

Coordination Chemistry of Acrylamide

2. Classical Complexes of Acrylamide with Manganese(II), Iron(II) and Nickel(II) Chlorides: Syntheses and Crystal Structures

K. B. Girma, Volker Lorenz, Steffen Blaurock, and Frank T. Edelmann*

Magdeburg, Chemisches Institut der Otto-von-Guericke-Universität

Received February 18th, 2005.

Dedicated to Professor Herbert W. Roesky on the Occasion of his 70th Birthday

Abstract. Metal complexes of manganese(II), iron(II), and nickel(II) chlorides with acrylamide, $[M(O-OC(NH_2)CH=CH_2)_4Cl_2]$ ($M = Mn$ (1), Fe (2) and Ni (3)), have been prepared and characterized by single crystal X-ray diffraction, IR spectroscopy and elemental analyses. The complexes crystallize in the cubic space group, $I\bar{4}3d$. The coordination geometries of the metal centers in

all three complexes involve tetragonally distorted octahedral structures with four O-donor atoms of acrylamide bonded in the equatorial positions and two chlorides in the apical positions.

Keywords: Acrylamide; Manganese; Iron; Nickel; Metal-amide complexes; Coordination chemistry; Crystal structure

Introduction

Complexes of acrylamide ($CH_2CHC(O)NH_2 = AAm$) [1, 2] and acrylamide based ligands [3–5] with transition metals are of interest due to the biological relevance of the amide group in peptides and proteins and their functions as models of metalloproteins active sites. The coordination chemistry of acrylamide has been reviewed with regard to recent public concerns on acrylamide exposure from food and its health effects [6]. The coordination of metal ions to acrylamide is also important since such complexes play catalytic roles in reactions of the monomer that is employed in the production of water-soluble polymers and copolymers [7].

Acrylamide is a special kind of ligand since it contains three donor sites that can form bonds with metal ions: the nitrogen atom of the amide group, the double bond between the carbon atoms and the oxygen atom of the carboxyl group [8]. Metal complexes of chlorides and nitrates of Cr^{III} , Mn^{II} , Fe^{III} , Co^{II} , Ni^{II} , Cu^{II} and Zn^{II} with acrylamide coordinating to the carbonyl oxygen atom are known mainly from elemental analysis, IR and electronic spectroscopy, and magnetic measurements [9]. To the contrary, some authors believed that complexes of Co^{II} , Mn^{II} , Ni^{II} , and Cu^{II} chlorides with acrylamide are coordinated through the nitrogen atom [10].

Despite the potential versatility of acrylamide as a ligand and conflicting conclusions as to MX_n coordination (where $M =$ metal atom; $X = Cl, NO_3$; $n = 2$ or 3), only few O-

bonded acrylamide complexes have been fully characterized by spectroscopic and single crystal X-ray diffraction studies. *Savost'yanov* et al. and *Evastratova* et al. have published the syntheses and single X-ray crystal structures of Co^{II} [9] and Cu^{II} [11] nitrates with O-bound acrylamide to the metal centers, respectively. Recently, we have reported two cobalt(II) chloride complexes with acrylamide, $[Co(O-OC(NH_2)CH=CH_2)_4Cl_2]$ and $[Co\{O-OC(NH_2)CH=CH_2\}_6][CoCl_4]$, in which the ligand is coordinated to the metal ions *via* the carbonyl oxygen atom which have been characterized using elemental analyses, infrared spectra and single crystal X-ray diffraction [12].

We now present in here the syntheses and single crystal X-ray structures of O-bonded manganese(II), iron(II) and nickel(II) chloride complexes with acrylamide. The IR frequencies observed for these complexes can be used as a reference in interpretation of spectral changes and assignments of the bands in acrylamide and their complexes upon coordination. The single X-ray crystal structures, spectroscopic and elemental analyses of **1**, **2** and **3** prove coordination of acrylamide through the carbonyl oxygen atom in these compounds.

Experimental Section

General Procedures. All preparations were done in an atmosphere of dry nitrogen with the use of standard Schlenk techniques. The starting materials acrylamide, the THF adduct of Mn^{II} chloride, $MnCl_2(THF)_2$, anhydrous iron(II) chloride, hexahydrated nickel(II) chloride and the solvent absolute ethanol were obtained from commercial suppliers and used as received. Diethylether was dried over $Na/benzophenone$ and freshly distilled under nitrogen before use. All compounds were basically prepared by the same method: To 300 mg of the anhydrous or hydrated metal(II) salt dissolved in 20 ml of absolute ethanol (and triethylorthoformate for dehydration in case of the hydrated nickel(II) chloride), acrylamide in a 1:6 metal salt to ligand ratio was added and stirred for 30 mi-

* Prof. Dr. F. T. Edelmann
Universitätsplatz 2
D-39106 Magdeburg/Germany
Tel.: +49-391-6718327
Fax: +49-391-6712933
E-mail address: frank.edelmann@vst.uni-magdeburg.de

Table 1 Characteristic absorption bands in the IR spectra of acrylamide and its complexes* a) (cm⁻¹, KBr disks).

AAM	[FeCl ₂ ·4AAM] (2)	[CoCl ₂ ·4AAM]	[NiCl ₂ ·4AAM] (3)	[MnCl ₂ ·4AAM] (1)	[Cu(NO ₃) ₂ ·4AAM]	[Co(AAM) ₆]- [CoCl ₄]
3354	3394	3394	3394	3400	3340	3392
	3336	3335	3334	3355		
	3305	3305	3305	3307		
	3265	3264	3264	3268		3264
	3226	3224	3224	3227		3224
3184	3189	3187	3185	3190	3183	3187
	3152	3152	3152	3156		3152
2814	2794	2793	2791	2789	2784	2756
	2755	2757	2756	2755		
1922	1921	1925	1928	1931	1932	1940
1673	1664	1664	1664	1664	1667	1667
	1629	1629	1630	1630	1623	1629
1614	1584	1583	1583	1585	1579	1582
1429	1452	1452	1452	1449	1456	1452
1353	1372	1372	1372	1370	1386	1371
					1365	
1281	1288	1287	1287	1286	1320	1288
1137	1133	1132	1131	1127	1118	1130
1052	1062	1061	1061	1059	1063	1059
					1040	
990	988	987	987	986	988	987
					971	
962	960	961	963	964	966	962
841	852	851	850	849	856	850
819	808	808	809	810	828	808
					812	
708	646	641	638	635	729	641
					707	
664	575	579	582	582	674	580
626	516	514	512	512	649	512
509	480	481	481	481	520	482
					502	

a) The spectra of [CoCl₂·4AAM] and [Co(AAM)₆][CoCl₄] from our previous work [12] and that of [Cu(NO₃)₂·4AAM], which we have measured after getting the complex as previously published by [11] are included.

notes. The solutions were then concentrated by removing part of the solvent under vacuum, and a few drops of dry diethylether were carefully layered. Cooling and slow diffusion of diethylether into the solution developed the corresponding single crystals of **1**, **2**, and **3**. The bulk purity of the complexes was verified by determining their carbon, hydrogen and nitrogen content by using a Leco CHNS 923 apparatus. Melting points were determined with a Büchi B-450 digital melting point apparatus. The IR spectra of the complexes were recorded using KBr pellets on a Perkin Elmer FT-IR spectrometer system 2000 between 4000 cm⁻¹ and 400 cm⁻¹.

[Mn(O-acrylamide)₄Cl₂] (1). Color: white. Yield: 220 mg (48 %). Elemental Anal. For **1** Calcd. (%): C, 35.1; H, 4.9; N, 13.6. Found (%): C, 34.8; H, 4.8; N, 13.6. Mp: 224 °C.

IR spectrum (KBr, cm⁻¹) for **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.

[Fe(O-acrylamide)₄Cl₂] (2). Color: yellow. Yield: 730 mg (75 %). Elemental Anal. For **2** Calcd. (%): C, 35.0; H, 4.9; N, 13.6. Found (%): C, 35.0; H, 4.9; N, 14. Mp: 116–118 °C.

IR spectrum (KBr, cm⁻¹) for **2**: 3394 vs; 3336 ms; 3306 ms; 3265 ms; 3226 ms; 3188 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.

[Ni(O-acrylamide)₄Cl₂] (3). Color: green. Yield: 340 mg (65 %). Elemental Anal. For **3** Calcd. (%): C, 34.8; H, 4.8; N, 13.5. Found (%): C, 34.9; H, 4.8; N, 13.6. Mp: 190 °C (dec.).

IR spectrum (KBr, cm⁻¹) for **3**: 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.

The IR spectra for a free AAM and the complexes analyzed in here are compared with each other to study the spectral changes observed on complexation. Measurement of the IR (KBr, cm⁻¹) for acrylamide include:

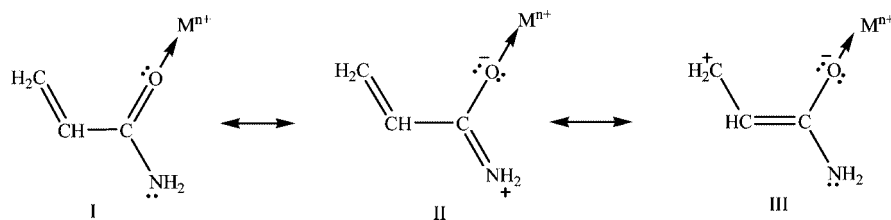
3354 vs; 3184 s; 3103 m; 3035 m; 2920 mw; 2814 m; 2525 w; 2427 w; 2279 w; 2192 w; 1922 mw; 1673 vs; 1614 vs; 1429 vs; 1353 vs; 1281 s; 1137 s; 1052 m; 990 s; 962 vs; 841 m; 819 m; 708 ms; 664 ms; 626 m and 509 ms.

The X-ray crystallographic study of the complexes was carried out using a Bruker AXS SMART CCD diffractometer with MoK_α radiation (λ = 0.71073 Å) and graphite monochromator. The structures were solved by direct methods using SHELXTL Version 5.1 [13]. Anisotropic thermal parameters were refined for all non-hydrogen atoms. All hydrogen atoms were found on the difference Fourier card and were refined freely.

Results and Discussion

Preparation

Crystalline hydrated or anhydrous MCl₂ compounds (where M = Mn, Fe, Co and Ni) form complexes with acrylamide in ethanol solution with diffusion of diethylether into the solution. Complexes of chlorides of Mn^{II}, Fe^{II}, Co^{II} [12], and Ni^{II} with acrylamide were obtained using this method



Scheme 1 Delocalized resonance structures of O-bonded acrylamide.

and characterized by IR spectroscopy and single X-ray diffraction. The complexes have the same composition, $[M(\text{AAm})_4\text{Cl}_2]$, in which the ligand is coordinated through the carboxyl oxygen atom. The molecular structures of **1**, **2**, **3** and the blue dichloro-tetrakis(acrylamide)cobalt(II) are all distorted octahedral. They all crystallize in cubic space groups with four O-donor atoms of acrylamide in the equatorial positions and two chloride ions in the apical positions around the central atom. The complexes of acrylamide are well soluble in water, alcohol, and acetone; and insoluble in toluene, ether, and other nonpolar solvents.

Infrared Spectroscopic Analysis

The IR spectra of free acrylamide and its complexes can be compared with each other to check spectral changes upon coordination and as a result predict the mode of coordination of acrylamide. There are some reports in the literature [14, 15] in which the spectrum of acrylamide has been recorded and the observed frequencies have been assigned to fundamental vibrations. However, even these recently proposed band assignments are not consistent in many cases. Review of the literature in this regard has shown that ambiguous band assignments and equivocal interpretations of the spectra of acrylamide and the spectral changes upon complexation caused contradictory opinions concerning the coordination of acrylamide *via* the oxygen or nitrogen atom. In Table 1, we have presented the spectra of acrylamide and the acrylamide complexes that are described in here and those that are completely characterized without taking a hard line on band assignments until the topic is settled in future studies with more experimental and theoretical results.

The electronic structure of O-coordinated acrylamide complexes may be represented by a resonance hybrid of structures **I**, **II** and **III**, with each contributing a certain amount depending on the intramolecular and intermolecular interactions (Scheme 1).

The presence of such resonance structures seems to be responsible for the fact that frequency changes of not only the stretching and bending modes of the CO, CN, and NH but also of the vinyl group are observed upon complexation. On coordination through oxygen, the contribution from the resonance forms **II** and **III** will increase; the contribution from either **II** or **III** may vary depending on the intermolecular and intramolecular interactions with

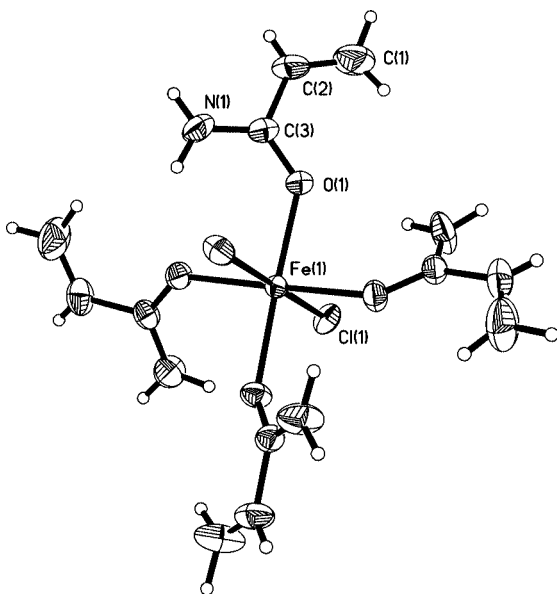
neighboring species. A strong contribution from **II** may result in a decrease in the CO stretching, increase in the CN stretching frequency but no appreciable change in the NH stretching. On the other hand, a strong contribution from **III** may result in a decrease in the CO stretching, decrease in the CN stretching and an appreciable change in NH stretching.

The position of the N–H stretching vibration in the infrared spectra is determined by the strength of the M–N–H bond and by the strength of the hydrogen bond (N–H···O or N–H···Cl) [16]. According to the literature [17], the NH_2 stretching vibrations shift to lower wavenumbers if these bonds become stronger. Comparison of the IR spectra of free acrylamide and the complexes in the NH_2 vibration region near $3400\text{--}3100\text{ cm}^{-1}$ reveals a significant increase in the positions of $\nu_{\text{as}}(\text{NH}_2)$ and appreciable increase in $\nu_{\text{s}}(\text{NH}_2)$ vibrations to higher wave numbers accompanied by splitting into more sharp components in the chloro-complexes. On the other hand, broad spectral shifts of the $\nu_{\text{as}}(\text{NH}_2)$ to lower wave numbers but no appreciable change in $\nu_{\text{s}}(\text{NH}_2)$ vibrations were reported for the O-coordinated tetrakis(O-acrylamide)-bis(O-nitrato)-copper(II) complex with coordinated nitrate. Instead of a sharp band, the spectra of substances in which the NH_2 groups are involved in strong hydrogen bond formation show only a weak and diffuse absorption band in these regions [18]. Substances which absorb strongly in these region (and are shown in this way not to be forming strong hydrogen bonds with the use of the hydroxyl or the amino groups) give curves of different types, involving pronounced frequency shifts and often splitting of the peak into two or more components. The five sharp bands around 3400 cm^{-1} in the chloro-complexes in contrast to the weak and diffuse absorption band in the spectra of acrylamide and copper(II) nitrate complex may suggest weak intra- and intermolecular hydrogen bonding between NH_2 groups and the neighboring species.

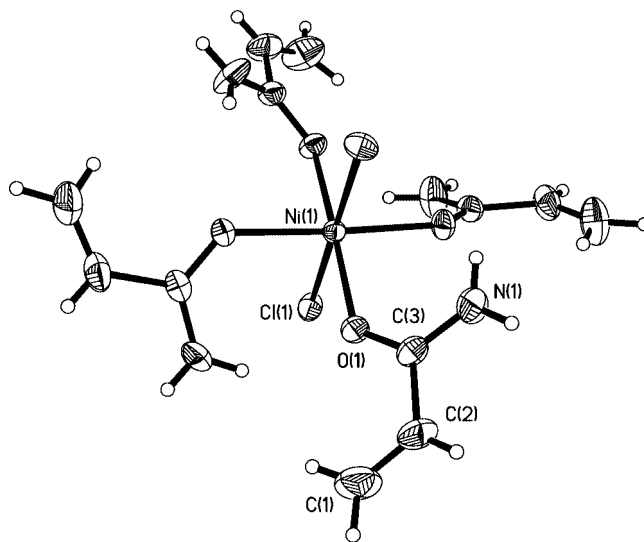
An important spectral change observed between the spectra of free acrylamide and the complexes investigated here is the shifting of a strong broad band observed at 1673 cm^{-1} in free acrylamide to lower wave numbers and its splitting into two bands at 1664 cm^{-1} and near 1629 cm^{-1} upon complexation. The vibration that is observed in the IR spectrum of free acrylamide at 1614 cm^{-1} has also shifted to lower wave numbers at 1582 cm^{-1} and at 1583 cm^{-1} in the spectra of the complexes. However, as-

Table 2 Crystal data and structure refinement for **1**, **2** and **3**.

Empirical formula	C ₁₂ H ₂₀ Cl ₂ Mn N ₄ O ₄	C ₁₂ H ₂₀ Cl ₂ Fe N ₄ O ₄	C ₁₂ H ₂₀ Cl ₂ N ₄ Ni O ₄
Formula weight	410.16	411.07	413.93
Temperature	210(2) K	200(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system, space group	cubic, I43d	cubic, I43d	cubic, I43d
Unit cell dimensions			
a, b, c Å	18.0239(4)	17.91440(10)	17.7548(5)
Volume	5855.3(2) Å ³	5749.19(6) Å ³	5596.9(3) Å ³
Z, Calculated density	12, 1.396 Mg/m ³	12, 1.425 Mg/m ³	12, 1.474 Mg/m ³
Absorption coefficient	0.970 mm ⁻¹	1.086 mm ⁻¹	1.348 mm ⁻¹
F(000)	2532	2544	2568
Crystal size	0.20 x 0.20 x 0.20 mm	0.50 x 0.50 x 0.30 mm	0.50 x 0.50 x 0.40 mm
Theta range for data collection	2.77 to 28.30 deg.	2.79 to 28.86 deg.	3.25 to 28.22 deg.
Limiting indices	-23 ≤ h ≤ 23, -15 ≤ k ≤ 23, -23 ≤ l ≤ 23	-24 ≤ h ≤ 23, -23 ≤ k ≤ 23, -23 ≤ l ≤ 23	-23 ≤ h ≤ 23, -23 ≤ k ≤ 23, -23 ≤ l ≤ 23
Reflections collected / unique	14678 / 1202 [R(int) = 0.0332]	21055 / 1231 [R(int) = 0.0329]	12304 / 1113 [R(int) = 0.0543]
Completeness to theta = 29.21	99.5 %	98.7 %	96.6 %
Absorption correction	SADABS	SADABS	SADABS
Max. and min. transmission	0.8296 and 0.8296	0.7364 and 0.6126	0.6147 and 0.5523
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	1202 / 0 / 73	1231 / 0 / 73	1113 / 0 / 73
Goodness-of-fit on F ²	1.065	1.103	1.099
Final R indices [I > 2σ(I)]	R1 = 0.0212, wR2 = 0.0528	R1 = 0.0197, wR2 = 0.0500	R1 = 0.0297, wR2 = 0.0708
R indices (all data)	R1 = 0.0236, wR2 = 0.0537	R1 = 0.0210, wR2 = 0.0505	R1 = 0.0315, wR2 = 0.0714
Absolute structure parameter	0.038(17)	0.009(12)	0.019(17)
Largest diff. peak and hole	0.218 and -0.137 e.Å ⁻³	0.160 and -0.198 e.Å ⁻³	0.475 and -0.338 e.Å ⁻³

**Fig. 1** Molecular structure of **1**, [Mn(O-OC(NH₂)CH=CH₂)₄Cl₂].

signments of these bands to the respective modes of vibrations have not been obvious. Sundaraganesan et al. [14] assigned the absorptions near 1673 cm⁻¹ to ν(C=O), ν(C=C) and δ(NH₂) vibration modes that are mixed in character; and the band near 1614 cm⁻¹ to C-C skeletal stretching (C=O and C=C with some contribution from CH₂ and HNC bending coordinates) for uncoordinated acrylamide. The assignment of the bands near 1664 cm⁻¹, 1629 cm⁻¹ and 1582 cm⁻¹ in the spectra of acrylamide complexes to ν(C=O), ν(C=C), δ(NH₂) or C-C skeletal stretching is not clear at this level.

**Fig. 2** Molecular structure of **2**, [Fe(O-OC(NH₂)CH=CH₂)₄Cl₂].

Nearly all bands at 1922 cm⁻¹, 1429 cm⁻¹, 1352 cm⁻¹ and 1280 cm⁻¹ in free acrylamide have shifted to higher wavenumbers upon complexation: 1931 cm⁻¹, 1449 cm⁻¹, 1371 cm⁻¹ and 1286 cm⁻¹ in **1**; 1921 cm⁻¹, 1452 cm⁻¹, 1372 cm⁻¹ and 1288 cm⁻¹ in **2**; and 1928 cm⁻¹, 1452 cm⁻¹, 1372 cm⁻¹ and 1287 cm⁻¹ in **3**, respectively. Shifts at 1456 cm⁻¹, 1385-1320 cm⁻¹ (three broad bands) and absence of a band near 1280 cm⁻¹ has been recorded for [Cu(NO₃)₂·4AAm]. The bands near 1352 cm⁻¹ and 1280 cm⁻¹ are assigned to NH₂ scissoring and NH₂ rocking, respectively. Bending motions of the NH₂ group contribute to several fundamentals; the strongest contribution

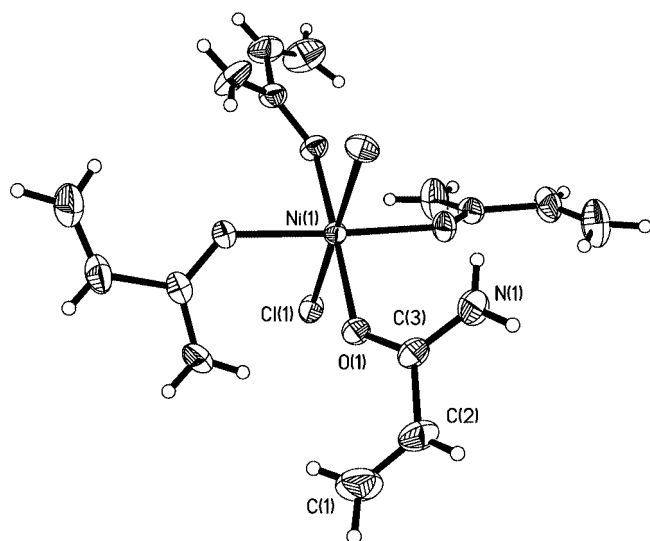


Fig. 3 Molecular structure of 3, $[\text{Ni}(\text{O-OC}(\text{NH}_2)\text{CH}=\text{CH}_2)_4\text{Cl}_2]$.

of this vibration was calculated for the band at 1138 cm^{-1} in free acrylamide [14]. This band has shifted to 1131 cm^{-1} in the chloro-complexes described in here, and a shift to 1119 cm^{-1} has been observed for the O-coordinated copper(II) nitrate complex with acrylamide. The $\omega(\text{H}_2\text{C}=\text{C})$ (CH_2 wagging) bands at 961 cm^{-1} or 962 cm^{-1} and the δCH and CH_2 twisting bands at about 990 cm^{-1} in both the spectra of acrylamide and the complexes indicate uncoordinated double bonds.

X-Ray Diffraction Analysis

The complexes, 1, 2, and 3, crystallize in the cubic space group $I\bar{4}3d$. The crystallographic data and structure refinement results of all crystals reported in here are presented in Table 2. A cobalt(II)-chloride complex with a similar composition and structure has been reported before [12]. The crystal structures of the complexes 1, 2 and 3 along with the atomic numbering schemes are shown in Figures 1, 2 and 3. The coordination geometries of the metal centers involve a tetragonally distorted octahedral structure with four O-donor atoms of acrylamide bonded in the equatorial positions and two chloride ions in the apical positions. Selected bond lengths and angles of complexes 1, 2 and 3 are summarized in Table 3. The equatorial M–O bond lengths in the manganese(II), iron(II), cobalt(II) and nickel(II) chloride complexes with acrylamide are 2.185 \AA , 2.130 \AA , 2.106 \AA and 2.076 \AA while the axial M–Cl bond lengths are 2.526 \AA , 2.497 \AA , 2.462 \AA and 2.419 \AA respectively. This sequence is in accordance with the general order of stability found by *Irving* and *Williams* for such compounds [19]. The longer M–Cl bonds slightly extend the metal polyhedron in to a tetragonally distorted octahedron. The angular distortions of the octahedrons are no more than 2.5° in all cases. Stronger metal-ligand bond is obtained in the copper(II) nitrate complex with acrylamide

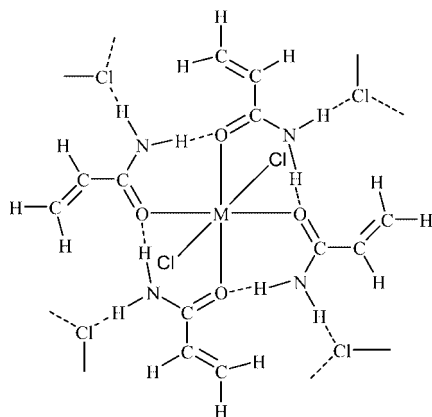
Table 3 Selected bond lengths/ \AA and angles/deg. for 1, 2 and 3.

1. $[\text{Mn}(\text{O-acrylamide})_4\text{Cl}_2]$			
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)–(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. $[\text{Fe}(\text{O-acrylamide})_4\text{Cl}_2]$			
Fe(1)–O(1)	2.130(8)	O(1)–Fe(1)–Cl(1)	87.8(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)–(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)
3. $[\text{Ni}(\text{O-acrylamide})_4\text{Cl}_2]$			
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)

where Cu–O bond lengths were found in the range between 1.952 \AA – 1.958 \AA .

The molecular structure of a free acrylamide without the coordinates of hydrogen atoms, which is a planar to a good approximation, is available in the literature [20] for comparison with coordinated acrylamide. The bond lengths C=O (1.190 \AA), C–N (1.272 \AA) and C–C (1.760 \AA) which are reported for a *syn* uncoordinated acrylamide molecule, are either significantly shorter or longer than the usual bond lengths of 1.24 \AA , 1.34 \AA and 1.53 \AA for C=O, C–N, and C–C, respectively, in the structures of amides and peptides. There is also an essential freedom of rotation about the single bond between the amide group and the alpha carbon atom, which may allow acrylamide to assume many configurations.

The coordinated acrylamide molecules in the crystal structures of the complexes studied here are planar. The C(3)–O(1) bond lengths for coordinated acrylamide molecules in the manganese(II), iron(II), cobalt(II) and nickel(II)



Scheme 2 Schematic drawing of $[M(\text{AAm})_4\text{Cl}_2]$ showing intramolecular and intermolecular interactions. Weak intermolecular interactions of the chlorine atoms in the apical positions are omitted for clarity.

chloride complexes are 1.250 Å, 1.252 Å, 1.256 Å and 1.250 Å, respectively. The C(3)–O(1) bond lengths (1.250 Å–1.256 Å) for coordinated acrylamide molecules in the complexes suggest weakening upon complexation. This bond is even weaker in the copper(II) nitrate complex with acrylamide where its length was found in the range between 1.256 Å–1.273 Å. The bond lengths of the terminal carbon atoms with the double bonds of the coordinated acrylamide molecules in the manganese(II), iron(II), cobalt(II) and nickel(II) chloride complexes are 1.288 Å, 1.295 Å, 1.301 Å and 1.297 Å respectively. These bond lengths show that the double bonds in coordinated acrylamide, although they are still shorter than the usual C=C bond (1.34 Å), are weakened during complexation relative to the C=C bond in uncoordinated acrylamide (1.261 Å). The copper(II) nitrate complex with acrylamide show C=C terminal bond lengths in the range between 1.294 Å – 1.311 Å.

The central C(3)–C(2) bond length (1.760 Å) for uncoordinated acrylamide molecule becomes very short (about 1.475 Å) upon complexation which may be due to delocalization of electrons from the double bond. The middle C(2)–H(2) bond lengths in the coordinated acrylamide molecules in the manganese(II), iron(II), cobalt(II) and nickel(II) chloride complexes are 0.80 Å, 0.77 Å, 0.82 Å and 0.78 Å, respectively. The couple C(3)–H(1A) and C(3)–H(1B) bond lengths in the coordinated acrylamide molecules are the weakest in the manganese(II) complex. The H(1A)–C(3)–H(1B) bond angles in the coordinated acrylamide molecules are 113°, 117° and 108° in manganese(II), iron(II) and nickel(II) complexes, respectively. The C(3)–N(3) bond lengths (1.302 Å–1.310 Å) in coordinated acrylamide molecules are relatively longer than the C–N bond length (1.272 Å) in uncoordinated acrylamide.

The structures of the complexes are composed of molecules and unit cells united by a system of intramolecular and intermolecular N–H···X hydrogen bonds (X = O or Cl) (Scheme 2). The couple N(1)–H(N1A) and N(1)–H(B)

bond lengths in the coordinated acrylamide molecules are 0.86 Å and 0.89 Å in the iron(II), 0.88 Å and 0.79 Å in the nickel(II) and 0.92 Å and 0.83 Å in the manganese(II) complexes, respectively. The H(N1A)–N(1)–H(N1B) bond angles in the coordinated acrylamide molecules are 117°, 120°, and 116° in **1**, **2**, and **3**, respectively. One of the amine-NH₂ hydrogen atoms is bonded to a neighboring oxygen atom of acrylamide that is coordinated to the metal atom, and the other one is weakly associated to the chloride anion in the neighboring unit cell.

Biologically relevant metal ions such as manganese, iron, cobalt, nickel and copper form coordination compounds with acrylamide. Few O-bonded transition metal complexes, $[\text{Co}(\text{O}-\text{OC}(\text{NH}_2)\text{CH}=\text{CH}_2)_4(\text{H}_2\text{O})_2](\text{NO}_3)_2$, $[\text{Cu}(\text{O}-\text{OC}(\text{NH}_2)\text{CH}=\text{CH}_2)_4(\text{NO}_3)_2]$, $[\text{Co}(\text{O}-\text{OC}(\text{NH}_2)\text{CH}=\text{CH}_2)_6][\text{CoCl}_4]$ and $\text{Co}[\text{O}-\text{OC}(\text{NH}_2)\text{CH}=\text{CH}_2)_4\text{Cl}_2$ have been fully characterized by spectroscopic and single crystal X-ray diffraction in previous studies. The single X-ray crystal structures, spectroscopic and elemental analyses of **1**, **2** and **3** described in here also prove coordination of acrylamide through the carbonyl oxygen atom in these compounds.

Supplementary Material. Crystallographic data for the crystal structures reported in this paper can be obtained from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or [www.http://ccdc.cam.ac.uk](http://ccdc.cam.ac.uk)) by referring the CIF deposition codes 258910 for **1**, 258909 for **2** and 258908 for **3**.

References

- [1] P. M. Angus, D. P. Fairlie, W. G. Jackson, *Inorg. Chem.* **1993**, *32*, 450.
- [2] D. P. Fairlie, P. M. Angus, M. D. Fenn, W. G. Jackson, *Inorg. Chem.* **1991**, *30*, 1564.
- [3] D.-Y. Kong, Y.-Y. Xie, *Polyhedron* **2000**, *19*, 1527.
- [4] T. Weyhermüller, K. Weighardt, P. Chaudhuri, *J. Chem. Soc., Dalton Trans.* **1998**, 3805.
- [5] R. W. Hay, N. Govan, A. Perotti, O. Carugo, *Trans. Metal Chem.* **1997**, *22*, 389.
- [6] a) A. D. Pomogailo, G. I. Dzhardimalieva, *Polym. Sci. Ser. A* **2004**, *46*, 250; b) D. Wöhrle, A. D. Pomogailo, *Metal complexes and metals in macromolecules. Synthesis, structure and properties*, VCH, **2003**, 96; c) G. I. Dzhardimalieva, A. D. Pomogailo and V. A. Volpert, *J. Inorg. Organomet. Polym.* **2002**, *12*, 1.
- [7] K. B. Girma, V. Lorenz, S. Blaurock, F. T. Edelmann, *Coord. Chem. Rev.* **2005**, *249*, 1283.
- [8] J. R. Allan, A. D. Paton, K. Turvey, *Thermochimica Acta.* **1992**, *200*, 355.
- [9] V. S. Savost'yanov, V. I. Ponomarev, A. D. Pomogailo, B. S. Selenova, I. N. Ivleva, A. G. Starikov, L. O. Atovmjan, *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)*, **1990**, *39*, 674.
- [10] M. S. Barvinok, L. V. Mashkov, *Russ. J. Inorg. Chem.* **1974**, *19*, 310.
- [11] S. I. Evstratova, G. V. Shilov, G. I. Dzhardimalieva, A. D. Pomogailo, I. E. Uflyand, S. M. Aldoshin, *Russ. J. Coord. Chem.* **2001**, *27*, 375.
- [12] K. B. Girma, V. Lorenz, S. Blaurock, F. T. Edelmann, *Z. Anorg. Allg. Chem.* **2005**, *631*, 1419.

- [13] SHELXTL Version 5.1, Bruker Analytical X-ray Systems, **1998**.
- [14] N. Sundaraganesan, N. Puviarasan, S. Mohan, *Talanta* **2001**, *54*, 233.
- [15] K.-M. Marstokk, H. Mollendal, S. Samdal, *J. Mol. Struct.* **2000**, *524*, 69.
- [16] P. M. Van Berkel, W. L. Driessen, R. Hämäläinen, J. Reedijk, U. Turpeinen, *Inorg. Chem.* **1994**, *33*, 5920.
- [17] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed.; Wiley Sons Inc.: New York, **1997**.
- [18] L. Pauling, *The Nature of Chemical Bond*, 3rd ed.; Cornell University Press, New York, **1960**.
- [19] H. Irving, R. J. Williams, *J. Chem. Soc.* **1953**, 3192.
- [20] I. V. Isakov, *J. Struct. Chem. (USSR)* **1966**, *7*, 836.