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The Coordination Chemistry of 2-imidazolidinone

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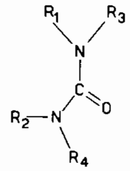
A number of complexes having the general formula $M(EU)_n(anion)_2$ is described, in which M^{2+} = Mg, Mn, Co, Ni, Cu, Zn and Cd, EU stands for 2-imidazolidinone (also called N, N'-ethyleneurea), n varies from 1 to 7, and the anions are ClO_4^-, BF_4^-, NO_3^-, NCS^-, Br^- and Cl^-. The compounds have been analysed and characterized by chemical analyses, infrared spectra, ligand-field spectra, X-ray powder diagrams and ESR spectra. In compounds with 6 or 7 ligands per metal ion, the metal ions are found to be octahedrally coordinated by six EU ligands. A seventh ligand is sometimes held in the crystal lattice. In compounds with less than six ligands per metal ion, the geometry around the metal ion is tetrahedral or distorted octahedral, depending upon the particular combination of M and anion. The position of the C=O stretching frequency in the infrared, which is unusually taken as a measure for the coordination site of amides, appears to be not indicative for the present ligand. The origin seems to be intense mixing of the amide vibrations, making that both the cation and the anion (coordinating respectively with the C=O and N–H groups) influence these vibrations in opposite directions. All spectral data agree with oxygen coordinated imidazolidinone ligands, this is usually observed with this type of ligands in combination with first-row transition metal ions, although bridging ligands with one C=O and N–H as coordinating site may also occur.

Introduction

Among the ligands having a $>$C=O group as the donor site, the amides and lactams are particularly interesting, since these molecules possess also an amine group, which potentially may (also) act as a donor to the metal ion. However, with transition metal ions thus far only compounds have been isolated that contain oxygen-coordinated lactams and amides. This was concluded from infrared spectra (shift to lower frequencies of the C=O stretching vibration), ligand-field spectra (the position of the ligands in the spectrochemical and nephelauxetic series), ESR spectra (magnitude of *g*- and A-values), and several X-ray structure determinations[1–10]. Since nitrogen is more electronegative than oxygen, it is rather unexpected that amides coordinate *via* the carbonyl group. The origin may be a combination of steric effects and hydrogen bonding of the N–H protons with the anions.

Introducing a second amine group in the ligand at the other side of the C=O group, produces another type of ligands, *i.e.* the urea's:



R = H or alkyl

This class of ligands is also very interesting, since now three possible bonding sites are present, which – especially in the cases where $R_3 = R_4$ is H and steric effects are assumed to be small – may yield several types of complexes, *e.g.* monodentate *via* either oxygen or nitrogen, bridging bidentate *via* oxygen and nitrogen, or bridging bidentate *via* two nitrogen atoms. In addition, hydrogen bonds with the anions may occur, even when coordination *via one* nitrogen occurs (contrasted with amides and lactams). In fact it has been shown some 17 years ago, that nitrogen coordination of urea occurs with $PtCl_2$ and $PdCl_2$ only, and that oxygen coordination occurs with first-row transition metal ions[1]. However, this was never proven by X-ray analyses. Gentile[2] on the other hand, has very recently shown by X-ray analysis that in $Co(urea)_4(NO_3)_2$ both monodentate oxygen coordinated and bidentate urea occurs; such a structure was predicted from IR and UV–VIS spectroscopy[3]. In only a few cases in literature, nitrogen coordination has been proposed, mainly based on IR evidence[4].

Because of the fact that the C=O stretching frequency in urea's is highly mixed with other "amide" vibrations, and because of the fact that hydrogen bonding of N–H protons with anions also influences these "amide" vibrations, conclusions about the bonding site of the ligand from IR spectra only, are seldomly unambigious. An illustrating example is the compound $HgCl_2$ (ethyleneurea)$_2$, which was suggested to be nitrogen coordinated and for which a very recent X-ray structure determination has shown that the ligand is bridging between the metal ions *via* one nitrogen and one oxygen[11]. We therefore decided to study the ligand properties of some urea-type ligands in more detail, with respect the several metal ions, several anions and with the aid of a variety of spectroscopic techniques. We selected the ligands ethylene urea (imidazolidinone-2) and propylene urea (2(1H)-tetrahydropyrimidinone), abbreviated as EU en PU respectively, for the following reasons: a) Only a few complexes containing these ligands have been reported in the literature; b) The shape of the ligands is determined by the 5 (or 6) membered rings, which allows no rotations about the OC–NH bonds; and therefore restricts the possible modes of coordination; c) The industrial use of these types of ligands in imparting crease resistance properties of several textiles.

Fortunately, during the course of this investigation a few crystal structure determinations of compounds containing these ligands appeared[8, 10–12], which could be used to verify our conclusions.

In the present paper we describe the characterization and identification of a number of EU complexes with the general formula $M(EU)_x(anion)_2$.

Experimental

Starting Materials

The ligand 2-imidazolidinone was obtained from Merck A.G. Darmstadt and was used without purification. Metal(II) salts were used as the commercially available hydrated products.

Preparation of the Complexes

All compounds were prepared by basicly the same procedure. An amount of metal(II) salt (usually 0.01 mol) was dissolved in ethanol and sufficient triethylorthoformate was added for dehydration. The ligand (0.04 or 0.06 mol) was dissolved in hot ethanol, upon which the metal salt solution was added.

In most cases crystals of the complexes appeared spontaneously upon cooling to room temperature. In a few cases cooling to about –10° C was necessary, or addition of diethyl ether. The crystals were collected on a glass funnel, washed with ethanol and sodium dried diethyl ether and finally dried *in vacuo* at room temperature. During later preparations it was found that methanol as a solvent (in which EU is much more soluble) often produces better crystalline powders.

Physical Measurements

Infrared spectra of the compounds were obtained on a Unicam SP-1200 spectrometer in the 4000–400 cm^{-1} region, using Nujol mulls between potassium bromide windows. It was found that most compounds decomposed when recorded as KBr discs. Far-infrared spectra of several compounds were recorded on a Hitachi EPI-Lspectrometer in the 700–200 cm^{-1} region (as Nujol mulls between polythene windows), or on a Beckman-RIIC IR-720 interferometer in the 450–50 cm^{-1} region (as pressed discs within polythene).

X-ray powder diagrams were obtained with a Guinier–de Wolff camera using CuKαradiation. The samples were protected from atmospheric moisture by adhesive tape.

ESR spectra of the Cu(II) and Mn(II) compounds were recorded on Varian instruments at X-band and Q-band frequencies. The powder samples were investigated at room temperature.

Ligand-field spectra of the solid compounds were obtained by the diffuse reflectance technique on Beckman DK-2 and DK-2A instruments.

Analyses

The metal content of the compounds was analysed by complexometric titration with EDTA, in a few cases Carbon, Hydrogen, Nitrogen or Halogen determinations were carried out.

Results and Discussion

General

All found compounds in the systems studied are listed in Tables I and II, together with analytical data, colours, melting points and X-ray types. The division into the several X-ray types was made according to the very similar Guinier photographs with regard to line spacings and intensities. It must be noticed, however, that the line patterns for the perchlorates and tetrafluoroborates are very diffuse and very complex and the quality of the samples was different from sample to sample and appeared to dependent upon the degree of crystallization. This may have something to do with the fact that especially the perchlorates may contain some extra EU which may slightly alter the crystalstructure. During the course of the investigation, when methanol was used instead of ethanol, samples which much better resolved X-ray powder patterns were obtained.

All compounds appeared to be quite stable in the atmosphere, and only a few samples appeared to be hygroscopic.

Considering the stoichiometries of the compounds in Tables I and II it is seen that all molar ratio's between 1 : 1 and 1 : 7 occur, and that for several metal (II) salts more than one complex exists, depending

TABLE I. Perchlorate, Tetrafluoroborate and Nitrate Compounds Containing the Ligand Ethyleneurea. Colours, Melting Points, Analytical Data and X-ray Types.

Compound	Colour	Melting point (° C)	% Metal Calcd	Found	X-ray Type	Remarks
$Mg(EU)_6(ClO_4)_2$	white	200–202	3.29	3.31	A	
$Mn(EU)_6(ClO_4)_2$	white	165–168	7.13	6.62	B	a
$Co(EU)_6(ClO_4)_2$	rose	223–226	7.61	7.58	A	
$Ni(EU)_6(ClO_4)_2$	light green	235–236	7.59	7.47	A	
$Cu(EU)_4(ClO_4)_2$	light blue	175–177	10.47	10.52	C	
$Cu(EU)_5(ClO_4)_2$	light blue	153–155	9.17	9.32	D	b
$Zn(EU)_6(ClO_4)_2$	white	166–167	8.50	8.37	A	
$Cd(EU)_6(ClO_4)_2$	white	154–155	13.58	13.53	B	c
$Mn(EU)_6(BF_4)_2$	white	168–169	7.37	7.21	A	
$Co(EU)_6(BF_4)_2$	rose	191–192	7.86	7.60	A	
$Ni(EU)_6(BF_4)_2$	light green	217–218	7.84	7.81	A	d
$Cu(EU)_4(BF_4)_2$	light blue	155–156	10.93	10.76	C	
$Cu(EU)_5(BF_4)_2$	light blue	150–151	9.52	9.97	D	
$Zn(EU)_6(BF_4)_2$	white	136–139	8.65	8.77	A	
$Cd(EU)_6(BF_4)_2$	white	161–162	14.01	14.14	A	
$Mg(EU)_6(NO_3)_2$	white	154–155	3.66	3.72	–	
$Mn(EU)_4(NO_3)_2$	white	145–146	10.50	10.53	–	
$Co(EU)_6(NO_3)_2$	rose	140–141	8.42	8.47	E	e
$Ni(EU)_6(NO_3)_2$	light green	154–155	8.40	8.32	E	
$Cu(EU)_3(NO_3)_2$	blue green	134–135	14.25	14.00	–	
$Cu(EU)_4(NO_3)_2$	light blue	125–126	11.95	11.80	–	
$Zn(EU)_6(NO_3)_2$	white	114–115	9.26	9.26	E	
$Cd(EU)_4(NO_3)_2$	white	115–116	19.35	20.4	–	
$Cd(EU)_6(NO_3)_2$	white	120–122	14.93	14.81	–	

[a] % C: 28.2 (calcd. 28.1); % H: 4.8 (calcd. 4.7); % N: 21.7(calcd. 21.8). [b] The crystal structure of this compound was recently described by Majeste[10]. [c] The crystal structure of this compound has been published by Brown *et al.*[8] [d] % C: 29.0 (calcd. 28.9); % H: 5.0 (calcd. 4.9); % N:22.5(calcd. 22.5). [e] A dihydrate of this compounds was described by Costamagna and Levitus[13].

upon the used molar ratio of ligand and metal salt. In most cases the proposed structure of the compounds is already expressed in their chemical formulae. These structure proposals are based upon the interpretation of the several physical methods, which will be described below.

Ligand-field Spectra

For a first structural characterization of the coloured compounds, ligand-field spectra of the Co(II), Ni(II) and Cu(II) compounds were recorded by the diffuse reflectance technique. This method provided direct evidence for the coordination geometry and for the spectrochemical position of the coordinating ligands. Spectral data for the several compounds are listed in Table III, together with assignments and calculated parameters. ESR spectra for the Cu(II) compounds are also listed in Table III; these will be discussed below.

The ligand-field spectral data of the Cobalt and Nickel compounds are all in agreement with octahedrally coordinated cations; even for the isothiocyanate and chloride compounds which have less than six ligands, the distortion is too small to yield band splittings. Therefore, for all compounds the spectral parameters were calculated assuming octahedral geometry. As expected, the spectral parameters for the compounds $M(EU)_6(anion)_2$, fall in the usual range for oxygen-donor urea and amide-type ligands[6,9]. The fluctuations in the Dq and B values for the several compounds are all within experimental error, except for the nitrates, which show significantly higher Dq values, although fairly well within the usual range[9]. Such an anion effect has been observed in a few other cases[9,17], and may be due to a different, small distortion from octahedral (*e.g.* trigonal *versus* tetragonal), or due to different hydrogen bonding with the N–H protons (*vide infra*). The somewhat higher Dq values for the isothiocyanate compounds, confirms the nitrogen-coordination of this anion (see also IR spectra).

The Dq value for $Ni(EU)_2Cl_2$ is somewhat smaller because of the weaker ligand-field strength of the chloride ion. A similar effect is observed for the smaller B-value, due to the more pronounced nephelauxetic character of Cl^-.

Since many compounds are isomorphous with these

TABLE II. Metal Chlorides, Bromides and Thiocyanates Coordinated by Ethyleneurea. Colours, Melting Points, Analytical Data and X-ray Types.

Compound Type	Colour	Melting Point (° C)	% Metal		% Anion		X-ray	Remarks
			Calcd	Found	Calcd	Found	Type	
$Mg(EU)_6Cl_2$	white	220–221	3.97	3.90	11.59	11.48	–	
$Mn(EU)_4Cl_2$	white	148–150	11.68	11.77	15.08	15.46	–	
$Co(EU)_6CoCl_4$	violet	158–160	15.20	15.34	18.27	18.34	–	a,b
$Ni(EU)_6Cl_2(EU)_{1\frac{1}{2}}$	light green	164–165	7.66	7.65	9.00	8.95	F	
$Cu(EU)Cl_2$	brown	192–193	28.81	28.38	32.2	32.3	–	
$Cu(EU)_2Cl_2$	green	160–161	20.72	20.66	23.1	23.0	–	b
$Zn(EU)_2Cl_2$	white	186–188	21.2	21.2	23.0	23.4	G	b
$Cd(EU)Cl_2$	white	>270	41.7	41.6	26.3	26.0	–	b
$Cd(EU)_2Cl_2$	white	>270	31.6	32.4	20.0	20.8	–	b
$Ni(EU)_2Cl_2$	yellow	240–242	19.5	19.3	23.5	23.2	–	c
$Mg(EU)_4Br_2$	white	169–171	4.60	4.54	30.2	30.0	–	
$Mg(EU)_6Br_2(EU)$	white	221–224	3.09	3.04	20.3	20.8	F	
$Mn(EU)_4Br_2$	white	164–165	9.83	10.10	28.6	28.1	–	
$Mn(EU)_6Br_2(EU)$	white	156–158	6.72	6.77	19.6	19.7	F	
$Co(EU)_6CoBr_4$	violet	177–178	12.35	12.34	33.5	33.4	–	
$Co(EU)_6Br_2(EU)$	rose–violet	155–156	7.17	7.14	19.5	19.1	F	
$Ni(EU)_6Br_2(EU)$	light green	200–201	7.15	6.94	19.5	19.2	F	
$Zn(EU)_2Br_2$	white	195–196	16.45	16.67	40.2	40.8	G	
$Cd(EU)_2Br_2$	white	208–216	25.3	25.6	36.0	36.0	–	d
$Mn(EU)_4(NCS)_2$	white	188–189	10.66	10.58	22.5	21.9	H	
$Co(EU)_4(NCS)_2$	rose	174–175	11.35	11.33	22.4	22.1	H	
$Ni(EU)_4(NCS)_2$	light green	224–225	11.31	11.35	22.4	22.3	H	
$Zn(EU)_6Zn(NCS)_4$	white	140–141	14.86	14.82	26.4	26.0	–	
$Cd(EU)_2(NCS)_2$	white	179–180	28.1	28.4	29.0	29.9	–	

[a] This compound was also reported by Calvaca *et al.*[14] [b] This compound was also reported by Berni *et al.*[15] [c] This compound can also be obtained with 1–3 additional EU ligands, which are bound in the lattice. [d] This compound was also reported by Berni *et al.*[16]

Co and Ni compounds we propose similar structures for the other similar compounds in Tables I and II. The ligand-field spectra of the Cu(II) compounds are all very similar in band width, band shape and approximate band position. Only small, but clear differences occur in the position of the band maxima. It is well known that the band maximum is a function of both the spectrochemical position of the ligands and the distortion from octahedral geometry[18]. Since we know that Cu $(EU)_5(ClO_4)_2$ is tetragonal[10] with four ligands in the equatorial position, one ligand in the axial position at a longer distance, and one perchlorate ion in the other axial position at "semi-coordinating" distance[18], we propose similar geometries for the compounds of formula $Cu(EU)_4(anion)_2$, but now with two anions in the axial positions at a quite long distance (see also IR spectra).

From the spectra of the compounds with less than four ligands nothing else about their structures can be said than that they are octahedrally or square planar based.

Infrared Spectra

As said in the introduction, infrared spectra in the amide region have been frequently used for distinguishing between O and N coordination. However, since earlier measurements[4,8,11,15,19,20] indicated that decisions about the bonding site of the ligand are ambiguous, and since preliminary data of our compounds showed very broad bands in the amide region (1500–1700 cm^{-1}), we decided to draw no direct conclusions about the donor site of EU from IR spectra. Moreover, two fundamental objections can be raised against the use of C=O and N–H frequency positions for the determination of the bonding site of EU, since both frequencies are influenced by hydrogen bonding between the N–H protons and the anions: a) This hydrogen bonding may cause a much greater shift in the N–H stretchings and bendings, than coordination of the metal on the nitrogen; this is due to a simple mass effect; b) Since it is known that in urea's a strong coupling occurs between the C=O stretching and the N–H bending[1], it is to be expected that hydrogen bond-

TABLE III. Ligand-field and ESR Spectra of Co(II), Ni(II) and Cu(II) Compounds Containing ethyleneurea; band maxima are in kK; Dq and B are in cm^{-1} and are accurate to 10 cm^{-1}; g-values are accurate to 0.01; A∥ is expressed in Gauss and accurate to about 5 G.

Compounds	Assignments[a]					Absorbing Species	Dq	B
	$^4T_{2g}\leftarrow$	$^4A_{2g}\leftarrow$		$^4T_{1g}(P), {}^2G\leftarrow{}^4T_{1g}(F)$				
$Co(EU)_4(NCS)_2$	8.3	16.7 sh		19.2	21.0 sh	CoO_4N_2	900	830
$Co(EU)_6(NO_3)_2$	8.0	15.8 sh		19.5	21.0 sh	CoO_6	870	850
$Co(EU)_6CoBr_4$[b]	7.8			19.5		CoO_6	850	850
$Co(EU)_6Br_2(EU)$	7.75			19.4	20.8 sh	CoO_6	845	850
$Co(EU)_6CoCl_4$[c]	7.7 sh			19.5		CoO_6	840	855
$Co(EU)_6(ClO_4)_2$	7.7	15.2 sh		19.3	20.8 sh	CoO_6	840	850
$Co(EU)_6(BF_4)_2$	7.65	15.1 sh		19.2	20.6 sh	CoO_6	835	850
	$^3T_{2g}\leftarrow$	$^3T_{1g}(F), {}^1E_g\leftarrow$		$^1T_{2g}\leftarrow$	$^3T_{1g}(P)\leftarrow{}^3A_{2g}$			
$Ni(EU)_4(NCS)^2$	8.75	15.1	13.8 sh		25.0	NiO_4N_2	875	890
$Ni(EU)_6(NO_3)_2$	8.35	13.5	14.7 sh	21.5 sh	24.8	NiO_6	835	915
$Ni(EU)_6(BF_4)_2$	8.20	13.6	14.9 sh	21.4 sh	24.8	NiO_6	820	920
$Ni(EU)_6(ClO_4)_2$	8.20	13.5	14.8 sh	21.3 sh	24.8	NiO_6	820	920
$Ni(EU)_6Br_2(EU)$	8.15	13.6	14.9 sh	21.3 sh	24.6	NiO_6	815	925
$Ni(EU)_6Cl_2(EU)_{1\frac{1}{2}}$	8.10	13.6	15.0 sh	21.2 sh	24.5	NiO_6	810	925
$Ni(EU)_2Cl_2$	7.6	12.2	13.5 sh		23.0	$NiCl_4O_2$	760	850
	$^2T_{2g}\leftarrow$	$^2A_{1g}\leftarrow{}^2B_{1g}$		ESR Parameters				
				$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$	g_{iso}	
$Cu(EU)_4(ClO_4)_2$	13.45	11.0 sh		2.38	2.07	100		
$Cu(EU)_4(BF_4)_2$	13.45	11.1 sh		2.39	2.07	100		
$Cu(EU)_3(NO_3)_2$	12.9	10.0 sh, br		2.41	2.11	80		
$Cu(EU)_4(NO_3)_2$	12.8	10.8 sh		2.40	2.10	100		
$Cu(EU)_5(ClO_4)_2$	12.35	10.3 sh		2.42	2.08	108		
$Cu(EU)_5(BF_4)_2$	12.30	10.5 sh		2.41	2.08	110		
$Cu(EU)Cl_2$	11.75						2.14 br	
$Cu(EU)_2Cl_2$	11.65	9.5 sh, br		2.29	2.10	u		

[a] sh = shoulder; br = broad; u = unresolved. [b] Bands due to the $CoBr_4^{2-}$ ion at 5.0 and 14.2 kK are omitted. [c] Bands due to the $CoCl_4^{2-}$ ion at 5.4 and 14.8 kK are omitted.

ing between the anions and the N–H group of the ligands will affect also the position of the C=O stretching.

Recently, Singh and Pande[19] showed that shifts compared with free EU in a very dilute solution, where hydrogen bonding can be neglected, are easier to use. Nevertheless, apart from these amide frequencies, a lot of other information can be obtained from the IR spectra of our compounds, *i.e.* presence or absence of water; possible coordination of anions and their donor site; possible presence of solvent molecules; possible isomorphism between certain compounds; presence and strength of hydrogen bonding. In addition far-IR spectra may yield direct information about the strength of the metal–ligand bond. We will discuss some of these subjects in more detail below.

The presence of water in some products from early preparations (without triethylorthoformate) and in some products recrystallized from ethanol was easily seen from bands around 3600 cm^{-1}. Further the presence of a seventh, uncoordinated molecule of EU in some complexes was accompagnied by weak bands around 1700 cm^{-1} and 1275 cm^{-1}, and a clear splitting of the bands at 1030 and 930 cm^{-1}.

The spectra of all compounds of formula $M(EU)_6(anion)_2$ with ClO_4^-, BF_4^- and NO_3^- as the anions showed some additional bands, which can be assigned to anion vibrations. The characteristics of these anions bands, *viz.* unsplit degenerate stretchings and unobserved forbidden bands, indicate uncoordinated anions[20] and confirm the occurrence of cations $M(EU)_6^{2+}$. Compared with other ligands that yield groups $M(ligand)_6^{2+}$, however, the bands due to the anions are rather broad in our complexes. This must be due to hydrogen bonding between the anions and the N–H groups of the ligands, as recently shown by X-ray analyses[8]. Such an effect has been observed previously for pyrazole ligands[21]. The perchlorate and tetrafluoroborate compounds of Cu(II) which have only five or four coordinated ligands, do not show the characteristics of coordinated anions either; this is in agreement with the X-ray structure[10] and the ligand-field spectra (*vide supra*), which indicate only "semi-coordinated" anions. The nitrate compounds of formula $M(EU)_4(NO_3)_2$ show clear splittings in the N–O stretches near 1300–1450 cm^{-1} and the presence of a "forbidden" band around 1030–1050 cm^{-1}. Similar spectra are observed for $Cu(EU)_3(NO_3)_2$, although no conclusions are allowed about the possibility of bidentate nitrate in this latter compound.

The thiocyanate compounds of formula $M(EU)_4(NCS)_2$ that are all isomorphous (Table II), show a single C=N stretching near 2080–2095 cm^{-1}. This band position is indicative for nitrogen coordination of the NCS anion[20]. The fact that the band is unsplit, is indicative for a *trans*-location of the anions, as is usually observed in compounds $M(ligand)_4(NCS)_2$. The spectrum of $Zn(EU)_3(NCS)_2$ shows a single C=N stretch around 2090 cm^{-1}. Since this peak is close to the value of $Zn(NCS)_4^{2-}$ [22], and since the remaining part of the spectrum agrees with $Zn(EU)_6^{2+}$ (see below), we tentatively suggest a structure $Zn(EU)_6Zn(NCS)_4$ for this compound. The C=N stretch in $Cd(EU)_2(NCS)_2$ occurs at about 2110 cm^{-1}, from which can be concluded that either bridging or sulfur-coordinated NCS^- groups occur.

It is well known that compounds containing similar groups of ligands around cations, may yield similar infrared spectra regarding line shape and relative intensities. This is sometimes called infrared isomorphism. The IR spectra of the compounds that were mentioned in Table I and II as being isomorphous, indeed are very similar – neglecting differences between vibrations of ClO_4^- and BF_4^- of course. Moreover, it appeared

TABLE IV. Infrared Spectra of EU and Complex Ions $M(EU)_6^{2+}$ with Assignments.

Free Ethyleneurea[a, b, c]			Assignment[23]	$M(EU)_6^{2+}X_2^-$ $X = ClO_4$, BF_4 Cl, Br, MY_4	$M(EU)_6(NO_3)_2$	$M(EU)_6X_2$ (EU)
Nujol mull	KBr disc	CCl_4[19]				
3300 br, s	3280 s	3467 s	N–H stretchings	3390 ± 20 vs	3360 ± 10 vs	3410 s
						3340 sh
					3290 ± 10 vs	3270 vs
						3200 vs
N	2945 m		CH_2 stretchings	N	N	N
	2880 m					
1670 vs	1680 vs	1718 vs	C=O stretch (amide I)	1665–1690 vs	1670 ± 5 vs	1690 sh
						1665 vs
1510 s	1510 s	1550 s	N–H bending (amide II)	1510 ± 5 s	1510 ± 5 s	1510 s
1490 s	1485 sh		CH_2 bending	1500 ± 5 sh	1500 ± 5 sh	1500 sh
N	1455 s		CH_2 bending	N	N	N
–	–		unassigned	1400 w	1400 w	1403 vw
1275 vs	1275 vs	1275 s	Ring deformation	1282 ± 5 vs	1301 ± 2 w	1286 vs
					1275 ± 3 s	1268 m, sh
1203 vw	1203 vw		CH_2 deformation	1208 ± 4 w	1206 vw	1205 w
1105 m	1105 m		Ring deformation	1100 ± 4 s	1098 ± 2 s	1102 s
1039 w	1038 w		Ring deformation	1030 ± 3 m	1030 ± 2 m	1040 m
						1030 w
990 w	990 w		CH_2 rocking	1000 ± 10 vw	1002 ± 2 w	1012 vw
932 vw	934 w		Ring deformation	930 ± 2 w	933 ± 2 w	935 w
						928 w
885 br, w	885 br, w		unassigned	895 vw, vbr	893 ± 2 w	893 w
						880 w
772 m	770 m		Ring deformation	765 ± 3 s	766 ± 2 m	767 s
705 vs, vbr	710–630 vs		N–H rocking	725 ± 5 vs	730 s	730 vs
				600–630 vs, vbr	711 vw	705 sh
					665 vs	630–600 vs, vbr
					600 s	
						560 s
516 m	514 w		Ring deformation	530–540 s, br	527 ± 3 s	530 m
						500 m

[a] Far-infrared spectra are listed in Table V. [b] s = strong, m = medium, w = weak, v = very, br = broad, sh = shoulder. [c] N = obscured by Nujol absorptions; unless otherwise indicated, accuracies are ± 5 cm^{-1}; bands due to the anions have been omitted from this Table.

that all compounds that contain the group $M(EU)_6^{2+}$ showed very similar spectra with respect to the bands that could be described to EU. Only the nitrates $M(EU)_6(NO_3)_2$ and the compounds with more than six EU ligands showed clear splittings in some bands. The characteristic bands in the 4000–500 cm^{-1} region for these types of compounds are listed in Table IV, together with the spectra of the free ligand and a literature assignment.

The inequivalence of the EU ligands in the compounds $M(EU)_6X_2(EU)$ is clear from the structure. The split N–H vibrations in the nitrates, however, are rather surprising, and indicate that not all N–H groups are symmetrically equivalent. This means a distortion of the cation from octahedral symmetry, which is imposed by the anion. This distortion may also explain the unexpected increase in the apparent Dq values for the compounds $M(EU)_6(NO_3)_2$ (Table III).

Hydrogen bonding between the N–H groups of the ligands and the anions appears also to be important in compounds containing less than six EU ligands per metal ion. These compounds generally have two N–H stretches, one around 3400 cm^{-1} and one around 3300 cm^{-1}. From these two bands, that around 3400 cm^{-1} is usually very sharp. At this stage, however, no conclusions about the structures of these compounds can be drawn from the IR spectra alone. For more information on these compounds, far-IR spectra were recorded, which will be described below.

Far-infrared Spectra

For additional information about the structures of some compounds containing less than six EU ligands per metal ion, and for a study of the strength of the metal–ligand bond far-IR spectra were recorded for several compounds. The main results are listed in Table V. From the fact that the ligand EU itself has several absorptions below 240 cm^{-1}, it is clear that all assignments below 250 cm^{-1} must be ambiguous. Nevertheless, a number of conclusions can be drawn.

The spectral data of $Zn(EU)_2Cl_2$ and $Zn(EU)_2Br_2$, combined with their powder isomorphism, fully agree with Zn(II) ions tetrahedrally coordinated by two halide anions and two ligands[24]. Further, in $Co(EU)_6CoX_4$ the CoX_4^{2-} species must be responsible for the bands at 310 and 288 cm^{-1} (X = Cl) and 230 cm^{-1} (X = Br)[24]. The bands around 280 cm^{-1} in $Zn(EU)_6Zn(NCS)_4$ agree with $Zn(NCS)_4^{2-}$. The observed broad bands in the compounds $Cu(EU)_2Cl_2$ and $Cu(EU)Cl_2$ are in the usual range for Cu–Cl, Cu–O and Cu–N stretching frequencies[24].

TABLE V. Far-infrared Spectra of Some Selected EU Complexes.

Compounds	Metal–anion Bands	Metal–Ligand Stretching	Ligand Bands and Unassigned Bands
Ethyleneurea (EU)			230 s, 191 vs, 140 vs, 118 vs, 90 sh
$Zn(EU)_2Cl_2$	326 vs, 304 vs	253 s	230 sh, 197 w, 135 vs, br, 90 sh
$Zn(EU)_2Br_2$	220 sh, 205 m	249 s	230 sh, 140 sh, 125 s, 90 m
$Zn(EU)_6Zn(NCS)_4$	286 vs, 275 sh	250 s	230 sh, 195 sh, 157 vs, br, 103 s
$Cu(EU)_2Cl_2$	295 vs, vbr	266 s, 241 s	174 vs, 145 s, 120 s, 100 s, 80 sh
$Cu(EU)Cl_2$	307 sh, 287 vs	273 sh	223 s, 187 w, 153 s, 112 vs, br, 88 sh
$Cd(EU)_2Br_2$			235 s, br, 178 s, 158 s, 118 s, 84 s, br
$Cd(EU)_2Cl_2$			230 sh, 220–170 vs, vbr, 112 s, 82 s
$Co(EU)_6CoCl_4$	310 s, 288 s		240 sh, 224 s, 160–140 vs, vbr, 90 sh
$Co(EU)_6CoBr_4$	230 s		240 sh, 222 s, 148 sbr, 91 s
$Mg(EU)_6(ClO_4)_2$		320 vs	230 sh, 213 s, 167 vs[b], 112 s, 92 sh
$Ni(EU)_6(ClO_4)_2$		247 vs	230 sh, 169 s[b], 124 s, 90 sh
$Co(EU)_6(ClO_4)_2$		245 s, sh, 224 s	162 vs,[b] 110 s, 85 sh
$Zn(EU)_6(ClO_4)_2$		195 s	226 sh, 157 vs[b], 108 s, 80 sh
$Mn(EU)_6(ClO_4)_2$		240–205 vs, vbr	144 s,[b] br, 100 m, br
$Cd(EU)_6(ClO_4)_2$		198 vs, vbr	235 m, 132 vs, vbr[b], 100 sh
$Ni(EU)_6(NO_3)_2$		295 vs	232 s, br, 170 s, br, 130–110 s, br, 80 s
$Ni(EU)_6(BF_4)_2$		260 s, sh	231 vs, 168 s, 120–100 s, br
$Ni(EU)_6Br_2(EU)$		270 m	243 s, 218 s, 179 s, 117 s, 85 m
$Ni(EU)_6Cl_2(EU)_{1^1/_2}$		243 s	228 sh, 190 m, 162 s, 125 s, 85 sh
$Cu(EU)_5(ClO_4)_2$		302 vs	256 m, 238 m, 178 vs, 120–80 m, br
$Cu(EU)_4(ClO_4)_2$		314 sh, 303 s, 255 vs	195 sh, 177 vs, 130–80 m, br
$Cu(EU)_4(NO_3)_2$		313 s, 302 s, 255 s	236 vs, 191 s, 173 vs, 140 s, 112 s, 98 s
$Cu(EU)_3(NO_3)_2$		329 vs, 275 s	248 m, 224 m, 211 m, 175 s, 137 m, 100 sh, br

[a] For abbreviations see Table IV. [b] This band is also strongly dependent upon the particular metal ion in $M(EU)_6(ClO_4)_2$.

Unfortunately, the far-IR data of the Cd compounds do not allow assignments of Cd–X, Cd–O or Cd–N vibrations. Polymeric structures just as found for $HgCl_2(EU)_2$[11] may be possible for these compounds, and probably also for the Cu(II) compounds, as deduced from the split N–H stretches (*vide supra*). In compounds containing uncoordinated anions, all bands in the far-IR region must be due to the cation $M(EU)_6^{2+}$, *i.e.* metal–ligand vibrations and ligand deformation modes. Because of the fact that the number of ligand modes is very large, even metal–ligand stretches are difficult to assign. An attempt has been made for an isomorphous series of perchlorates (Table V). The very similar line patterns and the fact that the Irving–Williams series of metal ions is found, seems to justify the assignment. Moreover, the observed region agrees with literature data for other C=O donor ligands, like acrylamide[5] and methyl formate[25]. Compared with 2-pyridone[7], however, our values are slightly smaller, whereas compared with ketones[26], our values are somewhat higher. Such a variation in metal–ligand stretches is also observed when the several Ni(II) compounds are compared. As is seen from Table V, the band positions and band shapes alter considerably upon variation of the anions in $Ni(EU)_6(anion)_2$. This indicates that hydrogen-bonding between the ligand and the anion influences also the spectral bands in this region. It is further observed that the very high M–O stretch in $Ni(EU)_6(NO_3)_2$ agrees nicely with the unusually large Dq value for this compound (Table III).

For the perchlorates a second metal-ion dependent band with a very high intensity is found from 170 (Ni) to 130 (Cd) cm^{-1}, which is marked in the colum of unassigned absorptions. Whether this band is a metal–ligand bending, or a ligand deformation mode cannot be deduced from these data. The Irving–Williams sequence of metal ions, however, is beautifully observed.

Electron Spin Resonance Measurements

For more detailed information about the structure of the Mn(II) and Cu(II) compounds, ESR spectroscopy can be particularly useful. The spectral data of our Cu(II) compounds were already listed in Table III. The observed parameters fall in the usual region for oxygen-donor ligands[5,7], at least for the nitrates, perchlorates and tetrafluoroborates. A clear difference between the species $Cu(EU)_4(anion)_2$ and $Cu(EU)_5(anion)_2$ is observed, which may be related to the magnitude of the tetragonal distortion.

The spectral data of $Cu(EU)_2Cl_2$ and $Cu(EU)Cl_2$ do not yield direct information about the coordinating atoms around Cu(II), although the spectrum of the latter compound indicates a considerable exchange between the Cu(II) ions. The spectra of the manganese compounds with formula $Mn(EU)_6(anion)_2$, $Mn(EU)_6Br(EU)$ and $Mn(EU)_4(NCS)_2$ all showed a single line centered around $g = 2.0$, which – given the monomeric nature of the compounds – agrees with rather regular octahedrally coordinated metal ions.

The compounds with formula $Mn(EU)_4X_2$, with X = Cl, Br, NO_3 showed very complex spectra at both X-band and Q-band frequencies. This is indicative for a distorted geometry[27]. Given the stoichiometry of the compounds, we must have to do with distorted octahedral compounds. With the aid of literature methods[27,28], we calculated the zero-field splitting parameters for these compounds, which yielded for the nitrate: $D = 0.065 \pm 0.002$ cm^{-1} and $E \leqq 0.002$ cm^{-1}; for the chloride: $D = 0.13 \pm 0.01$ cm^{-1} and $E = 0.013 \pm 0.003$ cm^{-1}; for the bromide: $D = 0.12 \pm 0.02$ cm^{-1} and $E = 0.025 \pm 0.008$ cm^{-1}. These values are of intermediate size compared with other compounds of this geometry[28]. The rhombic splitting E of the bromide is quite large, which might indicate that the anions are in a *cis*-arrangement. Unfortunately this could not be confirmed by far-IR spectra, because of the very intense ligand absorptions in this region (*vide supra*).

Conclusion

From the results described in the present paper, the following conclusions can be drawn: a) Ethylene urea forms coordination compounds with a large number of metal salts; b) In compounds of formula $M(EU)_{3-6}(anion)_2$, the EU molecules are coordinated to the metal ions *via* the carbonyl oxygen; c) In compounds containing less than 3 ligands per metal ion, the EU ligands are at least oxygen coordinated to the metal ions, although additional nitrogen coordination (bidentate) may occur in some cases; d) Hydrogen bonding between the N–H groups of the ligand and the anions seems to be extremely important in these compounds. It probably dictates the stoichiometries, allowing more than one compound to be formed in many cases; e) Conclusions about the bonding site of the ligand – and probably all amides and urea's – from the shifts in the C=O and N–H stretching vibrations are ambiguous and should be avoided; f) Metal–ligand vibrations are difficult to distinguish from ligand deformation modes. Hydrogen-bonding between ligands and anions also influences metal–ligand stretches.

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