Contribution from the Department of Inorganic Chemistry,
The University, P.O. Box 75, Leyden, The Netherlands

Acrylamide, an Oxygen-donor Ligand to Divalent Transition-metal Ions

J. Reedijk

Received June 8, 1971

The preparation and spectral properties of a number of compounds with general formula $M(acrylamide)_n^{2+}(anion)_2$ is reported; in this formula M = Mn, Fe, Co, Ni, Cu, Zn, and Cd, n = 4 or 6 and the anions are ClO_4^-, BF_4^-, and NO_3^-.

The ligand acrylamide is shown to behave as a normal amide donor, with the oxygen of the carbonyl group coordinated to the metal ions, as concluded from infrared spectra, ligand-field spectra, E.P.R.-spectra, and X-ray powder diagrams. The results are different from earlier reports about the ligand properties of acrylamide.

Introduction

Some time ago two papers, appeared[1,2] concerning the ligand properties of acrylamide (hereafter called AA). In that work some arguments were presented for nitrogen coordination rather than oxygen coordination of this ligand to Lewis acids. The main argument came from the analysis of the mass spectrum of $SnCl_4(AA)_2$, with additional evidence from NMR spectra, photoelectron spectroscopy, infrared spectra and qualitative M.O. calculations. Ligand-field spectra of the metal complexes[2], however, did not agree with that picture.

This prompted us to reinvestigate this subject in the scope of other work in this field from this laboratory[3]. Therefore a number of compounds of formula $M(AA)_n(anion)_2$ was prepared and investigated with the aid of several physical methods.

Experimental Section

(in co-operation with Mr. J.A. Smit)

Starting Materials. Acrylamide (Fluka) was used without purification. Metal (II) nitrates and perchlorates were commercially available as the hydrates. Hydrates of the metal (II) tetrafluoroborates were prepared from the metallic powders and hydrofluoroboric acid.

Preparation of the Complexes. All compounds were prepared basicly by same method, *i.e.* from the hydrated metal(II) salt dissolved in ethanol and triethylorthoformate (for dehydration[4]) to which excess of ligand in ethanol is added. The preparation of $Co(AA)_6(ClO_4)_2$ will be given as an example.

So, 1.7 g of $Co(H_2O)_6(ClO_4)_2$ (0.005 mole) was dissolved in 2 ml of ethanol and 5.5 g of triethylorthoformate (0.04 mole), upon which 2.5 g of acrylamide (0.035 mole) in 3 ml of ethanol was added. Upon the addition of a few ml of diethylether pink crystals separated, which were collected by filtration, washed with three portions of dry diethylether and finally dried *in vacuo*.

Analyses. The metal content of all compounds was determined by complexometric titrations. In a few cases carbon, hydrogen and nitrogen were also determined; (by the Organisch Chemisch Instituut TNO, P.O. Box 5009, Utrecht).

Measurements. Infrared spectra (4000-200 cm^{-1}) were obtained with a Unicam SP 1200 (4000-400 cm^{-1}) and a Hitachi EPI-L (700-200 cm^{-1}) as Nujol mulls sandwiched between NaCl or polythene. Ligand-field spectra were obtained by the diffuse reflectance method on a Beckman DK-2A instrument. X-ray powder diagrams were obtained by the Guinier method.[5] Paramagnetic resonance spectra (X- and Q-band) were recorded on Varian instruments, as described elsewhere.[6]

Results and Characterization

General. The compounds of the present investigation are listed in Table I, together with analytical results, colours, melting points and X-ray types. Ligand-field spectral data are listed in Table II.

Several compounds of Table I were found to have mutually similar X-ray powder diagrams, both in *d*-values and intensities. This strongly suggest the same metal-ion environment and ion packings in these compounds. This kind of powder isomorphy occurs in many first-row transition-metal compounds.[3,7-9]

---

[1] M.F. Farona, J.G. Grasselli, H. Grossman, and W.M. Ritchey, *Inorg. Chim. Acta*, 3, 495 (1969).
[2] M.F. Farona, W.T. Ayers, B.G. Ramsey, and J.G. Grasselli, *Inorg. Chim. Acta*, 3, 503 (1969).
[3] J. Reedijk, *Rec. Trav. Chim. 88*, 1139 (1969).
[4] P.W.N.M. van Leeuwen and W.L. Groeneveld, *Inorg. Nucl. Chem. Letters*, 3, 145 (1967).
[5] J. Reedijk and W.L. Groeneveld, *Rec. Trav. Chim.*, *86*, 1103 (1967).
[6] R.D. Dowsing, B. Nieuwenhuyse, and J. Reedijk, *Inorg. Chim. Acta* 5, 301 (1971).
[7] P.W.N.M. van Leeuwen and W.L. Groeneveld, *Rec. Trav. Chim.*, *86*, 721 (1967).

Table I. Coordination compounds of AA, with analyses, colours melting points and X-ray types.

Compound	% Metal fnd.	% Metal calc.	Colour	Melting point (°C.)	X-ray type
$Mn(AA)_6(ClO_4)_2$	8.20	8.08	white	110-111	A
$Fe(AA)_6(ClO_4)_2$	8.00	8.20	dark yellow	90 dec.	—
$Co(AA)_6(ClO_4)_2$	8.67	8.61	pink	180 dec.	B
$Ni(AA)_6(ClO_4)_2$	8.52	8.58	light green	188-190	B
$Cu(AA)_6(ClO_4)_2$	9.12	9.22	light blue	98-100	C
$Zn(AA)_6(ClO_4)_2$	9.60	9.46 [a]	white	126-127	B
$Cd(AA)_6(ClO_4)_2$	15.38	15.24	white	96-100	A
$Mn(AA)_6(BF_4)_2$	8.41	8.39	white	100-102	A
$Fe(AA)_6(BF_4)_2$	8.81	8.51	dark yellow	102 dec.	—
$Co(AA)_6(BF_4)_2$	8.89	8.94	pink	140 dec.	B
$Ni(AA)_6(BF_4)_2$	8.95	8.91 [b]	light green	180 dec.	B'
$Cu(AA)_6(BF_4)_2$	9.80	9.57	light blue	106-107	C
$Zn(AA)_6(BF_4)_2$	9.95	9.82	white	114-115	B
$Cd(AA)_6(BF_4)_2$	15.95	15.78	white	88-90	A
$Co(AA)_6(NO_3)_2$	9.86	9.67	pink	78-79	D'
$Ni(AA)_6(NO_3)_2$	9.85	9.64	green	114-116	D
$Zn(AA)_6(NO_3)_2$	10.67	10.62	white	81-82	D
$Cu(AA)_4(ClO_4)_2$	11.69	11.62	blue green	142-144	—
$Mn(AA)_4(NO_3)_2$	11.90	11.86	white	88-89	—
$Cu(AA)_4(NO_3)_2$	13.29	13.40 [c]	light blue	126-127	—
$Cd(AA)_3(NO_3)_2$	25.0	25.0	white	55-60	—

[a] %C: 31.44 (calc. 31.30; %H: 4.53 (calc. 4.38); %N: 12.31 (calc. 12.17). [b] %C: 32.85 (calc. 32.81); %H: 4.82 (calc. 4.59) %N: 12.62 (calc. 12.76). [c] %C: 30.89 (calc. 30.54); %H: 4.18 (calc. 4.28) %N: 17.50 (calc. 17.81).

Table II. Diffuse reflectance spectra of AA complexes; band maxima are in kK and Dq and B are in cm^{-1}.

Compound	Assignments and maxima					Calculated Dq	Parameters B
			$^5E_g \leftarrow {}^5T_{2g}$				
$Fe(AA)_6(ClO_4)_2$			9.9	7.6 sh			
$Fe(AA)_6(BF_4)_2$			10.0	8.0 sh			
	$^2P, {}^4T_{1g}(P) \leftarrow$		$^4A_{2g} \leftarrow$		$^4T_{2g} \leftarrow {}^4T_{1g}(F)$		
$Co(AA)_6(ClO_4)_2$	21.0 sh	19.4	16.0 sh		8.0	875	840
$Co(AA)_6(BF_4)_2$	20.9 sh	19.3	15.0 sh		7.9	870	840
$Co(AA)_6(NO_3)_2$	20.8 sh	19.4	15.5 sh		8.0	875	840
	$^3T_{1g}(P) \leftarrow$		$^3T_{1g}(F), {}^1E_g \leftarrow$		$^3T_{2g} \leftarrow {}^3A_{2g}$		
$Ni(AA)_6(ClO_4)_2$	25.3		14.9	13.6	8.6	860	900
$Ni(AA)_6(BF_4)_2$	25.3		15.0	13.6	8.6	860	900
$Ni(AA)_6(NO_3)_2$	25.3		15.1	13.7	8.65	865	900
			$^2T_{2g}, {}^2A_{1g} \leftarrow {}^2B_{1g}$				
$Cu(AA)_6(ClO_4)_2$			13.8	11.6 sh			
$Cu(AA)_6(BF_4)_2$			13.5	11.0 sh			
$Cu(AA)_4(ClO_4)_2$			13.2	11.9 sh			
$Cu(AA)_4(NO_3)_2$			13.0	11.3 sh			

The analyses of $Zn(AA)_6(ClO_4)_2$ are clearly different from the results of Farona *et al.*[2] for $Zn(AA)_5(ClO_4)_2$-(H_2O); this supports the suggestion[4] that triethyl orthoformate is a better dehydrating agent than 2,2-dimethoxypropane.

With Cu^{II} perchlorate two different compounds could be obtained depending upon the used mole ratio between the metal and the ligand; this has been found for many oxygen-donor ligands in combination with Cu^{II} salts.[7,9,10]

Despite of several attempts, the nitrate of Mn, Cu, and Cd did not yield $M(AA)_6(NO_3)_2$, even when large excesses of ligand were used.

The band maxima in the ligand-field spectra of the iron(II), cobalt(II), nickel(II), and copper(II) compounds agree with six-coordinate metal ions.[11-13] The magnitude of the parameters Dq and B will be discussed below.

The infrared spectra of our compounds appeared to be superpositions of the spectra of the ligands and the anions, with some ligand bands shifted to higher

---

(8) J. Reedijk, *Rec. Trav. Chim.*, *88*, 1451 (1969).
(9) J. Reedijk, *Rec. Trav. Chim.*, *88*, 499 (1969).
(10) P.W.N.M. van Leeuwen, *Thesis*, Leyden, 1967.
(11) J. Reedijk, W.L. Driessen, and W.L. Groeneveld, *Rec. Trav. Chim.*, *88*, 1095 (1969).
(12) J. Reedijk, P.W.N.M. van Leeuwen, and W.L. Groeneveld, *ibid.*, *87*, 129 (1968).
(13) B.J. Hathaway and D.E. Billing, *Coord. Chem. Rev.*, *5*, 143 (1970).

Table III. Comparison of spectral parameters Dq and B for some octahedral complexes $M(L)_6(anion)_2$ with M = Co and Ni.

Ligand	Co Dq	Co B	Ref.	Ni Dq	Ni B	Ref.
N-methylacetamide	785	845	3	785	895	3
ε-caprolactam	840	845	3	820	890	3
2-Pyridone	875	840	3	845	890	3
Acrylamide	875	840	this work	860	900	this work
Acetamide	890	840	3,11	875	890	3,12
N,N-dimethylformamide	895	835	11	885	895	12
NH_3	—	—	—	1075	890	12
$R\text{-}NH_2$	—	—	—	1040	890	22
Pyrazole	1075	800	8	1100	875	8

or lower wave numbers. The details of these spectra will be discussed below.

Arguments for Oxygen Rather than Nitrogen Coordination of AA. The ligand-field spectra (Table II) of the coloured compounds resemble the compounds with oxygen-donor amide ligands very much; this is easily seen from Table III where Dq and B values for a number of oxygen-donor and nitrogen-donor ligands have been listed, for Co^{II} and Ni^{II}. The differences between the spectrochemical values of our AA complexes and the complexes with nitrogen donor ligands are very large, eliminating the possibility of nitrogen coordination.

Another argument for oxygen coordination comes from the stoichiometry of the Cu^{II} compounds. Many amides and oxygen-donor ligands containing N=O or S=O groups, show the stoichiometry $CuL_6(ClO_4)_2$ whereas no complexes of Cu^{II} coordinated by six NH_2–R groups are known. The only compounds containing CuL_6^{2+} and nitrogen-donor ligands occur with nitriles,[14,15] pentamethylene tetrazole[16] and with the small ligands NH_3[17] and NO_2^-.[18] Since AA yields $Cu(AA)_6(ClO_4)_2$, this is another argument for oxygen coordination of AA.

Finally some arguments were obtained from paramagnetic resonance powder spectra of the Mn^{II} and Cu^{II} compounds. The spectra of the pure manganese compounds consisted of a single line near $g_{eff} = 2$; this is common for Mn^{II} compounds and does not decide between oxygen or nitrogen coordination. However, when Mn^{2+} is doped in the lattices of $Cd(AA)_6(ClO_4)_2$ or $Zn(AA)_6(ClO_4)_2$ the EPR-spectrum showes some fine structure and a very clear hyperfine splitting of the central $S=\frac{1}{2} \rightarrow S=-\frac{1}{2}$ transition. The magnitude of the hyperfine splitting constant (A) was found to be 96±1 Gauss; this A value is in the usual range for oxygen-donor ligands coordinated to Mn[19,20] and outside the range of nitrogen-donor ligands coordinated to Mn^{II}, (in that case A-values are in the 88-92 Gauss region[20,21]).

Undiluted $Cu(AA)_6(ClO_4)_2$ yields an asymmetric E.P.R.-spectrum with $g_{\parallel} = 2.37$ and $g_{\perp} = 2.07$; no hyperfine structure upon $g_{\parallel}$ is resolved. When Cu^{II} is doped in the lattice of $Cd(AA)_6(ClO_4)_2$ an E.P.R.-spectrum consisting of three signals is observed, from which the parameters g and A can be calculated; these parameters are: $g_{\parallel} = 2.390$, $A_{\parallel} = 128$ Gauss, $g_{\perp} = 2.076$, and $g_{iso} = 2.230$. The value of g_{iso} is due to regular octahedral Cu^{2+} ions, upon which a dynamical Jahn-Teller distortion works.[17,20] The other parameters correspond to a static Jahn-Teller distortion of the species $Cu(AA)_6^{2+}$. The magnitude of the several parameters[23] agree with oxygen-coordinated ligands to Cu^{II}, since we know[20] that nitrogen donor ligands usually yield: $g_{\parallel} = 2.20\text{-}2.30$, $A_{\parallel} = 140\text{-}180$ Gauss, and $g_{\perp} = 2.04\text{-}2.06$;[17,20] for oxygen-donor ligands coordinated to Cu^{II} these parameters are: 2.35-2.45, 80-130 Gauss, and 2.06-2.09 respectively. In addition no superhyperfine splittings of the E.P.R. lines were found, which would be expected in the case of nitrogen coordination.[17,20]

Infrared Spectra. Because of the fact that Farona *et al.*[1] concluded that IR spectra of the AA coordination compounds did not disagree with N-coordination, it seemed worthwhile to study these spectra and that of our new compounds.

As stated above, the IR spectra of the AA complexes appear to be additions of the free ligand spectra[24] and the anion spectra with a few alterations. These alterations are:

1. The N–H stretching frequencies. The position of these vibrations appeared to be dependent upon the particular anion; this indicates hydrogen bonding with the anions.[25] The strongest hydrogen bond occurs with the nitrates, whereas perchlorates and tetrafluoroborates are considerably weaker hydrogen bonded. This picture agrees with oxygen coordinated AA, since in that case the NH_2 groups are at the outer coordination sphere, close to the anions.

2. The amide frequencies near 1600 cm^{-1}. In this region three rather strong bands are found, *viz.* near 1675 cm^{-1}, near 1650 cm^{-1} and near 1610 cm^{-1}. These three bands can be assigned to a C=O stretching, a C=C stretching and a NH_2 bending vibration[1,24] respectively. However, since considerable mixing between these vibrations occur it is not possible to speak of pure C=O stretches and C=C stretches, nor of pure N–H bendings; this is illustrated by the

---

(14) A.P. Zuur and W.L. Groeneveld, *Rec. Trav. Chim.*, *86*, 1089 389 (1971).

(15) C.A.A. van Driel and W.L. Groeneveld, *Rec. Trav. Chim.*, *90*, (1971).

(16) F.M. D'Itri and A.I. Popov, *Inorg. Chem.*, *6*, 597 (1967).

(17) C.I. Shyrr, *Thesis*, Illinois, 1969.

(18) B.J. Hathaway and R.C. Slade, *J. Chem. Soc. (A)*, 85 (1968)

(19) S.I. Chan, B.M. Fung, and H. Lutje, *J. Chem. Phys.*, *47*, 2121 (1967).

(20) J. Reedijk and B. Nieuwenhuijse, to be published.

(21) J. Reedijk, *Inorg. Chim. Acta*, *3*, 517 (1969).

(22) B. Rapp and S.F. Pavkovic, *Inorg. Chem.*, *9*, 2801 (1970).

(23) B.R. McGarvey, Transition-metal Chemistry, ed R.L. Carlin, vol. 3, pag. 89 (1966), Dekker Inc. New York.

(24) N. Jonathan, *J. Mol. Spectr.*, *6*, 205 (1961).

(25) J. Reedijk, *Rec. Trav. Chim.*, *90*, 117 (1971).

fact that upon deuteration of the NH_2 group bands appear[1] at 1655 and 1615 cm^{-1} and upon methylation[1] at 1648 and 1610 cm^{-1}. Upon coordination of AA to metal ions it is observed first that all three ligand bands appear again, without important anion influence. This supports the idea of mixing between these three vibrations, since one of then (the NH bending) should be anion dependent. The observed bands in the complexes are: 1670 ± 5 cm^{-1}, 1627 ± 3 cm^{-1} and 1585 ± 10 cm^{-1}; compared with the free ligand these are shifts of about -5 cm^{-1}, -23 cm^{-1}, and -25 cm^{-1} respectively, with the band sequence as given above. When the band sequence is altered *i.e.* C=C higher than C=O, as Farona *et al.*[1] did for dimethyl acrylamide, the shifts are -58 cm^{-1}, $+20$ cm^{-1}, and -25 cm^{-1} for the C=O, C=C, and NH_2 vibrations respectively. These shifts are just as expected for oxygen-coordinated ligands,[26,27] although the initial assignment with the small C=O shift does not exlude this coordination site.

3. The N–H deformation vibrations. In the free ligand a very broad band near 700 cm^{-1} occurs, which can be assigned to a N–H deformation in the solid state.[25] In the complexes this band is shifted to lower wave numbers, indicating less hydrogen bonding. For the nitrates this band occurs near 650 cm^{-1}, and for the perchlorates and tetrafluoroborates near 600 cm^{-1}; this picture agrees with the N–H stretching results (*vide supra*) and with the picture of oxygen coordination.

4. Anion vibrations. In all compounds IR bands due to the anion absorptions were found. In none of our cases these bands were split into two or more components, in agreement with the picture of uncoordinated anions. However, the spectra of compounds with less than six moles of AA per metal ion, showed broadened anion bands, although no splittings were found. Weak « forbidden » anion bands on the other hand, indicate that in these compounds anions are slightly coordinated to the metal ions.[28]

5. Metal-ligand vibrations. Usually,[29] coordination compounds yield vibrations in the low-frequency region that can be assigned neither to the ligand nor to the anion. In fact metal-oxygen vibrations have not been extensively investigated for amide ligands; for most ligands mixing with other vibrations occurs, allowing no unambigious assignment. The 300-200 cm^{-1} region seems to be common for metal-oxygen vibrations in divalent metal-ion complexes with C=O donor ligands.[3,26] Metal-ammine vibrations occur at somewhat higher frequencies[29] for the species $M(L)_6^{2+}$. So, no *a priori* decision about the coordination site of AA seems to be allowed from far-infrared spectra. Our present compounds, showed two metal-ion dependent absorptions in this region. The highest one varies from 335 cm^{-1} (Cd) to 400 cm^{-1} (Cu), but seems to originate from the free ligand band at 308 cm^{-1}. The lowest band occurs near 250 cm^{-1} for the Cu compounds, near 225 cm^{-1} for the nickel compounds, near 210 cm^{-1} for the cobalt compounds and still at lower frequencies for the other compounds. The strong metal-ion dependence of the latter vibrations allows a tentative assignment to metal-oxygen stretching vibrations. An extensive study of these vibrations in the region below 200 cm^{-1} is left for future investigation.

Final Remarks and Conclusion

Because of the fact that our conclusions about the coordination site of acrylamide are rather different from that of Farona *et al,*[2] although the spectra for the several coordination compounds do not or hardly differ, it seemed interesting to reinvestigate the mass spectrum of $SnCl_4(AA)_2$, since this yielded primary evidence[1] for nitrogen rather than oxygen coordination of AA.

However, several runs recorded with a double focussing A.E.I. M.S. 902 mass spectrometer (at the organic chemistry department), at temperatures between 100 and 150°C., did not show the peaks at m/e = 130, 131, 132, 133, 134, and 135 as found by Farona.[1] So, from those measurements no conclusions were possible about the bonding site of AA.

The several measurements carried out with the metal(II) coordination compounds, on the other hand, unambigiously showed that AA behaves as a normal amide ligand, with the oxygen atom of the carbonyl group coordinated to the metal ions.

Acknowledgement. The investigations were supported in part by the Netherlands Foundation for Chemical Research (SON) with financial ai from the Netherlands Organization for the Advancement of Pure Research. The assistance with recording the mass spectra of Mr. J.J. van Houte, and with the infrared spectra of Mr. J.v.d. Linden is gratefully acnowledged. Mr. P.G. v.d. Akker and Drs. B. Nieuwenhuijse are thanked for help with the paramagnetic resonance spectra. Dr. W.L. Groeneveld and Dr. W.L. Driessen are thanked for their interest in this study. The author is indebted to Prof. M.F. Farona for his comments on the manuscript prior to submittance.

(26) W.L. Driessen, *Thesis*, Leyden, 1971.
(27) K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1970.
(28) J. Reedijk, *Rec. Trav. Chim.*, in the press.
(29) J.R. Ferraro, Low-frequency vibrations of Inorganic and Coordination Compounds, Plenum, New York, 1971 .