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

Alcohols as Ligands. III.[1] Complexes of Ethylene Glycol with some Divalent Metal Halides

D. Knetsch and W. L. Groeneveld

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A number of divalent metal halides with ethylene glycol as the ligand is reported. The general formula is $M(EG)_nX_2$, where $M = Mn, Co, Ni, Cu, Mg, Ca, Sr$; $n = 1 - 4$; and $X = Cl, Br$. The compounds are characterized by means of physical measurements and chemical analyses.

Ligand field parameters are calculated for the Co, Ni and Cu compounds and the ligand is placed in the spectrochemical and nephelauxetic series.

Infrared spectra indicated that both the symmetric and the asymmetric C-O stretching vibrations are shifted to lower frequencies and the symmetric CCO bending vibration is shifted to higher frequency. The assignments of the vibrational spectrum of the ligand as appeared in the literature, are discussed.

It is shown that ethylene glycol behaves as a normal oxygen donor, and that the ligand can serve as a bidentate chelating as well as a monodentate coordinating agent. Bidentate coordination is deduced for seven compounds and monodentate coordination for eight compounds. The gauche form with respect to the C-C bond is present in the complexes.

Introduction

Complexes of ethylene glycol (EG) with metal salts are known since more than sixty years. Around 1910 *Grün et. al.*[2,3] synthesized a number of compounds with the general formula $M(EG)_nX_2$, where M $=$Co, Ni, Cu; X $=$ Cl, Br, NO_3, $\frac{1}{2}SO_4$; and n $=$ 2,3 or 4. *Gomer* and *Tyson*[4] dealed with the preparation and magnetic moments of a series of complexes with general formula $M(EG)_nSO_4 \cdot mH_2O$, where M $=$ Fe, Co, Ni, Cu; n $=$ 1,2,3, or 4; and m $=$ 0,1 or 2. They also reported the magnetic moments of the compounds $Co(EG)_2Cl_2$, $Co(EG)_2Cl_2.H_2O$ and $Mn(EG)_2Cl_2.H_2O$. Recently, *Nylander*[5] reported the preparation and physical properties of some nickel halide complexes of EG and of some oxygen-substituted derivatives. The Lewis adducts $SnCl_4$-2EG and $SnBr_4$. 2EG were reported by *Pfeiffer.*[6]

Spectroscopic investigations in the uvv region on solutions of $Co(NO_3)_2$,[7] $NiCl_2$,[8] and $Co(ClO_4)_2$[9] in ethylene glycol were carried out.

Grün suggested that EG could behave as a bidentate ligand. This was confirmed by *Hieber* and *Woerner,*[10] who determined the heat of formation of complexes of EG with $CoCl_2$ and $CoBr_2$. However, there is also evidence for monodentate coordination.[11,12] In addition ethylene, glycol can serve as a bridging agent, as was pointed out by x-ray analyses of the compound (1 phenyl-1,3 dionato)(etylene glycol) sodium by *Bright et. al.*[13].

They also proved that the conformation of ethylene glycol was *gauche.* This was already suggested by *Myake,*[11] who investigated the infrared spectra of some ethylene glycol complexes.

Several investigators[3,4,10] observed the somewhat extra-ordinary behaviour of the compound $Co(EG)_3Cl_2$. This compound is very hygroscopic, possesses a low melting point, and shows a deep blue colour. No attempt has been made to explain these properties as far as known to the authors.

Although some of the complexes presented here have already been studied, they were not fully investigated, especially the infrared and ligand field spectra. In addition, the complex forming behaviour of ethylene glycol with many salts had not been studied at all. As an extension of previous investigations on methanol[1] and ethanol,[14] and because not very much is known about the coordination chemistry of diols, we wish to report here the preparation and properties of a series of complexes of ethylene glycol with some divalent metal halides. The properties of the compounds and the bonding between the metal ions and the ligand has been studied by means of physical measurements.

This work is part of our investigation on the coordination chemistry of diols.

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Table I. Complexes of ethylene glycol with metal(II) halides; analyses, colours, synthetical methods, melting points, X-ray and IR types.

Compound	Metal anal.		Halogen anal.		Colour	Synth. meth.	Melt. point[a]	X ray type	IR type[f]	First prep. by ref.[c]
	found	calc.	found	calc.						
$Mg(EG)_3Cl_2$	8.64	8.64	24.1	25.2	white	1	168-9	—	A	*
$Ca(EG)_4Cl_2$	11.18	11.15	19.5	19.7	white	1	94-5	I	A'	*
$Mn(EG)_2Cl_2$	22.2	22.0	28.0	28.4	pink	1	122-3	II	B	*
$Co(EG)_2Cl_2$	23.4	23.3	27.3	27.9	lilac	2	100 d	III	B	3
$Co(EG)_3Cl_2$	18.8	18.6	21.5	22.4	deep blue	3	67-8	—	A'	3
$Ni(EG)_2Cl_2$	23.1	23.2	26.7	26.9	green	1	200 d	III	B	5
$(Ni(EG)_3Cl_2)$	19.0	18.6	22.2	22.4	green	1	200 d	—	B	*
$Cu(EG)_1Cl_2$	32.4	32.3	35.2	36.1	green	1	130 d	—	C	*
$Cd(EG)_{4/3}Cl_2$[d]	42.4	42.2	26.2	26.6	white	1	145 d	—	D	*
$Mg(EG)_3Br_2$	6.67	6.57	42.6	43.1	white	1	195 d	—	A	*
$Ca(EG)_4Br_2$	9.04	8.94	35.4	35.7	white	1	142-3	I	A'	*
$Sr(EG)_2Br_2$	23.9	23.6	42.6	43.0	white	1	160-1	—	B	*
$Mn(EG)_2Br_2$	16.3	16.2	46.8	47.2	pink	1	125-6	II	B	3
$Co(EG)_2Br_2$	17.2	17.2	45.7	46.6	lilac	2	96-7	III	B	3
$Co(EG)_3Br_2$	14.7	14.6	40.0	39.5	deep blue	2,3	80-1	—	A'	5
$Ni(EG)_2Br_2$	17.3	17.1	45.8	46.6	green	1	200 d	III	B	3
$Ni(EG)_3Br_2$	14.2	14.5	39.4	39.5	green	3	85 d	—	A	3
$Cd(EG)_{4/3}Br_2$[e]	32.0	31.7	44.6	45.0	white	1	146-7	—	D	5

[a] d = decomposes; [b] — denotes: type different from any other; [c] * denotes: this work; [d] %C: found: 11.86, calcd: 12.02; %H: found: 3.09, calcd: 3.06. [e] %C: found: 8.84, calcd: 9.02; %H: found: 2.62, calcd: 2.28. [f] A and A' monodentate; B: bidentate; C and D: Not sure (see infrared spectra).

Experimental Section

Most of the compounds are hygroscopic and must therefore handled in a P_2O_5 dried glove-box.

Starting materials. Commercially available ethylene glycol was dried over anhydrous $CaSO_4$ and purified by distillation at atmospheric pressure.

The metal salts were commercially available as hydrates. They were used without further purification.

Preparation of the compounds. 1) The metal hydrate (0.01 mole) was dissolved either in an excess of the ligand, or in a solution of 4 gram EG in 15 ml methanol. Than triethyl orthoformate (EOF) was added for dehydration.[14] Crystals appeared after addition of sodium dried diethylether of THF (tetrahydrofuran) on cooling to –20°C. The solution had to be evaporated first when no crystallisation occured.

2) The metal hydrate (0.01 mole) was treated with trimethyl orthoformate (Me(OF) and an equivalent amount of EG was added. The solution was evaporated and the remaining syrup was allowed to stand under sodium dried diethylether till a solid compound could be isolated.

3) The metal hydrate (0.01 mole) was dissolved in an equivalent amount of the ligand. Crystals appeared after some days of standing in vacuo over P_2O_5.

The obtained solid compounds were filtered and whased several times with sodium dried diethylether and finally dried in vacuo.

Analyses. Metal(II) analyses were carried out by complexometric titrations as described by *Vogel*[15] and *Schwarzenbach*.[16] Halogen analyses were performed according to the Volhard method as described by Vogel.[15] Carbon and hydrogen analyses were carried out under the supervision of *Mr. W.J. Buis* at the Micro-analitical Department of the Organic Chemistry Institute TNO, P.O. Box 5009 Utrecht.

Physical measurements. Diffuse reflectance spectra were recorded on a Beckman DK2A double beam spectrophotometer, equipped with a standard reflectance set and with MgO as a reference.

Infrared spectra in the 4000-700 cm^{-1} region were recorded on a Hitachi EPI-G2 and on a Unicam Sp 1200 spectrophotometer. A Hitachi EPI-L spectrophotometer was used for the 700-200 cm^{-1} region.

The samples were measured as nujol mulls between NaCl plates and polythene plates or as KBr disks. The mulling of the compounds containing more than two molecules of the ligand was somewhat difficult.

X-ray powder diagrams of the compounds were obtained with a Guinier type camera and with Cu-Kα radiation. These samples were mounted with vasilline and protected from moisture by adhesive tape.

Magnetic susceptibility measurements were carried out on a Gouy balans, equipped with a temperature control set. The field was callibrated with $HgCo(CNS)_4$[17]. $\mu_{eff.}$ was calculated from the formula $\mu_{eff.} = (8\chi_{corr.}\ T)^{1/2}$ in which $\chi_{corr.} = \chi_{mol} + \chi_{dia.} + \chi_{TIP}$. Diamagnetic corrections were taken from literature.[18,19]

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Table II. Ligand field spectra of complexes of ethylene glycol with metal(II) halides; bandmaxima are in kK, Dq and B values are in cm^{-1}, Dq/B and β are real numbers.

Compound	Bandmaxima and assignment[a]			Dq	B	Dq/B	β[b]
	$^4T_{2g} \leftarrow {}^4T_{1g}(F)$	$^4A_{2g} \leftarrow {}^4T_{1g}(F)$	$^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$				
$Co(EG)_2Cl_2$	7.30	(14.4)	18.2 (19.6)	800	810	0.99	0.83
$Co(EG)_2Br_2$	(7.45)	?	18.35 (19.8)	810	790	1.02	0.82
(T_d species)[c]	6.7-4.5 ($^4T_1(F) \leftarrow {}^4A_2$);		14.4 ($^4T_1(P) \leftarrow {}^4A_2$)	340	720	0.47	0.74
	$^3T_{2g} \leftarrow {}^3A_{2g}$	$^1E_g, {}^3T_{1g}(F) \leftarrow {}^3A_{2g}$	$^3T_{1g}(P) \leftarrow {}^3A_{2g}$				
$Ni(EG)_2Cl_3$	8.20	(14.00) 12.95	24.2	820	870	0.94	0.84
$Ni(EG)_2Br_2$	8.00	(13.70) 12.80	23.5	800	845	0.95	0.81
$Ni(EG)_3Br_2$	8.80	15.40 14.00	26.0	880	940	0.94	0.90
$Ni(EG)_3Cl_2$[d]	8.10	(13.90) 12.90	23.9	815	860	0.95	0.83
		$^2T_{2g} \leftarrow {}^2E_g$					
$Cu(EG)_1Cl_2$		11.00 (asymmetric band)		1100	—	—	—

[a] shoulders are in parentheses. [b] $\beta = B_o = B_{obs}$; $B_o(Ni^{2+}) = 1041$ cm^{-1}; $B_o(Co^{2+}) = 972$ cm^{-1}. [c] see text. [d] impure.

Results and Discussion

General. The complexes of metal(II) halides with ethylene glycol as the ligand are listed in Table I, together with their analitical data, colours, melting points, X-ray types and type of the infrared spectrum. The synthetical method (see above) is also indicated in the Table.

No solid compounds could be isolated in the case of iodides, $SrCl_2$, $CuBr_2$, FeX_2, BaX_2 and ZnX_2 (X=Cl,Br). Also with trivalent halides only syrupy oils were obtained.

The compound $Co(EG)_2X_2$ (X = Cl, Br) can also be prepared by stirring the compound $Co(EG)_3X_2$ with sodium dried diethylether. Than a dark blue syrup is formed, which solidifies after some time. The compound $Co(EG)_3Cl_2$ con also be prepared by dissolving anhydrous $CoCl_2$) (0.01 mole) in an equivalent amount of the ligand (0.03 mole). The properties of the compounds $Co(EG)_3X_2$ (X = Cl, Br) will be published later.[20]

With method 1, we synthesized with $NiCl_2$ a complex which was first characterized as $NiCl_2 . 3EG$ because of the metal and anion analyses (Table I). In view of the infrared spectra however, and on grounds of the carbon and hydrogen analyses (%C: found 20.8; calcd 22.7; %H: found 5.21; calcd 5.74) it was pointed out that this compound was an impure product.

Stirring for several hours with dry diethylether yielded the compound $Ni(EG)_2Cl_2$.

The X-ray patterns indicate isomorphism for the compounds $M(EG)_2X_2$ (M = Ni, Co; X = Cl, Br). Furthermore the compounds $Ca(EG)_4X_2$ (X = Cl, Br) are isomorph, as well as the compounds $Mn(EG)_2X_2$ (X = Cl, Br). The other compounds form types by thermselves.

Ligand Field Spectra. For evidence about the surrounding of the metal ions, the diffuse reflectance spectra of the solid Co, Ni, and Cu compounds were taken.

In order to locate the infrared overtones of ligand vibrations in the 5-10 kK region we recorded the reflectance spectra of the Mn compounds. Overtones were observed at approximately 6450 and 5900 cm^{-1}. The band at 6450 cm^{-1} can be assigned to an overtone of the OH stretching vibration and the band at 5900 cm^{-1} is due to overtones of modes of the methylene group.[1]

Most of the compounds show spectra that are typical for octahedral coordination. The band maxima of the Co, Ni and Cu compounds and the assignment in terms of octahedral coordination[21,22] are given in Table II. Calculations of the spectral parameters were made according to ref. 21 and 22. The Cu compound shows an asymmetric band as is common for octahedral Cu^{II} complexes. The Dq value is taken directly from the band maximum. The spectra of $Co(EG)_3X_2$ (X = Cl, Br) are not included in the Table; these compounds will be discussed later.[20]

The diffuse reflectance spectrum of $Co(EG)_2Br_2$ consists of an intense doublet with bands at 14.40 and 18.35 kK with a shoulder at 19.80 kK, and of a broad band at 6.0 kK with a shoulder at 7.45 kK. This spectrum could not be explained in terms of distorted tetrahedral environment, since calculation of the spectral parameters yielded unacceptable values, for Dq and B. Nevertheless, this spectrum can be explained by accepting that the compound contains both tetrahedral and octahedral species. The T_d content is probably small, because the intensity of the observed bands is almost equal and because it is well known that the absorption bands for tetrahedral compounds are in general about a hundred times more intense than the absorption bands for octahedral complexes ($\varepsilon(T_d) \approx 1000$; $\varepsilon(O_h) \approx 10$). So, the absorption bands of this spectra can be assigned as follows: the bands at 14.40 and 6.0 k are due to the T_d species and the bands at 18.35 and 7.45 kK can be assigned to absorptions of the octahedral species.

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Table III. Comparison of spectral parameters of some octahedral complexes of cobalt and nickel. Dq and B values are in cm^{-1}, Dq/B and β are real numbers

	Co				Ni				
Compound [a]	Dq	B	Dq/B	β	Dq	B	Dq/B	β	Ref.
$M(PyNO)_6(BF_4)_2$	890	780	1.14	0.80	820	840	0.98	0.82	23
$M(EtOH)_6(ClO_4)_2$	905	845	1.07	0.87	835	910	0.92	0.87	21, 22
$M(MeOH)_6(BF_4)_2$	920	850	1.08	0.87	855	910	0.93	0.87	1
$M(PG)_3Cl_2$	—	—	—	—	870	920	0.95	0.88	20
$M(EG)_2Cl_2$	800	810	0.99	0.83	820	870	0.94	0.84	this work
$M(EG)_2Cl_2$	—	—	—	—	820	860	0.95	0.83	5
$M(EG)_3Cl_2$	—	—	—	—	865	910	0.95	0.87	8 [b]
$M(EG)_3Br_2$	—	—	—	—	880	940	0.94	0.90	this work
$M(EG)_3(NO_3)_2$	885	840	1.05	0.86	880	925	0.95	0.87	20
$M(H_2O)_6(ClO_4)_2$	920	850	1.08	0.87	885	920	0.96	0.87	21, 22
$M(en)_3Cl_2$	—	—	—	—	1150	860	1.33	0.83	21

[a] PyNO = pyridine-N-oxyde; PG = propylene glycol; EG = ethylene glycol; en = ethylenediamine. [b] transmission spectrum in solution.

Table IV. Infrared spectra of ethylene glycol in the vapour and liquid phase, together with the assignment and the range of the bands on coordination.

Vapour (ref. 27)	Liquid	Assignment (ref. 25) [a]	Range on coordination
3677 s	3350 vs	νOH	3300-3200
3644 s			
2941 s	2935 s	νCH	2935
2878 s	2875 s	νCH	2875
1456 w	1460 m	δCH_2 75	1460
	1410 m	δCOH 47, γCH_2 21	1415-1405 [b]
1385 w	1375 sh	γCH_2 42, τCH_2 32, δCOH 18	1380-1375 [b]
1279 w	1335 m	γCH_2 41, δCOH 23, τCH_2 20	1325-1305 [b]
1254 w	1255 w	τCH_2 51, γCH_2 43	1290-1220 [b]
	1207 w	τCH_2 61, γCH_2 19	1215-1200 [b]
1166 m			
1141 sh			
1085 vs	1089 s	ρCH_2 57	1085-1060 [b]
1055 vs			
1036 w	1045 s	νCO 51, νCC 27	1043-1012 [b]
876 sh	886 s	ρCH_2 40, νCO 24	890-880
861 m	867 s	νCC 60, νCO 17	880-860
	±630 br	t-CO 74	690-550
522 w	517 w	δCCO 62	545-519
375 s	347 w(br)	δCCO 72	?

v = very; s = strong; m = medium; w = weak; br = broad; sh = shoulder; t = torsion; ν = stretching; δ = bending; γ wagging; τ = twisting; ρ = rocking. [a] numbers give potential energy distributions in %. [b] splitting of the bands may occur.

Spectral parameters calculated according to this assignment are included in Table II. The Dq and B values are not very accurate, because observation of the bands at 6.0 and 7.45 kK is seriously hampered by the infrared overtones of ligand vibrations, and because the T_d/O_h ratio is not exactly known.

5-coordination in this compound can also be ruled out because of the following reasons:

1) the X-ray types of the compounds $M(EG)_2X_2$ (X = Cl, Br; M = Ni, Co) are very similar (see Table I); As the Ni-compound and $Co(EG)_2Cl_2$ show ligand-field spectra that are typical for octahedral or pseudo-octahedral coordination, 5-coordination is highly unreasonable.

2) The temperature dependance of the magnetic moment of this compound indicates pseudo octahedral coordination (see below).

In Table III a comparison is made between ethylene glycol and some other ligands. As can be seen from the table, ethylene glycol behaves as a normal OH donor. The position of EG in the spectrochemical series is very close to the position of H_2O[21,22] and PG[24] (= propylene glycol). Average environment calculations[5] for $M(EG)_2X_2$ (M = Ni, Co; X = Cl, Br) were performed to obtain more realistic values for Dq and B, yielding for Co: Dq = 865, B = 815, and for Ni: Dq = 880 and B = 940 cm^{-1}. The values for the Co compounds are to low.

Spectral parameters calculated from literature data[8] obtained from solutions are in agreement with our results (Table III). The Dq and B values as obtained by Nylander[5] are also in good agreement with our results. Abu-Eittah and Arafa[9] did not give the first absorption band and therefore no spectral parameters could be calculated from their data of solutions of $Co(ClO_4)_2$ in ethylene glycol.

As can be seen from Table II, $NiCl_2 . 3EG$ and

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(25) H. Matsuura and T. Miyazawa, *Bull. Chem. Soc. Japan*, *40*, 85 (1967).

$NiCl_2 . 2EG$ have the same ligand field parameters. This should indicate the same surrounding of the metal ion: 2 EG and 2Cl. On grounds of the infrared spectra however (see below) it must be concluded that this compound is impure.

Infrared Spectra. The infrared spectra of ethylene glycol have been subject of extensive investigations. A normal coordinate analysis was performed by Matsuura and Miyazawa.[25] They analysed several conformations of the glycol molecule, e.g. TGG which means that the internal rotational forms along the bands HO-CH_2-CH_2OH are trans, gauche and gauche. Assignments were also published by Sawodny *et al,*[26] Buckley and Giguère[27] and Krishnan and Krishnan.[28] There are however some relevant differences between the various assignments (see below). All investigators concluded that the gauche conformation with respect to the CC bond was the most common in the liquid.

The infrared spectra of ethylene glycol, both in the liquid and the vapour phase are collected in Table IV, together with the assignment as published by Matsuura.[25] Furthermore the range of the absorption bands as they occur in the complexes is indicated in the table.

Spectra of the Complexes. The CH and OH stretching vibrations: All compounds show a broad intense band at about 3300 cm^{-1}, which is due to the ν(OH). In the free ligand the absorption occurs at 3350 cm^{-1}.

In the complexes it is shifted about 50-150 cm^{-1} to lower frequences. This suggests coordination of EG via one or two of the oxygen atoms. The compounds $Cd(EG)_{4/3}X_2$ show no shift of the OH stretching. The CH_2 stretching vibrations are not shifted on coordination.

The COH and CH_2 twisting and wagging vibrations: All these vibrations are coupled in the uncomplexed ligand.[25] Because of this coupling, nothing definite can be said about shifts in the region where these absorptions occur.

The spectra of the compounds $M(EG)_2X_2$ (M = Sr, Mn, Co, Ni) and $Cd(EG)_{4/3}X_2$ (X = Cl, Br) in this region are similar to the spectrum of the free ligand. They also resemble very well with the spectra of the complexes with less than 15% water as reported by Miyake,[11] indicating bidentate coordination. The other complexes show splittings and considerable shifts of the absorption bands. The spectra of most of these compounds resemble those of the complexes with more than 15% water, for which Miyake[11] concluded bidentate coordination. This is not fully supported by the behaviour of the CO stretching vibration (see below). No compound shows a shift of the absorption bands at 1460, 1410, and 1375 cm^{-1}, although splittings may occur.

A peak at about 1610 cm^{-1} was observed when the spectra were recorded as KBr pellets. This absorption is probably due to water[30] adsorbed to the KBr. No peak at this frequency was observed when the spectra were obtained from nujol mulls.

The CO stretching vibrations: The assignment of these vibrations and of the CH_2 rockings and CC stretchings will be discussed below.

In the free ligand these vibrations, which are coupled for a certain amount with other vibrations, occur at probably 1089 and 1045 cm^{-1} as strong and somewhat broad bands.[25-28] In the compounds $M(EG)_2X_2$ (M = Sr, Mn, Co, Ni) and $Cd(EG)_{4/3}X_2$ (X = Cl, Br) these bands are shifted 20-30 cm^{-1} to lower frequencies. Since no splittings of the bands are observed, bidentate coordination can be deduced.[11]

The spectra of the complexes $Ca(EG)_4X_2$ and $Co(EG)_3X_2$ (X = Cl, Br) are very similar; they show downfield shifts of 10-30 cm^{-1} but no splittings are observed. This would indicate bidentate coordination, however this is contradicted by the shape of the spectra in the 1700-1200 cm^{-1} region (see above). The spectra of the compounds $Mg(EG)_3X_2$ and $Ni(EG)_3Br_2$ show shifts of 10-30 cm^{-1} and a splitting of both the absorption bands, indicating monodentate coordination.

The CH_2 rocking and CC stretching vibrations: These bands probably occur at 886 and 867 cm^{-1} in the free ligand. Small shifts to higher as well as to lower frequencies are observed, while no splitting of the bands occurs. In most complexes two sharp peaks are observed except for the compound $Cu(EG)Cl_2$, where the band at 886 cm^{-1} is shifted to 898 cm^{-1} and for the compound $Sr(EG)_2Br_2$, where only one band is observed at 868 cm^{-1}.

The CO torsional and CCO bending vibrations: The t-CO occurs as a very broad band at about 630 cm^{-1} in the free ligand. In the complexes this band appears as a very broad continuous absorption, centered at about 630 (±50) cm^{-1}. No shifts or splittings can be observed.

The symmetric CCO bending occurs at 517 cm^{-1} in the free ligand, and is shifted to higher frequencies on complexing (0-30 cm^{-1}). The shape and intensity in the complexes are the same as in the free ligand.

The asymmetric CCO bending is observed at 437 cm^{-1} as a weak and rather broad absorption in the free ligand. Assignment of obsorption bands in the complexes is not possible, because observation of the ν_{as}(CCO) is seriously hampered by other vibrations which occur in this region, for instance the M-L and M-X modes.[34-35]

Metal-ligand and metal-halogen vibrations: M-O stretching vibrations are usually found in the 450-200 cm^{-1} region and M-X vibrations, including bridging halogens, are expected to occur below 350 cm^{-1}.

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Table V. Comparision of the assignments of some absorption bands in the infrared spectrum of ethylene glycol.

Band (ref.)	25 [a]	26	27	28
1089 [b]	$\rho CH_2(57)$ [c]	$\nu_s CO$	νCO	νCO
1045	$\nu CO(51)$, $\nu CC(27)$	$\nu_{as} CO$	νCC	νCO
886	$\rho CH_2(40)$, $\gamma CO(24)$	ρCH_2	ρCH_2	ρCH_2
867	$\nu CC(60)$, $\nu CO(17)$	νCC	ρCH_2	νCC

[a] numbers in parenthesis are potential energy distributions in %. [b] numbers are in cm^{-1}. [c] ν = stretching; ρ = rocking; s = symmetric; as = asymmetric.

Table VI. Magnetic susceptibilities and magnetic moments of some complexes of ethylene glycol.

Compound	T(°K)	χmol. ($\times 10^6$ cgs)	χcorr. ($\times 10^6$ cgs)	μeff. (BM)
$Ni(EG)_2Cl_2$	291	4540	4435	3.21
$(Ni(EG)_3Cl_2)$	291	4575	4435	3.21
$Ni(EG)_2Br_2$	291	4395	4480	3.23
$Ni(EG)_3Br_2$	291	4515	4355	3.18
$Co(EG)_2Cl_2$	291	11040	11180	5.10
	100	28630	28770	4.80
$Co(EG)_2Br_2$	291	11400	11560	5.19
	100	29580	29740	4.86

All compounds show a broad absorption below 250 cm^{-1}, probably due to M-L and M-X vibrations. The compounds $M(EG)_2X_2$ and $Cd(EG)_{4/3}X_2$ have a broad band in the region 455-348 cm^{-1}, which is anion and metal dependent. This band can be due to the δCCO, although this is not quite sure, because the observed bands are more intense than those in the free ligand, and furthermore, M-O vibrations can occur in this region. The Ni compounds show extra bands at 330 and 280 cm^{-1}.

The compounds $Co(EG)_3X_2$ and $Ca(EG)_4X_2$ afforded very poor spectra due to the bad mulling properties of this compounds.

The coopper complex and the compounds $Mg(EG)_3X_2$ and $Ni(EG)_3Br_2$ show three rather sharp bands between 450 and 300 cm^{-1}, probably due to M-L and M-X vibrations.

In addition it may be remarked that the spectra of the compounds $Cd(EG)_{4/3}X_2$ are very similar to the EG spectrum, suggesting bidentate coordination, although some sort of clathrate compound may not be excluded here.

The spectrum of $Ni(EG)_3Cl_2$ is similar to that of $Ni(EG)_2Cl_2$, however extra bands are observed at 1730 and 1180 cm^{-1}, which are probably due to absorptions of ethylformate, formed by the reaction of EOF with water.[14] So it is clear that this compound is impure. An attempt has been made to prepare this complex with MeOF (methylorthoformate) as the dehydrating agent,[1] but additional absorptions were observed again.

The assignment of the CO and CC stretching and CH_2 rocking vibrations: There is some disagreement about the assignment of the bands at 1089, 1045, 886 and 867 cm^{-1} in the literature. The various assignments are collected in Table V.

Coordination of molecules to metal ions induces alterations in the infrared spectra of these molecules. This is well known for ligands like sulfoxides[31] and nitriles.[32] The origin of shifts in IR absorptions are in general:[33]

1) formation of a coordination bond (σ or π), ultimately resulting in a shift to lower frequencies of the stretching modes and a shift to higher frequencies of the bending modes of the bands between the donor atom and the rest of the ligand.

2) changes in coupling of ligand modes and kinematic coupling.

3) coupling of ligand modes with metal-ligand vibrations.

4) anion effects (e.g. H-bonding)

5) lattice effects.

Usually[33] effect 1) predominates the others, but effect 3) can be rather important, especially in the low frequency region (500 cm^{-1}). Shifts due to effects 2), 4), and 5) can not simply be determined and predicted.

Upon coordination, we expect because of effect 1) a shift to lower frequency for the CO stretching modes ,and a small shift to higher frequency for the ν(CC)because of effect 2)[33]. Only a small or no shift is expected to occur for the $\rho(CH_2)$.

Now we observe in the IR spectra of the complexes shifts to lower wavelength of 30-20 cm^{-1} for the band at 1089 cm^{-1} and of 10-25 cm^{-1} for the band at 1045 cm^{-1}. The bands at 886 and 867 cm^{-1} show only small shifts. The observed shifts should indicate considerable amounts of ν(CO) in the vibrational modes at 1089 and 1045 cm^{-1}, while the bands at 886 and 867 cm^{-1} should consist of predominantly CC stretching and CH_2 rocking vibrations . This is supported by the assignments of other investigators.[26-28] On basis of the normal coordinate treatment of Matsuura and Miyazawa[25] however, we expect shifts of

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(36) B.N. Figgis, « Introduction to ligand Fields », Interscience, New York (1966).

the bands at 1045 and 886 cm^{-1}. This is not observed however.

The various types of IR spectra are indicated in Table I. Spectra denoted by A or A′ give evidence for monodentate coordinated ethylene glycol, and the spectra indicated by B suggest bidentate coordination. C and D are different types and nothing definite can be said about coordination of the glycol molecule. No *Irving-Williams* sequence[30] was observed in the complexes.

Magnetic susceptibility measurements. Magnetic moments have been determined for the Ni-compounds and for $Co(EG)_2X_2$ (X = Cl, Br). The results are given in Table VI. The magnitudes of the magnetic moments indicate octahedral coordination for all metal ions, which is in agreement with the results from ligand field spectra.

The results for the Ni-compounds are in reasonable agreement with literature values[5,36]. TIP contributions are taken to be 240 cgs units.

Temperature dependence of the magnetic moment for the Co compounds also indicates O_h symmetry This supports our conclusions as obtained from ligand field spectra, for the compound $Co(EG)_2Br_2$. TIP contributions are ignored.

Conclusion

The results of this study show that ethylene glycol acts as a normal OH-donor ligand, which coordinates via one or two oxygen atoms.

Magnetic measurements and ligand field spectra indicate octahedral or pseudo octahedral coordination of the Co, Ni and Cu compounds. Ethylene glycol and water are in the same position in the spectrochemical series.

Infrared spectra give evidence for monodentate and for bidentate coordination. The observed shifts of some ligand vibrations can not be explained on basis of a literature normal coordinate treatment.

In a number of cases, synthesis of solid complexes of ethylene glycol with metal(II) halides is somewhat difficult, because of crystallisation problems.

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