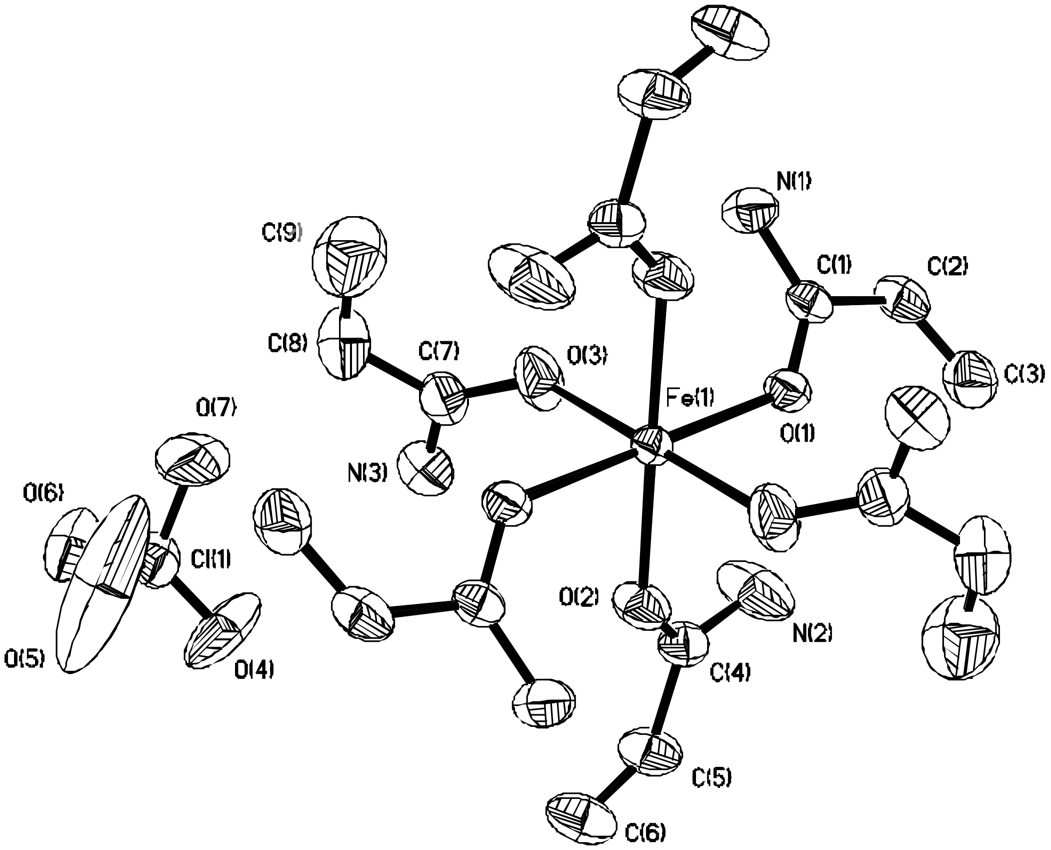
Girma Kibatu Berihie

Coordination Chemistry of Acrylamide and N-Pyrazolylpropanamide: Syntheses and Structures



Coordination Chemistry of Acrylamide and N-Pyrazolylpropanamide: Syntheses and Structures

Dissertation

Zur Erlangung des akademischen Grades

Doctor rerum naturalium
(Dr. rer. nat.)

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Genehmigt durch die Fakultät für Verfahrens-und Systemtechnik
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Promotionskolloquium am 06. 12. 2006

Dedicated to my mother and to my wife

For their love and affection

Acknowledgement

This thesis has been carried out under the guidance and supervision of Professor Dr. rer. nat. habil. Frank T. Edelmann at the Institut für Chemie, Fakultät für Verfahrens- und Systemtechnik der Otto-von-Guericke-Universität Magdeburg, between January 2003 and August 2006.

My sincere thanks and gratitude are to

Professor Dr. rer. nat. habil. Frank T. Edelmann

for his constant guidance, motivation, suggestions, and discussions throughout this work. I also thank him for the financial support offered through working with his group during my stay at Magdeburg.

I thank Dr. rer. nat. Steffen Blaurock for crystallographic measurements and refinements. I also respect the support from and discussions with Dr. rer. nat. Volker Lorenz, Dr. rer. nat. Jochen Gottfriedsen and Dr. rer. nat. Stephan Gießmann during this research work.

I thank Ms. Ute Gutknecht (IR Spectra measurements), Dr. rer. nat. Liane Hilfert and Ms. Ines Sauer (NMR), Ms. Christina Jäger and Ms. Sabine Preiß (Elemental analysis) for their timely support. Support from laboratory technicians Ms. Viola Herrmann and Marlies Spoida and from chemical store Mr. Jens Küger and Ms. Christel Knoche are acknowledged.

The support, care and encouragement received from my wife were always tremendous. The encouragement and financial support from Ms. Sonia and Sr. M. Cecilia in working this thesis are gratefully acknowledged.

Girma

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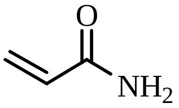
1. Introduction

Acrylamide (2-propenamide) is a white and odorless crystalline solid with a melting point of 84.5 °C. It is soluble in many polar solvents, including acetone, ethanol, acetonitrile, and water, where 215.5 g can be dissolved in 100 ml of water at 30 °C. The compound has a high mobility in soil and groundwater, and is biodegradable [1]. Acrylamide contains two principle functional groups, the vinyl carbon-carbon double bond and an amide group (Scheme 1).



Scheme 1. Structure of acrylamide.

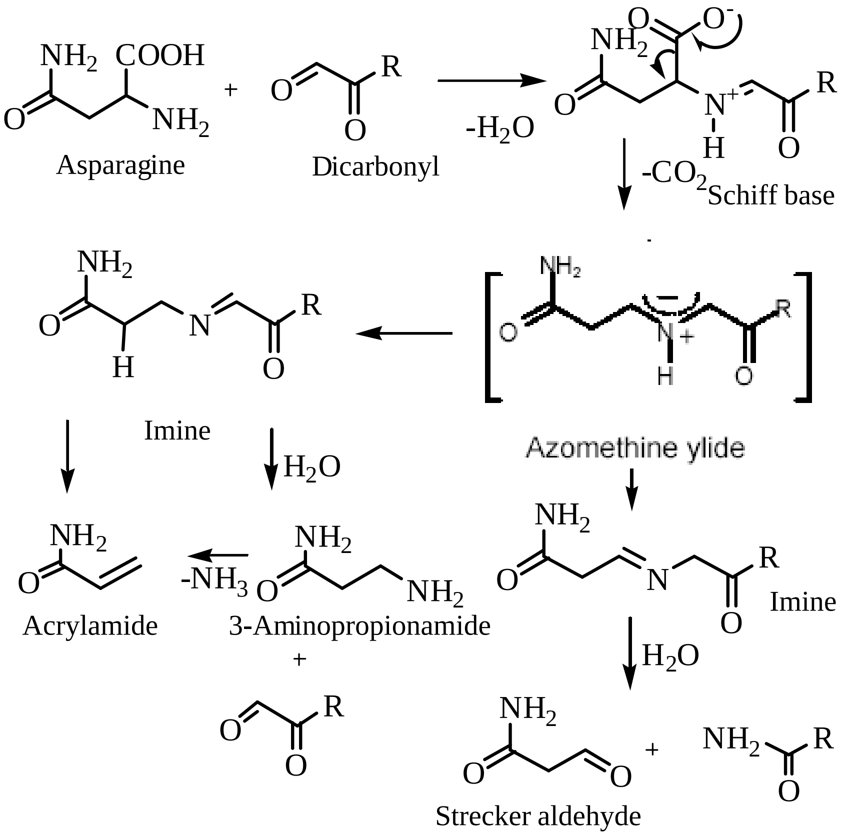
The German scientist C. Moureu first synthesized acrylamide in 1893 by slowly adding dry ammonia to a saturated benzene solution of acrylyl chloride at 10°C [2]. After boiling and filtration to remove the ammonium chloride, acrylamide precipitated upon cooling. However, it was not widely commercially available until the 1950s, when Hercules started marketing commercial quantities. Acrylamide is generally formed upon hydration of acrylonitrile with either sulfuric acid at 90 to 100 °C or more recently by catalytic hydration using a copper catalyst (Scheme 2) [3].

$$CH_2{=}CHCN \quad + \quad H_2O \xrightarrow{\text{Catalyst}} CH_2{=}CHCONH_2$$

Scheme 2. Hydration of acrylonitrile.

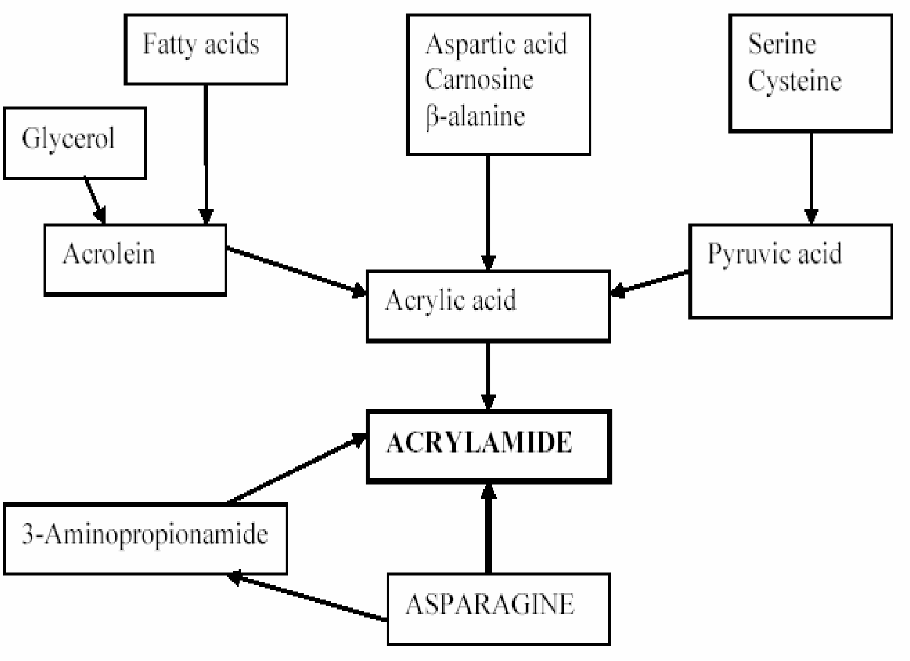
Analogous routes of conversion of acrylonitrile to acrylamide are also performed by various microorganisms [4]. Nitrilase produces acid and ammonia directly from a nitrile, whereas, the nitrile hydratase catalyzes the hydration of acrylonitrile to acrylamide. This reaction has been used for low-temperature production of acrylamide with minimal by-products. An amidase can then hydrolyze the acrylamide into acrylic acid and ammonia. The presence of metal ions from an acrylamide-degrading *Rhodococcos sp.* amidase may represent a crucial role in the mechanism of acrylamide hydrolysis. Such an enzyme may detoxify acrylamide and may also be useful as a biocatalyst for the production of acrylic acid. Microbial genera known to effect this reaction include *Nocardia*, *Brevibacterium*, *Arthrobacter*, *Rhodococcos*, and *Pseudomonas*.

Recently, it has been reported that acrylamide may also form in certain foods cooked at high temperatures above 120 °C [5]. This report of the presence of acrylamide in a range of fried and oven cooked foods has caused worldwide concern because this compound has been classified as probably carcinogenic in humans. The highest concentrations of acrylamide have been identified in potato- and grain-based foods that are cooked at very high temperatures (e.g., frying, grilling or baking). Acrylamide levels as high as 3500 µg/kg has been reported in potato chips and French fries. A number of mechanisms for acrylamide formations in foods are mainly described in [6] (a) for the interaction of the amino acid asparagines with glucose or other carbohydrates (Scheme 3). (b) for free aspartic acid in foods that could lead to the formation of acrylic acid, that in turn could undergo amino hydroxylation to acrylamide, provided ammonia is present (thermal reaction), and (c) for the decomposition of triglycerides which afford acrolein. Acrolein in turn reacts with asparagines to give acrylamide.



Scheme 3. Formation of acrylamide from asparagines in the presence of a- hydroxycarbonlys. R represents the rest of the carbonyl moiety (adapted from STADLER et al. [7]).

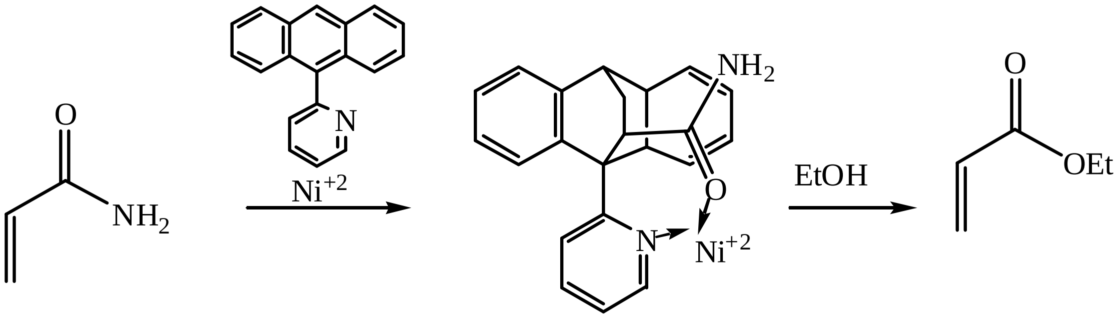
Even though formation of acrylamide in foods has its dominating routes through asparagines and reducing sugars, there are also other minor routes suggested for the formation from many different food constituents in addition to amino acids (Scheme 4). Routes below show components that react with available amino-groups from the Maillard reaction system.



Scheme 4. Formation routes of acrylamide.

Acrylamide has been extensively investigated and has a large database of very complex toxicity, pharmacokinetic, and mode of action studies [8-9]. The results of animal complex toxicity studies indicated that acrylamide is carcinogenic in rodents and produces toxic effects on the reproductive and nervous systems. Acrylamide is toxic and probably carcinogenic to human beings. Acrylamide has been classified as Group B2 probable carcinogen by U. S. Environmental Protection Agency (EPA). Exposures to acrylamide may occur via the inhalation, oral or dermal routes. In the manufacture of polyacrylamide, workers may be exposed via inhalation. However, exposures via the oral (food and water) and dermal (use of polyacrylamide-containing products) routes also may occur.

To fully evaluate the health effects and risks associated with acrylamide exposure, it is important to understand the chemistry and biology of pure acrylamide and acrylamide-based (metabolites) compounds. Metal ion coordination to acrylamide also enhances the electrophilicity of acrylamide and increases its reactivity. Nickel-containing 2-pyridylanthracene, for example, which models the activity of metal containing enzymes that are involved in the conversion of carboxamides to carboxylic ester or acids, is known to catalyze the conversion of acrylamide to ethyl acrylate (Scheme 5) [10]. Alcoholysis of acrylamide with methanol has also been reported in the presence of rare earth transitions metal complexes [11]. Acrylamide and few biologically relevant adducts of acrylamide with ethylenediamine, cycelen and pyrazole are able to coordinate to biologically relevant metal ions.



Scheme 5. Metal ion prompted conversion of acrylamide to ethyl acrylate.

Hence, this thesis is concerned particularly with the coordination chemistry of acrylamide and an acrylamide-based compound, N-pyrazolylpropanamide with biologically relevant metal ions such as Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II). The solution and solid-state chemistry of acrylamide or acrylamide-based ligands (metabolites) with less acidic biologically relevant metal ions are of great interest due to the biological relevance of the amide group in peptides and proteins [12-14], their function as models of metalloproteins active sites and their relevance in elucidating the mechanism of acrylamide metabolism in biological systems and its health effects. From the industrial point of view metal complexes of acrylamide are employed in the production of water-soluble polymers and copolymers that are used in many commercial and scientific applications [15-21].

1.1. Physical properties

Acrylamide is an odorless, white crystalline solid at room temperature, with molecular formula of C_3H_5NO and weight 71.08. Acrylamide is readily soluble in water (2155g/l at 30 °C) and polar solvents (e.g., acetone, methanol, and ethanol), but not in non-polar solvents (e.g., carbon tetrachloride). Acrylamide has a density of 1.27 g/l (25 °C), a boiling point of 136 °C at 3.3 kPa and a melting point of 84-85 °C. The solubility of acrylamide in 100 grams of solvent is summarized below [1, 22]:

Solvent	Grams/100 g of solvent at 30 °C
Acetonitrile	39.6
Acetone	63.1
Benzene	0.346
Ethylene glycol monobutylether	31
Chloroform	2.666
1,2-Dichloroethane	1.50
Dimethyl formamide	119
Dimethylsulfoxide	124
Dioxane	30
Ethanol	86.2
Ethyl acetate	12.6
Heptane	0.0068
Methanol	155
Pyridine	61.9
Water	215.5
Carbon tetrachloride	0.038

Acrylamide, as compared to some other vinyl monomers, has good thermal stability and long shelf life. There is no evidence of polymer formation and only slight yellowing after three weeks of storage at 50 °C and even after 24 hours at 80 °C (slightly below the melting point) a pure sample shows little or no polymer formation.

The stability of acrylamide to light has been evaluated by exposing several samples in soft glass vials to irradiation under a General Electric sun lamp for 40 hours at a distance of six inches. The results indicate some polymer formation under these conditions.

Solutions of acrylamide can be stabilized when necessary by incorporation of cupferron-Fe(II) complex (ferrous salt(II) of N-nitrosophenylhydroxylamine) [23], sodium nitrite [24], and potassium hexacyanoferrate [25], a chelating agent such as EDTA [26], butylated hydroxyanisole [27], or tetramethylthiuram monosulfide [28]. Aqueous salt-containing solutions of acrylamide may be stabilized, even at elevated temperatures, by addition of iron complexes of cyanogen or thiocyanogen [29].

1.2. Chemical properties

Acrylamide is an interesting difunctional monomer containing a reactive electron-deficient double bond and an amide group, and it undergoes reactions typical of those two functionalities. It exhibits both weak acidic and basic properties. The double bond of acrylamide is susceptible to a wide range of chemical reactions including nucleophilic additions, Diels-Alder, and radical reactions. Thus, ammonia, aliphatic amines, phosphines, chlorine, bromine, bisulfite, and dithiocarbamates readily react with the vinylic double bond as do alkylation of proteins, non-protein SH groups, and N-terminal NH_2 groups of the valine residue of haemoglobin and NH_2 of guanine and other nucleic acids, hence the reasons for concern in biological systems. Reactions of the amide group include hydrolysis, dehydration, alcoholysis, and condensations with aldehydes.

Reactions with Ammonia and Aliphatic Amines

A tris-compound can be obtained with ammonia. Acrylamide reacts with concentrated aqueous ammonia at 10-20 °C, to give a 90% yield of 3,3',3''-nitrilotrispropionamide [30, 31].

$3\ CH_2{=}CHCONH_2 \quad + \quad NH_3 \quad ? \quad N(CH_2CH_2CONH_2)_3$

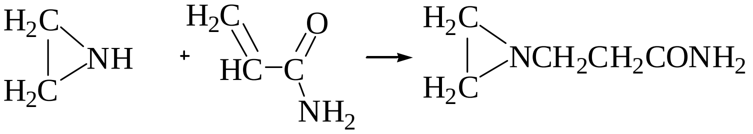
Acrylamide adds to the active hydrogens of these compounds. 3-(Alkylamino-propionamide) can be prepared by reactions of primary or secondary aliphatic amines with acrylamide [32-34].

$RNH_2 \quad + \quad CH_2{=}CHCONH_2 \quad ? \quad RNHCH_2CH_2CONH_2$

$RNH_2 \quad + \quad 2\ CH_2{=}CHCONH_2 \quad ? \quad RN(CH_2CH_2CONH_2)_2$

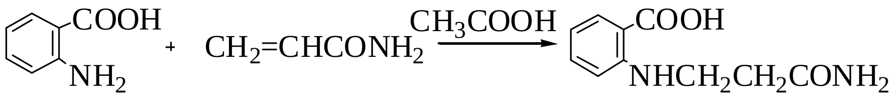
$R_2NH \quad + \quad CH_2{=}CHCONH_2 \quad ? \quad R_2NCH_2CH_2CONH_2$

Carbamolylethylation of ethylenimine with acrylamide, for example, yields 3-(1-aziridinyl)propionamide [35].



Scheme 6. Carbamoylethylation of ethylenimine with acrylamide.

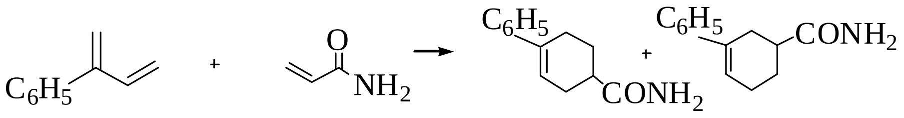
Anthranilic acid reacts with acrylamide in the presence of acetic acid to give N- 2-carbamolylethylanthranilic acid [36].



Scheme 7. Carbamolylethylation of anthranilic acid with acrylamide.

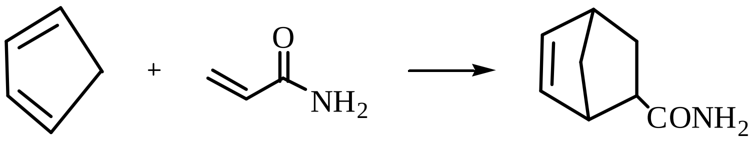
Diels-Alder Reactions

Acrylamide reacts with 2-phenyl-1,3-butadiene in the presence of N-phenyl-2-naphthyl amine to give two isomeric adducts [37]. These adducts are obtained in the ratio of approximately 7 parts *para* and 2 parts *meta*.



Scheme 8. The reaction of acrylamide with 2-phenyl-1,3-butadiene.

With acrylamide and trans-1-phenyl-1,3-butadiene, the major adducts formed is *trans*-2-phenyl-1,2,5,6-tetrahdrobenzamide [38]. Bicyclo [2.2.1] hept-5-ene-2-carboxamide can be prepared readily from acrylamide and cylopentadiene.

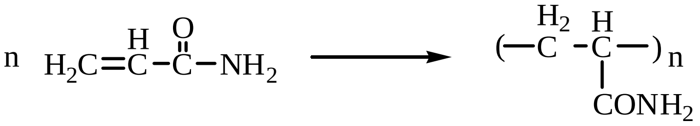


Scheme 9. The reaction of acrylamide with cylopentadiene.

9-Cyanoanthracene adds to acrylamide to give 9-cyano-9,10-ethanoanthracene-12-carboxamide [39].

Free Radical Polymerization of Acrylamide

Acrylamide is readily polymerized in the presence of free radicals. The free radically induced polymerization of acrylamide follows the classical vinyl polymerization mechanism involving initiation, propagation, and termination processes. The basic mechanism involved in the free radical polymerization of acrylamide is outlined in Scheme 10.



$$n\ H_2C{=}\overset{H}{C}{-}\overset{O}{\overset{\|}{C}}{-}NH_2 \longrightarrow (-\overset{H_2}{C}-\underset{CONH_2}{\overset{H}{C}}-)_n$$

Scheme 10. Free radical polymerization of acrylamide.

Polymerization can be initiated by a number of systems including peroxides, persulfates, redox couples, azo compounds, photochemical systems, perborates, percarbonates, and radiation.

Formation of Esters of Acrylic Acid

Acrylamide sulphate, which may be prepared from acrylonitrile or from acrylamide and concentrated sulphuric acid, reacts with alcohols to give esters of acrylic acid.

$CH_2{=}CHCN + H_2SO_4 + H_2O$? $CH_2{=}CHCONH_2{\cdot}H_2SO_4$

$CH_2{=}CHCONH_2 + H_2SO_4$? $CH_2{=}CHCONH_2{\cdot}H_2SO_4$

$CH_2{=}CHCONH_2{\cdot}H_2SO_4 + ROH$? $CH_2{=}CHCOOR + NH_4HSO_4$

Salt Formation

Alkali metal salts of acrylamide can be prepared under conditions. Thus, N-potassium acrylamide is obtained by treating acrylamide with a potassium alkoxide [40].

$CH_2{=}CHCONH_2 + KOC(CH_3)_3$? $CH_2{=}CHCONHK + (CH_3)_3COH$

The above reaction takes place in t-BuOH at room temperature. The corresponding N-sodium acrylamide is more readily prepared by reacting acrylamide with sodamide in liquid ammonia.

When mercuric oxide is refluxed with an excess of acrylamide in ethanol for 90 minutes, there is obtained a 23% yield of N-N'-mercuribis(acrylamide) [41]. This compound is easily polymerized or copolymerized.

$$CH_2{=}CHCONH_2 \quad + \quad HgO \quad ? \quad CH_2{=}CHCONHHgNHCOCH{=}CH_2$$

Hydrolysis

Acid- or base- catalyzed hydrolysis of acrylamide yields acrylic acid

$$CH_2CHCONH_2 + H_2O \xrightarrow{H^+ \text{ or } OH^-} CH_2CHCOOH + NH_3$$

Dehydration

Acrylamide has been converted to acrylonitrile by treatment with fused manganese dioxide at 500^{0}C [42] or with phosphorus pentoxide [43]. The reaction can be formally viewed as a ß-elimination of water from the enol form to form a new triple bond. Dehydration of amides to nitriles is one of the oldest known reactions in organic chemistry.

$$R\text{-}C(=O)\text{-}NH_2 \; ? \quad R\text{-}C(\text{-}OH)=NH \; ? \quad R\text{-}C=N + H_2O$$

$$CH_2{=}CHCONH_2 \xrightarrow{\text{fused } MnO_2 \text{ or } P_2O_5} CH_2{=}CHCN \quad + \quad H_2O$$

Condensations with aldehydes

Depending on the conditions employed, a variety of products may be obtained by the reaction of acrylamide with formaldehydes or other aldehydes. Reaction of acrylamide with formaldehyde under different conditions gives N-methylolacrylamide. The reaction is preferably carried out by heating a concentrated aqueous solution (more than 60%

acrylamide) with formaldehyde at a pH of 9.6 for 2 hr. at 50 °C in the presence of cupferron or methyl ether of hydroquinone (MEHQ) inhibitor [44].

$$CH_2{=}CHCONH_2 \quad + \quad HCHO \xrightarrow{\text{Base}} CH_2{=}CHCONHCH_2OH$$

The rate of methylolation increases with increases in pH and formaldehyde to acrylamide ratio.

Under acidic conditions, acrylamide with aldehydes give the corresponding alkylidene-bis(acrylamides) [45, 46].

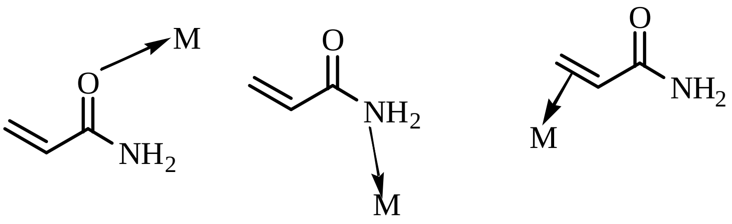
$$CH_2{=}CHCONH_2 \quad + \quad RCHO \xrightarrow{H^+} (CH_2{=}CHCONH)_2CHR \; + \; H_2O$$

The reaction of acrylamide with glyoxal in the presence of alkali yields N,N'-(1, 2-dihydroxyethylene) bis acrylamide [47, 48].

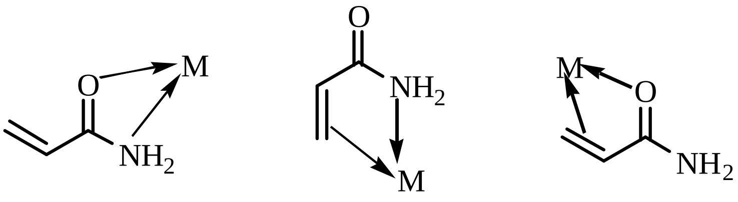
$$OHCCHO + \quad 2CH_2{=}CHCONH_2 \; ? \quad CH_2{=}CHCONHCH(OH)CH(OH)NHCOCH{=}CH_2$$

Coordination modes of acrylamide with metal salts

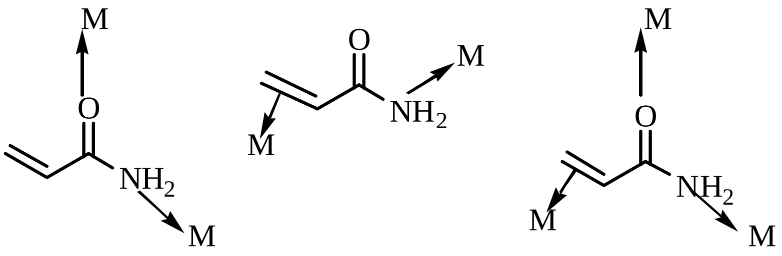
Acrylamide is also capable of coordinating with metal ions through the carbonyl oxygen atom, the nitrogen atom, or the olefin in an ?^{2}-mode. It could be monodentate O- or N-bonded, or exhibit a bidentate chelate rings or bridging complexes. It can be in the amide or the hydroxyimine tautomeric forms, and may be neutral, or deprotonated.



Scheme 11. Possible monodentate coordination modes in acrylamide complexes.



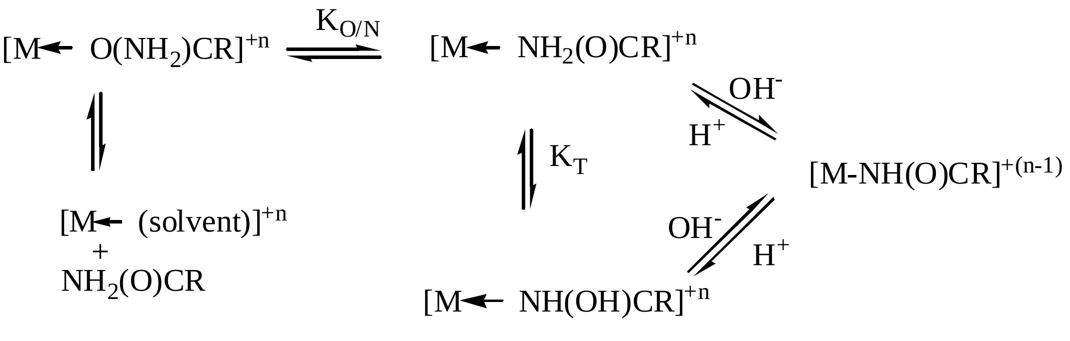
Scheme 12. Possible chelate rings in acrylamide complexes.



Scheme 13. Possible bridging coordination modes in acrylamide complexes.

Metal complexes of acrylamide are generally prepared by direct reaction of metal ions with acrylamide [49-61] or base-catalyzed hydrolysis of coordinated acrylonitrile, $[M\text{-}N{=}C\text{-}CH{=}CH_2]^{n+}$ (where $M^{n+3} = Co^{+3}$) [62]. The first route usually gives complexes in which the metal is coordinated through oxygen, although coordination through nitrogen or the olefin has been reported in some cases. The second route usually forms a more stable deprotonated N-amidate, $[M\text{-}NHC(O)CH{=}CH_2]^{(n-1)+}$, which is protonated instantaneously in acidic conditions to give *N*- or *O*-coordinated complexes.

The most basic site in acrylamide is oxygen, where protonation or metallation occurs in neutral conditions. However, the basicity of the amide nitrogen may also make protonation or complexation at this site a possibility, where the amide oxygen then becomes the most basic centre calling for additional rapid protonation or complexation at the oxygen. Thus, the *O*- to *N*-linkage isomerization or the *vice versa*, tautomerization, solvolysis and hydrolysis to the corresponding *N*-amidate complexes in solutions are typical characteristics in metal-amide complexes. Complexation of amides can be summarized as shown in Scheme 14 [63]. In general, changes in the acidity and oxidation states of the metal centre, substitute groups, temperature, and solvent system influence the stability and mode of coordinations in metal-amide complexes [64, 65].



Scheme 14. Chemistry of amide complexes.

1.3. Uses

Most uses for high molecular weight polyacrylamide in water treatment, mineral processing, and paper manufacture are based on the ability of these polymers to flocculate small suspended particles by charge neutralization and bridging. Low molecular weight polymers are employed as dispersants, crystal growth modifiers, or selective mineral depressants. In oil recovery, polyacrylamide adjusts the rheology of injected water so that the polymer solution moves uniformly through the rock pores, sweeping the oil ahead of it. Other applications such as superabsobents and soil modification rely on the very hydrophilic character of polyacrylamide.

1.4. Toxicity

Acrylamide may be absorbed into the body by passage through the intact skin, by inhalation of air containing dust or droplets of solutions of the material, or by swallowing. Small, single doses of acrylamide are not hazardous (the actual oral LD50 for rats is 200 mg/Kg), and health experience in the manufacture of acrylamide has been good. The result of the animal toxicity studies indicate that acrylamide is carcinogen in rodents and produces toxic effects on the reproductive and nervous systems [66, 67]. Acrylamide is a compound, with a potential to cause a spectrum of effects, including neurotoxic effects as has been observed in humans. Acrylamide has also been classified as “a probable human carcinogen” [68]. The mutagenic and carcinogenic properties of acrylamide are assumed to depend on the epoxy metabolite, glycidamide [69].

1.5. Scope and objectives of the present work

Acrylamide has been known for a long time as a monomer in plastic industry as starting material in making polyacrylamide. However, it appeared also as environmental danger in bread or potato chips which are cooked or frit at high temperatures. The presence of this toxic acrylamide in many foods increased health concerns from the compound. The risk from acrylamide has been studied. Much less investigation of the coordination of acrylamide with different metals has been performed. The exact coordination sites of acrylamide with main group and sub-group metals are not clear. Thus, coordination of acrylamide with metals is the main objective of this work. This dissertation comprises an actual research subject in bioinorganic chemistry.

Acrylamide is a multifunctional molecule which combines a carbonyl group, an amino group and an olefin double bond. All three groups are ordered over free electron pairs and enable coordination with metals. For monodentate coordination to metal complex-fragments; acrylamide has three different possibilities. Oxophilic metals, such as alkali and alkaline earth metals, aluminium, gallium or lanthanide elements bind with the carbonyl oxygen. Metal ions which have strong affinity for N- over O-donor ligands may favor N-coordination modes. Metals in low oxidation states may form p-coordination *via* back donation in an ?^{2}-mode.

O-Bonded interactions are more favored in the presence of a primary anchoring group capable of forming five-membered chelate rings with a metal ion and the carbonyl oxygen in the metal amide complexes. However, chelation between a very weakly activated double bond and the carbonyl oxygen or the amide nitrogen to form a five-membered ring in acrylamide is only probable. Chelation between the carbonyl oxygen and the amine nitrogen or the deprotonated nitrogen in rare four-membered chelate rings is an unlikely but imaginable structural possibility. Another possibility is the simultaneous coordination of two or all donor sites in acrylamide where the ligand acts as a bridge between two or more metal atoms.

Based on the aforementioned background material, acrylamide was reacted with metal salts and the products are analyzed by spectroscopic methods. The isolated products were mainly structurally characterized using single X-ray structures.

Acrylamide and few biologically relevant adducts of acrylamide are able to coordinate to biologically relevant metal ions such as Co, Ni, Cu, and Zn. Hence this investigation included the coordinations of acrylamide and metabolites with metals which have some role in biological system. The possibility of biologically relevant metal ions coordinated with acrylamide or its metabolites, thus activating or deactivating the reaction of substrates and/or dysfunction a metal ion due to coordination with acrylamide or its metabolites can be used in elucidating the mechanism of acrylamide metabolism and its health effects in future studies.

2. Results and Discussions

2.1. Syntheses and characterizations of complexes of metal(II) chlorides with acrylamide, $[M(O\text{-}OC(NH_2)CH=CH_2)_4Cl_2]$

2.1.1. Synthesis and characterization of the complex of Mn(II) chloride with acrylamide

The THF adduct of Mn^{II} chloride, $MnCl_2(THF)_2$, was dissolved in absolute ethanol and reacted with acrylamide in a 1:6 metal salt to ligand ratio [70]. The solution was then concentrated by removing part of the solvent under vacuum, and a few drops diethyl ether were carefully layered. Cooling and slow diffusion of diethyl ether into the solution developed single crystals of $[Mn(O\text{-acrylamide})_4Cl_2]$. The compound has been characterized by elemental analysis, IR spectroscopy and single crystal X-ray diffraction.

Compound **1** is a white crystalline solid melting at 224 °C. The elemental analysis of **1** showed that the contents found of C and H are slightly lower than the calculated ones and that of calculated N is equal to those found in **1**. The IR spectra of free acrylamide and its complexes can be compared with each other to check spectral changes upon coordination. The comparison of the IR spectra of free acrylamide and the complexes in the NH_2 vibration region near 3400-3100 cm^{-1} reveals a significant increase of the positions of $?_{as}(NH_2)$ and appreciable increase in $?_{s}(NH_2)$ vibrations to higher wave numbers accompanied by splitting into more sharp components.

An important spectral change observed between the spectra of free acrylamide and the complex investigated here is the shifting of a strong broad band observed at 1673 cm^{-1} in free acrylamide to lower wave numbers and its splitting into bands at 1664 cm^{-1} and near 1629 cm^{-1} upon complexation. The $?(H_2C=C)$ (CH_2 wagging) bands at 961 cm^{-1} or 962 cm^{-1} and the dCH and CH_2 twisting bands about 990 cm^{-1} in both the spectra of acrylamide and the complex indicate uncoordinated double bonds.

The molecular structure of **1** is shown in Figure **1**, and selected bond lengths and angles are presented in Table **1**. Compound **1** crystallizes in the cubic space group I43d. The coordination geometry of the metal centre in the complex involves a tetragonally distorted octahedral structure with four O-donor atoms of acrylamide bonded in the equatorial positions and two chlorides in the apical positions. The equatorial M-O bond lengths in the manganese(II) chloride complex with acrylamide are 2.185Å while the axial M-Cl bond length is 2.526Å. The longer M-Cl bonds slightly extend the polyhedron into a tetragonally distorted octahedron. The central C(3)-C(2) bond length (1.760Å) for the uncoordinated acrylamide molecule becomes very short (1.475Å) upon complexation which may be due to delocalization of electrons from the double bond. The C(3)-N(3) bond lengths (1.302Å-1.310Å) in coordinated acrylamide are relatively longer than the C-N bond length (1.272Å) in uncoordinated acrylamide.

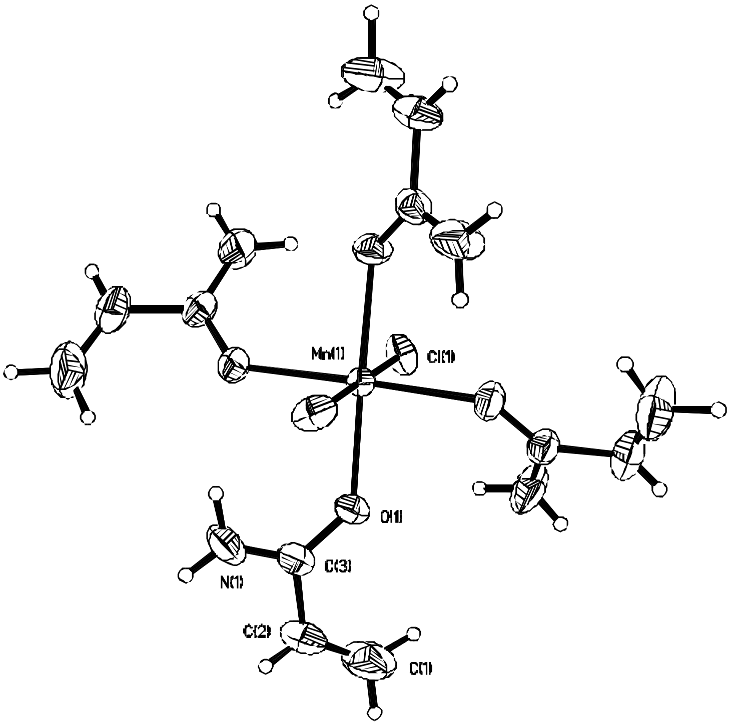


Figure **1**. Molecular structure of [Mn(O-OC(NH_2)CH=CH_2)$_4$$Cl_2$], **1**

Table **1**. Selected bond lengths (Å) and angles (°) for **1**

Mn(1)-O(1)	2.186(1)	O(1)-Mn(1)-Cl(1)	88.0(3)
Mn(1)-Cl(1)	2.526(4)	C(3)-O(1)-Mn(1)	131.8(1)
O(1)-C(3)	1.251(2)	C(3)-N(1)-H(1NA)	120(2)
N(1)-C(3)	1.302(2)	C(3)-N(1)-H(1NB)	120.8(2)
N(1)-H(1NA)	0.92(3)	H(1NA)-N(1)-H(1NB)	117(2)
N(1)-H(1NB)	0.83(2)	C(2)-C(1)-H(1A)	122.9(2)
C(1)-C(2)	1.288(3)	C(2)-C(1)-H(1B)	123.0(2)
C(1)-H(1A)	0.90(2)	H(1A)-C(1)-H(1B)	113(2)
C(1)-H(1B)	0.99(2)	C(1)-C(2)-C(3)	122.4(2)
C(2)-C(3)	1.475(2)	C(1)-C(2)-H(2)	117.4(2)
C(2)-H(2)	0.80(2)	C(3)-C(2)-H(2)	120.2(2)
		O(1)-C(3)-N(1)	122.4(1)
		O(1)-C(3)-C(2)	121.2(2)
		N(1)-C(3)-C(2)	116.4(2)

2.1.2. Synthesis and characterization of the complex of Fe(II) chloride with acrylamide

To anhydrous iron(II) chloride acrylamide in absolute ethanol in a 1:6 metal salt to ligand ratio was added and stirred for 30 minutes. The solution was then concentrated by removing part of the solvent under vacuum, and a few drops of diethyl ether were carefully layered. Cooling and slow diffusion of diethyl ether into the solution developed single crystals of [Fe(*O*-acrylamide)$_4$Cl$_2$]. The compound has been characterized by elemental analysis, IR spectroscopy and single crystal X-ray diffraction [70].

Compound **2** is a yellow crystalline solid melting at 116-118 ^{o}C. Comparison of the IR spectra of free acrylamide and the complex in the NH_2 vibration region near 3400-3100 cm^{-1} reveals a significant increase in the positions of ?$_{as}$(NH_2) and appreciable increase in ?s(NH_2) vibrations to higher wavenumbers accompanied by splitting into more sharp components.

An important spectral change observed between the spectra of free acrylamide and the complex is the shifting of a strong broad band observed at 1673 cm^{-1} in free acrylamide to lower wavenumbers and its splitting into bands at 1664 cm^{-1} and near 1629 cm^{-1} upon complexation. The ?($H_2C=C$) (CH_2 wagging) bands at 961 cm^{-1} or 962 cm^{-1}and the dCH and CH_2 twisting bands about 990 cm^{-1} in both the spectra of acrylamide and the complex indicate uncoordinated double bonds.

The molecular structure of **2** is shown in Figure **2**, and selected bond lengths and angles are presented in Table **2**. Compound **2** crystallizes in the cubic space group I43d. The coordination geometries of the metal centre in the complex involve tetragonally distorted octahedral structures with four O-donor atoms of acrylamide bonded in the equatorial positions and two chlorides in the apical positions. The equatorial M-O bond lengths in the iron (II) chloride complex with acrylamide are 2.130Å while the axial M-Cl bond length is 2.497Å. The longer Fe-Cl bonds slightly extend the polyhedron into a tetragonally distorted octahedron.

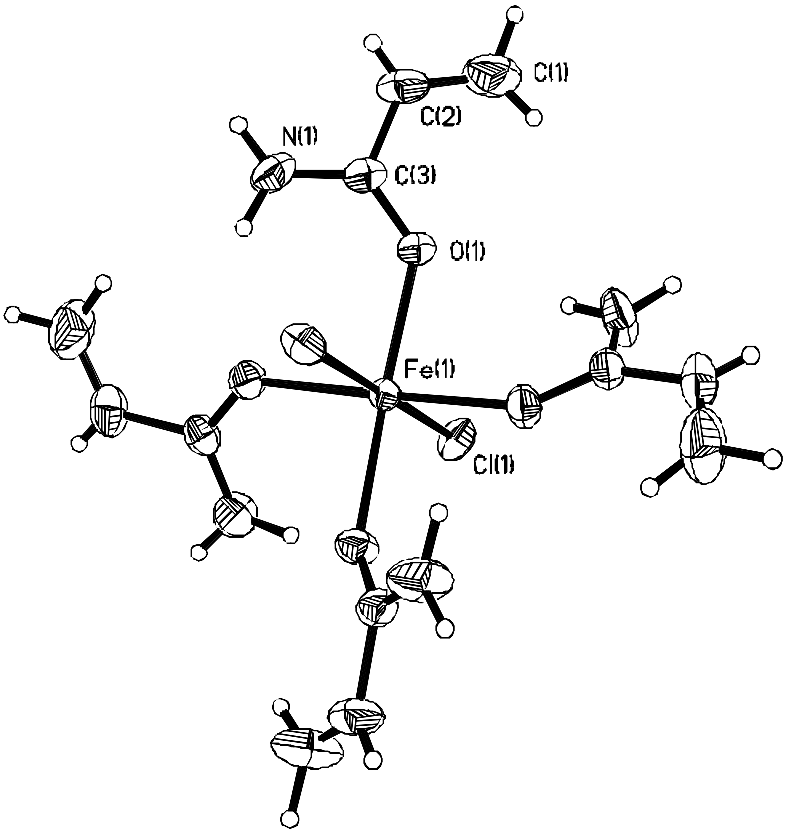


Figure **2**. Molecular structure of [Fe(O-OC(NH_2)CH=CH_2)$_4$$Cl_2$], **2**

Table **2**. Selected bond lengths (Å) and angles (°) for **2**

Fe(1)-O(1)	2.130(8)	O(1)-Fe(1)-Cl(1)	87.0(3)
Fe(1)-Cl(1)	2.497(3)	C(3)-N(1)-H(1NA)	118.5(1)
N(1)-C(3)	1.310(2)	C(3)-N(1)-H(1NB)	120.1(2)
N(1)-H(1NA)	0.86(2)	H(1NA)-N(1)-H(1NB)	120(2)
N(1)-H(1NB)	0.89(2)	C(3)-O(1)-Fe(1)	131.8(8)
O(1)-C(3)	1.252(1)	C(2)-C(1)-H(1A)	120.5(1)
C(1)-C(2)	1.295(2)	C(2)-C(1)-H(1B)	120.7(1)
C(1)-H(1A)	0.99(2)	H(1A)-C(1)-H(1B)	117.7(2)
C(1)-H(1B)	0.868(2)	C(1)-C(2)-C(3)	122.6(2)
C(2)-C(3)	1.477(2)	C(1)-C(2)-H(2)	113.5(1)
C(2)-H(2)	0.767(2)	C(3)-C(2)-H(2)	123.9(1)
		O(1)-C(3)-N(1)	122.6(1)
		O(1)-C(3)-C(2)	121.1(1)
		N(1)-C(3)-C(2)	116.3(1)

2.1.3 Synthesis and characterization of the complexes of Co(II) chloride with acrylamide

The direct reaction between $CoCl_2 \cdot 6H_2O$ and acrylamide in absolute ethanol and crystallization by slow diffusion of diethyl ether in the solution gave blue crystals of **3**, [Co(*O*-OC(NH_2)CH=CH_2)$_4$$Cl_2$]. The molecular structure of **3** contains a distorted octahedral Co^{2+} centre coordinated by four *O*-donor atoms of acrylamide in the equatorial positions and two chlorides in the apical positions [71].

A similar reaction in the solid state by grinding the reagents together in a mortar followed by washing with boiling toluene to remove the excess acrylamide from the dry crude product and crystallization from hot ethanol and few drops of diethyl ether gave the violet, ionic form [Co(*O*-OC(NH_2)CH=CH_2)$_6$][$CoCl_4$], **4**. The molecular structure of **4** contains an octahedral Co^{2+} cations surrounded by six *O*-bound acrylamide and a counter tetrachlorocobaltate (II) anion.

The comparison of the IR spectra of the free acrylamide and these complexes in the 3400-3100 cm^{-1} region reveals changes in $?_{as}$(NH) to higher wavenumbers on complexation. The ?(C=O) band at 1673 cm^{-1} in the spectrum of the free acrylamide has moved to lower wavenumbers on complexation, indicating that bonding is taking place between the oxygen of the C=O group and the metal ion.

The crystal structures of the complexes **3** and **4** along with the atomic numbering schemes are shown in Fig. **3** and Fig. **4**, respectively. The coordination of Co^{II} in **3** involves a tetragonally distorted octahedral structure with four *O*-donor atoms of acrylamide in the equatorial positions and two chloride ions in the apical positions. The equatorial Co-O bond lengths are 2.1026(10) Å, while the axial Co-Cl bond lengths are 2.4621(5) Å, corresponding to a distorted octahedron. Selected bond lengths and angles of complex **3** are summarized in Table **3**. The structure is composed of molecules and unit cells united by a system of intramolecular and intermolecular hydrogen bonds where the amine hydrogen atoms are bonded to a neighbouring coordinated oxygen atom and the chloride in the second unit cell.

The crystal structure of **4** contains Co^{2+} cations surrounded by an octahedral array of *O*-coordinated acrylamide ligands, accompanied by a $[CoCl_4]^{2-}$ anion. The Co-O bond lengths are 2.0699(15) Å – 2.1086(13) Å. Two of the six Co-O bond distances are longer than the rest of these bonds in **4** indicating non-equivalence of the ligands and energetic differences between the Co-O bonds. The tetrachlorocobaltate (II) anion is distorted tetrahedral with the Co-Cl bond lengths variable between 2.2582(9) Å and 2.2783(7) Å. Selected bond lengths and angles of complex **4** are summarized in Table **4**.

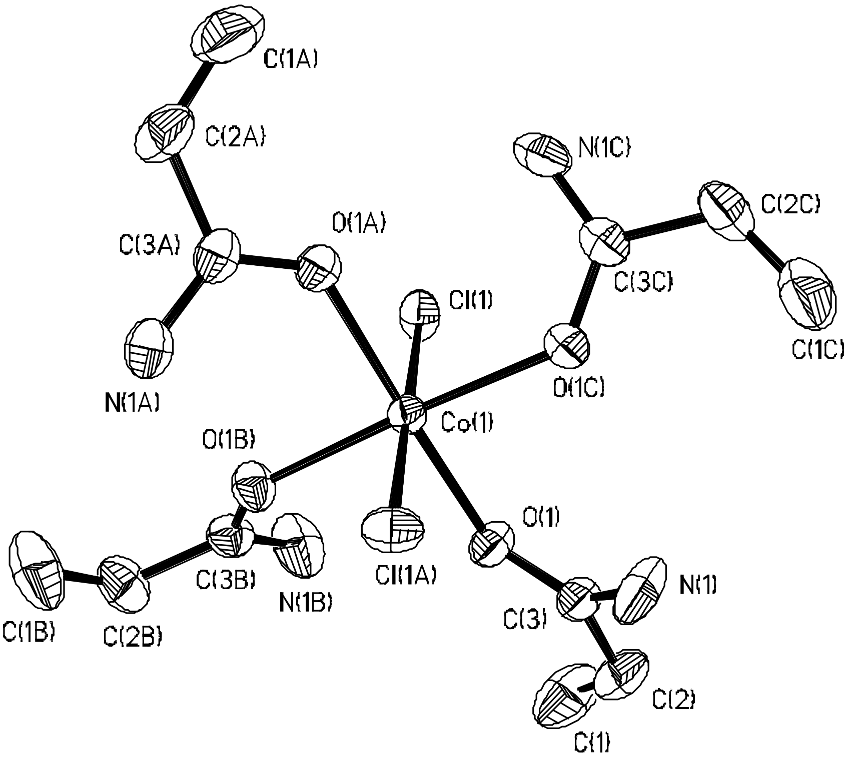


Figure **3**. Molecular structure of [Co(*O*-OC(NH$_2$)CH=CH$_2$)$_4$Cl$_2$], **3**

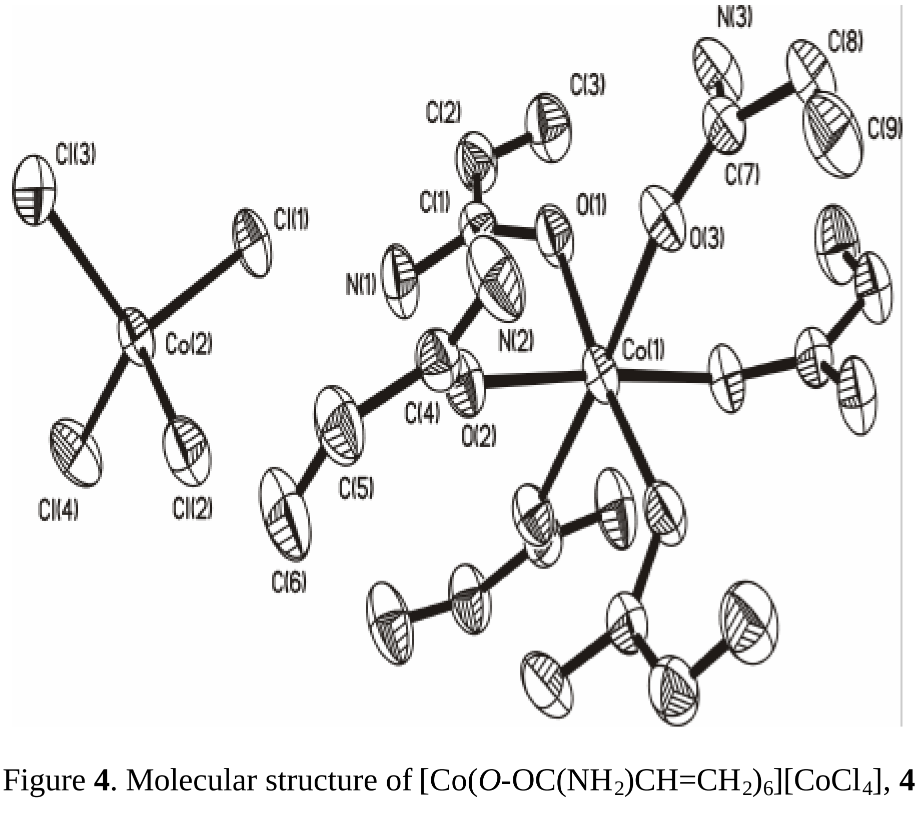


Figure **4**. Molecular structure of [Co(*O*-OC(NH$_2$)CH=CH$_2$)$_6$][CoCl$_4$], **4**

Table **3**. Selected bond lengths (Å) and angles (°) for **3**

Co(1)-O(1)	2.1026(10)	O(1)-Co(1)-Cl(1)	87.65(3)
Co(1)-Cl(1)	2.4621(5)	O(1A)-Co(1)-O(1)	175.30(6)
N(1)-C(3)	1.308(2)	O(1B)-Co(1)-O(1)	90.096(3)
O(1)-C(3)	1.26(2)	O(1)-Co(1)-Cl(1A)	92.35(3)
C(1)-C(2)	1.301(1)	Cl(1)-Co(1)-Cl(1A)	180.0
C(2)-C(3)	1.475(2)	C(3)-O(1)-Co(1)	131.76(11)
		C(1)-C(2)-C(3)	122.4(2)
		O(1)-C(3)-N(1)	122.6(2)
		O(1)-C(3)-C(2)	121.2(2)
		N(1)-C(3)-C(2)	116.2(2)

Table **4**. Selected bond lengths (Å) and angles (°) for **4**

Co(1)-O(1)	2.0699(15)	O(1)-Co(1)-O(2)	95.49(5)
Co(1)-O(2)	2.1011(13)	O(1)-Co(1)-O(3)	90.41(5)
Co(1)-O(3)	2.1086(13)	C(9)-C(8)-C(7)	121.8(2)
Co(2)-Cl(3)	2. 2582(9)	Cl(3)-Co(2)-Cl(2)	107.60(4)
Co(2)-Cl(2)	2.2597(8)	Cl(3)-Co(2)-Cl(4)	111.86(3)
Co(2)-Cl(4)	2.2705(8)	Cl(2)-Co(2)-Cl(4)	112.28(3)
Co(2)-Cl(1)	2.2783(7)	Cl(3)-Co(2)-Cl(1)	109.02(3)
O(1)-C(1)	1.258(2)	Cl(2)-Co(2)-Cl(1)	110.05(2)
O(2)-C(4)	1.248(2)	Cl(4)-Co(2)-Cl(1)	106.00(4)
O(3)-C(7)	1.255(2)	C(1)-O(1)-Co(1)	129.89(11)
N(1)-C(1)	1.315(2)	C(4)-O(2)-Co(1)	132.31(12)
N(2)-C(4)	1.318(3)	C(7)-O(3)-Co(1)	129.31(12)
N(3)-C(7)	1.316(2)	O(1)-C(1)-N(1)	122.6(2)
C(1)-C(2)	1.474(3)	O(1)-C(1)-C(2)	120.0(2)
C(2)-C(3)	1.302(3)	N(1)-C(1)-C(2)	117.4(2)
C(4)-C(5)	1.484(3)	C(3)-C(2)-C(1)	122.1(2)
C(5)-C(6)	1.299(3)	O(2)-C(4)-N(2)	122.7(2)
C(7)-C(8)	1.477(3)	O(2)-C(4)-C(5)	120.8(2)
C(8)-C(9)	1.302(3)	N(2)-C(4)-C(5)	116.4(2)
		C(6)-C(5)-C(4)	121.8(2)
		O(3)-C(7)-N(3)	122.2(2)
		O(3)-C(7)-C(8)	120.3(2)
		N(3)-C(7)-C(8)	117.6(2)
		O(2)-Co(1)-O(3)	93.02(6)

2.1.4. Synthesis and characterization of the complex of Ni(II) chloride with acrylamide

The reaction between hydrated nickel(II) chloride, $NiCl_2·6H_2O$, dissolved in absolute ethanol (and triethylorthoformate for dehydration) and acrylamide in a 1:6 metal salt to ligand ratio resulted in formation of the complex of Ni(II) chloride with acrylamide [70]. Cooling and slow diffusion of diethyl ether into the solution developed single crystals of **5**, $[Ni(O\text{-}OC(NH_2)CH{=}CH_2)_4Cl_2]$.

The comparison of the IR spectra of the free acrylamide and this complex in the 3400-3100 cm^{-1} region reveals changes in $?_{as}$(NH) to higher wavenumbers on complexation. The ?(C=O) band at 1673 cm^{-1} in the spectrum of free acrylamide has moved to lower wavenumbers on complexation, indicating that bonding is taking place between the oxygen of the C=O group and the metal ion. The ?($H_2C{=}C$) (CH_2 wagging) bands at 961cm^{-1} or 962 cm^{-1} and the dCH and CH_2 twisting bands at about 990 cm^{-1} in both the spectra of acrylamide and the complexes indicate uncoordinated double bonds.

The molecular structure of **5** is shown in Figure **5**, and selected bond lengths and angles are presented in Table **5**. Compound **5** crystallizes in the cubic space group I43d. The coordination geometry of the metal centre in the complex involves a tetragonally distorted octahedral structure with four O-donor atoms of acrylamide bonded in the equatorial positions and two chlorides in the apical positions. The equatorial M-O bond lengths in the nickel (II) chloride complex with acrylamide are 2.076Å, while the axial M-Cl bond length is 2.491Å. The longer M-Cl bonds extend the polyhedron slightly into a tetragonally distorted octahedron. Selected bond lengths and angles of complex **5** are summarized in Table **5**.

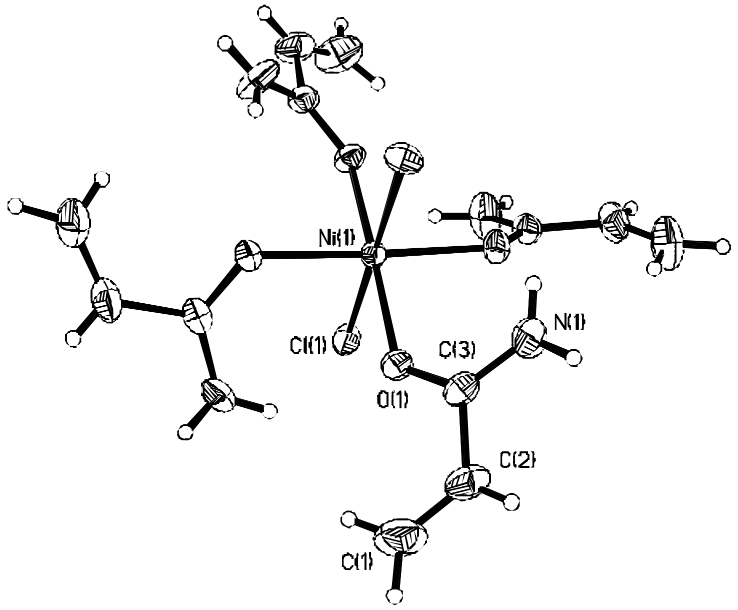


Figure **5**. Molecular structure of [Ni(*O*-OC(NH$_2$)CH=CH$_2$)$_4$Cl$_2$], **5**

Table **5**. Selected bond lengths (Å) and angles (°) for **5**

Ni(1)-O(1)	2.076(1)	O(1)-Ni(1)-Cl(1)	87.5(4)
Ni(1)-Cl(1)	2.420(6)	C(3)-O(1)-Ni(1)	131.3(1)
O(1)-C(3)	1.250(2)	C(3)-N(1)-H(1NA)	124(3)
N(1)-C(3)	1.308(3)	C(3)-N(1)-H(1NB)	120(3)
N(1)-H(1NA)	0.88(4)	H(1NA)-N(1)-H(1NB)	116(4)
N(1)-H(1NB)	0.79(4)	C(2)-C(1)-H(1A)	129(3)
C(1)-C(2)	1.297(4)	C(2)-C(1)-H(1B)	122(2)
C(1)-H(1A)	0.91(5)	H(1A)-C(1)-H(1B)	108(4)
C(1)-H(1B)	0.86(3)	C(1)-C(2)-C(3)	122.7(2)
C(2)-C(3)	1.482(3)	C(1)-C(2)-H(2)	115(3)
C(2)-H(2)	0.78(4)	C(3)-C(2)-H(2)	122(3)
		O(1)-C(3)-N(1)	123.3(2)
		O(1)-C(3)-C(2)	120.7(2)
		N(1)-C(3)-C(2)	116.0(2)

2.1.5. Synthesis and characterization of the complex of Cu(II) chloride with acrylamide

Single crystals of $[Cu(AAm)_4Cl_2]$ were obtained in acetonitrile-ether mixture upon substitution of crystal water in hydrated $CuCl_2·2H_2O$ by acrylamide molecules [72]. The IR spectrum of the Cu(II) acrylamide complex is quite similar to the spectra of the Mn(II), Fe(II), Co(II), and Ni(II) complexes of the same general formula $[M(AAm)_4Cl_2]$. The formation of the oxygen-to-metal coordination bond in the complex was confirmed by shifts of the coupled CO stretching band to a lower wavenumber, 1663 cm^{-1}, in comparison with the IR spectrum of the free ligand in which this band is observed at 1673 cm^{-1}. Complexation tends to reduce the coupling among the CO stretching, C=C stretching and NH_2 bending vibrations causing them to become more separable.

The molecular structure of **6** is shown in Figure **6**, and selected bond lengths and angles are presented in Table **6**. Compound **6** crystallizes in the cubic space group I43d. The coordination geometry of the metal centre in the complex involves a tetragonally distorted octahedral structure with four O-donor atoms of acrylamide bonded in the equatorial positions and two chlorides in the apical positions. The equatorial M-O bond lengths in the copper (II) chloride complex with acrylamide are 1.996Å, while the average axial M-Cl bond length is 2.691Å. The longer M-Cl bonds extend the polyhedron slightly into a tetragonally distorted octahedron. Selected bond lengths and angles of complex **6** are summarized in Table **6**. The most unique result in the copper(II) complex is the average bond obtained for the vinyl group, C=C, 1.313 Å, in the coordinated acrylamide molecules, which is somewhat longer than those observed in both the free acrylamide ligand and in the Mn(II), Fe(II), Co(II), and Ni(II) chloride complexes.

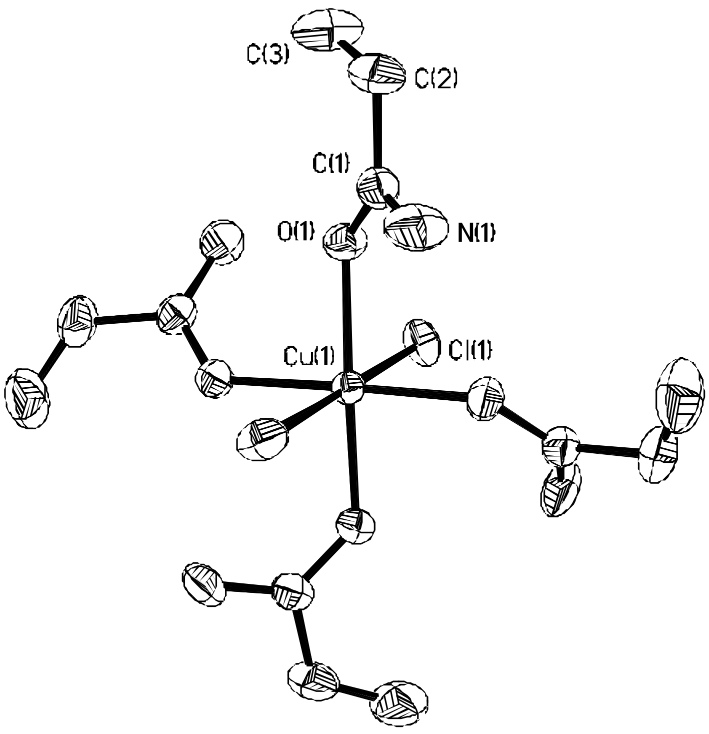


Figure **6**. Molecular structure of [Cu(*O*-OC(NH$_2$)CH=CH$_2$)$_4$Cl$_2$], **6**

Table **6**. Selected bond lengths (Å) and angles (°) for **6**

Cu(1)-O(1)	1.996(1)	O(1)-Cu(1)-Cl(1)	88.1(1)
Cu(1)-Cl(1)	2.691(1)	C(1)-O(1)-Cu(1)	131.2(1)
O(1)-C(1)	1.258(2)	C(1)-N(1)-H(1NA)	121.9(2)
N(1)-C(1)	1.308(2)	C(1)-N(1)-H(1NB)	122.3(2)
N(1)-H(1NA)	0.82(2)	H(1NA)-N(1)-H(1NB)	116(2)
N(1)-H(1NB)	0.80(2)	O(1)-C(1)-N(1)	123.0(2)
C(1)-C(2)	1.470(2)	O(1)-C(1)-C(2)	120.6(2)
C(3)-H(3A)	0.94(2)	N(1)-C(1)-C(2)	116.4(2)
C(3)-H(3B)	1.00(3)	C(3)-C(2)-C(1)	122.5(2)
C(2)-C(3)	1.313(3)	C(3)-C(2)-H(2)	121(3)
C(2)-H(2)	0.70(3)	C(1)-C(2)-H(2)	117(3)
		C(2)-C(3)-H(3A)	117.5(2)
		C(2)-C(3)-H(3B)	116.9(2)
		H(3A)-C(3)-H(3B)	126(2)

2.2. Syntheses and characterization of complexes of metal(II) nitrates with acrylamide, [M(*O*-OC(NH_2)CH=CH_2)$_6$][NO_3]$_2$ or [M(*O*-OC(NH_2)CH=CH_2)$_4$(H_2O)$_2$][NO_3]$_2$

2.2.1. Synthesis and characterization of the complex of Co(II) nitrate with acrylamide

The complex [Co(*O*-OC(NH_2)CH=CH_2)$_6$](NO_3)$_2$,**7**, was prepared from the hexahydrated salt dissolved in ethanol and triethyl orthoformate (for dehydration) to which an excess acrylamide in ethanol was added [73]. Single crystals of **7** were grown by slow vapor diffusion of diethyl ether into the reaction solution at room temperature.

The infrared spectrum of the complex **7** with non-coordinating nitrate anions shows an increase in the wavenumbers of asymmetric NH_2 stretching bands, and an unchanged or a slight shift towards higher wavenumbers in the symmetric NH_2 stretching bands from the bands in spectrum of the free ligand. Upon coordination of acrylamide to cobalt, the bands at 1673 cm^{-1} (which may have hidden the overlapped C=C stretching at 1650 cm^{-1}) and 1614 cm^{-1} in the spectrum of the free acrylamide move to lower wave numbers and split into three sharp bands, at 1667 cm^{-1}, 1620 cm^{-1}, and 1585 cm^{-1}. These shifts are just as expected for oxygen-coordinated ligands, although the C=O shift is small compared to the shifts observed for O-bound metal complexes with simple amides. The shifts in the C=O band are rather small because of the conjugation of the C=O bond with vinyl bond and the free electron pair on the nitrogen atom.

The complex crystallizes in the triclinic space group P1. The crystal structure of the complex **7** along with the atomic numbering scheme is shown in Figure **7**. Bond lengths and angles of the complex are summarized in Table **7**. The structure of **7** comprises octahedral cations [Co(AAm)$_6$]$^{2+}$ and nitrate anions. The octahedral environment of the metal centre includes six oxygen atoms of acrylamide molecules. The spread in the Co-O bond lengths (2.075, 2079 and 2.116 for Co-O) reflects non-equivalence of the ligands and energetic differences between the M-O bonds. Two of the weakly coordinated acrylamide molecules can be lost extremely readily, and exposure to water in the solvent should result in the formation of [Co(AAm)$_4$(H_2O)$_2$](NO_3)$_2$. The analysis of selected bond lengths and angles of different metal acrylamide complexes with nitrates show that the CO bond, the CN bond and the vinyl C=C bond are longer and the middle C-C bond is shorter in the coordinated ligands than the corresponding bond lengths in free acrylamide. The changes in the bond lengths and the associated frequency shifts are in agreement with the contribution of the charge-separated resonance forms in the acrylamide structure that are enhanced by oxygen atom coordination and intramolecular and intermolecular interaction of the coordinated acrylamide ligand, coordinated crystal water and anionic ligands.

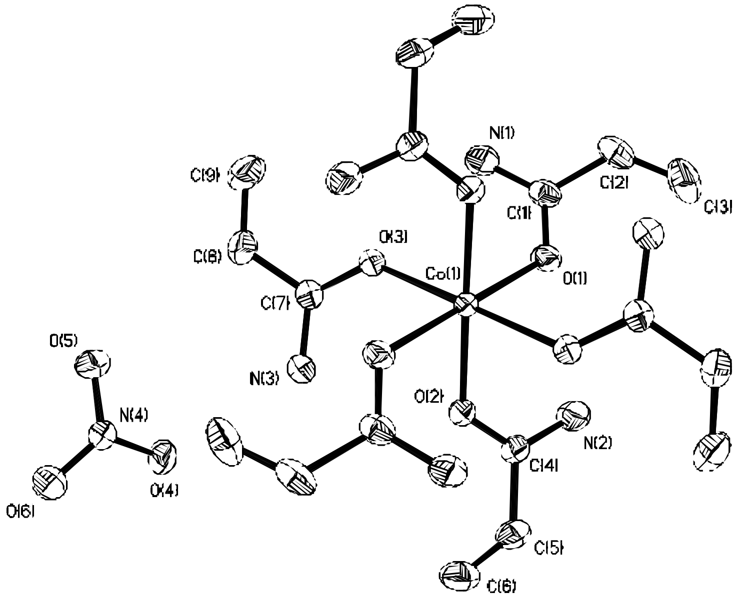


Figure **7**. Molecular structure of [Co(O-OC(NH$_2$)CH=CH$_2$)$_6$](NO$_3$)$_2$, **7**

Table **7**. Selected bond lengths (Å) and angles (°) for **7**

Co(1)-O(3)	2.075(9)	O(3)-Co(1)-O(2)	93.1(4)
Co(1)-O(2)	2.079(9)	O(3)-Co(1)-O(1)	92.7(4)
Co(1)-O(1)	2.117(1)	O(2)-Co(1)-O(1)	93.8(4)
O(1)-C(1)	1.257(2)	C(1)-O(1)-Co(1)	127.0(9)
O(2)-C(4)	1.257(2)	C(4)-O(2)-Co(1)	129.7(9)
O(3)-C(7)	1.257(2)	C(7)-O(3)-Co(1)	129.0(9)
N(1)-C(1)	1.312(2)	O(1)-C(1)-N(1)	122.5(1)
N(2)-C(4)	1.315(2)	O(1)-C(1)-C(2)	120.5(1)
N(3)-C(7)	1.314(2)	N(1)-C(1)-C(2)	116.9(1)
C(1)-C(2)	1,484(2)	C(3)-C(2)-C(1)	121.7(2)
C(2)-C(3)	1.307(3)	O(2)-C(4)-N(2)	122.8(1)
C(4)-C(5)	1.481(2)	O(2)-C(4)-C(5)	120.1(1)
C(5)-C(6)	1.310(3)	N(2)-C(4)-C(5)	117.0(1)
C(7)-C(8)	1.474(2)	C(6)-C(5)-C(4)	121.0(1)
C(8)-C(9)	1.313(3)	O(3)-C(7)-N(3)	123.1(1)
		O(3)-C(7)-C(8)	119.7(1)
		N(3)-C(7)-C(8)	117.1(1)
		C(9)-C(8)-C(7)	121.3(2)

2.2.2. Synthesis and characterization of the complex of Ni(II) nitrate with acrylamide

The complex $[Ni(O\text{-}OC(NH_2)CH{=}CH_2)_6](NO_3)_2$, **8**, was prepared from the hexahydrated salt $Ni(NO_3)_2{\cdot}6H_2O$, dissolved in ethanol and triethyl orthoformate (for dehydration) to which excess acrylamide in ethanol was added [73]. Single crystals of **8** were grown by slow vapor diffusion of diethyl ether into the reaction solution at room temperature.

The infrared spectrum of the complex **8** with non-coordinating nitrate anions shows an increase in the wavenumbers of the asymmetric NH_2 stretching bands, and an unchanged or a slight shift towards higher wavenumbers in the symmetric NH_2 stretching bands compared to the bands in the spectrum of the free ligand. Upon coordination of acrylamide to nickel, the bands at 1673 cm^{-1} (which may have hidden the overlapped C=C stretching at 1650 cm^{-1}) and 1614 cm^{-1} in the spectrum of the free acrylamide move to lower wavenumbers and split into three sharp bands at 1671 cm^{-1}, 1627 cm^{-1}, and 1587 cm^{-1}.

The complex crystallizes in the triclinic space group P1. The crystal structure of the complex **8** along with the atomic numbering scheme is shown in Figure **8**. Bond lengths and angles of the complex are summarized in Table **8**. The structure of **8** represents octahedral cations $[Ni(AAm)_6]^{2+}$ and nitrate anions. The octahedral environment of the metal centre includes bound oxygen atoms of the six acrylamide molecules. The spread in the Ni-O bond distances (2.044, 2.050 and 2.078 for Ni-O) reflects non-equivalence of the ligands and energetic differences between the M-O bonds.

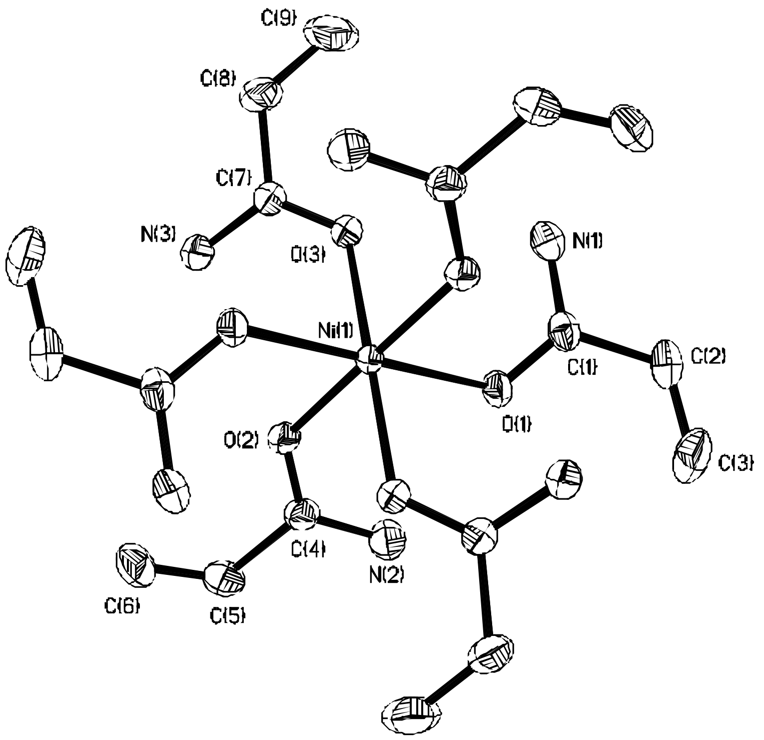


Figure **8**. Molecular structure of $[\mathrm{Ni}(\mathit{O}\text{-}\mathrm{OC(NH_2)CH{=}CH_2})_6](\mathrm{NO_3})_2$, **8**

Table **8**. Selected bond lengths (Å) and angles (°) for **8**

Ni(1)-O(3)	2.045(1)	O(3)-Ni(1)-O(2)	93.3(4)
Ni(1)-O(2)	2.050(1)	O(3)-Ni(1)-O(1)	92.8(5)
Ni(1)-O(1)	2.078(1)	O(2)-Ni(1)-O(1)	93.9(4)
O(1)-C(1)	1.258(2)	C(1)-O(1)-Ni(1)	127.4(1)
O(3)-C(7)	1.258(2)	C(7)-O(3)-Ni(1)	129.1(1)
O(2)-C(4)	1.255(2)	C(4)-O(2)-Ni(1)	130.0(1)
N(1)-C(1)	1.312(2)	C(1)-N(1)-H(1NA)	122.5(2)
N(1)-H(1NA)	0.83(3)	C(1)-N(1)-H(1NB)	114.1(2)
N(1)-H(1NB)	0.89(3)	H(1NA)-N(1)-H(1NB)	122(2)
N(2)-C(4)	1.318(2)	C(4)-N(2)-H(2NA)	123.0(2)
N(2)-H(2NA)	0.86(3)	C(4)-N(2)-H(2NB)	122.3(2)
N(2)-H(2NB)	0.87(3)	H(2NA)-N(2)-H(2NB)	115(2)
N(3)-C(7)	1.312(2)	C(7)-N(3)-H(3NA)	117.5(2)
N(3)-H(3NA)	0.80(3)	C(7)-N(3)-H(3NB)	121.7(2)
N(3)-H(3NB)	0.85(3)	H(3NA)-N(3)-H(3NB)	121(2)
C(1)-C(2)	1.484(2)	O(1)-C(1)-N(1)	122.8(1)
C(2)-C(3)	1.316(3)	O(1)-C(1)-C(2)	120.4(2)
C(2)-H(2)	0.93(2)	N(1)-C(1)-C(2)	116.8(1)
C(3)-H(3A)	0.94(3)	C(3)-C(2)-C(1)	121.6(2)
C(3)-H(3B)	1.00(3)	C(3)-C(2)-H(2)	120.6(1)
C(4)-C(5)	1.479(2)	C(1)-C(2)-H(2)	117.8(1)
C(5)-C(6)	1.312(3)	C(2)-C(3)-H(3A)	121.3(2)
C(5)-H(5)	0.92(3)	C(2)-C(3)-H(3B)	120.9(2)
C(6)-H(6A)	0.93(3)	H(3A)-C(3)-H(3B)	118(2)
C(6)-H(6B)	0.96(3)	O(2)-C(4)-N(2)	123.1(1)

C(7)-C(8)	1.479(2)	O(2)-C(4)-C(5)	120.1(1)
C(8)-C(9)	1.310(3)	N(2)-C(4)-C(5)	116.8(1)
C(8)-H(8)	0.91(3)	C(6)-C(5)-C(4)	121.0(2)
C(9)-H(9A)	0.89(4)	C(6)-C(5)-H(5)	125.2(2)
C(9)-H(9B)	0.96(4)	C(4)-C(5)-H(5)	113.7(2)
		C(5)-C(6)-H(6A)	123.8(2)
		C(5)-C(6)-H(6B)	122.0(2)
		H(6A)-C(6)-H(6B)	114(2)
		O(3)-C(7)-N(3)	123.5(1)
		O(3)-C(7)-C(8)	119.5(1)
		N(3)-C(7)-C(8)	116.99(1)
		C(9)-C(8)-C(7)	121.51(2)
		C(9)-C(8)-H(8)	124.2(2)
		C(7)-C(8)-H(8)	114.0(2)
		C(8)-C(9)-H(9A)	117(2)
		C(8)-C(9)-H(9B)	125(2)
		H(9A)-C(9)-H(9B)	119(3)

2.2.3. Synthesis and characterization of the complex of Zn(II) nitrate with acrylamide

The complex $[Zn(\textit{O}\text{-}OC(NH_2)CH{=}CH_2)_4(H_2O)_2](NO_3)_2$, **9**, was prepared from hexahydrated salt $Zn(NO_3)_2{\cdot}6H_2O$, dissolved in ethanol and triethyl orthoformate (for dehydration) to which excess acrylamide in ethanol was added [73]. A white solid was obtained by slow vapor diffusion of diethyl ether into the reaction solution at room temperature. Single crystals of **9** were obtained by recrystallizing the white solid obtained in the previous procedure by slow evaporation from methanol. In the case of the zinc complex, a structure with six O-coordinated acrylamide molecules might have formed at the beginning and should be the main structure of the complex in absolute ethanol. However, in an attempt to recrystallizing the complex from methanol a product which contains two coordinated water molecules was formed probably by replacing the weakly bonded acrylamide molecules by water from the solvent to give the aqua complex.

The infrared spectrum of complex **9** with non-coordinating nitrate anions and coordinated water shows an increase in the wavenumbers of the asymmetric NH_2 stretching bands, and an unchanged or a slight shift towards higher wavenumbers in the symmetric NH_2 stretching bands from the bands in spectrum of the free ligand. Upon coordination of acrylamide to zinc, the bands at 1673 cm^{-1} (which may have hidden the overlapped C=C stretching at 1650 cm^{-1}) and 1614 cm^{-1} in the spectrum of the free acrylamide move to lower wavenumbers and split into three sharp bands at 1667 cm^{-1}, 1615 cm^{-1}, and 1575 cm^{-1}. These bands correspond to shifts that are traditionally assigned to C=O, C=C, and NH_2 bending, respectively. The C=C and NH_2 bending shifts in **9** are significant. These shifts are just as expected for oxygen-coordinated ligands, although the C=O shift is small as compared to the shifts observed for O-bound metal complexes with simple amides. The shift of the C=O band is rather small because of the conjugation of the C=O bond with the vinyl bond and the free electron pair on the nitrogen atom.

The complex crystallizes in the triclinic space group P1. The crystal structure of complex **9** along with the atomic numbering scheme is shown in Figure **9**. Bond lengths and angles of the complex are summarized in Table **9**. The structure of **9** consists of octahedral cations $[Zn(AAm)_4(H_2O)_2]^{2+}$ and nitrate anions. The octahedral environment of the metal centre includes bound oxygen atoms of the four acrylamides and two water molecules. The long Zn-O(amide) bond length of 2.133Å is associated with the larger Zn-O-C angle of 139°, while the short Zn-O(amide) bond length of 2.076Å is associated with the smaller Zn-O-C angle of 135°. The Zn-O(water) bond lengths are 2.073Å.

An analysis of the bond lengths and angles of different metal acrylamide complexes with nitrates and comparison with the structural parameters of free acrylamide show that the CO bond, the CN bond and the vinyl C=C bond are longer and the middle C-C bond is shorter in the coordinated ligands than the corresponding bond lengths in the free acrylamide. The changes in the bond lengths and the associated frequency shifts are in agreement with the contribution of the charge-separated resonance forms in the acrylamide structure that are enhanced by oxygen atom coordination and intramolecular and intermolecular interaction of the coordinated acrylamide ligand with coordinated crystal water and anionic ligands.

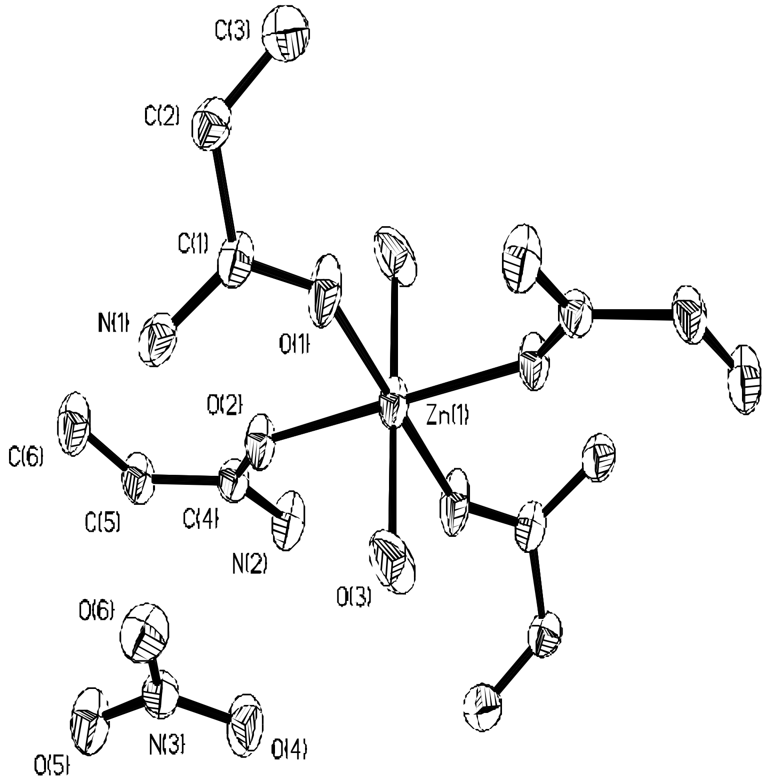


Figure **9**. Molecular structure of $[Zn(\mathit{O}\text{-}OC(NH_2)CH=CH_2)_4(H_2O)_2](NO_3)_2$, **9**

Table **9**. Selected bond lengths (Å) and angles (°) for **9**

Zn(1)-O(3)	2.073(2)	O(3)-Zn(1)-O(2)	90.0(1)
Zn(1)-O(2)	2.076(2)	O(3)-Zn(1)-O(1)	92.3(1)
Zn(1)-O(1)	2.133(2)	O(2)-Zn(1)-O(1)	88.07(7)
O(1)-C(1)	1.248(3)	C(1)-O(1)-Zn(1)	138.8(2)
O(2)-C(4)	1.258(3)	C(4)-O(2)-Zn(1)	134.8(2)
O(3)-H(3OA)	0.87(3)	Zn(1)-O(3)-H(3OA)	122(2)
O(3)-H(3OB)	0.70(4)	Zn(1)-O(3)-H(3OB)	125(4)
N(1)-C(1)	1.310(4)	H(3OA)-O(3)-H(3OB)	105(4)
N(1)-H(1NA)	0.69(3)	C(1)-N(1)-H(1NA)	123(3)
N(1)-H(1NB)	0.73(4)	C(1)-N(1)-H(1NB)	117(3)
N(2)-C(4)	1.318(3)	H(1NA)-N(1)-H(1NB)	120(4)
N(2)-H(2NA)	0.83(4)	C(4)-N(2)-H(2NA)	124(3)
N(2)-H(2NB)	0.72(5)	C(4)-N(2)-H(2NB)	127(4)
N(3)-O(4)	1.240(3)	H(2NA)-N(2)-H(2NB)	109(5)
N(3)-O(5)	1.243(3)	O(4)-N(3)-O(5)	120.3(2)
N(3)-O(6)	1.259(3)	O(4)-N(3)-O(6)	120.4(2)
C(1)-C(2)	1.483(3)	O(5)-N(3)-O(6)	119.3(2)
C(2)-C(3)	1.313(4)	O(1)-C(1)-N(1)	123.2(2)
C(2)-H(2)	0.87(4)	O(1)-C(1)-C(2)	120.3(2)
C(3)-H(3A)	1.00(4)	N(1)-C(1)-C(2)	116.5(2)
C(3)-H(3B)	0.95(4)	C(3)-C(2)-C(1)	122.5(3)
C(4)-C(5)	1.474(4)	C(3)-C(2)-H(2)	122(2)
C(5)-C(6)	1.309(4)	C(1)-C(2)-H(2)	116(2)

C(5)-H(5)	0.76(5)	C(2)-C(3)-H(3A)	121(2)
C(6)-H(6A)	0.90(4)	C(2)-C(3)-H(3B)	118(2)
C(6)-H(6B)	0.87(5)	H(3A)-C(3)-H(3B)	121(3)
		O(2)-C(4)-N(2)	122.4(2)
		O(2)-C(4)-C(5)	121.3(2)
		N(2)-C(4)-C(5)	116.3(2)
		C(6)-C(5)-C(4)	122.3(3)
		C(6)-C(5)-H(5)	119(4)
		C(4)-C(5)-H(5)	119(4)
		C(5)-C(6)-H(6A)	124(3)
		C(5)-C(6)-H(6B)	122(3)
		H(6A)-C(6)-H(6B)	114(4)

2.3. Syntheses and characterizations of complexes of metal(II) perchlorates and tetrafluoroborates with acrylamide, [M(*O*-OC(NH_2)CH=CH_2)$_6$][X]$_2$ (X = ClO_4 or BF_4)

2.3.1. Synthesis and characterization of the complex of Fe(II) perchlorate with acrylamide

Complex **10** was prepared by the previously published method from the hexahydrated perchlorate salt and the ligand in an absolute ethanol/triethyl orthoformate (for dehydration) solution in a 1:6 metal salt:ligand ratio (**Scheme 15**) [74]. Single crystals were grown by slow vapor diffusion of diethyl ether into the reaction solution at room temperature.

$$6L + M(H_2O)_6X_2 + 6HC(OC_2H_5)_3$$

$$\xrightarrow{C_2H_5OH} [ML_6]X_2 + 6HCO_2C_2H_5 + 12C_2H_5OH$$

Where L = $CH_2CHCONH_2$, X = ClO_4 or BF_4 and M = Mn, Fe, Co, Ni, Cu and Zn

Scheme 15. Synthesis of acrylamide complexes with metal perchlorates and tetrafluoroborates.

In the IR spectra of the perchlorate complexes the bands at 3354 $cm^{-1}$and 3184 cm^{-1} due to the NH_2 symmetric and NH_2 asymmetric stretching vibration of free acrylamide are either slightly shifted to higher wavenumbers or remain unchanged without significant splitting. A large triplet band at about 1110 cm^{-1} characterizes the perchlorates in the spectra of the complexes described here. The splitting of this broad band into three or more bands is in agreement with the picture of anions which are in weak intermolecular interactions with the amide NH_2 groups of the ligands at the outer coordination sphere. When acrylamide is bonded to a metal ion through its oxygen atom, a weakening of the C=O bond and a strengthening of the adjacent C-C bond must be expected, according to a description of resonance and inductive effects on chemical bonds. A shift to higher frequencies is also expected for the CO bending vibration, as this vibration will be “hindered” by bond formation. The magnitude of the shifts in these vibrations should be dependent on the electronegativity of the metal ion. In all the complexes described in this work the amide I band (consisting primarily the C=O vibration) is shifted from 1673 cm^{-1} in the free ligand and is splitting into two lower bands occurring at about 1664-1667 cm^{-1} and about 1620 cm^{-1}. The C-C stretching is shifted from about 1052 cm^{-1} in the free ligand to higher frequencies of about 1088-1091 cm^{-1} in all the perchlorate complexes.

The complex **10** crystallizes in the monoclinic space group $P2_1/c$. The single crystal X-ray structure of the complex described in this work demonstrates that the ligands are coordinated via the carbonyl oxygen. The crystal structure of the cation in the complex along with the atomic numbering scheme is shown in Figs. **10**. Bond lengths and angles of the complex are summarized in Table **10**. The structure consists of octahedral cations $[Fe(AAm)_6]^{2+}$ and non coordinating perchlorates in ionic forms. The anions do not participate in coordination with the divalent transition metal ions but take part in secondary interactions such as hydrogen bonds with the amide NH_2 groups at the outer coordination sphere.

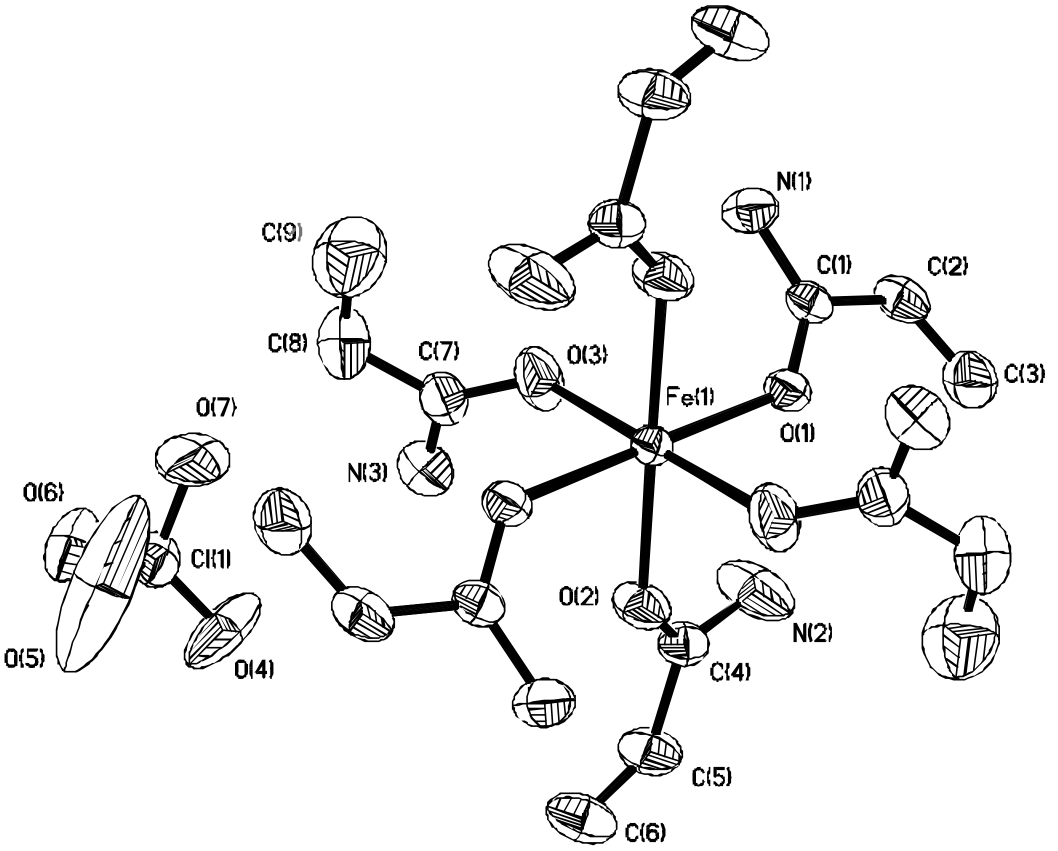


Figure **10**. Molecular structure of $[Fe(\mathit{O}\text{-}OC(NH_2)CH{=}CH_2)_6](ClO_4)_2$, **10**

The long Fe–O(amide) bond lengths of 2.143 and 1.128 Å are associated with the larger Fe–O–C angles of 136° for the equatorial ligands, while the short Fe–O(amide) bond length of 2.085 Å is associated with the smaller Fe–O–C angle of 135° for the ligands in the apical position. In general, the effect of coordination on structural parameters is paralleled by the changes in vibrational frequencies assigned as NH_2 stretching, amide I mode (consisting primarily of ?C=O), C=C stretching and amide II mode (consisting primarily of NH_2 bending and CN stretching). The changes in the bond lengths and the associated frequency shifts are in agreement with the contribution of the charge-separated resonance form in which the terminal carbon which exists as a carbonium ion is enhanced by oxygen coordination.

Table **10**. Selected bond lengths (Å) and angles (°) for **10**

Fe(1)-O(3)	2.085(2)
O(3)-C(7)	1.240(2)
N(3)-C(7)	1.311(3)
N(3)-H(3NA)	0.79(4)
N(3)-H(3NB)	0.86(5)
C(7)-C(8)	1.463(4)
C(8)-C(9)	1.303(5)
C(8)-H(8)	0.89(4)
C(9)-H(9A)	0.92(5)
C(9)-H(9B)	0.91(5)
Fe(1)-O(1)	2.143(1)
O(1)-C(1)	1.252(2)
N(1)-C(1)	1.318(2)
N(1)-H(1NA)	0.86(3)
N(1)-H(1NB)	0.89(3)
C(1)-C(2)	1.484(3)
C(2)-C(3)	1.305(3)
C(2)-H(2)	0.93(3)
C(3)-H(3A)	0.98(3)
C(3)-H(3B)	0.90(3)
Fe(1)-O(2)	2.128(1)
O(2)-C(4)	1.232(2)
N(2)-C(4)	1.308(3)
N(2)-H(2NA)	0.88(4)
N(2)-H(2NB)	0.80(4)
C(4)-C(5)	1.484(3)
C(5)-C(6)	1.296(4)
C(5)-H(5)	0.99(3)
C(6)-H(6A)	0.90(4)
C(6)-H(6B)	0.98(3)
Cl(1)-O(4)	1.295(17)
Cl(1)-O(7)	1.389(11)
Cl(1)-O(5)	1.446(15)
Cl(1)-O(6)	1.417(11)

O(3)-Fe(1)-O(2)	90.21(7)
O(3)-Fe(1)-O(1)	89.06(6)
O(2)-Fe(1)-O(1)	92.76(5)
C(7)-O(3)-Fe(1)	135.89(14)
C(7)-N(3)-H(3NA)	126(3)
C(7)-N(3)-H(3NB)	124(3)
H(3NA)-N(3)-H(3NB)	109(4)
O(3)-C(7)-N(3)	121.9(2)
O(3)-C(7)-C(8)	122.4(2)
N(3)-C(7)-C(8)	115.7(2)
C(9)-C(8)-C(7)	121.8(3)
C(9)-C(8)-H(8)	122(3)
C(7)-C(8)-H(8)	117(3)
C(8)-C(9)-H(9A)	119(3)
C(8)-C(9)-H(9B)	125(3)
H(9A)-C(9)-H(9B)	111(4)
C(1)-O(1)-Fe(1)	134.48(12)
C(1)-N(1)-H(1NA)	121(2)
C(1)-N(1)-H(1NB)	118.6(15)
H(1NA)-N(1)-H(1NB)	120(2)
O(1)-C(1)-N(1)	123.06(17)
O(1)-C(1)-C(2)	119.98(16)
N(1)-C(1)-C(2)	116.96(17)
C(3)-C(2)-C(1)	121.99(19)
C(3)-C(2)-H(2)	120.1(18)
C(1)-C(2)-H(2)	117.8(18)
C(2)-C(3)-H(3A)	119.9(18)
C(2)-C(3)-H(3B)	121.7(18)
H(3A)-C(3)-H(3B)	118(2)
C(4)-O(2)-Fe(1)	135.86(14)
C(4)-N(2)-H(2NA)	121(2)
C(4)-N(2)-H(2NB)	125(3)
H(2NA)-N(2)-H(2NB)	114(3)
O(2)-C(4)-N(2)	122.16(19)
O(2)-C(4)-C(5)	121.54(19)
N(2)-C(4)-C(5)	116.29(19)
C(6)-C(5)-C(4)	122.5(2)
C(6)-C(5)-H(5)	118.8(19)
C(4)-C(5)-H(5)	118.7(19)
C(5)-C(6)-H(6A)	127(2)
C(5)-C(6)-H(6B)	123(2)
H(6A)-C(6)-H(6B)	109(3)
O(4)-Cl(1)-O(7)	118.5(11)
O(4)-Cl(1)-O(5)	116.3(8)
O(7)-Cl(1)-O(5)	106.6(11)
O(4)-Cl(1)-O(6)	111.0(13)
O(7)-Cl(1)-O(6)	97.9(13)
O(5)-Cl(1)-O(6)	104.2(9)

2.3.2. Synthesis and characterization of the complex of Ni(II) perchlorate with acrylamide

Complex **11** was prepared by the previously described method from the hexahydrated perchlorate salt and the ligand in an absolute ethanol/triethyl orthoformate (for dehydration) solution in a 1:6 metal salt:ligand ratio [74]. Single crystals were grown by slow vapor diffusion of diethyl ether into the reaction solution at room temperature.

In the IR spectrum of the Ni(II) perchlorate complex, the band at 3383 cm^{-1} due to the NH_2 symmetric and NH_2 asymmetric stretching vibration of free acrylamide have either slightly shifted to higher wavenumbers or remain unchanged without significant splitting. A large triplet band at about 1110 cm^{-1} characterizes the perchlorate in the spectrum of the complex described in here. The splitting of this broad band into three or more bands is in agreement with the picture of anions which are in weak intermolecular interactions with the amide NH_2 groups of the ligands at the outer coordination sphere. The amide I band (consisting primarily of the C=O vibration) is shifted from 1673 cm^{-1} in the free ligand and is splitting into two lower bands occurring at about 1664 cm^{-1} and about 1625 cm^{-1}. The C-C stretching is shifted from about 1052 cm^{-1} in the free ligand to higher frequencies of about 1091 cm^{-1} in all the perchlorate complexes.

Complex **11** crystallizes in the triclinic space group P-1. The single crystal X-ray structure of the complex demonstrates that the ligands are coordinated via the carbonyl oxygen. The crystal structure of the cation in the complex along with the atomic numbering scheme is shown in Fig. **11**. Bond lengths and angles of the complex are summarized in Table **11**. The structure consists of octahedral cations $[M(AAm)_6]^{2+}$ and non-coordinating perchlorates in ionic forms. The anions do not participate in coordination with the divalent transition metal ions but take part in secondary interactions such as hydrogen bonds with the amide NH_2 groups at the outer coordination sphere.

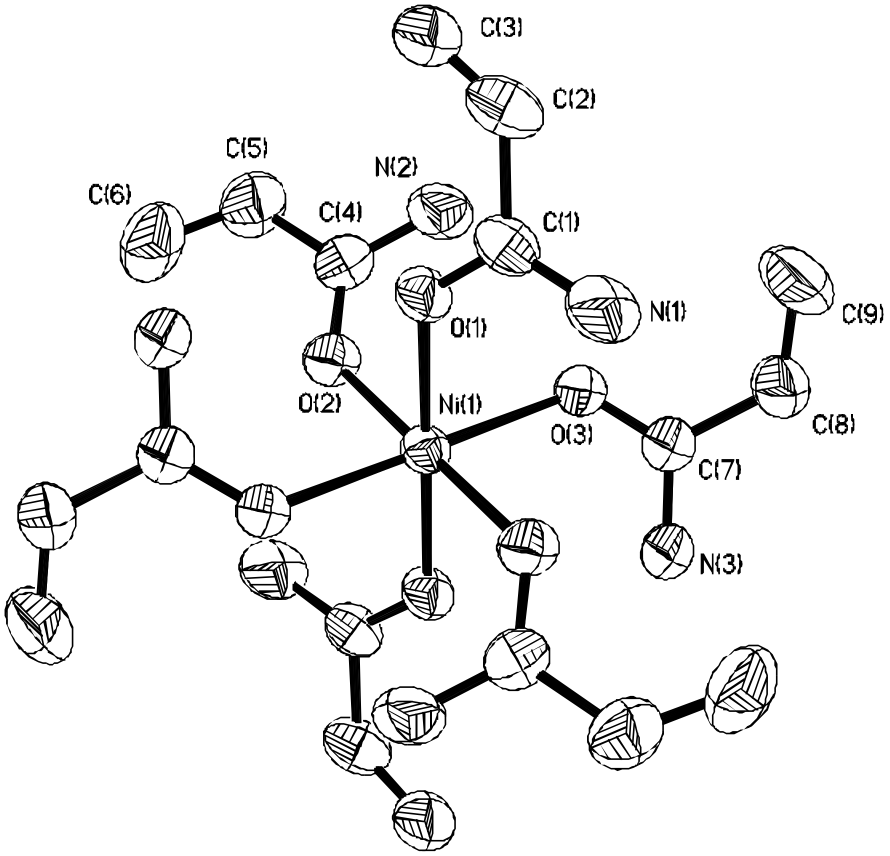


Figure **11**. Molecular structure of $[\mathrm{Ni}(\mathit{O}\text{-}\mathrm{OC(NH_2)CH{=}CH_2})_6](\mathrm{ClO_4})_2$, **11**

Table **11**. Selected bond lengths (Å) and angles (°) for **11**

Ni(1)-O(2)	2.0509(17)	O(2)-Ni(1)-O(1)	86.34(7)
O(2)-C(4)	1.261(3)	O(2)-Ni(1)-O(3)	93.61(7)
N(2)-C(4)	1.307(4)	O(1)-Ni(1)-O(3)	86.70(7)
N(2)-H(2NA)	0.76(3)		
N(2)-H(2NB)	0.69(4)	C(4)-O(2)-Ni(1)	130.35(18)
C(4)-C(5)	1.453(4)	C(4)-N(2)-H(2NA)	117(3)
C(5)-C(6)	1.306(6)	C(4)-N(2)-H(2NB)	123(3)
C(5)-H(5)	1.01(4)	H(2NA)-N(2)-H(2NB)	119(4)
C(6)-H(6A)	0.84(5)	O(2)-C(4)-N(2)	121.7(3)
C(6)-H(6B)	1.08(4)	O(2)-C(4)-C(5)	121.0(3)
		N(2)-C(4)-C(5)	117.2(3)
Ni(1)-O(3)	2.0713(18)	C(6)-C(5)-C(4)	122.0(3)
O(3)-C(7)	1.254(3)	C(6)-C(5)-H(5)	121(3)
N(3)-C(7)	1.302(4)	C(4)-C(5)-H(5)	117(3)
N(3)-H(3NA)	0.82(3)	C(5)-C(6)-H(6A)	123(3)
N(3)-H(3NB)	0.69(3)	C(5)-C(6)-H(6B)	127(2)
C(7)-C(8)	1.475(4)	H(6A)-C(6)-H(6B)	110(4)
C(8)-C(9)	1.289(6)		
C(8)-H(8)	1.06(6)	C(7)-O(3)-Ni(1)	130.18(17)
C(9)-H(9A)	??????	C(7)-N(3)-H(3NA)	120(2)
C(9)-H(9B)	0.86(6)	C(7)-N(3)-H(3NB)	114(3)
		H(3NA)-N(3)-H(3NB)	125(3)
		O(3)-C(7)-N(3)	122.7(3)
Ni(1)-O(1)	2.0501(17)	O(3)-C(7)-C(8)	121.0(3)
O(1)-C(1)	1.255(3)	N(3)-C(7)-C(8)	116.3(3)
N(1)-C(1)	1.301(4)	C(9)-C(8)-C(7)	122(2)
N(1)-H(1NA)	0.68(4)	C(9)-C(8)-H(8)	118(3)
N(1)-H(1NB)	0.72(3)	C(7)-C(8)-H(8)	120(4)
C(1)-C(2)	1.476(4)	C(8)-C(9)-H(9A)	?????
C(2)-C(3)	1.296(5)	C(8)-C(9)-H(9B)	127(4)
C(2)-H(2)	0.93(4)	H(9A)-C(9)-H(9B)	?????
C(3)-H(3A)	0.92(3)		
C(3)-H(3B)	0.92(4)	C(1)-O(1)-Ni(1)	129.78(18)
		C(1)-N(1)-H(1NA)	121(3)
Cl(1)-O(8)	1.397(3)	C(1)-N(1)-H(1NB)	120(3)
Cl(1)-O(9)	1.403(2)	H(1NA)-N(1)-H(1NB)	118(4)
Cl(1)-O(7)	1.420(3)	O(1)-C(1)-N(1)	122.9(3)
Cl(1)-O(10)	1.436(3)	O(1)-C(1)-C(2)	119.7(3)
		N(1)-C(1)-C(2)	117.4(3)
		C(3)-C(2)-C(1)	122.7(3)
		C(3)-C(2)-H(2)	120(2)
		C(1)-C(2)-H(2)	117(2)
		C(2)-C(3)-H(3A)	121.1(19)
		C(2)-C(3)-H(3B)	124(2)
		H(3A)-C(3)-H(3B)	115(3)
		O(8)-Cl(1)-O(9)	110.74(19)
		O(8)-Cl(1)-O(7)	108.8(3)
		O(9)-Cl(1)-O(7)	112.03(19)
		O(8)-Cl(1)-O(10)	105.8(2)
		O(9)-Cl(1)-O(10)	110.55(16)
		O(7)-Cl(1)-O(10)	108.67(18)

2.3.3. Synthesis and characterization of the complex of Zn(II) perchlorate with acrylamide

Complex **12** was prepared by the previously described method from the hexahydrated perchlorate salt and the ligand in an absolute ethanol/triethyl orthoformate (for dehydration) solution in a 1:6 metal salt:ligand ratio [74]. Single crystals were grown by slow vapor diffusion of diethyl ether into the reaction solution at room temperature.

In the IR spectrum of the Zn(II) perchlorate complex the bands at 3352 cm^{-1} and at 3180 cm^{-1}, due to the NH_2 symmetric and NH_2 asymmetric stretching vibration of free acrylamide, have either slightly shifted to higher wavenumbers or remain unchanged without significant splitting. A large triplet band at about 1110 cm^{-1} characterizes the perchlorate in the spectrum of the complex. The splitting of this broad band into three or more bands is in agreement with the picture of anions which are in weak intermolecular interactions with the amide NH_2 groups of the ligands at the outer coordination sphere. The amide I band (consisting primarily of the C=O vibration) is shifted from 1673 cm^{-1} in the free ligand and is splitting into two lower bands occurring at about 1664 cm^{-1} and about 1620 cm^{-1}. The C-C stretching is shifted from about 1052 cm^{-1} in the free ligand to higher frequencies of about 1089 cm^{-1} in the perchlorate complex.

The complex **12** crystallizes in the triclinic space group P-1. The single crystal X-ray structure of **12** demonstrates that the ligands are coordinated via the carbonyl oxygen. The crystal structure of the cation in the complex along with the atomic numbering scheme is shown in Fig. **12**. Bond lengths and angles of the complex are summarized in Table **12**. The structure displays octahedral cations $[Zn(AAm)_6]^{2+}$ and non-coordinating perchlorates in ionic forms. The anions do not participate in coordination with the zinc ion but take part in secondary interactions such as hydrogen bonds with the amide NH_2 groups at the outer coordination sphere.

Table **12**. Selected bond lengths (Å) and angles (°) for **12**

Zn(1)-O(3)	2.0847(11)	O(3)-Zn(1)-O(2)	86.23(4)
O(3)-C(7)	1.254(2)	O(3)-Zn(1)-O(1)	86.37(5)
N(3)-C(7)	1.314(3)	O(2)-Zn(1)-O(1)	92.58(5)
C(7)-C(8)	1.473(2)	C(7)-O(3)-Zn(1)	128.24(10)
C(8)-C(9)	1.301(4)	O(3)-C(7)-N(3)	122.23(15)
Zn(1)-O(1)	2.0971(12)	O(3)-C(7)-C(8)	120.69(17)
O(1)-C(1)	1.2562(19)	N(3)-C(7)-C(8)	117.07(17)
N(1)-C(1)	1.313(2)	C(9)-C(8)-C(7)	121.97(19)
C(1)-C(2)	1.475(2)	C(1)-O(1)-Zn(1)	127.66(11)
C(2)-C(3)	1.298(3)	O(1)-C(1)-N(1)	121.90(15)
Zn(1)-O(2)	2.0906(11)	O(1)-C(1)-C(2)	120.53(16)
O(2)-C(4)	1.2516(18)	N(1)-C(1)-C(2)	117.57(16)
N(2)-C(4)	1.310(2)	C(3)-C(2)-C(1)	122.0(2)
C(4)-C(5)	1.478(3)	C(4)-O(2)-Zn(1)	128.80(11)
C(5)-C(6)	1.293(3)	O(2)-C(4)-N(2)	123.08(15)
Cl(1)-O(7)	1.383(5)	O(2)-C(4)-C(5)	120.01(15)
Cl(1)-O(5)	1.4242(13)	N(2)-C(4)-C(5)	116.91(15)
Cl(1)-O(4)	1.4275(14)	C(6)-C(5)-C(4)	121.5(2)
Cl(1)-O(6)	1.501(6)	O(7)-Cl(1)-O(5)	113.9(3)
		O(7)-Cl(1)-O(4)	116.8(3)
		O(5)-Cl(1)-O(4)	110.72(8)
		O(7)-Cl(1)-O(6)	107.3(3)
		O(5)-Cl(1)-O(6)	102.6(4)
		O(4)-Cl(1)-O(6)	103.9(2)

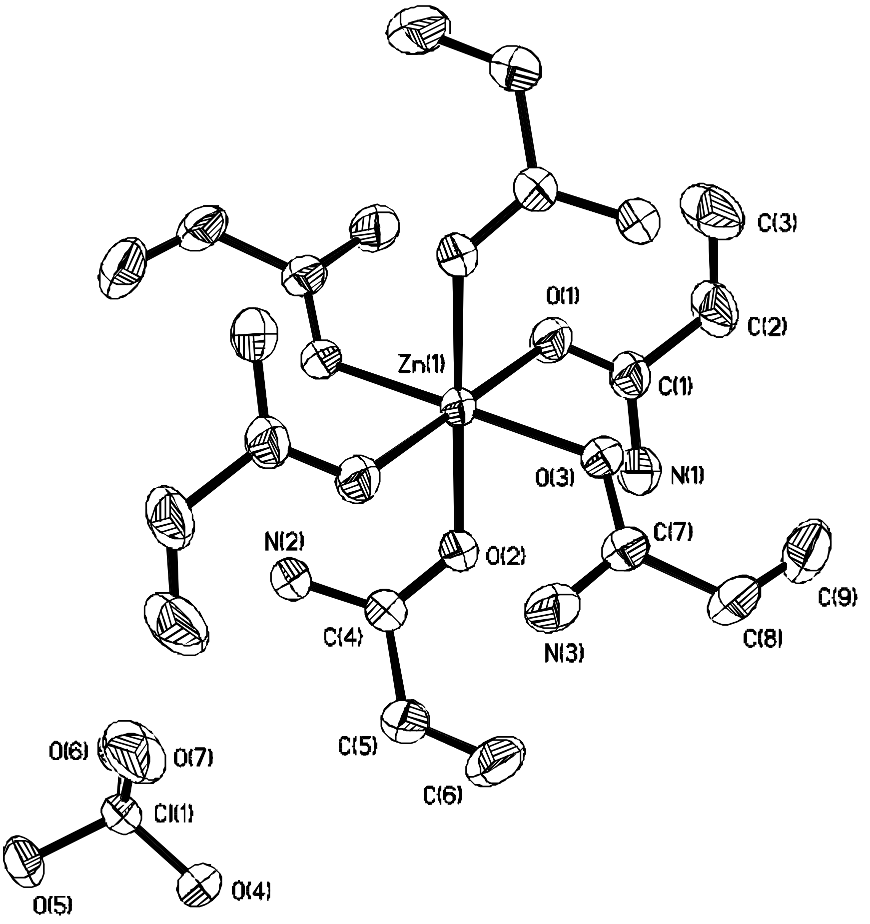


Figure **12**. Molecular structure of [Zn(O-OC(NH_2)CH=$CH_2$$)_6$]($ClO_4$$)_2$, **12**

2.3.4. Synthesis and characterization of the complex of Co(II) tetrafluoroborates with acrylamide

Complex **13** was prepared from the hexahydrated tetrafluoroborate salt and the ligand in an absolute ethanol/triethyl orthoformate (for dehydration) solution in a 1:6 metal salt:ligand ratio [74]. Single crystals were grown by slow vapor diffusion of diethyl ether into the reaction solution at room temperature.

In the IR spectrum of the Co(II) tetrafluoroborate complex the bands at 3351 cm^{-1} and at 3186 cm^{-1}, due to the NH_2 symmetric and NH_2 asymmetric stretching vibration of free acrylamide, have either slightly shifted to higher wavenumbers or remain unchanged without significant splitting. A broad band with multiple shoulders at about 1100 cm^{-1} and other two bands at ca. 534 and 522 cm^{-1} may be assigned to characterize the tetrafluoroborate ions. The splitting of this broad band into three or more bands is in agreement with the picture of anions which are in weak intermolecular interactions with the amide NH_2 groups of the ligands at the outer coordination sphere. The amide I band (primarily the C=O vibration) is shifted from 1673 cm^{-1} in the free ligand and is splitting into two lower bands occurring at about 1667 cm^{-1} and about 1615 cm^{-1}. The C-C stretching is shifted from about 1052 cm^{-1} in the free ligand to higher frequencies of about 1061 cm^{-1} in the tetrafluoroborate complex.

The complex **13** crystallizes in the triclinic space group P-1. The single crystal X-ray structure of the complex described in this work demonstrates that the ligands are coordinated via the carbonyl oxygen. The crystal structure of the complex along with the atomic numbering scheme is shown in Fig. **13**. Bond lengths and angles of the complex are summarized in Table **13**. The structure comprises octahedral cations $[Co(AAm)_6]^{2+}$ and non coordinating tetrafluoroborates in ionic forms. The anions do not participate in coordination with the divalent transition metal ions but take part in secondary interactions such as hydrogen bonds with the amide NH_2 groups at the outer coordination sphere.

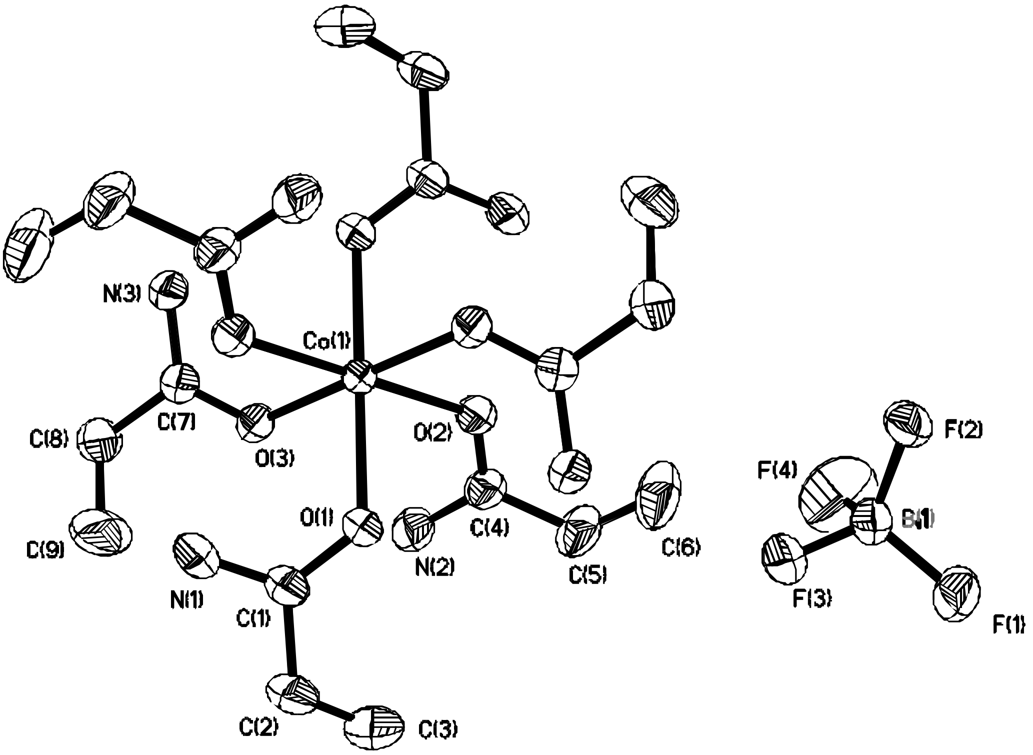


Figure **13**. Molecular structure of [Co(*O*-OC(NH_2)CH=CH_2)$_6$](BF_4)$_2$, **13**

Table **13**. Selected bond lengths (Å) and angles (°) for **13**

Co(1)-O(3)	2.0888(10)	O(1)-Co(1)-O(3)	85.78(4)
O(3)-C(7)	1.2524(17)	O(1)-Co(1)-O(2)	85.87(4)
N(3)-C(7)	1.3131(19)	O(3)-Co(1)-O(2)	93.16(4)
N(3)-H(3NA)	0.77(2)		
N(3)-H(3NB)	0.81(2)	C(7)-O(3)-Co(1)	129.32(9)
C(7)-C(8)	1.480(2)	C(7)-N(3)-H(3NA)	117.4(16)
C(8)-C(9)	1.305(3)	C(7)-N(3)-H(3NB)	123.1(15)
C(8)-H(8)	0.84(3)	H(3NA)-N(3)-H(3NB)	119(2)
C(9)-H(9A)	0.94(3)	O(3)-C(7)-N(3)	122.86(13)
C(9)-H(9B)	0.92(3)	O(3)-C(7)-C(8)	120.16(13)
		N(3)-C(7)-C(8)	116.97(14)
Co(1)-O(2)	2.0948(10)	C(9)-C(8)-C(7)	121.29(19)
O(2)-C(4)	1.2584(17)	C(9)-C(8)-H(8)	120.1(17)
N(2)-C(4)	1.313(2)	C(7)-C(8)-H(8)	118.6(17)
N(2)-H(2NA)	0.87(3)	C(8)-C(9)-H(9A)	120.5(19)
N(2)-H(2NB)	0.82(2)	C(8)-C(9)-H(9B)	122(2)
C(4)-C(5)	1.474(2)	H(9A)-C(9)-H(9B)	118(3)
C(5)-C(6)	1.304(3)		
C(5)-H(5)	0.76(2)		
C(6)-H(6A)	0.96(3)	C(4)-O(2)-Co(1)	127.98(9)
C(6)-H(6B)	0.91(3)	C(4)-N(2)-H(2NA)	124.5(16)
		C(4)-N(2)-H(2NB)	119.7(15)
Co(1)-O(1)	2.0856(9)	H(2NA)-N(2)-H(2NB)	115(2)
O(1)-C(1)	1.2529(16)	O(2)-C(4)-N(2)	122.04(14)
N(1)-C(1)	1.315(2)	O(2)-C(4)-C(5)	120.42(14)
N(1)-H(1NA)	0.87(2)	N(2)-C(4)-C(5)	117.54(14)
N(1)-H(1NB)	0.82(2)	C(6)-C(5)-C(4)	122.00(17)
C(1)-C(2)	1.482(2)	C(6)-C(5)-H(5)	122.9(18)

C(2)-C(3)	1.300(3)	C(4)-C(5)-H(5)	115.1(18)
C(2)-H(2)	0.90(3)	C(5)-C(6)-H(6A)	121.0(17)
C(3)-H(3A)	0.91(3)	C(5)-C(6)-H(6B)	122.0(18)
C(3)-H(3B)	0.94(3)	H(6A)-C(6)-H(6B)	117(2)
F(1)-B(1)	1.3847(19)	C(1)-O(1)-Co(1)	128.14(9)
F(2)-B(1)	1.418(11)	C(1)-N(1)-H(1NA)	119.6(15)
F(3)-B(1)	1.332(4)	C(1)-N(1)-H(1NB)	123.5(16)
F(4)-B(1)	1.420(4)	H(1NA)-N(1)-H(1NB)	116(2)
		O(1)-C(1)-N(1)	122.53(13)
		O(1)-C(1)-C(2)	120.66(14)
		N(1)-C(1)-C(2)	116.80(14)
		C(3)-C(2)-C(1)	121.56(16)
		C(3)-C(2)-H(2)	121.7(15)
		C(1)-C(2)-H(2)	116.6(15)
		C(2)-C(3)-H(3A)	122.2(16)
		C(2)-C(3)-H(3B)	122.3(19)
		H(3A)-C(3)-H(3B)	115(2)
		F(3)-B(1)-F(1)	115.3(3)
		F(3)-B(1)-F(4)	108.7(3)
		F(1)-B(1)-F(4)	104.7(4)
		F(3)-B(1)-F(2)	109.0(5)
		F(1)-B(1)-F(2)	112.0(5)
		F(4)-B(1)-F(2)	106.5(6)

2.3.5. Synthesis and characterization of the complex of Zn(II) tetrafluoroborates with acrylamide

Complex **14** was prepared analogously from the hexahydrated tetrafluoroborate salt and the ligand in an absolute ethanol/triethyl orthoformate (for dehydration) solution in a 1:6 metal salt:ligand ratio [74]. Single crystals were grown by slow vapour diffusion of diethyl ether into the reaction solution at room temperature.

In the IR spectrum of the Zn(II) tetrafluoroborate complex, the bands at 3350 cm^{-1} and at 3195 cm^{-1}, due to the NH_2 symmetric and NH_2 asymmetric stretching vibration of free acrylamide, have either slightly shifted to higher wavenumbers or remain unchanged without significant splitting. A broad band with multiple shoulders at about 1100 cm^{-1} and other two bands at ca. 534 and 522 cm^{-1} may be assigned to characterize the tetrafluoroborate ions in the spectrum of **14**. The splitting of this broad band into three or more bands is in agreement with the picture of anions which are in weak intermolecular interactions with the amide NH_2 groups of the ligands at the outer coordination sphere. The amide I band (primarily the C=O vibration) is shifted from 1673 cm^{-1} in the free ligand and is splitting into two lower bands occurring at about 1667 cm^{-1} and about 1615 cm^{-1}. The C-C stretching is shifted from about 1052 cm^{-1} in the free ligand to higher frequencies of about 1084 cm^{-1} in the tetrafluoroborate complex.

The complex **14** crystallizes in the triclinic space group P-1. The single crystal X-ray structure of the complex described in this work demonstrates that the ligands are coordinated via the carbonyl oxygen. The crystal structure of the complex along with the atomic numbering scheme is shown in Fig. **14**. Bond lengths and angles of the complex are summarized in Table **14**. The structure comprises octahedral cations $[Zn(AAm)_6]^{2+}$ and non-coordinating tetrafluoroborates in ionic forms. The anions do not participate in coordination with the divalent transition metal ions but take part in secondary interactions such as hydrogen bonds with the amide NH_2 groups at the outer coordination sphere.

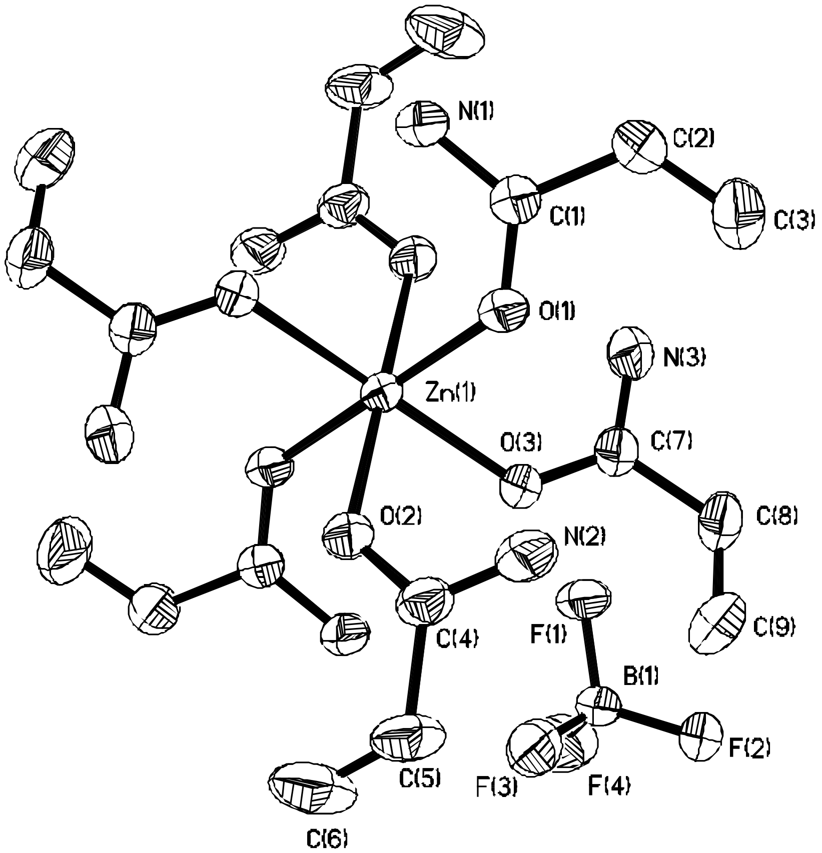


Figure **14**. Molecular structure of $[Zn(O\text{-}OC(NH_2)CH=CH_2)_6](BF_4)_2$, **14**

Table **14**. Selected bond lengths (Å) and angles (°) for **14**

Zn(1)-O(3)	2.0906(11)	O(3)-Zn(1)-O(1)	86.31(5)
O(3)-C(7)	1.252(2)	O(3)-Zn(1)-O(2)	86.39(5)
N(3)-C(7)	1.318(3)	O(1)-Zn(1)-O(2)	92.73(5)
N(3)-H(3NA)	0.80(3)		
N(3)-H(3NB)	0.95(3)	C(7)-O(3)-Zn(1)	128.08(11)
C(7)-C(8)	1.480(2)	C(7)-N(3)-H(3NA)	122(2)
C(8)-C(9)	1.303(4)	C(7)-N(3)-H(3NB)	120.1(19)
C(8)-H(8)	0.90(3)	H(3NA)-N(3)-H(3NB)	116(3)
C(9)-H(9A)	0.95(3)	O(3)-C(7)-N(3)	122.17(16)
C(9)-H(9B)	0.95(4)	O(3)-C(7)-C(8)	121.01(17)
		N(3)-C(7)-C(8)	116.83(16)
Zn(1)-O(1)	2.0943(12)	C(9)-C(8)-C(7)	121.40(19)
O(1)-C(1)	1.247(2)	C(9)-C(8)-H(8)	120.7(18)
N(1)-C(1)	1.317(2)	C(7)-C(8)-H(8)	117.9(19)
N(1)-H(1NA)	0.80(3)	C(8)-C(9)-H(9A)	124.5(17)
N(1)-H(1NB)	0.81(3)	C(8)-C(9)-H(9B)	120(2)
C(1)-C(2)	1.484(3)	H(9A)-C(9)-H(9B)	116(3)
C(2)-C(3)	1.305(4)		
C(2)-H(2)	0.85(4)	C(1)-O(1)-Zn(1)	129.23(10)
C(3)-H(3A)	0.86(4)	C(1)-N(1)-H(1NA)	116.4(19)
C(3)-H(3B)	0.95(5)	C(1)-N(1)-H(1NB)	119(2)
		H(1NA)-N(1)-H(1NB)	124(3)
Zn(1)-O(2)	2.0992(12)	O(1)-C(1)-N(1)	122.84(16)
O(2)-C(4)	1.256(2)	O(1)-C(1)-C(2)	120.37(16)
N(2)-C(4)	1.312(2)	N(1)-C(1)-C(2)	116.79(17)
N(2)-H(2NA)	0.82(3)	C(3)-C(2)-C(1)	120.9(2)
N(2)-H(2NB)	0.88(3)	C(3)-C(2)-H(2)	124(3)
C(4)-C(5)	1.483(3)	C(1)-C(2)-H(2)	114(3)
C(5)-C(6)	1.303(4)	C(2)-C(3)-H(3A)	121(3)
C(5)-H(5)	0.85(3)	C(2)-C(3)-H(3B)	120(3)
C(6)-H(6A)	0.92(3)	H(3A)-C(3)-H(3B)	119(3)
C(6)-H(6B)	0.93(3)		
		C(4)-O(2)-Zn(1)	127.69(11)
B(1)-F(4)	1.302(9)	C(4)-N(2)-H(2NA)	123.3(17)
B(1)-F(2)	1.383(2)	C(4)-N(2)-H(2NB)	118.9(18)
B(1)-F(1)	1.384(2)	H(2NA)-N(2)-H(2NB)	117(2)
B(1)-F(3)	1.455(9)	O(2)-C(4)-N(2)	122.22(16)
		O(2)-C(4)-C(5)	117.46(16)
		C(6)-C(5)-C(4)	122.0(2)
		C(6)-C(5)-H(5)	117.8(19)
		C(4)-C(5)-H(5)	120(2)
		C(5)-C(6)-H(6A)	121(2)
		C(5)-C(6)-H(6B)	126.4(18)
		H(6A)-C(6)-H(6B)	113(3)
		F(4)-B(1)-F(2)	118.6(6)
		F(4)-B(1)-F(1)	115.7(4)
		F(2)-B(1)-F(1)	110.77(16)
		F(4)-B(1)-F(3)	106.5(4)
		F(2)-B(1)-F(3)	102.2(5)
		F(1)-B(1)-F(3)	100.1(7)

2.4. Synthesis and characterization of a complex of Fe(II) with acrylamide stabilized by oxo-bridged diiron(III) chloride dianion.

The complex [Fe(O-OC(NH_2)CHCH_2)$_6$][Fe_2OCl_6] **15** was obtained by the reaction of a mixture of anhydrous $FeCl_2$ and anhydrous $FeCl_3$ with acrylamide (1:2:6 ratio) in 98% pure commercial nitromethane under nitrogen atmosphere. Although the reaction was carried out to prepare [Fe(O-OC(NH_2)CHCH_2)$_6$][$FeCl_4$]$_2$ as suggested for this kind of complexes with ligands containing a carbonyl group, an iron(II) complex cation stabilized by diiron(III) oxo anion was obtained. Both the cation in this system, [Fe(O-OC(NH_2)CHCH_2)$_6$]$^{2+}$, stabilized by perchlorates or tetraflouroborates, and the diiron(III) oxo anion are well known. The diiron(III) oxo anion is may be either the result of partial hydrolysis of $FeCl_3$ or [$FeCl_4$]$^-$ by small amounts of water in the nitromethane and/or by the nitromethane itself.

The molecular structure of **15** is shown in Figure 15 and selected bond lengths and angles are presented in Tables 15 and 16. The compound crystallizes in the cubic space group I-43d with a = 17. 8310(2) Å, ß = 90°, and V = 5669.27(11) Å^3 for Z = 12. The [Fe(*O*-OC(NH_2)CHCH_2)$_6$]$^{2+}$ ion contains six acrylamide molecules that bind to the iron(II) centre via the carbonyl oxygen atom (Fe–O 1.996 Å).

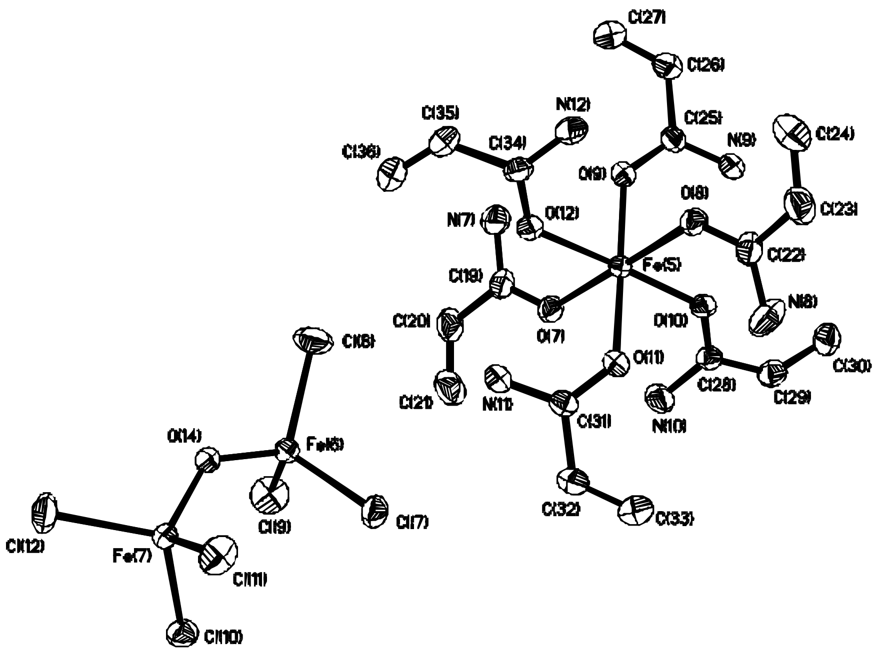


Figure 15. Crystal structure of [Fe(AAm)$_6$] [Fe_2OCl_6]. Thermal ellipsoids are drawn at the 50% probability level

The structure of the $[Cl_3Fe^{III}OFe^{III} Cl_3]^{2-}$ ion in the solid state is dependent on the nature of the counter cations. The iron(III) atoms, Fe(6) and Fe(7), have approximately tetrahedral geometries, with angles ranging from 107° to 110° and from 107° to 112° , respectively. The Fe-O-Fe bond angle is 133°. The $FeCl_3$ moieties are somewhat unevenly bridged by the oxo ion (Fe-O 1.7906 Å and 1.7909 Å), but the Fe-O distances are close to the average value observed for this anion (1.767(6) Å). The Fe-Cl bonds are close to the average observed for $[Cl_3Fe\text{-}O\text{-}FeCl_3]^{2-}$ ion (2.21Å). In addition the free Fe-Cl distances within each $FeCl_3$ moiety of the diiron anion are not equivalent: for both iron atoms, one of the three Fe-Cl bonds is somewhat longer than the other two.

Table 15. Selected bond lengths (Å) and angles (deg.) of the $[Fe(O\text{-}acrylamide)_6]^{2+}$ cations in $[Fe(O\text{-}acrylamide)_6][Fe_2OCl_6]$.

Fe(5)-O(9)	2.0848(15)	O(9)-Fe(5)-O(11)	179.23(6)
Fe(5)-O(11)	2.0919(15)	O(9)-Fe(5)-O(8)	87.60(6)
Fe(5)-O(8)	2.1235(14)	O(9)-Fe(5)-O(7)	93.32(6)
Fe(5)-O(12)	2.1285(14)	C(19)-O(7)-Fe(5)	130.10(13)
Fe(5)-O(7)	2.1312(14)	C(22)-O(8)-Fe(5)	130.68(13)
Fe(5)-O(10)	2.1353(13)	C(25)-O(9)-Fe(5)	129.53(13)
O(7)-C(19)	1.247(2)	C(19)-N(7)-H(7A)	120.7(18)
O(8)-C(22)	1.253(2)	C(19)-N(7)-H(7B)	117.6(18)
O(9)-C(25)	1.257(2)	H(7A)-N(7)-H(7B)	121(3)
N(7)-C(19)	1.322(3)	C(22)-N(8)-H(8A)	118(2)
N(7)-H(7A)	0.87(3)	C(22)-N(8)-H(8B)	121(2)
N(7)-H(7B)	0.90(3)	H(8A)-N(8)-H(8B)	121(3)
N(8)-C(22)	1.313(3)	C(25)-N(9)-H(9A)	121.6(16)
N(8)-H(8A)	0.83(3)	C(25)-N(9)-H(9B)	122.0(17)
N(8)-H(8B)	0.81(3)	H(9A)-N(9)-H(9B)	116(2)
N(9)-C(25)	1.310(2)	O(7)-C(19)-N(7)	122.24(19)
N(9)-H(9A)	0.82(2)	O(7)-C(19)-C(20)	120.7(2)
N(9)-H(9B)	0.83(3)	N(7)-C(19)-C(20)	117.10(19)
C(19)-C(20)	1.473(3)	C(21)-C(20)-C(19)	122.6(2)
C(20)-C(21)	1.295(4)	C(21)-C(20)-H(20)	122.0(19)
C(20)-H(20)	0.94(3)	C(19)-C(20)-H(20)	115.4(19)
C(21)-H(21A)	0.94(3)	C(20)-C(21)-H(21A)	122.0(17)
C(21)-H(21B)	0.98(3)	C(20)-C(21)-H(21B)	119.6(17)
C(22)-C(23)	1.465(3)	H(21A)-C(21)-H(21B)	118(2)
C(23)-C(24)	1.291(4)	O(8)-C(22)-N(8)	122.29(19)
C(23)-H(23)	0.98(3)	O(8)-C(22)-C(23)	122.14(19)
C(24)-H(24A)	0.99(3)	N(8)-C(22)-C(23)	115.5(2)
C(24)-H(24B)	1.00(4)	C(24)-C(23)-C(22)	122.3(2)
C(25)-C(26)	1.472(3)	C(24)-C(23)-H(23)	108.7(19)
C(26)-C(27)	1.306(3)	C(22)-C(23)-H(23)	128.9(19)
C(26)-H(26)	0.95(3)	C(23)-C(24)-H(24A)	120.4(15)
C(27)-H(27A)	0.95(3)	C(23)-C(24)-H(24B)	112(2)
C(27)-H(27B)	0.96(3)	H(24A)-C(24)-H(24B)	128(3)

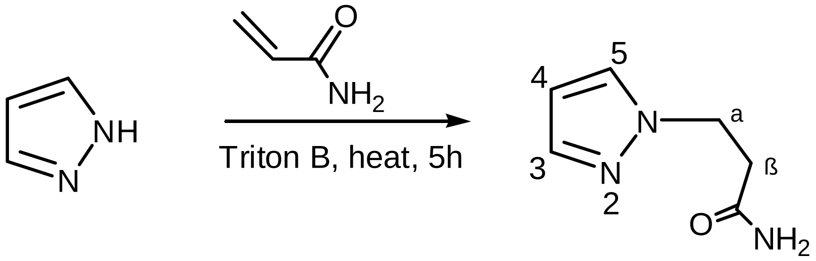
Table 16. Selected bond lengths (Å) and angles (deg.) of the $[Fe_2OCl_6]^{2-}$ anion in $[Fe(O\text{-acrylamide})_6][Fe_2OCl_6]$.

Fe(6)-O(14)	1.7906(12)	O(14)-Fe(6)-Cl(9)	109.65(5)
Fe(6)-Cl(9)	2.1856(7)	O(14)-Fe(6)-Cl(8)	107.51(5)
Fe(6)-Cl(8)	2.1938(8)	Cl(9)-Fe(6)-Cl(8)	113.37(4)
Fe(6)-Cl(7)	2.2338(7)	O(14)-Fe(6)-Cl(7)	107.86(5)
Fe(7)-O(14)	1.7909(14)	Cl(9)-Fe(6)-Cl(7)	107.95(3)
Fe(7)-Cl(11)	2.1896(7)	Cl(8)-Fe(6)-Cl(7)	110.37(3)
Fe(7)-Cl(12)	2.1897(7)	O(14)-Fe(7)-Cl(11)	109.41(5)
Fe(7)-Cl(10)	2.2367(7)	O(14)-Fe(7)-Cl(12)	107.06(4)
		Cl(11)-Fe(7)-Cl(12)	112.90(3)
		O(14)-Fe(7)-Cl(10)	108.97(5)
		Cl(11)-Fe(7)-Cl(10)	108.91(3)
		Cl(12)-Fe(7)-Cl(10)	109.51(3)
		Fe(6)-O(14)-Fe(7)	133.02(7)

3. Synthesis and characterization of complexes of metal(II) chlorides with the acrylamide-based ligand N- pyrazolylpropanamide

3.1. Synthesis and characterization of N-pyrazolylpropanamide

The ligand **16** was prepared by Michael addition of pyrazole to acrylamide in the presence of trimethylbenzylammonium hydroxide (Triton B, 40% in methanol) as a basic catalyst (Scheme **16**). After about five hours of reflux in a boiling water bath the ligand was obtained in good yield (94%). Single crystals of the compound suitable for X-ray diffraction analysis were obtained from dichloromethane/ether solution in a 4:1 ratio. Recently, de la Cruz et al. [75] have reported the synthesis and spectroscopic properties of several N-azolylpropanamides including N-pyrazolylpropanamide (Yield: 82%) obtained from acrylamide and the corresponding azoles using pyridine-sodium methoxide as a basic catalyst. Here trimethylbenzylammonium hydroxide has been used as a basic catalyst in a high-yield synthesis and the compound was recrystallized from dichloromethane/ether solution in 4:1 ratio which also afforded single crystals suitable for X-ray diffraction analysis.



Scheme 16. The synthesis of N-pyrazolylpropanamide

The ^{1}H and ^{13}C NMR data for **16** are reported in Table 17 and Table 18 respectively. The chemical shifts and coupling constants are consistent with the spectral data reported for this ligand [75]. The infrared spectrum of the ligand shows characteristic bands of the amide group. Fundamental bands which are observed at 3374 cm^{-1} and 3170 cm^{-1} can be assigned to NH_2 asymmetric and NH_2 symmetric stretching, respectively. The doublets which are observed at 1690 cm^{-1} and 1666 cm^{-1} are the amide I absorption bands which is mainly due to the CO absorption.

Table 17. ^{1}H NMR spectral data for N-pyrazolylpropanamide in Me_2SO-d_6 at 20°C*

Chemical shift (ppm)	Coupling Constants (Hz)	Assignments+
2.59	$^{3}J = 6Hz$	H-ß
4.28	$^{3}J = 6Hz$	H-a
6.18	-	H-4
6.89	broad singlet	NH_2
7.40	-	H-3
7.60	-	H-5

Table 18. ^{13}C NMR spectral data for N-pyrazolylpropanamide in Me_2SO-d_6 at 20°C*

Chemical shift (ppm)	Coupling Constants (Hz)	Assignments+
35.69	$^{1}J = 126.3$ $^{2}J = 7.2$	C-ß
47.36	$^{1}J = 141.3$ $^{2}J = 5.0$	C-a
104.92	$^{1}J = 174.5$ $^{2}J = 9.4$ $^{2}J = 10.3$	C-4
129.87	$^{1}J = 184.4$ $^{2}J = 7.7$	C-5
138.58	$^{1}J = 183.5$ $^{2}J = 7.8$ $^{3}J = 7.8$	C-3
171.72	$^{2}J = 4.0$	C=O

*Shifts downfield from TMS +Numbering in scheme 2

The ligand **16** crystallizes in the monoclinic space group, P2($_1$)/n. The molecule consists of a conjugated N-propylamide moiety ($N\text{-}{}^{a}CH_2{}^{\text{ß}}CH_2C(O)NH_2$) which can adopt conformation changes at the ß-carbon suggesting that the bidentate ligand is flexible and can accommodate metals for coordination. However, the amide moiety is planar and remains unperturbed even after complexation. The C=O and C-NH$_2$ bond lengths of the amide group are 1.2286(10) Å and 1.33281(11) Å, respectively. The molecular structure together with the coordinate atom labelling is shown in Figure **16**. The bond lengths in the pyrazolyl group of the compound **16** are more or less equivalent suggesting that the ring is highly conjugated and that there is less interaction between the coordinating nitrogen in the ring and the amide moiety. Selected bond lengths and angles of **16** are summarized in Table **19**.

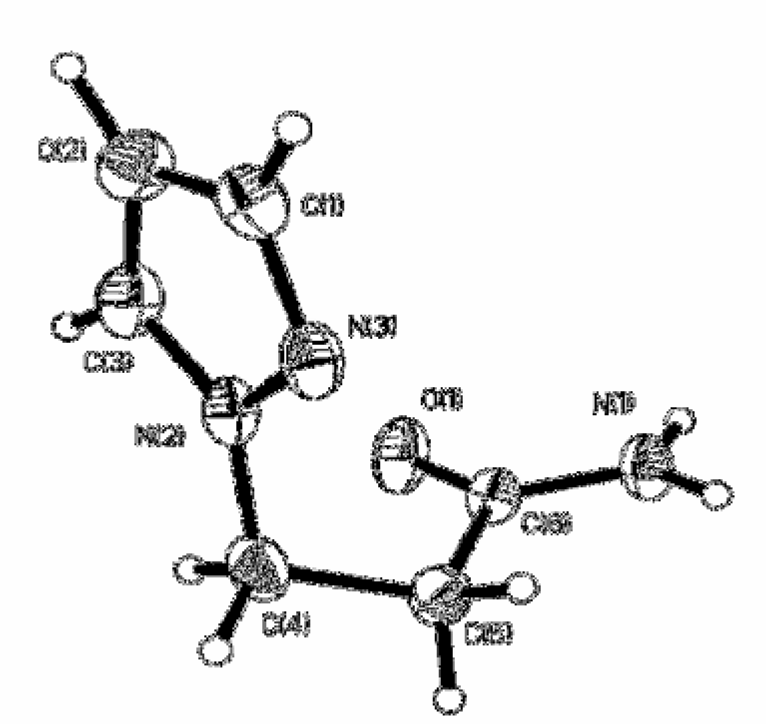


Figure **16**. Crystal structure for ligand **16** with atomic labelling. Thermal ellipsoids are drawn at the 50% probability level.

Table **19**. Selected bond lengths (Å) and angles (°) for **16**

O(1)-C(6)	1.2286(10)	C(6)-N(1)-H(1N)	120.4(10)
N(1)-C(6)	1.3281(11)	C(6)-N(1)-H(2N)	120.0(9)
N(1)-H(1N)	0.869(15)	H(1N)-N(1)-H(2N)	119.6(13)
N(1)-H(2N)	0.883(14)	C(3)-N(2)-N(3)	111.86(8)
N(2)-C(3)	1.3445(12)	C(3)-N(2)-C(4)	127.62(8)
N(2)-N(3)	1.3486(10)	N(3)-N(2)-C(4)	120.48(7)
N(2)-C(4)	1.4548(12)	C(1)-N(3)-N(2)	104.58(7)
N(3)-C(1)	1.3314(13)	N(3)-C(1)-C(2)	111.66(9)
C(1)-C(2)	1.3932(13)	N(3)-C(1)-H(1)	119.3(8)
C(1)-H(1)	0.975(13)	C(2)-C(1)-H(1)	128.9(8)
C(2)-C(3)	1.3683(15)	C(3)-C(2)-C(1)	104.59(9)
(2)-H(2)	0.971(13)	C(3)-C(2)-H(2)	126.7(8)
C(3)-H(3)	0.938(14)	C(1)-C(2)-H(2)	128.6(8)
(4)-C(5)	1.5139(12)	N(2)-C(3)-C(2)	107.31(8)
(4)-H(4A)	0.980(12)	N(2)-C(3)-H(3)	119.6(9)
(4)-H(4B)	0.981(12)	C(2)-C(3)-H(3)	132.8(9)
(5)-C(6)	1.5139(11)	N(2)-C(4)-C(5)	112.40(7)
(5)-H(5A)	0.987(13)	N(2)-C(4)-H(4A)	105.3(7)
(5)-H(5B)	1.011(13)	C(5)-C(4)-H(4A)	110.6(7)
		N(2)-C(4)-H(4B)	109.4(7)
		C(5)-C(4)-H(4B)	110.1(7)
		H(4A)-C(4)-H(4B)	108.8(10)
		C(6)-C(5)-C(4)	113.44(7)
		C(6)-C(5)-H(5A)	106.1(7)
		C(4)-C(5)-H(5A)	108.8(7)
		C(6)-C(5)-H(5B)	110.7(7)
		C(4)-C(5)-H(5B)	110.3(7)
		H(5A)-C(5)-H(5B)	107.3(10)
		O(1)-C(6)-N(1)	123.06(8)
		O(1)-C(6)-C(5)	121.47(7)
		N(1)-C(6)-C(5)	115.43(7)

3.2. Synthesis and characterization of the complex of Co(II) chloride with N-pyrazolylpropanamide

The novel coordination compound [$Co_3L_4Cl_6$] (L = N-pyrazolylpropanamide) **17** was prepared by dissolving hexahydrated cobalt(II) chloride in hot absolute ethanol, followed by adding a few millilitres of triethyl orthoformate for dehydration. To this solution, a solution of the ligand N-pyrazolylpropanamide in absolute ethanol was added. The complex crystallized after the reaction mixture was allowed to stand at room temperature for a few days. The crystal structure of complex **17** along with the atomic numbering scheme is shown in Figure **17**. Selected bond lengths and angles of the cobalt complex **17** are summarized in Table **20**.

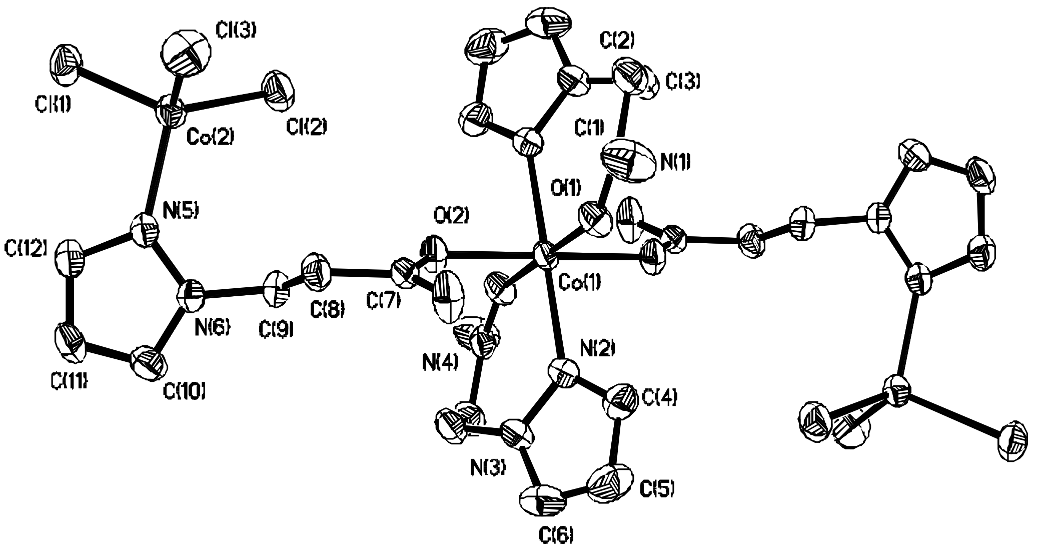


Figure **17**. Crystal structure for complex **17** with atomic labelling. Thermal ellipsoids are drawn at the 50% probability level.

Table 20. Selected bond lengths [Å] and angles [deg] for **17**

Co(1)-N(2)	2.091(3)	N(2)-Co(1)-O(2)	92.29(10)
Co(1)-O(2)	2.115(2)	N(2)-Co(1)-O(1)	88.17(10)
Co(1)-O(1)	2.119(2)	O(2)-Co(1)-O(1)	90.78(9)
Co(2)-N(5)	2.030(3)	N(5)-Co(2)-Cl(3)	110.47(8)
Co(2)-Cl(3)	2.2338(12)	N(5)-Co(2)-Cl(1)	101.71(8)
Co(2)-Cl(1)	2.2763(10)	Cl(3)-Co(2)-Cl(1)	113.62(5)
Co(2)-Cl(2)	2.2835(13)	N(5)-Co(2)-Cl(2)	112.63(8)
O(1)-C(1)	1.241(4)	Cl(3)-Co(2)-Cl(2)	109.21(5)
O(2)-C(7)	1.235(4)	Cl(1)-Co(2)-Cl(2)	109.10(5)
N(1)-C(1)	1.315(5)	C(1)-O(1)-Co(1)	143.5(2)
N(1)-H(1NA)	0.87(5)	C(7)-O(2)-Co(1)	132.82(19)
N(1)-H(1NB)	0.78(4)	C(1)-N(1)-H(1NA)	122(3)
N(2)-C(4)	1.325(4)	C(1)-N(1)-H(1NB)	120(3)
N(2)-N(3)	1.357(4)	H(1NA)-N(1)-H(1NB)	119(5)
N(3)-C(6)	1.345(5)	C(4)-N(2)-N(3)	105.1(3)
N(4)-C(7)	1.318(4)	C(4)-N(2)-Co(1)	126.4(2)
N(4)-H(4NA)	0.83(4)	N(3)-N(2)-Co(1)	127.8(2)
N(4)-H(4NB)	0.90(5)	C(6)-N(3)-N(2)	110.3(3)
N(5)-C(12)	1.341(4)	C(7)-N(4)-H(4NA)	120(3)
N(5)-N(6)	1.349(4)	C(7)-N(4)-H(4NB)	119(3)
N(6)-C(10)	1.338(4)	H(4NA)-N(4)-H(4NB)	121(4)
C(1)-C(2)	1.499(5)	C(12)-N(5)-N(6)	105.2(3)
C(2)-C(3)	1.510(5)	C(12)-N(5)-Co(2)	123.4(2)
C(2)-H(2A)	0.95(4)	N(6)-N(5)-Co(2)	131.46(19)
C(2)-H(2B)	0.84(5)	C(10)-N(6)-N(5)	111.1(3)
C(3)-H(3A)	0.92(4)	O(1)-C(1)-N(1)	120.3(3)
C(3)-H(3B)	0.97(5)	O(1)-C(1)-C(2)	123.8(3)
C(4)-C(5)	1.380(5)	N(1)-C(1)-C(2)	116.0(3)
C(4)-H(4)	0.9300	C(1)-C(2)-C(3)	115.6(3)
C(5)-C(6)	1.351(6)	C(1)-C(2)-H(2A)	105(3)
C(5)-H(5)	0.9300	C(3)-C(2)-H(2A)	107(3)
C(6)-H(6)	0.9300	C(1)-C(2)-H(2B)	101(3)
C(7)-C(8)	1.497(4)	C(3)-C(2)-H(2B)	114(3)
C(8)-C(9)	1.508(5)	H(2A)-C(2)-H(2B)	113(4)
C(8)-H(8A)	0.95(4)	C(2)-C(3)-H(3A)	112(2)
C(8)-H(8B)	0.83(4)	C(2)-C(3)-H(3B)	110(3)
C(9)-H(9A)	0.90(4)	H(3A)-C(3)-H(3B)	102(3)
C(9)-H(9B)	0.91(4)	N(2)-C(4)-C(5)	111.4(3)
C(10)-C(11)	1.362(5)	N(2)-C(4)-H(4)	124.3
C(10)-H(10)	0.9300	C(5)-C(4)-H(4)	124.3
C(11)-C(12)	1.378(5)	C(6)-C(5)-C(4)	105.1(3)
C(11)-H(11)	0.9300	C(6)-C(5)-H(5)	127.4
C(12)-H(12)	0.9300	C(4)-C(5)-H(5)	127.4
N(7)-C(13)	1.105(6)	N(3)-C(6)-C(5)	108.1(3)
C(13)-C(14)	1.443(7)	N(3)-C(6)-H(6)	125.9
C(14)-H(14A)	0.9600	C(5)-C(6)-H(6)	125.9
C(14)-H(14B)	0.9600	O(2)-C(7)-N(4)	123.5(3)
C(14)-H(14C)	0.9600	O(2)-C(7)-C(8)	120.2(3)
		N(4)-C(7)-C(8)	116.3(3)
		C(7)-C(8)-C(9)	112.5(3)
		C(7)-C(8)-H(8A)	111(2)
		C(9)-C(8)-H(8A)	112(2)
		C(7)-C(8)-H(8B)	108(3)
		C(9)-C(8)-H(8B)	110(3)
		H(8A)-C(8)-H(8B)	103(3)
		C(8)-C(9)-H(9A)	111(2)
		C(8)-C(9)-H(9B)	114(2)
		H(9A)-C(9)-H(9B)	104(3)
		N(6)-C(10)-C(11)	107.5(3)

N(6)-C(10)-H(10)	126.3
C(11)-C(10)-H(10)	126.3
C(10)-C(11)-C(12)	105.6(3)
C(10)-C(11)-H(11)	127.2
C(12)-C(11)-H(11)	127.2
N(5)-C(12)-C(11)	110.5(3)
N(5)-C(12)-H(12)	124.7
C(11)-C(12)-H(12)	124.7
N(7)-C(13)-C(14)	177.9(6)
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5

3.3. Synthesis and characterization of the complex of Cu(II) chloride with N-pyrazolylpropanamide

The coordination compound [CuL_2Cl_2] (L = N-pyrazolylpropanamide) **18** was prepared by dissolving dihydrated copper(II) chloride in hot absolute ethanol, followed by adding a few millilitres of triethyl orthoformate for dehydration. To this solution, a solution of the ligand N-pyrazolylpropanamide in absolute ethanol was added. The complex crystallized after the reaction mixture was allowed to stand at room temperature for a few days.

Comparison of the IR spectra of the free ligand and the complex revealed a significant decrease to lower wavenumbers at 1660 cm^{-1} and 1601 cm^{-1} in the CO absorptions and an increase in the positions of the NH_2 vibrations to higher wavenumbers at 3447 cm^{-1} and 3287 cm^{-1} upon complexation. This is in good agreement with the shifts observed in metal-amide complexes upon oxygen coordination of the carbonyl oxygen of the amide group.

The crystal structure of **18** along with the atomic numbering scheme is shown in Figure **18**. The coordination geometry of the metal centre in the complex involves an octahedral structure with two chelate ligands in the equatorial positions and two chlorides in the apical positions. Each ligand is coordinated to the metal via the coordinating nitrogen of the pyrazolyl group and the carbonyl oxygen of the amide group in a seven-membered chelate ring. The bond lengths of the N(3)-Cu(1) and O(1)-Cu(1) are 1.991(2) Å and 2.441(2) Å, respectively. The bond lengths in the pyrazolyl group of the compound **18** are elongated and less conjugated compared to the bond lengths in the free ligand due to coordination of the nitrogen of the pyrazolyl group of the ligand to the metal centre. Only a slight increase in the bond lengths of the C=O and C-N bonds of the amide group has been observed upon coordination. Selected bond lengths and angles of the copper complex **18** are summarized in Table **21**.

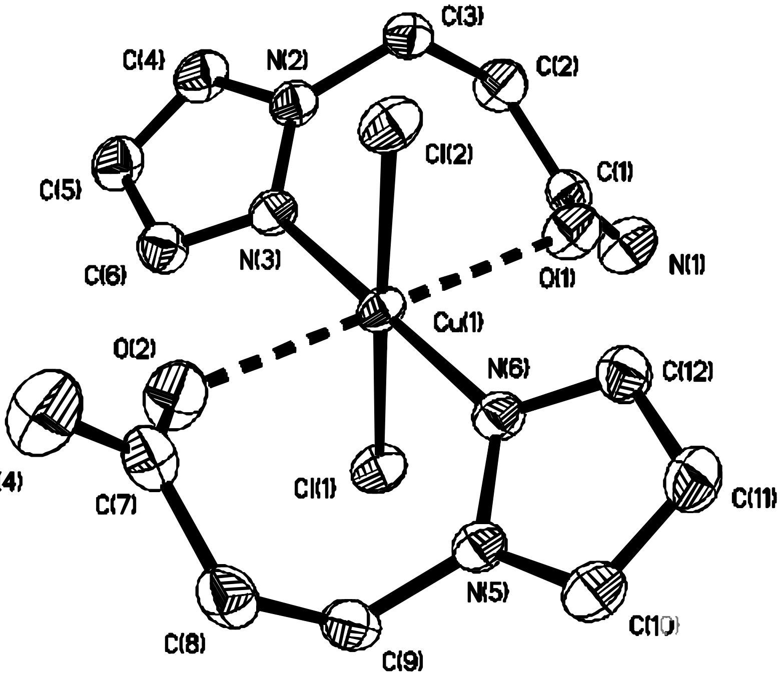


Figure **18**. Crystal structure for complex **18** with atomic labelling. Thermal ellipsoids are drawn at the 50% probability level.

Table 21. Selected bond lengths [Å] and angles [deg] for **18**

Cu(1)-N(6)	1.989(2)	N(3)-Cu(1)-Cl(2)	92.45(7)
Cu(1)-N(3)	1.991(2)	N(3)-Cu(1)-Cl(1)	87.35(7)
Cu(1)-Cl(2)	2.3233(9)	Cl(2)-Cu(1)-Cl(1)	178.43(3)
Cu(1)-Cl(1)	2.3466(9)	C(1)-N(1)-H(1NA)	116(3)
O(1)-C(1)	1.236(4)	C(1)-N(1)-H(1NB)	113(4)
O(2)-C(7)	1.224(4)	H(1NA)-N(1)-H(1NB)	130(5)
N(1)-C(1)	1.336(4)	C(4)-N(2)-N(3)	110.3(2)
N(1)-H(1NA)	0.86(5)	C(4)-N(2)-C(3)	125.9(3)
N(1)-H(1NB)	0.86(7)	N(3)-N(2)-C(3)	123.6(2)
N(2)-C(4)	1.351(4)	C(6)-N(3)-N(2)	106.2(2)
N(2)-N(3)	1.358(3)	C(6)-N(3)-Cu(1)	124.5(2)
N(2)-C(3)	1.465(4)	N(2)-N(3)-Cu(1)	129.30(18)
N(3)-C(6)	1.335(3)	O(1)-C(1)-N(1)	121.7(3)
N(4)-C(7)	1.338(4)	O(1)-C(1)-C(2)	122.8(3)
N(4)-H(4NA)	0.90(4)	N(1)-C(1)-C(2)	115.5(3)
N(4)-H(4NB)	0.96(4)	C(1)-C(2)-C(3)	114.3(3)
N(5)-C(10)	1.340(4)	C(1)-C(2)-H(2A)	111(3)
N(5)-N(6)	1.359(3)	C(3)-C(2)-H(2A)	107(3)
N(5)-C(9)	1.464(4)	C(1)-C(2)-H(2B)	104(4)
N(6)-C(12)	1.338(4)	C(3)-C(2)-H(2B)	116(4)
C(1)-C(2)	1.508(5)	H(2A)-C(2)-H(2B)	104(5)
C(2)-C(3)	1.521(5)	N(2)-C(3)-C(2)	113.4(2)
C(2)-H(2A)	0.97(5)	N(2)-C(3)-H(3A)	106(2)
C(2)-H(2B)	0.88(6)	C(2)-C(3)-H(3A)	114(2)
C(3)-H(3A)	0.94(3)	N(2)-C(3)-H(3B)	108(2)

C(3)-H(3B)	1.01(4)	C(2)-C(3)-H(3B)	114(2)
C(4)-C(5)	1.367(4)	H(3A)-C(3)-H(3B)	100(3)
C(4)-H(4)	0.95(5)	N(2)-C(4)-C(5)	108.0(3)
C(5)-C(6)	1.401(4)	N(2)-C(4)-H(4)	125(3)
C(5)-H(5)	0.94(5)	C(5)-C(4)-H(4)	127(3)
C(6)-H(6)	0.96(4)	C(4)-C(5)-C(6)	105.3(3)
C(7)-C(8)	1.516(4)	C(4)-C(5)-H(5)	129(3)
C(8)-C(9)	1.526(4)	C(6)-C(5)-H(5)	126(3)
C(8)-H(8A)	0.93(4)	N(3)-C(6)-C(5)	110.2(3)
C(8)-H(8B)	0.98(4)	N(3)-C(6)-H(6)	120(2)
C(9)-H(9A)	0.96(4)	C(5)-C(6)-H(6)	130(2)
C(9)-H(9B)	0.98(4)		
C(10)-C(11)	1.371(4)		
C(10)-H(10)	0.93(4)		
C(11)-C(12)	1.387(4)		
(11)-H(11)	0.90(4)		
C(12)-H(12)	1.02(4)		

While the exact mechanism by which the enzymes from Rhodococcus sp. Pseudomonos sp. and X. malthophilia metabolize acrylamide remained to be unknown, there are studies by Czarnik et al. [76] on metal catalyzed and/or metal mediated hydrolysis of acrylamide specially using copper(II) salts which mimic the activity of amidases that must break amide linkages in biological systems. The catalysis in these studies involves an additional ligand covalently linked to the substrate acrylamide so that an intramolecular, oxygen-coordinated 7- or 6- membered metal chelate can be formed. One proposed mechanism in such catalysis utilizes bound metal ions to polarize the amide carbonyl group via oxygen ligation, thereby increasing the rate of attack by oxygen nucleophiles at the carbon. The structures in this work can provide further insights into the mechanism of acrylamide hydrolysis catalysis via conjugate adducts of acrylamide ligands by metal(II) ions.

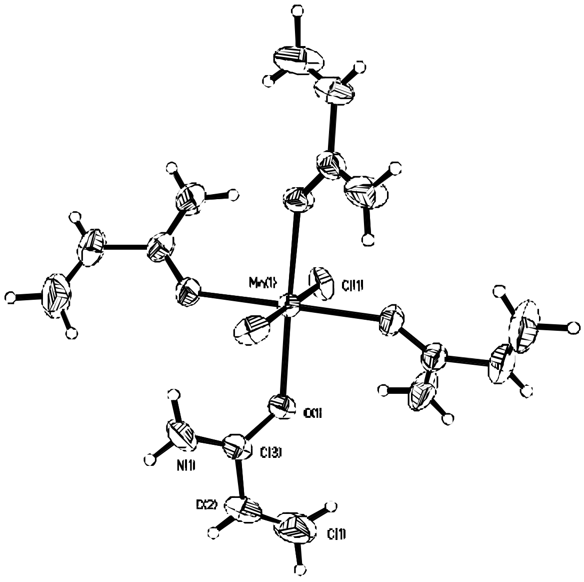
4. Summary and Outlook

4.1 Summary

The research into the coordination of acrylamide and N-pyrazolylpropanamide chemistry in this work has resulted in the synthesis and characterization of a number of coordination compounds of acrylamide, **1-15**, N-pyrazolylpropanamide, **16**, and cobalt and copper complexes of N-pyrazolylpropanamide, **17-18**.

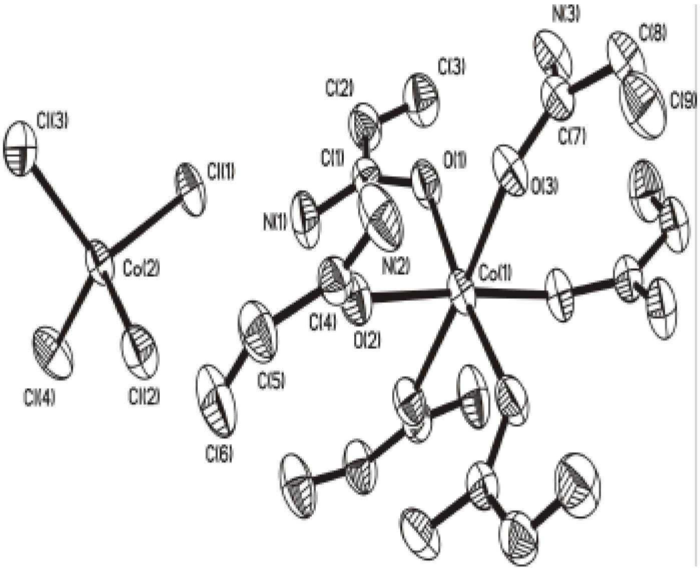
Complexes of acrylamide with chlorides, nitrates, perchlorates and tetrafluoroborates of divalent manganese, iron, cobalt, nickel, copper and zinc have been prepared and the single crystal structures of these compounds was determined using X-ray diffraction. The ligand acrylamide is shown to behave as a normal amide donor, with the oxygen of the carbonyl group coordinated to the metal ions.

The syntheses and structures of classical complexes of acrylamide with manganese(II), iron(II), cobalt(II) and nickel(II) chlorides are developed by direct reaction between salts and acrylamide in absolute ethanol and crystallization by slow diffusion of diethyl ether into the solution. Single crystals of $[Cu(AAm)_4Cl_2]$ were obtained in acetonitrile-ether mixture upon substitution of crystal water in $CuCl_2{\cdot}2H_2O$ by acrylamide molecules. The elemental analyses of these compounds show that the complexes of the metal chlorides have the composition $MCl_2{\cdot}4AAm$. The complexes $MnCl_2{\cdot}4AAm$, $FeCl_2{\cdot}4AAm$, $CoCl_2{\cdot}4AAm$, $NiCl_2{\cdot}4AAm$ and $CuCl_2{\cdot}4AAm$ crystallize in the cubic space group. The coordination of the metal centers in these complexes involves tetragonally distorted octahedral structures with four O-donor atoms of acrylamide and two chlorides.



Molecular structure of **1**

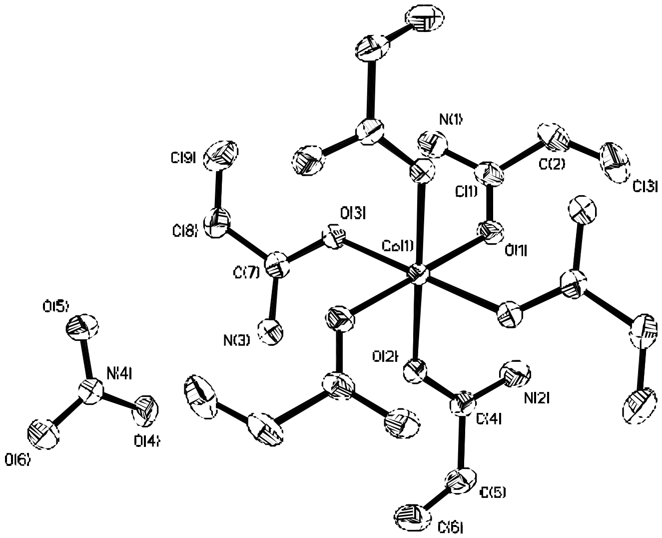
Comparison among these complexes of acrylamide show a decrease in M-O bond lengths in the order of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) accompanied by an increase in the C=O bond lengths in the same order. A good correlation between the ionic radii of the metal ions and the M-O(amide) bond lengths has been observed. Another reaction in the solid state by grinding $CoCl_2{\cdot}6H_2O$ and acrylamide together in a mortar followed by washing with boiling toluene to remove the excess acrylamide from the crude product and crystallization from hot ethanol and a few drops of diethyl ether gave violet crystals of ionic $[Co(AAm)_6][CoCl_4]$, **4**. The crystal structure of the complex contains Co^{+2} cations surrounded by an octahedral array of O-coordinated acrylamide ligands, accompanied by a $[CoCl_4]^{2-}$ anion.



Molecular structure of **4**

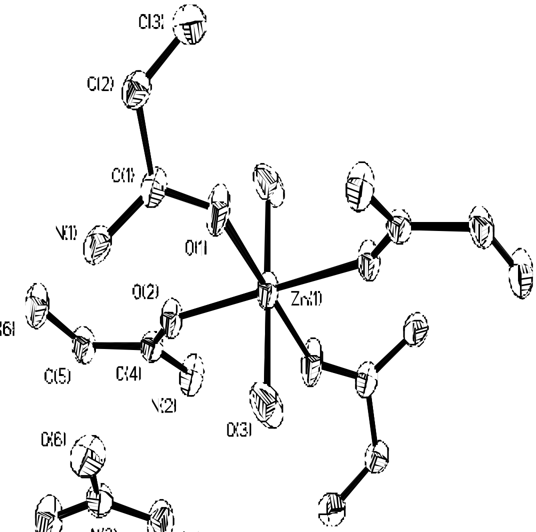
Complexes of acrylamide with the nitrates of manganese(II), iron(III), cobalt(II), nickel(II), copper(II), and zinc(II) have been prepared. The spectra of complexes of acrylamide with salts of these metals containing four acrylamide and two water molecules or six coordinated acrylamide molecules without water of crystallization have been obtained. The infrared absorption spectra of the complexes having the general formula $M(NO_3)_2{\cdot}4L$, where M = Co, Ni, Cu, or Zn, and L = acrylamide show that acrylamide acts as an oxygen donor ligand. The nitrate ion forms an ionic bond with the cationic complex. In the copper complex this bond is covalent [53]. The crystal structure of the copper compound is composed of neutral centrosymmetric $[Cu\{(O)C(NH_2)CHCH_2\}_4(NO_3)_2]$ molecules united by a system of hydrogen bonds. The copper(II) polyhedron includes four acrylamide O atoms coplanar with the Cu atom and two nitro O atoms.

Crystal structures and IR spectroscopic properties of acrylamide complexes having the general formula $M(NO_3)_2 \cdot 6L$, where M = Co and Ni and L = acrylamide represent octahedral species $[M(AAm)_6]^{+2}$ and uncoordinated nitrate ions have been obtained.



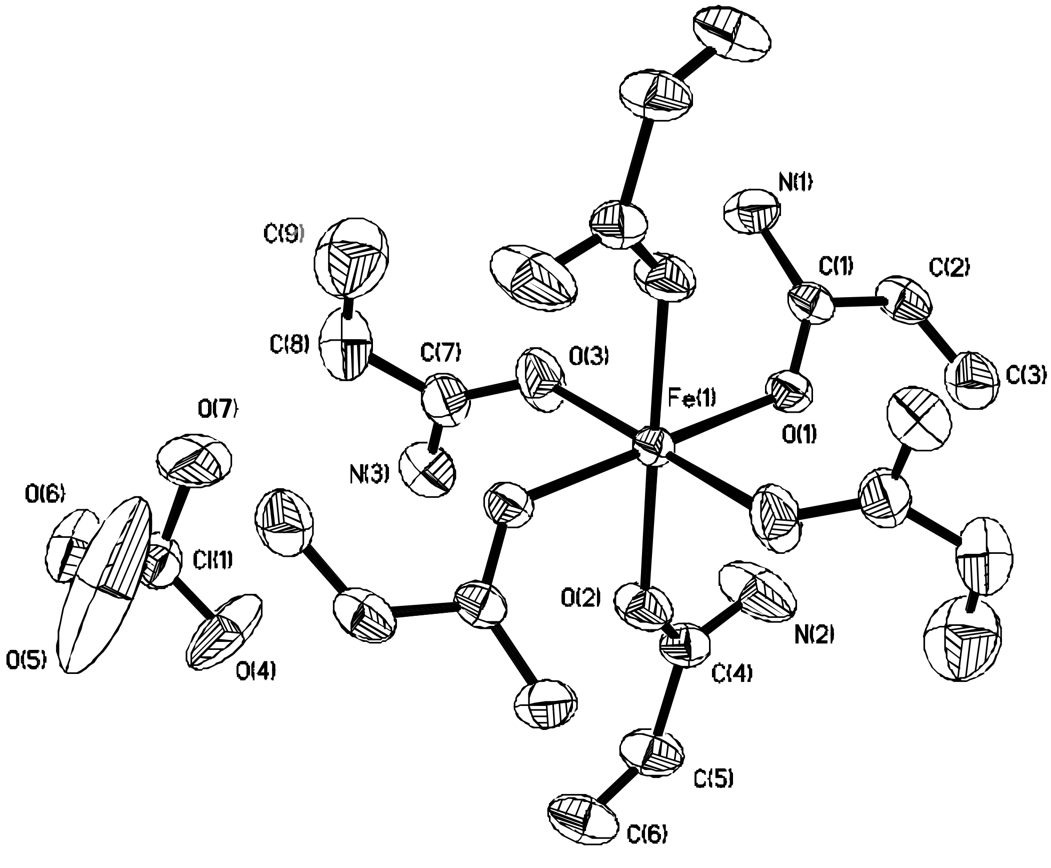
Molecular structure of **7**

Complexes of acrylamide with the nitrates of manganese(II), cobalt(II), nickel(II), and zinc(II) that contain water of crystallization are characterized by the composition $M(NO_3)_2 \cdot 4AAm \cdot 2H_2O$. The molecular structure of these metal nitrates was determined for the example of the adducts of Co(II) and Zn(II) by X-ray diffraction. The structures represent complex octahedral cations $[M(AAm)_4(H_2O)_2]^{+2}$ and NO_3^- anions joined together by a three dimensional system of hydrogen bonds. The octahedral environments of Co^{+2} and Zn^{+2} include the oxygen atoms of four acrylamide molecules and two water molecules, i.e., coordination of acrylamide is accomplished through the oxygen atoms of the amide group.



Molecular structure of **9**

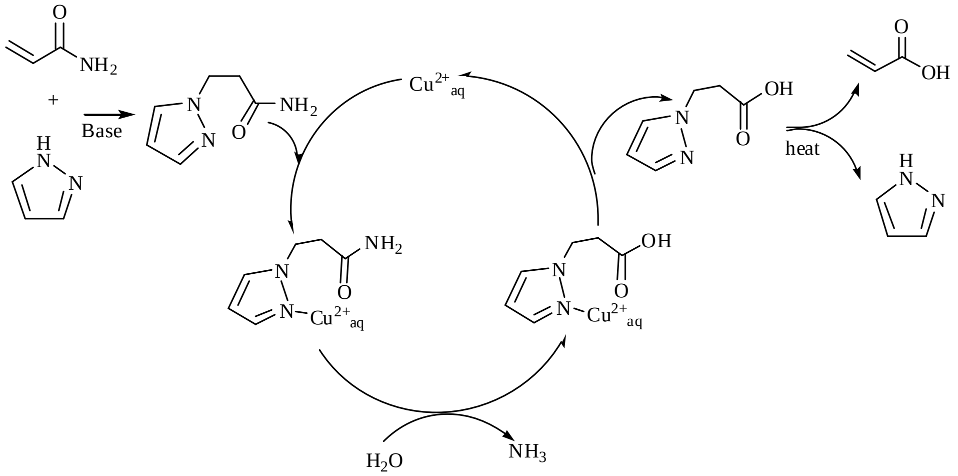
A variety of acrylamide complexes of first-row transition metal perchlorates and tetrafluoroborates were prepared and investigated with the purpose of determining the mode of attachment of the amide. Preparations, spectral properties and single X-ray structures of compounds with the general formula $[M(AAm)_6](anion)_2$, where M = Fe, Co, Ni and Zn and the anions are ClO_4^- and BF_4^-, are described. All compounds were prepared from the hydrated metal(II) salt dissolved in ethanol and triethylorthoformate (for dehydration) to which excess of ligand in ethanol is added. The single crystal X-ray structures of these complexes contain M(II) cations surrounded by an octahedral array of O-bonded acrylamide ligands accompanied by the corresponding anions.



Molecular structure of **10**

Michael-type addition reaction is responsible for the formation of several DNA and protein adducts of acrylamide that are used as biomarkers of acrylamide [77]. Base-catalyzed direct Michael-type addition reactions of acrylamide with adenine and cytosine in *vitro* can give 3-(adenin-9-yl) propionamide and 3-(1-cytosinyl) propionamide, respectively; which were also obtained indirectly by the reaction of adenine and cytosine with ß-propiolactone in the presence of N,N-dimethyl-4-pyridylamine in dimethyl sulfoxide at 383 K, esterification with HCl-saturated MeOH and then ammonolysis with NH_3-saturated MeOH in a long route

[78]. The development of transition metal complexes that can reproduce both the structural and functional properties of the metallic centers of enzymes that must break amide linkages is of a considerable interest in bioinorganic chemistry. One particular area of interest which has shown significant progress since 1980s' by Czarnik et al. [79] and other authors [80] is metal-catalyzed and/or metal-mediated ethanolysis and hydrolysis of acrylamide and urea by way of their conjugate adducts using Cu(II) or Ni(II) salts which mimic the activity of amidase and/or urease in biological systems. The catalysis in these studies involves direct alkylation of the substrate acrylamide or urea to another ligand which contains an adjacent nitrogen atom resulting in a hemilabile multidentate ligand which then forms intramolecular, weakly oxygen coordinated, 7- or 6- membered metal chelates with the active metallic cores.



Scheme 17. Proposed metal ion catalyzed hydrolysis of acrylamide by way of its conjugate adduct **16**.

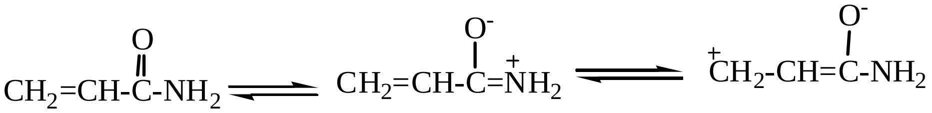
Currently there is a considerable attraction in the use of hemilabile ligands containing substituted pyrazole groups because of their potential application in catalysis and their ability to form complexes that mimic structural and catalytic functions in metalloproteins. As a part of interest in the coordination chemistry of acrylamide and acrylamide-based ligands an acrylamide substituted pyrazole ligand, N-pyrazolylpropanamide, and its complexes [CuL_2Cl_2] and [$Co_3L_4Cl_6$] (L = N-pyrazolylpropanamide) with copper(II) and cobalt(II) have been synthesized and fully characterized. In a similar context, microbial amidases (amidohydrolase, EC 3.5.1.4) from Rhodococcus sp., Pseudomonos sp. and X. malthophilia that catalyzes the hydrolysis of acrylamide into acrylic acid and ammonia have attracted much attention. However, the exact ligand donor environment and the reactivity of the active centers towards the substrate acrylamide in these enzymes remain unresolved.

All compounds **16**, **17** and **18** are characterized using elemental, IR, and X-ray diffraction analyses. In addition, the ^{1}H- and ^{13}C-NMR spectroscopic properties of the ligand were recorded. The structures of these compounds can provide further insights in to the mechanism of metal catalyzed/mediated hydrolysis catalysis of acrylamide *via* conjugate adducts of an acrylamide substituted ligand in a mononuclear nitrogen/oxygen-ligated metal centre that are relevant to enzyme activity.

4.2 Outlook

This work has been focused on the preparation, spectral and single crystal X-ray properties of a variety of acrylamide complexes of first-row transition chlorides, nitrates, perchlorates and tetrafluoroborates with the purpose of determining the mode of attachment of the amide. It is known that acrylamide is a special kind of ligand since its molecule contains simultaneously two *p*-donor groups, namely a carbonyl and an amine one which forms an amide group.

For the ligands of this type it is very essential where the coordination bond is localized. The existence of the double bond in acrylamide markedly effects the electronic state of the amide group. Assuming the resonance of the C=C and C=O groups with the participation of NH_2, the formation of three differing resonance structures is deemed likely.



$$CH_2{=}CH{-}\overset{O}{\overset{\|}{C}}{-}NH_2 \rightleftharpoons CH_2{=}CH{-}\overset{O^-}{\overset{|}{C}}{=}\overset{+}{N}H_2 \rightleftharpoons \overset{+}{C}H_2{-}CH{=}\overset{O^-}{\overset{|}{C}}{-}NH_2$$

I II III

In complexing via the oxygen atom structure II is preferred, whereas structures I and III are expected to exist in the case of N-coordination. The presence of such acrylamide resonance structures seems to be responsible for fact that during complexing one can observe frequency changes of not only the stretching and bending modes of the C=O, C-N, and N-H bonds but also those of the vinyl group. The change in the position of the NH_2 vibration to higher wavenumbers on complexation shows that no bonding has taken place between the nitrogen atoms of the NH_2 and the metal ions. The ?(C=O) vibration is found to move to lower wavenumbers on complexation, indicating that bonding is taking place between the oxygen atom of the C=O group and the metal ions. The C-N band is found to move to higher wavenumbers, compared with the values for pure acrylamide. It should be mentioned that the shifts in the C=O band are rather small because of the conjugation of the C=O bond with the vinyl bond and the free electron pair on the nitrogen atom.

A parallel shift of the ?(NH), ?(CO), and d(NH) bands to the long wave region caused by ligand complexing gives rise to conflicting conclusion as to MX_n coordination. Some authors believe that complexing takes place at the nitrogen atom, and others advocate the same process occurring at the carbonyl oxygen as in the case of saturated amines.

Nevertheless, X-ray structure studies of $M(AAm)_4Cl_2$, where M= Mn, Fe, Co, Ni or Cu; $[M(AAm)_4(H_2O)_2](NO_3)_2$, where M= Co(II) or Zn(II); $[Cu(AAm)_4(NO_3)_2]$ and $[M(AAm)_6]X_2$, where M= Fe(II), Co(II), Ni(II) and Zn(II) and X= NO_3^-, ClO_4^- or BF_4^- clearly demonstrate that acrylamide is coordinated *via* the oxygen atom. The measurements carried out with the metal(II) coordination compounds showed that acrylamide behaves as a normal amide ligand, with the oxygen of the carbonyl group coordinated to the metal ions.

A model study on a biologically relevant ligand based on acrylamide, N-pyrazolylpropanamide, has been shown to bind to metals that are available in biological systems. Solomon et. al [81] also reported the direct alkylation of acrylamide with deoxynucleosides via Michael-type addition reaction in *vitro* which showed a facile hydrolysis of an amide group to a carboxylic acid when acrylamide is alkylated to a ring nitrogen that is adjacent to an exocyclic nitrogen atom. The structures of **16**, **17** and **18** can provide further insights in to the mechanism of metal catalyzed/mediated hydrolysis of acrylamide *via* conjugate adducts of an acrylamide-substituted ligand in a mononuclear nitrogen/oxygen-legated metal centre that are relevant to enzyme activity.

5. Experimental Section

5.1 General Procedures

All preparations were done in an atmosphere of dry nitrogen with the use of standard Schlenk techniques. Starting materials: Acrylamide with the THF adduct of Mn(II) chloride, anhydrous Fe(II) chloride, hexahydrated Co(II) chloride, hexahydrated Ni(II) chloride, dihydrated Cu(II) chloride and Co(II), Ni(II) or Zn(II) nitrates and hexahydrated perchlorates of Fe(II), Ni(II) and Zn(II) or hexahydrated teraborofluoroborate of Co(II) and Zn(II) were dissolved in a minimum amounts of absolute ethanol, methanol or acetonitrile and stirred for 30 minutes. To a hydrated metal(II) salt triethylorthoformate for dehydration was added. The solutions were concentrated by removing part of the solvent under vacuum, and a few drops of dry diethyl ether were carefully layered. Cooling and slow diffusion of the diethyl ether into the solution developed single crystals.

The ligand N-pyrazolylpropanamide **16** has been prepared by Michael addition of pyrazole to acrylamide in the presence of trimethylbenzylammonium hydroxide (Triton B, 40% in methanol) as a basic catalyst. After about five hours of reflux in a boiling water bath the ligand were obtained in good yield (94%). Single crystals of the compound suitable for X-ray diffraction analysis were obtained from dichloromethane/ether solution in a 4:1 ratio. The coordination compounds $[CuL_2Cl_2]$ and $[Co_3L_4Cl_6]$ (L = N-pyrazolylpropanamide) were prepared by dissolving dihydrated copper(II) chloride and cobalt(II) chloride, respectively, in hot absolute ethanol, followed by adding a few millilitres of triethylorthoformate for dehydration. To these solutions, a solution of the ligand N-pyrazolylpropanamide in absolute ethanol was added. The complexes crystallized after the reaction mixtures were allowed to stand at room temperature for a few days.

5.2 Physical measurements

The *melting points* of the compounds were measured on a BÜCHI B-450 digital melting point apparatus.

The bulk purities of the compounds were verified by determining their carbon, hydrogen and nitrogen content by using a Leco CHNS 923 apparatus.

The *IR spectra* of the free acrylamide and complexes of the acrylamide were recorded using KBr pellets on a Perkin Elmer FT-IR spectrometer system 2000 between 4000 cm^{-1} and 400 cm^{-1}. Intensities are estimated as follows: w (weak), m (medium), s (strong), and vs (very strong).

The *^1H* and *^{13}C NMR* of the ligand **16** was recorded in D-DMSO solution at ambient temperature on a Bruker DPX 400 NMR spectrometer operating at basic frequencies 400 MHz and 101 MHz, respectively. The proton NMR spectra were referenced to internal tetramethylsilane (d = 0) whereas internal $CDCl_3$ was used for the calibration of the ^{13}C NMR spectra (d = 77.1). These were recorded with composite pulse decoupling. The degree of substitution of the carbon atoms was determined using the DEPT 135 method (q: CH_3, t: CH_2, d: CH, s: CR_4).

The *X-ray crystallographic* studies of the complexes were carried out using a Bruker AXS SMART CCD diffractometer with Mo-Ka radiation (?= 0.71073) and graphite monochromator. The structures were solved by direct methods using SHELXTL Version 5.1 [82]. Anisotropic thermal parameters were refined for all non-hydrogen atoms. All hydrogen atoms were found on the difference Fourier card and were refined freely. The crystal data for all the compounds related to data collection, structure solution, and refinement are listed in section 7 in tabular form.

5.3. Synthesis methods of complexes of metal(II) chlorides with acrylamide

5.3.1. Synthesis of [Mn(O-acrylamide)$_4$Cl$_2$] (1)

To 300 mg of the THF adduct of Mn(II) chloride, $MnCl_2(THF)_2$, dissolved in 20 ml absolute ethanol, acrylamide in a 1:6 metal salt to ligand was added and stirred for 30 minutes. The solution was then concentrated by removing part of the solvent under vacuum, and a few drops of dry diethyl ether were carefully layered. Cooling and slow diffusion of the diethyl ether into the solution developed white single crystals of **1** in 48% yields (220 mg).

Mp: 224 °C

IR spectrum (KBr, cm^{-1}): 3400 vs, 3335 ms, 3307 ms, 3268 ms, 3227 ms, 3190 s, 3156 s, 2789 w, 2755 w, 2640 vw, 2426 vw, 2257 vw, 1931 vw, 1664 vs, 1630 vs, 1585 vs, 1449 s, 1370 mw, 1286 m, 1127 m, 1059 w, 986 m, 964 ms, 849 mw, 810 ms, 635 m, 582 ms, 509 m, 481 mw.

Elemental analysis for $C_{12}H_{20}Cl_2MnN_4O_4$

	C	H	N
Calcd:	35.1	4.9	13.6
Found:	34.8	4.8	13.6

5.3.2. Synthesis of [Fe(O-acrylamide)$_4$Cl$_2$] (2)

To 300 mg of the anhydrous iron(II) chloride, $FeCl_2$, dissolved in 20 ml of absolute ethanol, acrylamide in 1:6 metal salt to ligand ratio was added and stirred for 30 minutes. The solution was then concentrated by removing part of the solvent under vacuum, and a few drops of dry diethyl ether were carefully layered. Cooling and slow diffusion of the diethyl ether into the solution developed yellow single crystals of **2** in 75% yields (730mg).

Mp: 116-118 °C

IR spectrum (KBr, cm^{-1}): 3394 vs, 3336 ms, 3305 ms, 3265 ms, 3226 ms, 3189 s, 3152 s, 2794 w, 2758 w, 2641 vw, 2428 vw, 2344 vw, 2266 vw, 1921 vw, 1665 vs, 1629 vs, 1584 vs, 1452 s, 1372 mw, 1288 m, 1133 m, 1062 w, 988 m, 960 ms, 852 mw, 808 ms, 646 m, 575 ms, 516 m, 480 mw.

Elemental analysis for $C_{12}H_{20}Cl_2FeN_4O_4$

	C	H	N
Calcd:	35.0	4.9	13.6
Found:	35.0	4.9	14

5.3.3. Synthesis of [Co(O-acrylamide)$_4$Cl$_2$] (3)

Hexahydrated violet cobalt(II) chloride (300 mg, 1.25 mmol) was dissolved in 2 ml of absolute ethanol and acrylamide (500 mg, 7 mmol), dissolved in a minimum amount of absolute ethanol was added. The solution was then concentrated by removing part of the solvent under vacuum, and a few drops of dry diethyl ether were carefully layered. Cooling and slow diffusion of the diethyl ether into the solution developed blue single crystals of **3** in 47 % yields (213 mg).

Mp: 122-124 °C

IR spectrum (KBr, cm^{-1}): 3394 vs, 3335 ms, 3305 ms, 3264 ms, 3224 ms, 3187 s, 3152 s, 2793 w, 2757 w, 2640 vw, 2427 vw, 2344 vw, 2263 vw, 1925 vw, 1664 vs, 1629 vs, 1583 vs, 1452 s, 1372 mw, 1288 m, 1132 m, 1061 w, 987 m, 961 ms, 851 mw, 808 ms, 641 m, 579 ms, 514 m, 481 mw.

Elemental analysis for $C_{12}H_{20}Cl_2CoN_4O_4$

	C	H	N
Calcd:	34.8	4.8	13.5
Found:	35.0	4.7	12.8

5.3.4. Synthesis of $[Co(O\text{-}acrylamide)_6][CoCl_4]$(4)

The crude product as powder was prepared by a published method [56]. Crystalline $CoCl_2.6H_2O$ (2.5g, 0.01mol) was ground and mixed with acrylamide (3.89g, 0.05mol). After some time, a homogeneous violet paste was produced. The homogeneous was placed for about 48h in a desiccator containing P_4O_{10} to remove moisture. The dried crude product was powdered and washed for 15 minutes using 100 ml boiling toluene in flask equipped with Celite filter aid and a reflux condenser in order to extract the excess acrylamide. A portion of the dark blue crude residue on the filter was then dissolved in 100 ml of boiling ethanol forming a clear dark blue solution. Slow evaporation of the clear ethanol solution, to which a few drops of diethyl ether were added, resulted in violet crystals. Yield: 0.79g (21%).

Mp: 112-114°C

IR spectrum (KBr, cm^{-1}): 3392 vs; 3264 ms; 3224 ms; 3187 s; 3152 s; 2792 w; 2756 w; 2425 vw; 2262 vw; 1940 vw; 1667 vs; 1629 vs; 1582 vs; 1452 s; 1371 mw; 1288 m; 1130 m; 1059 w; 987 m; 962 ms; 850 mw; 808 ms; 641 m; 580 ms; 512 m; 482 mw.

Elemental analysis for $C_{18}H_{30}Cl_4Co_2N_6O_6$

	C	H	N
Calcd:	31.51	4.41	12.28
Found:	31.52	4.37	12.14

5.3.5. Synthesis of [Ni(O-acrylamide)$_4$Cl$_2$](5)

To 300 mg of hexahydrated nickel (II) chloride dissolved in 20 ml of absolute ethanol and triethylorthoformate for dehydration, acrylamide in a 1:6 metal salt to ligand ratio was added and stirred for 30 minutes. The solution was then concentrated by removing part of the solvent under vacuum, and a few drops of dry diethyl ether were carefully layered. Cooling and slow diffusion of the diethyl ether into the solution developed green single crystals. Yield: 340 mg (65%).

Mp: 112-114 °C

IR spectrum (KBr, cm^{-1}): 3394 vs, 3334 vs, 3305 vs, 3264 vs, 3224 vs, 3185 vs, 3152 vs, 2791 w, 2756 w, 2639 vw, 2426 vw, 2346 vw, 2262 vw, 1928 vw, 1664 vs, 1630 vs, 1583 vs, 1452 vs, 1372 vs, 1287 m, 1137 m, 1061 w, 987 m, 963 ms, 850 mw, 808 mw, 638 m, 582 s, 512 m, 480 m.

Elemental analysis for $C_{12}H_{20}Cl_2N_4NiO_4$

	C	H	N
Cald:	34.8	4.8	13.5
Found:	34.8	4.8	13.5

5.3.6. Synthesis of [Cu(O-acrylamide)$_4$Cl$_2$] (6)

To 300 mg of dihydrated copper(II) chloride dissolved in 20 ml of acetonitrile, 750 mg of acrylamide (1:6 ratio), dissolved in the minimum volume acetonitrile was added and stirred for 30 minutes. The solution was then concentrated by removing part of the solvent under vacuum, and a few drops of dry diethyl ether were carefully layered. Cooling and slow diffusion of the diethyl ether into the solution developed light green single crystals. Yield: 200 mg (27%).

IR spectrum (KBr, cm^{-1}): 3379 vs, 3262 vs, 3124 vs, 2790 w, 2757 w, 1932 vw, 1663 vs, 1629 vs, 1570 vs, 1456 vs, 1377 vs, 1287 m, 1137 m, 1061 w, 987 m, 963 ms, 850 mw, 808 mw, 638 m, 582 s, 512 m, 480 m.

Elemental analysis for $C_{12}H_{20}Cl_2CuN_4O_4$

	C	H	N
Calcd:	34.4	4.8	13.4
Found:	33.8	4.8	12.5

5.4. Synthesis of complexes of metal(II) nitrates with acrylamide

5.4.1. Synthesis of $[Co(O\text{-acrylamide})_6][NO_3]_2$ (7)

The complex was synthesized according to the procedures described by *Reedijk* [49] and pink single crystals of the compound were grown by slow vapor diffusion of diethyl ether into the reaction solution at room temperature. Yield: 2.24 g (74%).

Mp: 78-79 °C

IR spectrum (KBr, cm^{-1}): 3378 vs, 3186 m, 2794 w, 2396 w, 1908 w, 1763 w, 1667 vs, 1620 s, 1585 s, 1447 s, 1384 vs, 1356 vs, 1287 m, 1115 m, 1055 m, 988 m, 971 m, 962 m, 848 m, 817 m, 638 m, 507 m.

Elemental analysis for $C_{18}H_{30}CoN_8O_{12}$

	C	H	N
Calcd:	35.5	5.0	18.4
Found:	35.3	4.8	17.8

5.4.2. Synthesis of $[Ni(O\text{-acrylamide})_6][NO_3]_2$ (8)

The complex was synthesized according to the procedures described by *Reedijk* [49] and green single crystals of the compound were grown by slow vapour diffusion of diethyl ether into the reaction solution at room temperature. Yield: 1.09 g (36%).

Mp: 114-116 °C

IR spectrum (KBr, cm^{-1}): 3374 vs, 3185 m, 2795 w, 2395 w, 1908 w, 1763 w, 1670 vs, 1627 s, 1587 s, 1448 s, 1384 vs, 1356 vs, 1288 m, 1117 m, 1056 m, 987 m, 971 m, 964 m, 850 m, 817 m, 669 m, 509 m.

Elemental analysis for $NiC_{18}H_{30}O_{12}N_8$

	C	H	N
Calcd:	35.5	5.0	18.4
Found:	35.6	4.9	17.7

5.4.3. Synthesis of [Zn(O-acrylamide)$_4$(H$_2$O)$_2$][NO$_3$]$_2$ (9)

The complex was synthesized according to the procedures described by *Reedijk* [49] and single crystals of the compound were obtained by recrystallizing the white solid obtained in the reaction by slow evaporation from methanol. Yield: 1.14 g (44%).

Mp: 75-76 °C

IR spectrum (KBr, cm^{-1}): 3351 s, 3191 s, 2814 w, 2428 vw, 2397 vw, 1922 vw, 1763 w (sharp), 1667 vs, 1616 s, 1575 s, 1430 vs, 1384 vs, 1355 s, 1281 m, 1137 m, 1122 m,1052 m, 989 m, 962 m, 841 m, 825 m, 810 m, 711 m, 637 m, 590 mw. 509 m.

Elemental analysis for $ZnC_{12}H_{24}O_{12}N_6$

	C	H	N
Calcd:	34.8	4.8	13.5
Found:	34.9	4.8	13.6

5.5. Synthesis of complexes of metal(II) perchlorates and tetrafluoroborates with acrylamide

5.5.1. Synthesis of [Fe(O-acrylamide)$_6$][ClO$_4$]$_2$ (10)

The complex was synthesized according to the procedures described by *Reedijk* [49]. To 0.005 mole of $Fe(H_2O)_6(ClO_4)_2$ dissolved in 2 ml ethanol and 0.04 mole of triethylorthoformate, 0.035 mole of acrylamide in 3 ml of ethanol were added. Upon the addition of a few ml of diethyl ether dark yellow single crystals of the compound were grown by slow vapor diffusion of the diethyl ether into the reaction solution at room temperature.

Mp: 90 °C (dec.)

IR spectrum (KBr, cm^{-1}): 3352 s, 3180 s, 2812 w, 2279 w, 1940 vw, 1922 vw,1664 vs, 1620 vs, 1589 vs, 1561 m, 1431 s, 1385 m, 1364 m, 1354 m, 1282 m, 1141 s, 1109 vs, 1089 vs, 987 m, 970 m, 941 w, 843 w, 809 m, 636 s, 627 s, 592 m, 509 m.

Elemental analysis for $FeC_{18}H_{30}O_{14}N_6Cl_2$

	C	H	N
Calcd:	31.7	4.4	12.3
Found:	32.6	4.8	12.2

5.5.2. Synthesis of [Ni(O-acrylamide)$_6$][ClO$_4$]$_2$ (11)

The complex was synthesized according to the procedures described by *Reedijk* [49]. To 0.005 mole of $Ni(H_2O)_6(ClO_4)_2$ dissolved in 2 ml ethanol and 0.04 mole of triethylorthoformate, 0.035 mole of acrylamide in 3 ml of ethanol were added. Upon the addition of a few ml of diethyl ether green single crystals of the compound were grown by slow vapor diffusion of the diethyl ether into the reaction solution at room temperature. Yield 2.58 g (75%).

Mp: 188-190 °C

IR spectrum (KBr, cm^{-1}): 3383 s,1948 vw, 1664 vs, 1625 vs, 1579 vs, 1445 s, 1370 m, 1285 m, 1091 vs, 973 m, 852 mw, 810 m, 637 ms, 627 s, 509 m.

Elemental analysis for $NiC_{18}H_{30}O_{14}N_6Cl_2$

	C	H	N
Calcd:	31.3	4.4	12.3
Found:	31.3	4.5	12.5

5.5.3. Synthesis of [Zn(O-acrylamide)$_6$][ClO$_4$]$_2$ (12)

The complex was synthesized according to the procedures described by *Reedijk* [49]. To 0.005 mole of $Zn(H_2O)_6(ClO_4)_2$ dissolved in 2 ml ethanol and 0.04 mole of triethylorthoformate, 0.035 mole of acrylamide in 3 ml of ethanol were added. Upon the addition of a few ml of diethyl ether white single crystals of the compound were grown by slow vapor diffusion of the diethyl ether into the reaction solution at room temperature.

Mp: 126-127 °C

IR spectrum (KBr, cm^{-1}): 3352 s, 3180 s, 2812 w, 2279 w, 1940 vw, 1922 vw,1664 vs, 1620 vs, 1589 vs, 1561 m, 1431 s, 1385 m, 1364 m, 1354 m, 1282 m, 1141 s, 1109 vs, 1089 vs, 987 m, 970 m, 941 w, 843 w, 809 m, 636 s, 627 s, 592 m, 509 m.

Elemental analysis for $FeC_{18}H_{30}O_{14}N_6Cl_2$

	C	H	N
Calcd:	31.3	4.4	12.2
Found:	31.2	4.4	11.7

5.5.4. Synthesis of [Co(O-acrylamide)$_6$][BF$_4$]$_2$ (13)

The complex was synthesized according to the procedures described by *Reedijk* [49]. To 0.005 mole of $Co(H_2O)_6(BF_4)_2$ dissolved in 2 ml ethanol and 0.04 mole of triethylorthoformate, 0.035 mole of acrylamide in 3 ml of ethanol were added. Upon the addition of a few ml of diethyl ether pink single crystals of the compound were grown by slow vapor diffusion of the diethyl ether into the reaction solution at room temperature. Yield 0.96 g (29%).

Mp: 140 °C (dec.)

IR spectrum (KBr, cm^{-1}): 3351 s, 3186 ms, 3104 mw, 2813 w, 1922 w, 1667 vs, 1615 vs, 1572 s, 1552 m, 1430 s, 1354 m, 1282 m, 1061 vs, 990 m, 962 m, 941 w, 845 w, 810 m, 717 mw, 640 m, 591 m, 534 w, 521 mw, 509 mw.

Elemental analysis for $CoC_{18}H_{30}O_6B_2F_8$

	C	H	N
Calcd:	32.8	4.6	12.8
Found:	32.6	4.6	12.5

5.5.5. Synthesis of [Zn(O-acrylamide)$_6$][BF$_4$]$_2$ (14)

The complex was synthesized according to the procedures described by *Reedijk* [49]. To 0.005 mole of $Zn(H_2O)_6(BF_4)_2$ dissolved in 2 ml ethanol and 0.04 mole of triethylorthoformate, 0.035 mole of acrylamide in 3 ml of ethanol were added. Upon the addition of a few ml of diethyl ether white single crystals of the compound were grown by slow vapor diffusion of the diethyl ether into the reaction solution at room temperature. Yield 1.18 g (36%).

Mp: 114-115 °C.
IR spectrum (KBr, cm^{-1}): 3350 s, 3195 ms, 2813 w, 1922 w,1667 vs, 1615 vs, 1575 s, 1430 vs,1354 m, 1282 m, 1084 s, 1034 s, 989 m, 962 m, 941 w, 844 mw, 811 m, 707 mw, 626 m, 591 m, 534 w, 522 mw, 508 m.
Elemental analysis for $ZnC_{18}H_{30}O_6B_2F_8$

	C	H	N
Calcd:	32.5	4.5	12.6
Found:	33.4	4.4	12.4

5.6. Synthesis of [Fe(*O*-acrylamide)$_6$][Fe$_2$OCl$_6$] (15)

In preparing **15**, $FeCl_2$ (0.01 mole) and $FeCl_3$ (0.02 mole) were placed a Schlenk flask purged with nitrogen, and nitromethane (5 ml) and acrylamide (0.06 mole) were added. This mixture was stirred with a magnetic stirrer until a bright yellow colored solution was obtained. After filtering and upon cooling in a refrigerator, well formed yellow brown crystals with the composition [Fe(*O*-OC(NH$_2$)CHCH$_2$)$_6$][Fe$_2$OCl$_6$] were obtained over several days. The yield of the compound obtained was 58 % based on $FeCl_2$.

5.7. Synthesis of an acrylamide based ligand, N-pyrazolylpropanamide, and its complexes of metal(II) chlorides.

5.7.1. Synthesis of N-pyrazolylpropanamide (16)

A mixture of 6.8 g (0.1 mole) of pyrazole, 7.1 g (0.1 mole) of acrylamide and 2ml of trimethylbenzylammonium hydroxide (Triton B, 40% in methanol) was heated for five hours in a boiling water-bath. The cooled reaction mixture was washed with diethyl ether and dried in *vacuo* to give 12.84 g (94 % of the theoretical amount) of analytically pure yellowish N-pyrazolylpropanamide. Single crystals of the ligand were obtained by cooling 3.14 g ligand solution of dichloromethane and diethyl ether as a precipitant (dichloromethane/diethyl ether in 4:1 ratio).

Mp: 80-82 °C.

IR spectra (KBr, cm^{-1}) for **16**: 3394 vs, 3334 vs, 3305 vs, 3264 vs, 3224 vs, 3185 vs, 3152 vs, 2791 w, 2756 w, 2639 vw, 2426 vw, 2346 vw, 2262 vw, 1928 vw, 1664 vs,1630 vs,1583 vs, 1452 vs, 1372 vs, 1287 m, 1137 m, 1061 w, 987 m, 963 s, 850 mw, 808 mw, 638 m, 582 s, 512 m, 480 m.

^{1}H NMR (400 MHz, DMSO-d_6): 2.59 (2H, J = 6Hz, H-ß), 4.28 (2H, J = 6Hz, H-a), 6.18 (1H, H-4), 6.89 (2H, bs, NH_2), 7.40 (1H, H-3), 7.60 (1H, H-5) ppm.
^{13}C NMR (101 MHz, DMSO-d_6): 35.69 (C-ß), 47.36 (C-a), 104.92 (C-4), 129. 87 (C-5), 138.58 (C-3), 171.72 (C=O) ppm.
Elemental Anal. for $C_6H_9N_3O$ **(16)**

	C	H	N
Calcd. (%):	51.79	6.52	30.2.
Found (%):	51.9	7.65	27.6.

5.7.2. Synthesis of Cobalt(II) chloride complex with N-pyrazolylpropanamide (17)

To an ethanol solution (10 ml) of hexahydrated cobalt(II) chloride (0.340 g, 0.002 mole) and 4 ml of triethylorthoformate for dehydration, an ethanol solution (10 ml) of N-pyrazolylpropanamide (0.557 g, 0.004 mole) was added and stirred for about 1h at room temperature. A blue-violet solid substance precipitated out of the reaction mixture. The solvent was then removed under vacuum and the solid was extracted using 150 ml acetonitrile. Evaporation of the acetonitrile solution at room temperature resulted in blue single crystals suitable for X-ray diffraction analysis after a few days. Yield: 462 mg (25 %).

Mp: 155 °C.

IR spectra (KBr, cm^{-1}): 3369 vs, 3005 vs, 2973 w, 2951 w, 2372 vw, 2170 vw, 2071 vw, 1647 vs,1592 vs, 1520 vs, 1442 vs, 1420 vs, 1406 vs, 1384 s, 1356 m, 1306 s, 1291 s, 1240 w, 1219 m, 1175 m, 1133 w, 1101 m, 1068 w, 1061 s, 990 m, 970 m, 921 w, 885 m, 853 m, 813 m, 761 s, 681 m, 654 m, 615 s, 536 s, 512 m, 493 s.

Elemental Anal. For $Co_3C_{24}H_{36}N_{12}O_4Cl_6$ (**17**):

	C	H	N
Calcd (%):	30.47	3.84	17.76
Found (%):	30.88	3.94	16.04

5.7.3. Synthesis of the copper(II) chloride complex with N-pyrazolylpropanamide (18)

The coordination compound [CuL_2Cl_2] (L = N-pyrazolylpropanamide) was prepared by dissolving 0.340 g (0.002 mole) dihydrated copper(II) chloride in 10 ml hot absolute ethanol, followed by adding 2ml of triethylorthoformate for dehydration. To this solution, a solution of 0.557 g (0.004 mole) of the ligand N-pyrazolylpropanamide in 10 ml of absolute ethanol was added without stirring. The complex crystallized after the reaction mixture was allowed to stand at room temperature for a few days. Yield: 220 mg (48 %).

Mp: 174 °C.

IR spectrum (KBr, cm^{-1}) for **18**: 3394 vs, 3334 vs, 3305 vs, 3264 vs, 3224 vs, 3185 vs, 3152 vs, 2791 w, 2756 w, 2639 vw, 2426 vw, 2346 vw, 2262 vw, 1928 vw, 1664 vs,1630 vs,1583 vs, 1452 vs, 1372 vs, 1287 m, 1137 m, 1061 w, 987 m, 963 s, 850 mw, 808 mw, 638 m, 582 s, 512 m, 480 m.

Elemental Anal. For **18**:

	C	H	N
Calcd. (%):	34.92	4.40	20.36
Found (%):	34.87	4.67	18.64

6. Special Handling Procedures and Storage Requirements

Acrylamide is a white, odorless, crystalline solid which can irritate the skin causing a rash or burning feeling on contact. Contact with the eye causes eye irritation, watering and inflammation and breathing the compound in air can irritate the nose and throat causing coughing and wheezing. In long terms, health effects such as damage of the testes and the nervous system causing numbness, loss of balance, heavy sweating and/or weakness in the hands and feet may occur upon exposure. Here are some recommendations on special handling procedures and storage requirements:

- Prior to working with acrylamide you should be trained on its proper handling and storage.
- Avoid skin contact with acrylamide. Wear protective gloves and clothing. All protective clothing (suits, gloves, footwear, headgear) should be clean, available each day, and put on before work.
- Wear impact resistant eye protection with side shields or goggles.
- Wear a face shield along with goggles when working with corrosive, highly irritating or toxic substances.
- A regulated, marked area should be established where acrylamide is handled, used or stored.
- When acrylamide is heated to its melting point or exposed to ultraviolet light, it may polymerize violently.
- Store in tightly closed containers in a cool, well-ventilated area away from heat, sun light and moisture.
- Sources of ignition, such as smoking and open flames, are prohibited where acrylamide is used, handled, or stored in a manner that could create a potential fire or explosion hazard.
- Wherever acrylamide is used, handled, or stored, use explosion-proof electrical equipments and fittings.

7. Crystal Data and Refinement Details

Table 22. Crystal data and structure refinement for 1

Empirical formula	$C_{12}H_{20}Cl_2MnN_4O_4$
Formula weight	410.16
Temperature	210(2)K
Wavelength	0.71073 Å
Crystal system	Cubic
Space group	I43d
Unit cell dimension a, b, c (Å)	18.0239(4)
Volume	5855.3(2) $Å^3$
Z	12
Density (calculated)	1,396 Mg/m^3
Absorption coefficient	0.970 mm^{-1}
F(000)	2532
Crystal size	0.20 x 0.20 x 0.20 mm^3
Theta range for data collection	2.77 to 28.30 deg.
Index ranges	-23<= h<=23, -15<= k <=23, -23<= l <=23
Reflections collected/ Unique	14678/1202 [R(int) = 0.0332]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1202/0/73
Goodness-of-fit on F^2	1.065
Final R indices [I>2s(I)]	R1 = 0.0212, wR2 = 0.0528
R indices (all data)	R1 = 0.0236, wR2 = 0.0537
Absolute structure parameter	0.038(17)
Large difference peak and hole	0.218 and -0.137 e $Å^{-3}$

Table 23. Crystal data and structure refinement for 2

Empirical formula	$C_{12}H_{20}Cl_2FeN_4O_4$
Formula weight	411.07
Temperature	200(2)K
Wavelength	0.71073 Å
Crystal system	Cubic
Space group	I43d
Unit cell dimension a, b, c (Å)	17.91440(10)
Volume	5749.19(6) $Å^3$
Z	12
Density (calculated)	1.425 Mg/m^3
Absorption coefficient	1.086 mm^{-1}
F(000)	2544
Crystal size	0.50 x 0.50 x 0.50 mm^3
Theta range for data collection	2.79 to 28.86 deg.
Index ranges	-24<= h <=23, -23<= k <=23, -23 <= l <=23
Reflections collected/ Unique	21055/1231 [R(int) = 0.0329]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1231/0/73
Goodness-of-fit on F^2	1.103
Final R indices [I>2s(I)]	R1 = 0.0197, wR2 = 0.0500
R indices (all data)	R1 = 0.0210, wR2 = 0.0505
Absolute structure parameter	0.009(12)
Large difference peak and hole	0.160 and -0.198 e $Å^{-3}$

Table 24. Crystal data and structure refinement for 3

Empirical formula	$C_{12}H_{20}Cl_2CoN_4O_4$
Formula weight	414.16
Temperature	210(2)K
Wavelength	0.71073 Å
Crystal system	Cubic
Space group	I43d
Unit cell dimension	
a, b, c (Å)	17.857(2)
Volume	5694.5(12) $Å^3$
Z	48
Density (calculated)	1.449 Mg/m^3
Absorption coefficient	1.206 mm^{-1}
F(000)	2556
Crystal size	0.40 x 0.30 x 0.20 mm^3
Theta range for data collection	2.79 to 29.23 deg.
Index ranges	-42<= h <= 44, -15<= k <=15, -24<= l <=24
Reflections collected/ Unique	16874/1260 [R(int) = 0.0475]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	260/0/73
Goodness-of-fit on F^2	1.033
Final R indices [I>2s(I)]	R1 = 0.0201, wR2 = 0.0458
R indices (all data)	R1 = 0.0290, wR2 = 0.0482
Large difference peak and hole	0.273 and -0.136 e $Å^{-3}$

Table 25. Crystal data and structure refinement for 4

Empirical formula	$C_{18}H_{30}Cl_4Co_2N_6O_6$
Formula weight	686.14
Temperature	210(2)K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	C2/c
Unit cell dimension	
a, b, c (Å)	33.67(11), 11.668(4), 18.556(8),
ß (°)	122.539(10)
Volume	6146(4) Å^3
Z	8
Density (calculated)	1.483 Mg/m^3
Absorption coefficient	1.467 mm^{-1}
F(000)	2800
Crystal size	0.50 x 0.50 x 0.30 mm^3
Theta range for data collection	1.89 to 29.21 deg.
Index ranges	-22<=h<=24, -24<=k<16, -22<=l<=24
Reflections collected/ Unique	30893/7708 [R(int) = 0.0233]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7708/0/447
Goodness-of-fit on F^2	1.012
Final R indices [I>2s(I)]	R1 = 0.0329, wR2 = 0.0775
R indices (all data)	R1 = 0.0522, wR2 = 0.0841
Large difference peak and hole	0.404 and -0.246 e Å^{-3}

Table 26. Crystal data and structure refinement for 5

Empirical formula	$C_{12}H_{20}Cl_2NiN_4O_4$
Formula weight	413.93
Temperature	293(2)K
Wavelength	0.71073 Å
Crystal system	cubic
Space group	I43d
Unit cell dimension	
a, b, c (Å)	17.7548(5)
Volume	5596.9(3)Å^3
Z	12
Density (calculated)	1.474 Mg/m^3
Absorption coefficient	1.348 mm^{-1}
F(000)	2568
Crystal size	0.50 x 0.50 x 0.40 mm^3
Theta range for data collection	3.25 to 28.22 deg.
Index ranges	-23<=h<=23, -23<=k<23, -23<=l<=23
Reflections collected/ Unique	12304/1113 [R(int) = 0.0543]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1113/0/73
Goodness-of-fit on F^2	1.099
Final R indices [I>2s(I)]	R1 = 0.0297, wR2 = 0.0708
R indices (all data)	R1 = 0.0315, wR2 = 0.0714
Large difference peak and hole	0.475 and -0.338 e Å^{-3}

Table 27. Crystal data and structure refinement for 6

Empirical formula	$C_{12}H_{20}Cl_2CuN_4O_4$
Formula weight	418.76
Temperature	293(2)K
Wavelength	0.71073 Å
Crystal system	cubic
Space group	I43d
Unit cell dimension	
a, b, c (Å)	17.8310(2)
Volume	5669.27(11)Å^3
Z	12
Density (calculated)	1.472 Mg/m^3
Absorption coefficient	1.459 mm^{-1}
F(000)	2580
Crystal size	0.50 x 0.40 x 0.30 mm^3
Theta range for data collection	2.80 to 28.30 deg.
Index ranges	-23<=h<=23, -23<=k<23, -23<=l<=23
Reflections collected/ Unique	21715/1166 [R(int) = 0.0328]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1166/0/73
Goodness-of-fit on F^2	1.075
Final R indices [I>2s(I)]	R1 = 0.0176, wR2 = 0.0488
R indices (all data)	R1 = 0.0196, wR2 = 0.0497
Large difference peak and hole	0.143 and -0.175 e Å^{-3}

Table 28. Crystal data and structure refinement for 7

Empirical formula	$C_{18}H_{30}CoN_8O_{12}$
Formula weight	609.43
Temperature	210(2)K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	P-1
Unit cell dimension	
a, b, c (Å)	6.9897(3), 11.1346(4), 11.2119(4)
a, ß, ? (°)	118.9220(10), 92.5700(10), 105.8420(20)
Volume	718.36(5)$Å^3$
Z	1
Density (calculated)	1.409 Mg/m^3
Absorption coefficient	0.666 mm^{-1}
F(000)	317
Crystal size	0.60 x 0.50 x 0.20 mm^3
Theta range for data collection	3.15 to 28.26 deg.
Index ranges	-9<=h<=9, -14<=k<14, -14<=l<=14
Reflections collected/ Unique	8259/3339 [R(int) = 0.0287]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3339/0/238
Goodness-of-fit on F^2	1.065
Final R indices [I>2s(I)]	R1 = 0.0382, wR2 = 0.0995
R indices (all data)	R1 = 0.0347, wR2 = 0.1012
Large difference peak and hole	0.376 and -0.387 e $Å^{-3}$

Table 29. Crystal data and structure refinement for 8

Empirical formula	$C_{18}H_{30}N_8NiO_{12}$
Formula weight	609.21
Temperature	210(2)K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	P-1
Unit cell dimension	
a, b, c (Å)	6.9897(3), 11.0943(4), 11.1747(4)
a, ß, ? (°)	118.9810(10), 92.7170(10),105.5370(10)
Volume	713.80(5)Å^3
Z	1
Density (calculated)	1.417 Mg/m^3
Absorption coefficient	0.748 mm^{-1}
F(000)	318
Crystal size	0.50 x 0.50 x 0.40 mm^3
Theta range for data collection	3.15 to 28.29 deg.
Index ranges	-9<=h<=8, -14<=k<14, -14<=l<=14
Reflections collected/ Unique	7440/3283 [R(int) = 0.0255]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3283/0/238
Goodness-of-fit on F^2	1.087
Final R indices [I>2s(I)]	R1 = 0.0327, wR2 = 0.1042
R indices (all data)	R1 = 0.0334, wR2 = 0.1049
Large difference peak and hole	0.413 and -0.462 e Å^{-3}

Table 30. Crystal data and structure refinement for 9

Empirical formula	$C_{12}H_{24}N_6O_{12}Zn$
Formula weight	509.74
Temperature	293(2)K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	P-1
Unit cell dimension	
a, b, c (Å)	7.2012(6), 8.8888(8), 9.6955(8)
a, ß, ? (°)	65.2790(10), 70.8870(10), 79.6220(10)
Volume	531.98(8)$Å^3$
Z	1
Density (calculated)	1.591 Mg/m^3
Absorption coefficient	1.226 mm^{-1}
F(000)	264
Crystal size	0.40 x 0.20 x 0.10 mm^3
Theta range for data collection	2.74 to 28.24 deg.
Index ranges	-9<=h<=9, -8<=k<11, -11<=l<=12
Reflections collected/ Unique	3247/2288 [R(int) = 0.0372]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2288/0/190
Goodness-of-fit on F^2	1.076
Final R indices [I>2s(I)]	R1 = 0.0513, wR2 = 0.1330
R indices (all data)	R1 = 0.0538, wR2 = 0.1354
Large difference peak and hole	1.829 and -0.529 e $Å^{-3}$

Table 31. Crystal data and structure refinement for 10

Empirical formula	$C_{18}H_{30}Cl_2FeN_6O_{14}$
Formula weight	681.23
Temperature	210(2)K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimension	
a, b, c (Å)	9.2072(4), 15.9552(7), 10.8233(4)
a, ß, ? (°)	90, 111.2310(10), 90
Volume	1482.06(11)Å^3
Z	2
Density (calculated)	1.527 Mg/m^3
Absorption coefficient	0.762 mm^{-1}
F(000)	704
Crystal size	0.50 x 0.40 x 0.30 mm^3
Theta range for data collection	2.37 to 28.30 deg.
Index ranges	-12<=h<=12, -21<=k<21, -14<=l<=14
Reflections collected/ Unique	20573/3696 [R(int) = 0.0403]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3696/0/284
Goodness-of-fit on F^2	0.984
Final R indices [I>2s(I)]	R1 = 0.0481, wR2 = 0.1249
R indices (all data)	R1 = 0.0457, wR2 = 0.1300
Large difference peak and hole	0.538 and -0.440 e Å^{-3}

Table 32. Crystal data and structure refinement for 11

Empirical formula	$C_{18}H_{30}Cl_2N_6NiO_{14}$
Formula weight	684.09
Temperature	293(2)K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimension	
a, b, c (Å)	11.3437(4), 11.5740(4), 14.3987(6)
a, ß, ? (°)	66.9560(10), 87.3390(10), 64.7660(10)
Volume	1557.02(10)$Å^3$
Z	2
Density (calculated)	1.459 Mg/m^3
Absorption coefficient	0.864 mm^{-1}
F(000)	708
Crystal size	0.50 x 0.40 x 0.30 mm^3
Theta range for data collection	3.11 to 28.32 deg.
Index ranges	-15<=h<=14, -15<=k<14, -19<=l<=19
Reflections collected/ Unique	17889/7241 [R(int) = 0.0329]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7241/0/511
Goodness-of-fit on F^2	1.044
Final R indices [I>2s(I)]	R1 = 0.0474, wR2 = 0.1372
R indices (all data)	R1 = 0.0629, wR2 = 0.1505
Large difference peak and hole	0.646 and -0.443 e $Å^{-3}$

Table 33. Crystal data and structure refinement for 12

Empirical formula	$C_{18}H_{30}Cl_2N_6O_{14}Zn$
Formula weight	690.75
Temperature	293(2)K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimension	
a, b, c (Å)	7.1910(5), 11.2388(8), 11.5159(8)
a, ß, ? (°)	109.9670(10), 102.769(2), 107.1540(10)
Volume	780.36(9)Å^3
Z	1
Density (calculated)	1.470 Mg/m^3
Absorption coefficient	1.027 mm^{-1}
F(000)	356
Crystal size	0.50 x 0.40 x 0.30 mm^3
Theta range for data collection	2.02 to 28.30 deg.
Index ranges	-8<=h<=9, -14<=k<14, -15<=l<=15
Reflections collected/ Unique	9365/3843 [R(int) = 0.0375]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3843/0/266
Goodness-of-fit on F^2	1.028
Final R indices [I>2s(I)]	R1 = 0.0351, wR2 = 0.1009
R indices (all data)	R1 = 0.0398, wR2 = 0.1041
Large difference peak and hole	0.484 and -0.334 e Å^{-3}

Table 34. Crystal data and structure refinement for 13

Empirical formula	$C_{18}H_{30}B_2CoF_8N_6O_6$
Formula weight	659.03
Temperature	210(2)K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimension	
a, b, c (Å)	7.2519(3), 11.1083(4), 11.3608(4)
a, ß, ? (°)	109.6030(10), 103.6090(10), 106.4390(10)
Volume	769.68(5)Å^3
Z	1
Density (calculated)	1.422 Mg/m^3
Absorption coefficient	0.646 mm^{-1}
F(000)	337
Crystal size	0.50 x 0.50 x 0.20 mm^3
Theta range for data collection	3.06 to 28.26 deg.
Index ranges	-9<=h<=9, -14<=k<14, -14<=l<=15
Reflections collected/ Unique	8843/3619 [R(int) = 0.0291]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3619/0/275
Goodness-of-fit on F^2	1.002
Final R indices [I>2s(I)]	R1 = 0.0345, wR2 = 0.0959
R indices (all data)	R1 = 0.0386, wR2 = 0.0990
Large difference peak and hole	0.579 and -0.354 e Å^{-3}

Table 35. Crystal data and structure refinement for 14

Empirical formula	$C_{18}H_{30}B_2F_8N_6O_6Zn$
Formula weight	665.47
Temperature	293(2)K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimension	
a, b, c (Å)	7.2361(3), 11.1022(5), 11.3826(5)
a, ß, ? (°)	109.7800(10), 103.5560(10), 106.1920(10)
Volume	769.73(6)Å^3
Z	1
Density (calculated)	1.436 Mg/m^3
Absorption coefficient	0.886 mm^{-1}
F(000)	340
Crystal size	0.70 x 0.40 x 0.30 mm^3
Theta range for data collection	3.52 to 28.30 deg.
Index ranges	-9<=h<=9, -14<=k<14, -15<=l<=15
Reflections collected/ Unique	7493/3543 [R(int) = 0.0359]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3543/0/266
Goodness-of-fit on F^2	1.051
Final R indices [I>2s(I)]	R1 = 0.0367, wR2 = 0.1074
R indices (all data)	R1 = 0.0386, wR2 = 0.1092
Large difference peak and hole	0.580 and -0.573 e Å^{-3}

Table 36. Crystal data and structure refinement for 15

Empirical formula	$C_{18}H_{30}Cl_{6}Fe_{3}N_{6}O_{7}$
Formula weight	822.73
Temperature	180(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C2/m
Unit cell dimensions	
a, b, c (Å)	41.231(8) 23.293(5) 15.018(3)
a, ß, ? (deg.)	90 108.30(3) 90
Volume	13694(5) $Å^3$
Z, Calculated density	16, 1.596 Mg/m^3
Absorption coefficient	1.765 mm^{-1}
F(000)	6656
Crystal size	0.60 x 0.40 x 0.30 mm
Theta range for data collection	3.32 to 32.01 deg.
Limiting indices	-61<=h<=30, -29<=k<=34, -21<=l<=22
Reflections collected / unique	46325 / 23522 [R(int) = 0.0258]
Completeness to theta = 32.01	98.8 %
Absorption correction	XRED32
Max. and min. transmission	0.6195 and 0.4173
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	23522 / 0 / 962
Goodness-of-fit on F^2	0.775
Final R indices [I>2sigma(I)]	R1 = 0.0308, wR2 = 0.0608
R indices (all data)	R1 = 0.0691, wR2 = 0.0675
Largest diff. peak and hole	0.726 and -0.577 $e \cdot Å^{-3}$

Table 37. Crystal data and structure refinement for 16

Empirical formula	$C_6H_9N_3O$
Formula weight	139.16
Temperature	180(2)K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimension	
a, b, c (Å)	7.6563(15), 7.7682(16), 12.838(3)
a, ß, ? (°)	90, 106.57(3), 90
Volume	731.8(3)Å^3
Z	4
Density (calculated)	1.263 Mg/m^3
Absorption coefficient	0.091 mm^{-1}
F(000)	296
Crystal size	0.60 x 0.40 x 0.40 mm^3
Theta range for data collection	3.82 to 30.50 deg.
Index ranges	-10<=h<=10, 0<=k<11, 0<=l<=18
Reflections collected/ Unique	2209/2209 [R(int) = 0.0000]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2209/0/127
Goodness-of-fit on F^2	1.047
Final R indices [I>2s(I)]	R1 = 0.0347, wR2 = 0.0988
R indices (all data)	R1 = 0.0450, wR2 = 0.1023
Large difference peak and hole	0.273 and -0.158 e Å^{-3}

Table 38. Crystal data and structure refinement for 17

Empirical formula	$C_{24}H_{36}Cl_6Co_3N_{12}O_4$
Formula weight	946.14
Temperature	293(2)K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimension	
a, b, c (Å)	8.078(2), 8.898(2), 15.624(3)
a, ß, ? (°)	103.42(3), 101.88(3), 92.52(3)
Volume	1064.0(4)$Å^3$
Z	1
Density (calculated)	1.605 Mg/m^3
Absorption coefficient	1.584 mm^{-1}
F(000)	523
Crystal size	0.60 x 0.40 x 0.30 mm^3
Theta range for data collection	2.36 to 23.98 deg.
Index ranges	-9<=h<=8, -10<=k<9, 0<=l<=17
Reflections collected/ Unique	3318/3318 [R(int) = 0.0000]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3318/0/299
Goodness-of-fit on F^2	1.153
Final R indices [I>2s(I)]	R1 = 0.0310, wR2 = 0.0862
R indices (all data)	R1 = 0.0368, wR2 = 0.0981
Large difference peak and hole	0.361 and -0.420 e $Å^{-3}$

Table 39. Crystal data and structure refinement for 18

Empirical formula	$C_{12}H_{18}Cl_2CuN_6O_2$
Formula weight	412.76
Temperature	180(2)K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimension	
a, b, c (Å)	8.0473(16), 14.544(3), 13.618(3)
a, ß, ? (°)	90, 94.48(3), 90
Volume	1588.9(5)$Å^3$
Z	4
Density (calculated)	1.725 Mg/m^3
Absorption coefficient	1.729 mm^{-1}
F(000)	844
Crystal size	0.50 x 0.50 x 0.40 mm^3
Theta range for data collection	3.78 to 31.93 deg.
Index ranges	-11<=h<=11, 0<=k<21, 0<=l<=20
Reflections collected/ Unique	5429/5429 [R(int) = 0.0000]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5429/0/280
Goodness-of-fit on F^2	0.963
Final R indices [I>2s(I)]	R1 = 0.0452, wR2 = 0.1168
R indices (all data)	R1 = 0.0729, wR2 = 0.1255
Large difference peak and hole	0.875 and -1.120 e $Å^{-3}$

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Appendix A: List of abbreviations

br	Broad
C	Celsius
Calcd.	Calculated
Dec.	Decomposition
IR	Infrared
L	Ligand
J	Coupling constant
M	Metal
MeOH	Methanol
m	Multiplet (NMR), medium (IR)
NMR	Nuclear magnetic resonance
s	Singlet (NMR), strong (IR)
t	Triplet
T	Temperature
THF	Tetrahydrofuran
w	weak
Z	Number of molecules in the unit cell

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