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Ethers as Ligands. Part II[1]. Metal(II) Dimethoxyethane Solvates

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A series of new complexes is reported with 1,2-dimethoxyethane as the ligand, viz. *$[M(1,2\text{-dimethoxyethane})_3]^{2+}(SbCl_6)_2^-$ where M is Mg(II), Ca(II), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II). The metal(II) ions are octahedrally surrounded by three dimethoxyethane molecules. The chelating dimethoxyethane ligands are in the* gauche *conformation.*

Introduction

Relatively few systematic studies have been devoted to the ligation properties of 1,2-dimethoxyethane (DME). Knowledge of the complex forming properties of dimethoxyethane and, in general, of ether molecules is not only of interest in coordination chemical respect but may also be of importance from a synthetical organic point of view. In order to obtain unambiguous results, we have tried to synthesize transition metal ion solvates* with dimethoxyethane as the ligand. Up till now only dimethoxyethane adducts have been reported, for example: $MCl_2(DME)$ where M is Mn, Fe, Co, and Ni [2–7], $ZnBr_2(DME)$ and $(C_6H_5)_2Zn(DME)$ [8], $(CH_3)_2Mg(DME)$ [9, 10], $NiI_2(DME)_2$ [3], and $SnCl_4(DME)$ [11, 12].

We succeeded in synthesizing a number of solvates by a still not very common method, which has been developed in our laboratories:

$$MCl_2 + 2SbCl_5 + 3DME \xrightarrow{DME} [M(DME)_3]^{2+}(SbCl_6)_2^-$$

The features of this method, without which it appears not to be possible to obtain solvates of ligands with poor donor properties, are: i) Dimethoxyethane is both ligand and solvent, which has the advantage that no other (potentially stronger) ligands are present. ii) The formation of a large anion forces the complete solvation of the metal ion by ligand molecules.

This work is part of our investigations on the existence of coordination compounds of weak ligands [13–15].

Experimental

Most of the divalent metal chlorides were available as hydrates. Dehydration was effected by heating them in a stream of dry HCl gas. Calcium(II) chloride, iron(II) chloride, and zinc(II) chloride were prepared as described by Brauer [16]. Antimony pentachloride was used without further purification. Dimethoxyethane was used after storage over anhydrous calcium sulphate.

The complexes were prepared by stirring the metal chlorides with antimony pentachloride in the ratio 1.00:2.05 in dimethoxyethane at room temperature. The solid compounds, which are poorly soluble in the parent solvent, separated as powders. These were collected on a glass filter, washed with sodium-dried n-pentane and dried *in vacuo* at 50 °C. The compounds decompose rapidly in the presence of water. All operations were therefore conducted in a P_2O_5-dried atmosphere. After a few weeks the solid compounds decomposed (they turned black). Crystalline solids can be obtained by adding DME slowly to a solution of $(M(CH_3NO_2)_6)^{2+}(SbCl_6)_2^-$ in nitromethane [13].

The divalent metals were determined complexometrically [17], antimony was determined iodometrically [18]. Diffuse reflectance spectra in the visible and near infrared region were recorded on a Beckman DK-2 spectrophotometer using the standard reflectance attachment. Infrared spectra were recorded on a Perkin Elmer 580 spectrophotometer (4000–180 cm^{-1}) as nujol mulls between KrS-5 plates and between polythene plates. The electron paramagnetic resonance (EPR) spectrum of the copper compound was obtained at room temperature on a Varian instrument as described elsewhere [19].

Results and Discussion

In Table I eight new coordination compounds of dimethoxyethane are listed with colours, melting

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*We understand by a SOLVATE: A solid coordination compound in which the central (transition) metal ion is coordinated completely by ligands of only one kind; *e.g.* $[Ni(NH_3)_6]^{2+}(BF_4)_2^-$, $[Ni(2,2'\text{-dipyridyl})_3]^{2+}Cl_2^-$.

TABLE I. Complexes of 1,2-Dimethoxyethane (DME), Their Analyses (% weight), Melting Points (°C), and Colours.

	Metal(II)		Melting Point, °C	Colour
	Calc.	Found		
$Mg(DME)_3(SbCl_6)_2$	2.52	2.43	>250	White
$Ca(DME)_3(SbCl_6)_2$	4.09	4.09	>250	White
$Mn(DME)_3(SbCl_6)_2$	5.53	5.44	>250	White
$Fe(DME)_3(SbCl_6)_2$	24.5[a]	24.1[a]	170 d.	Pale Yellow
$Co(DME)_3(SbCl_6)_2$	5.90	5.84	230 d.	Rose–Red
$Ni(DME)_3(SbCl_6)_2$	5.88	5.94	>250	Green
$Cu(DME)_3(SbCl_6)_2$	6.33	6.19	183 - 185	Greenish–Blue
$Zn(DME)_3(SbCl_6)_2$	6.51	6.48	199 - 201	White

[a] Antimony content. d. = decomposes.

TABLE II. Infrared Absorption Bands (cm^{-1}) of Dimethoxyethane (DME) and the Compounds $[M(DME)_3](SbCl_6)_2$.

DME	Mg	Ca	Mn	Fe	Co	Ni	Cu	Zn
1304	1281	1286	1281	1279	1281	1278	1279	1279
1248	1247	1248	1246	1245	1243	1241	1240	1243
1194	1191	1188	1189	1189	1190	1187	1188	1189
1120	1092	1106	1092	1091	1088	1088	1093 1082	1090
1092	1042	1052	1041	1044	1040	1037	1034	1039
982								
938								
852	864	860	856	861	857	857	859	859
541	560	558	561	562	562	558	562	562
	–	392	401	406	408	416	421	408
	342	337	338	338	338	338	342	334
	–	238	233	246	250	277	310 230	227

points, and analytical data. From the stoichiometry of the compounds a first indication is gained that the metal ions are hexacoordinated by the bidentate dimethoxyethane ligands.

In the far infrared spectra of all compounds a strong absorption band is present at about 340 cm^{-1}. This band is due to the $\nu_3(T_{1u})$ mode of the octahedral ion $(SbCl_6)^-$ [13, 14, 20].

When comparing the infrared spectrum of liquid dimethoxyethane with the infrared spectra of its complexes (see Table II) some significant differences are observed: the bands at 982 cm^{-1} and at 938 cm^{-1} of liquid dimethoxyethane are not present in the dimethoxyethane solvates. The disappearance, upon complexing, of the ligand vibration bands is in general indicative of a change in conformation of the ligand [21, 22]. In this case it is a strong indication that dimethoxyethane in its complexes occurs in the *gauche* (tgt) conformation [23, 24], which is to be expected when dimethoxyethane acts as a chelating ligand. Most of the other bands of dimethoxyethane shift upon complexing (see Table II), which is a general feature of ligands upon coordination [14, 15, 21, 25]. However, in the case of dimethoxyethane, the magnitudes of the shifts do not follow the Irving–Williams sequence [21, 26]. In general ligands are coordinated via a donor atom which is part of a distinct group of the ligand molecule, like C≡N in RCN ligands [15], C=O in RR'CO ligands [21], and S=O in RR'SO ligands [25]. The stretching and bending vibrations of such donor groups are coupled with other ligand (skeletal) modes only to a limited extent. The inductive effect of the metal ions is therefore reflected directly in a particular change of the stretching and bending frequencies of the donor group, thus producing an Irving–Williams sequence. In dimethoxyethane, on the other hand, the C–O stretching and bending vibration modes are strongly coupled with other (skeletal) modes [24], so that the influence of the metal ions on the 'C–O vibrations' is so much 'diluted', that it does not manifest itself. The non-occurrence of an Irving–Williams sequence in the magnitudes of the shifts of ligand vibration bands has also been observed for 1,2-ethanediol [27]. In the far infrared spectra of the complexes two absorption bands appear which are not present in the spectrum

TABLE III. Absorption Bands (cm^{-1}) in the Visible and Near Infrared, Their Assignments, and the Calculated Ligand Field Parameters of the Cobalt and Nickel Compounds.

$Co(DME)_3(SbCl_6)_2$	σ_1 = 8015	$^4T_{2g} \leftarrow {}^4T_{1g}(F)$	Dq = 875 cm^{-1}
	σ_2 = 15550	$^4A_{2g} \leftarrow {}^4T_{1g}(F)$	B = 805 cm^{-1}
	σ_3 = 19010	$^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$	Dq/B = 1.09
	= 20830sh	$^2A_{1g}(G) \leftarrow {}^4T_{1g}(F)$	β = 0.83
$Ni(DME)_3(SbCl_6)_2$	σ_1 = 8620	$^3T_{2g} \leftarrow {}^3A_{2g}$	Dq = 860 cm^{-1}
	σ_2 = 13515	$^1E_g \leftarrow {}^3A_{2g}$	B = 895 cm^{-1}
	= 14515	$^3T_{1g}(F) \leftarrow {}^3A_{2g}$	Dq/B = 0.96
	σ_3 = obscured by the anion (CT) band		β = 0.86

of liquid dimethoxyethane. The positions of both bands are metal dependent in the Irving–Williams sense [26]. Metal–ligand vibrations of metal(II) oxygen-donor complexes usually do not occur above 350 cm^{-1} [14, 21, 25]. Therefore we assign, tentatively, the band in the 227–310 cm^{-1} range to the M–O stretching vibration. Snyder and Zerbi [24] observed that at −196 °C in solid dimethoxyethane a band at 344 cm^{-1} is present with much COC bending character. This band is not present in the spectrum of liquid dimethoxyethane at room temperature. It might well be that this band becomes active again upon coordination. We propose to assign the band in the 392–421 cm^{-1} range to this COC bending vibration. The rather large upfield shift of this band in the complexes and the metal dependence in the Irving–Williams sense can be accounted for by the COC bending character of this vibration mode together with coupling of this mode with metal–ligand vibration modes. The infrared spectra of the complexes, with the exception of the copper compound, all show the same pattern of bands and (relative) intensities, which suggests that the compounds are largely isomorphous. In the far infrared spectrum of the copper compound some 'extra' bands are present. This indicates that the $[Cu(DME)_3]^{2+}$ species are distorted from octahedral symmetry [15, 19] (see below).

The reflectance spectrum of the iron compound consists of one rather asymmetrical band at 9570 cm^{-1} due to the $^5E_g \leftarrow {}^5T_{2g}$ transition. This band has definite doublet structure, with a peak separation of about 2000 cm^{-1}. The doublet structure is presumed to be due to a low symmetry ligand field component (Jahn–Teller effect), which lifts the twofold degeneracy of the ^5E_g term [14, 21, 28].

The reflectance spectra of the cobalt and nickel compounds are typical for octahedral coordination. Accordingly assingments of the bands and calculations of the ligand field spectral parameters [29, 30] were performed (see Table III). The values for the spectrochemical splitting parameter lie in a range which is normal for oxygen-donor ligands [29, 30].

The reflectance spectrum of the copper compound shows one strongly asymmetric band with its maximum at 10870 cm^{-1}, which indicates that the environment of the Cu^{2+} ion deviates from octahedral symmetry. To check this we performed an EPR measurement at room temperature on this compound. An asymmetric signal was obtained from which the following Landé factors were calculated: g_x = 2.10, g_y = 2.15, and g_z = 2.34. We conclude from these values that the environment of the Cu^{2+} ion can be described as elongated octahedral.

Conclusions

The existence of metal(II) solvates with dimethoxyethane as a bidentate chelating ligand has been proved. They can be synthesized quite easily if moisture is thoroughly excluded. From the similarity in the patterns of the infrared spectra of the compounds and from the ligand field spectra of the cobalt and nickel compounds it is clear that, with the exception of Cu(II), the metal ions are in a regular octahedral environment of six oxygen atoms.

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