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Ethers as Ligands.
Part VII*. Monomeric and Chloride-bridged Dimeric Metal(II) Triglyme Compounds

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A number of new coordination compounds is reported with triethyleneglycoldimethylether (tgm) as the ligand [1]. The compounds have the general formula $[M_2(tgm)_2Cl_2](SbCl_6)_2$ *where M is Mn(II), Co(II), Ni(II), Cu(II), and Zn(II). In these dimeric complexes the hexa-coordinated metal ions are bridged by two chloride ions. The chelating, tetradentate triglyme molecules are in the* $T\bar{G}T\bar{G}\bar{G}TTGT$ *and* $TGTGGTT\bar{G}T$ *conformation respectively. Other compounds isolated are* $[M(tgm)_2](SbCl_6)_2$ *where M is Ca(II) and Sr(II), and* $[M(tgm)_2](SbCl_6)_2(H_2O)_2$ *where M is Mg(II) and Mn(II). In these monomeric compounds the Ca(II), Sr(II), and Mn(II) ions seem to be octacoordinated by the oxygen atoms of the ether molecules which are in the* $TGTT\bar{G}TTGT$ *conformation.*

Introduction

Triglyme (tgm), or 2,5,8,11-tetraoxadodecane, is well known as a solvent for organic reactions and as a catalyst in many polymerization reactions [2–4]. Only a few coordination compounds with triglyme as the ligand have been reported [5–9]. So far no solvates [10] of triglyme are known. Investigations on the coordinating properties of cyclic and linear ethers have been carried in our laboratories, and many new ether solvates have been reported [1, 10–13]. On extending these studies with an investigation on the ligand properties of triglyme it was expected that metal(II) compounds would be analogous to those with dimethoxyethane, diglyme, and pentaglyme as the ligands [10, 13]. The various possibilities seemed to be either monomeric complexes in which the metal(II) ions would be octahedrally surrounded by one triglyme molecule and two solvent molecules or by two triglyme molecules with 'loose ends', or dimeric complexes in which three diglyme molecules would coordinate two metal(II) ions at a time. To exclude possible anion coordination, non-coordinating anions like $SbCl_6^-$ and $InCl_4^-$ have to be used. The present paper describes the results of a first study on compounds containing tgm and the $SbCl_6^-$ anion.

Experimental

Nitromethane, dichloromethane, and triglyme were used after storage over molecular sieve (3 Å). The complexes were prepared at room temperature by adding triglyme to solutions of 0.005 mol of $[M(CH_3NO_2)_6]^{2+}(SbCl_6)_2^-$ in about 30 ml of nitromethane [14]. Several metal to ligand ratios were tried, from which the following ratios give optimum results: 1:1 for the Co(II), Ni(II), and Zn(II) complexes, 1:0.5 for the Cu(II) and the dimeric Mn(II) complexes, 1:2 for the Mg(II), Ca(II), and Sr(II) complexes, and 1:4 for the monomeric Mn(II) complex. In all cases a clear solution was obtained. The solutions were concentrated by partly evaporating the solvent *in vacuo* at 50 °C. Upon standing at 4 °C crystals separated, which were collected on a porous glass filter, washed with a small amount of dichloromethane, and dried *in vacuo* below 50 °C. The complexes decompose in the presence of water; the Mg, Ca, Sr, and Mn compounds are especially moisture-sensitive. All preparations were therefore carried out in a P_2O_5-dried atmosphere. An X-ray structural analysis of one of the monomeric compounds was prevented by the extreme moisture-sensitivity of these compounds and the difficulty in obtaining single crystals. An iron(II) compound could not be isolated, as during the synthetical procedure Fe(II) was partly oxidized, apparently by Sb(V). The divalent metals were determined complexometrically [15], antimony iodometrically [16], and chloride by the Volhard method [16]. Infrared spectra were recorded on a Perkin Elmer 580 spectrophotometer (4000–300 cm^{-1}) as nujol mulls between KRS-5 windows and far-infrared spectra on a Beckman FIR

Dedicated to the late Prof. Dr. W. L. Groeneveld.

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TABLE I. Metal(II) Complexes of Triglyme (tgm), Their Analyses (% weight), Melting Points (°), and Colours.

Compound	Metal(II)		Antimony(V)		Chloride		Melting point (°)	Colour
	Calc.	Found	Calc.	Found	Calc.	Found		
$Mg(SbCl_6)_2(H_2O)_2(tgm)_2$	2.24	2.28	22.4	22.2	39.2	39.5	>250	white
$Ca(SbCl_6)_2(tgm)_2$[a]	3.76	3.74	22.9	22.7	39.9	40.0	>250	white
$Sr(SbCl_6)_2(tgm)_2$	7.87	7.89	21.9	21.8	38.2	38.3	>250	white
$Mn(SbCl_6)_2(H_2O)_2(tgm)_2$[b]	4.92	5.01	21.8	21.6	38.1	37.9	163–165[d]	white
$Mn_2(SbCl_6)_2Cl_2(tgm)_2$	9.13	8.96	20.2	20.5	41.2	40.8	178–180[d]	white
$Co_2(SbCl_6)_2Cl_2(tgm)_2$	9.71	9.51	20.1	20.2	40.9	40.2	221–223[d]	purple
$Ni_2(SbCl_6)_2Cl_2(tgm)_2$	9.68	9.46	20.1	20.2	40.9	40.1	224–226[d]	green
$Cu_2(SbCl_6)_2Cl_2(tgm)_2$[c]	10.4	10.8	–	–	40.6	39.8	186–189[d]	green-yellow
$Zn_2(SbCl_6)_2Cl_2(tgm)_2$	10.7	10.6	19.9	20.1	40.6	41.2	196–197[d]	white

[a] %C: 17.9 (calc. 18.0), %H: 3.48 (calc. 3.41). [b] %C: 15.4 (calc. 15.7), %H: 3.02 (calc. 2.97). [c] %C: 16.9 (calc. 17.2), %H: 3.69 (calc. 3.61), %O: 14.5 (calc. 14.3). [d] Dec.

720 interferometer (300–100 cm^{-1}) as polythene pellets. Diffuse reflectance spectra in the visible and near infrared region were recorded on a Beckman DK-2A spectrophotometer. EPR spectra were obtained at both room temperature and liquid nitrogen temperature on a Varian 4502 X-band spectrometer and at room temperature on a Varian E-line Century Series 110 (Q-band). Magnetic susceptibility measurements between 4 and 120 K were performed on a parallel-field vibrating-sample magnetometer (PAR model 150A). X-ray powder diagrams of the compounds were obtained with a Guinier type powder camera using Cu-Kα radiation. The samples were protected from atmospheric vapour by adhesive tape.

Results and Discussion

General

In Table I the new coordination compounds are listed with their analytical data, colours and melting points. For a few representative compounds C, H, and O percentages are also given. The stoichiometry already indicates that two types of compounds are obtained, of which the Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) compounds might be dimeric. From the similarity of the X-ray powder diffraction patterns it was concluded that these supposedly dimeric compounds are isomorphous.

In the far infrared spectra of all complexes two very strong bands are present at about 350 and 180 cm^{-1}. These bands are characteristic for the non-coordinating octahedral $SbCl_6^-$ anion and have been assigned to the ν_3 (T_{1u}) and ν_4 (T_{1u}) modes of this ion respectively [17, 18]. The infrared spectra of the Mg(II) compound and the monomeric Mn(II) compound show broad bands around 3600–3300 cm^{-1} and 1630 cm^{-1} due to water.

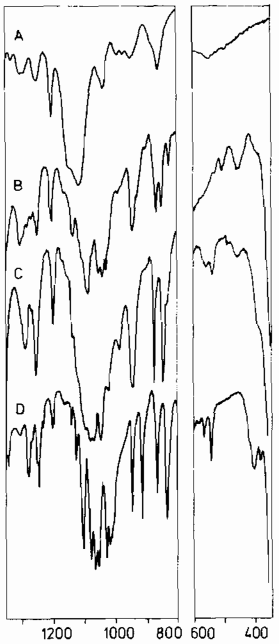

Fig. 1. Parts of the infrared spectra of liquid triglyme (A), $[Mg(tgm)_2](SbCl_6)_2(H_2O)_2$ (B), $[Ca(tgm)_2](SbCl_6)_2$ (C), and $[Ni_2(tgm)_2Cl_2](SbCl_6)_2$ (D).

Infrared Spectra, Conformation of the Ligand

Machida *et al.* [19, 20] concluded from the infrared spectra of triglyme that in the liquid state a random distribution occurs of *trans* (T) and *gauche* (G) around the C–C and C–O bonds, and that the conformation of triglyme in the solid state is more fixed, with a *trans* configuration around all C–O bonds and a *gauche* conformation around all C–C bonds.

In Fig. 1 the most important regions of the infrared spectra of liquid triglyme and of its Mg(II), Ca(II), and Ni(II) compounds are given. Iwamoto [5, 21] studied the conformation of linear ethers in several adducts. He found that triglyme has the TGTT$\bar{\mathrm{G}}$TTGT conformation in its HgCl$_2$ adduct and that any other conformation of triglyme must give rise to a more complex (split bands) infrared spectrum. In the infrared spectra of the monomeric Mn(II) compound and the Ca(II) (see Fig. 1) and Sr(II) compounds the same pattern of bands and relative intensities is observed as in the HgCl$_2$ adduct, in which the triglyme molecule acts as a tetradentate ligand. Recently the structure of a Mn(II) compound with 12-crown-4 (1,4,7,10-tetraoxacyclododecane) as the ligand has been reported [22]. In this compound the Mn(II) ion is 'sandwiched' between two 12-crown-4 ligands. The ligands are in the TGTT$\bar{\mathrm{G}}$TTGT conformation, and the Mn(II) ion is octa-coordinated by the ether oxygens. These observations suggest that in our Ca(II), Sr(II), and (monomeric) Mn(II) compounds the metal ions are also octa-coordinated by two tetradentate triglyme ligands in the TGTT$\bar{\mathrm{G}}$TTGT conformation. The infrared spectrum of the Mg(II) compound is more complex (see Fig. 1), indicating a different conformation for triglyme. Apparently triglyme does not act as a tetradentate but as a tridentate ligand in the Mg(II) compound, which is not unexpected due to the small ionic radius of Mg(II).

Apart from the anion bands, one band (at 230 cm^{-1}) of medium intensity for the Ca(II) compound and a shoulder on the ν_4-anion band (at 190 cm^{-1}) for the Sr(II) compound were observed in the far infrared region. These bands are tentatively assigned to the M–O stretching vibration. Bands due to this vibration were not observed for the Mg(II) and (monomeric) Mn(II) compounds; such bands are probably obscured by the (intense) anion band at 320–350 cm^{-1}.

The Dimeric Compounds

An X-ray structural analysis of the Co(II) compound, carried out recently in our laboratories [23], has shown that this compound is dimeric, the dimer being centrosymmetric. The cobalt ions are in a distorted octahedron of two bridging chloride ions and four triglyme oxygens (see Fig. 2). The conformations of the ligands are TGTGGTT$\bar{\mathrm{G}}$T and T$\bar{\mathrm{G}}$T$\bar{\mathrm{G}}\bar{\mathrm{G}}$TTGT respectively. The infrared spectra of the Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) compounds show exactly the same pattern of bands and relative intensities, with the exception of one band in the Cu(II) spectrum at 816 cm^{-1} which is present in the other spectra only as a small shoulder. Moreover, the X-ray powder diffraction patterns of these compounds are very similar (*vide supra*). From these observations it is concluded that these compounds are isomorphous and have the same dimeric structure. The conformation of the ligand in these compounds is different from that in the HgCl$_2$ adduct (*vide supra*), which is also clear from the infrared spectra (compare the Ca(II) and Ni(II) spectra in Fig. 1).

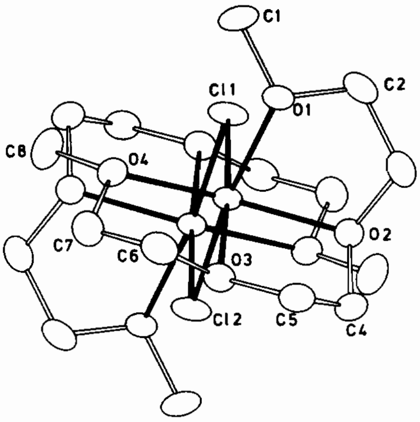

Fig. 2. Schematic representation of the structure of the dimer [Co$_2$(tgm)$_2$Cl$_2$](SbCl$_6$)$_2$ [23].

In the 300–190 cm^{-1} region of the infrared spectra of these dimeric compounds bands are present which follow the Irving–Williams sequence [24]. These bands are due to metal–ligand and metal–chloride stretching vibrations. A distinction between these vibrations cannot of course be made as these vibrations are supposed to be strongly coupled. Around 400 cm^{-1} a doublet band is present which also occurs in solid triglyme (342 cm^{-1}) and which is not present in liquid triglyme. The positions in the compounds are: Mn: 394 and 410 sh cm^{-1}, Co: 400 and 419 cm^{-1}, Ni: 403 and 421 sh cm^{-1}, Cu: 412 and 422 sh cm^{-1}, and Zn: 401 and 418 cm^{-1}. The large upfield shift together with its metal dependence (Irving–Williams sequence) can be accounted for by its COC-bending character together with some coupling with metal–ligand vibration modes. This phenomenon (of a band absent in the liquid ligand but present in its complexes) has also been encountered with the other linear ethers dimethoxyethane, diglyme, and pentaglyme [10, 13].

Ligand Field Spectra

The electronic absorption bands in the visible and near infrared region, their assignments and the calculated [25, 26] ligand field parameters of the Co(II) and Ni(II) compounds are listed in Table II. The values for the spectrochemical parameter Dq of cobalt and nickel fall in a range which can be expected for mixed oxygen–chloride coordination [25, 26]. The spectra of the cobalt and nickel compounds

TABLE II. Absorption Bands (cm^{-1}) in the Visible and Near Infrared, their Assignments, and the Calculated Ligand Field Parameters.

Compound	Band Maximum	Assignment ('octahedral')	Ligand Field Parameters
$Co_2(SbCl_6)_2Cl_2(tgm)_2$	7405	$^4T_{2g} \leftarrow {}^4T_{1g}(F)$	Dq = 805 cm^{-1}
	14290	$^4A_{2g} \leftarrow {}^4T_{1g}(F)$	B = 780 cm^{-1}
	18020	$^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$	
$Ni_2(SbCl_6)_2Cl_2(tgm)_2$	8065	$^3T_{2g} \leftarrow {}^3A_{2g}$	Dq = 805 cm^{-1}
	13070	$^1E_g \leftarrow {}^3A_{2g}$	B = 860 cm^{-1}
	14185	$^3T_{1g}(F) \leftarrow {}^3A_{2g}$	
	23700	$^3T_{1g}(P) \leftarrow {}^3A_{2g}$	

TABLE III. Bond Angles in the Cobalt Triglyme Dimer [23], see Fig. 2.

Angles	Degrees
Cl_1–Co–Cl_2	87.5
Cl_1–Co–O_1	87.9
Cl_1–Co–O_2	105.8
Cl_1–Co–O_3	176.1
Cl_1–Co–O_4	101.0
O_1–Co–Cl_2	170.5
O_1–Co–O_2	76.0
O_1–Co–O_3	95.1
O_1–Co–O_4	90.4
O_2–Co–Cl_2	97.3
O_2–Co–O_3	77.4
O_2–Co–O_4	149.3
O_3–Co–Cl_2	89.8
O_3–Co–O_4	76.5
O_4–Co–Cl_2	98.6

show a pattern characteristic for a significantly distorted octahedral coordination, which is reflected also in the low values for the nephelauxetic parameter B [25, 26]. This finding is in agreement with the bond angles around the Co(II) ion, found by the X-ray analysis [23] (see Table III). The spectrum of the Cu(II) compound shows one strongly asymmetrical band with its maximum at 10500 cm^{-1}.

Magnetic Measurements

Further evidence for the dimeric structure of the Mn, Co, Ni, and Cu compounds comes from low-temperature magnetic susceptibility measurements. No maxima were observed in the χ *versus* T curves down to 4 K, but the values of μ_{eff} diminish at low temperature, which points to a small exchange interaction for all four compounds. The interaction is antiferromagnetic for the Mn and Cu compounds and ferromagnetic for the Co and Ni compounds.

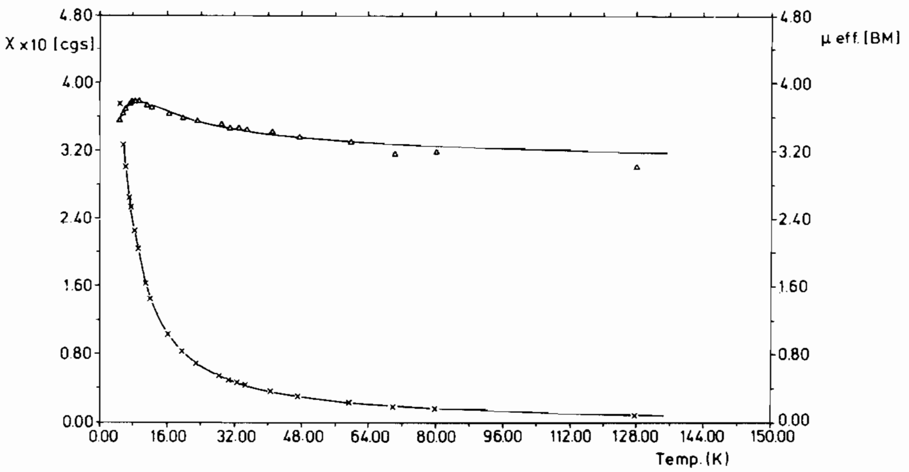

Fig. 3. χ *versus* T and μ_{eff} *versus* T curves for the dimeric compound $[Ni_2(tgm)_2Cl_2](SbCl_6)_2$: g = 2.20, J = 3.79 cm^{-1}, D = –12.48 cm^{-1}, Z'J' = 0.30 cm^{-1}, and μ_{eff}(max) = 3.79 BM at 8.0 K.

Ginsberg and co-workers [27] developed a theory concerning the magnetic exchange in dimeric nickel(II) complexes. A least squares procedure [28] was followed to fit the observed susceptibility data with the parameters J, g, D, and $Z'J'$, where $Z'J'$ represents the interdimer coupling. Formula 19 from ref. 27 was used in this program. Corrections for diamagnetism and temperature independent paramagnetism were made according to standard tables [29]. The results are presented in Fig. 3. The g-value calculated from the ligand field spectral data [26] was 2.24, which is in fair agreement with the g-value obtained from the susceptibility data.

From the X-band and Q-band EPR-spectra of the copper compound the following information was gained: the X-band spectra at room temperature and at the liquid nitrogen temperature showed no signal at half field. The following data were obtained from the rhombic signal resulting from the Q-band EPR measurement at room temperature: $g_1 = 2.25$, $g_2 = 2.20$, and $g_3 = 2.05$ with $D \leqslant 50$ G and $50 \text{ G} < J < 200$ G. These data suggest a copper environment of lower symmetry than concluded on the basis of the X-ray results (*vide supra*), which is due presumably to a dynamic Jahn–Teller effect.

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