Inorganica Chimica Acta, 33 (1979) 261–264

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

W. L. DRIESSEN and M. den HEIJER

Gorlaeus Laboratories of the State University of Leiden, 2300 RA Leiden, P.O. Box 9502, The Netherlands

Received September 12, 1978

A series of new complexes is reported with tetrahydrofuran (THF) as the ligand, viz. $\{M(THF)_6\}(SbCl_6)_2$ where M is Mg(II), Sr(II), Mn(II), Fe(II), Co(II), Ni(II), and Zn(II), $\{Ca(THF)_6\}(SbCl_6)_2(THF)$ and $\{Cu(THF)_6\}(SbCl_6)_2(THF)_2$. In all compounds the metal(II) ions are octahedrally surrounded by tetrahydrofuran molecules.

Introduction

Tetrahydrofuran (THF), or more correctly 1,4-epoxybutane, is a common solvent for many reactions. Its properties as such have been studied extensively. Its properties as a complex forming agent have also gotten some attention, as can be deduced from the large number of adducts that have been reported [2–8], *e.g.* $CoX_2(THF)$, $MX_2(THF)_{1.5}$ with M = Mn(II), Fe(II), and Co(II); $MX_2(THF)_2$ with M = Ti(II), Cr(II), Ni(II), and Zn(II); $MX_3(THF)_3$ with M = Ti(III), V(III), and Cr(III), and X = Cl, Br, or I; and $MHg(SCN)_4(THF)_2$ with M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II). Although thus many adducts have been prepared and characterized, only one coordination compound has been reported in which the metal ion is completely surrounded only by THF molecules. This solvate, $Mg(THF)_6I_2$, has been detected in a mixture with $Mg(AlH_4)_2(THF)_4$ [9].

The object of the present study has been to obtain a series of THF solvates. To stabilize solvates of (divalent) metal ions with weakly coordinating ligands large counter ions are needed [1, 10, 11], for which the very large hexachloroantimoniate(V) anions were choosen. This work is part of our investigations on the existence of complexes of divalent metals with weakly coordinating ligands [1, 10–12].

Experimental

Nitromethane was used after storage over anhydrous calcium sulphate. The ligand, tetrahydrofuran, was used after storage over 3A molecular sieve. The complexes were prepared by adding tetrahydrofuran at room temperature to a solution of $\{M(CH_3NO_2)_6\}(SbCl_6)_2$ in nitromethane [10, 11]. The complexes separated immediately as powders. These were collected on a glass filter, washed with sodium-dried n-pentane and dried *in vacuo* at slightly elevated

TABLE I. Complexes of Tetrahydrofuran (THF), Their Analyses (% weight), Melting points (°C), and Colours.

Compound	Metal(II)		Melting Point, °C	Colour
	Calc.	Found		
$Mg(THF)_6(SbCl_6)_2$	2.16	2.13	199 d.[b]	White
$Ca(THF)_7(SbCl_6)_2$	3.31	3.22	195 d.	White
$Sr(THF)_6(SbCl_6)_2$	20.9[a]	20.5[a]	162 d.	White
$Mn(THF)_6(SbCl_6)_2$	4.75	4.69	164 d.	White
$Fe(THF)_6(SbCl_6)_2$	21.0[a]	20.7[a]	146 d.	Pale-yellow
$Co(THF)_6(SbCl_6)_2$	5.08	5.06	158 - 160 d.	Light-purple
$Ni(THF)_6(SbCl_6)_2$	5.06	5.07	160 - 162 d.	Light-green
$Cu(THF)_8(SbCl_6)_2$	4.86	4.77	156 d.	Yellow-green
$Zn(THF)_6(SbCl_6)_2$	5.60	5.51	124 d.	White

[a] Antimony content. [b] d. = decomposes.

TABLE II. Some of the Infrared Absorption Bands (cm^{-1}) of Tetrahydrofuran in the Compounds M(THF)$_n$(SbCl$_6$)$_2$.

Assignment[a]	THF^{a}_{solid}	THF^{a}_{liquid}	THF_{liquid}	Sr	Ca	Mg	Mn	Fe	Co	Ni	Cu	Zn
CH_2-wag	1241 s	1234 m	1238 m	1247	1250	1247	1246	1244	1244	1244	1247	1246 m
ν_{ring}	1179 vs	1177 s	1182 s	1184	1185	1182	1179	1178	1178	1176	1172	1177 s
ν_{ring}	1058 vs	1067 vs	1069 vs	–	–	1038	1037	1037	1038	1038	1035	1037 w sh
ρ_{CH_2}	1043 vs	1030 m sh	1030 m sh	1024	1022	1014	1018	1016	1017	1017	1018	1016 vs
ν_{C-C}/ν_{C-O}	954 s 921 s			–	960	965	960	961	963	964	970	963 w
Ring-breathing	908s 891 s	908 vs	910 vs	917	922	922	920	920	923	924	918	921 m
ρ_{CH_2}	871 s			867	869	864	859	860	858	860	860	860 vs
ρ_{CH_2}	838 vs			844	847	844	843	846	845	845	–	843 w sh
$\delta_{ring\ in\ plane}$	662	654 s	658 s	668	675	674	673	674	674	677	680	674 m
ν_{Sb-Cl}				340	343	342	342	342	342	342	340	343 vs
ν_{M-O}				–	250	320	225	230	235	250	265	210 m

[a] Ligand assignment and values after ref. 14. w = weak, m = medium, s = strong, v = very, sh = shoulder.

temperatures (not exceeding 50 °C). Attempts to prepare tetrahydrofuran solvates directly by the method of chloride-ion transfer [1, 11] were not successful, as polymerization of tetrahydrofuran took place, apparently under the action of antimony pentachloride [13]. The compounds decompose rapidly in the presence of water. Therefore all preparations were carried out in a P_2O_5-dried atmosphere. The analytical and physical methods employed have been described elsewhere [1]. No nitromethane was detectable in the solid compounds by infrared measurements.

Results and Discussion

In Table I nine new coordination compounds of tetrahydrofuran are listed with colours, melting points and analytical data. From the stoichiometry and colours of the compounds a first indication is gained that the metal(II) ions are hexacoordinated by tetrahydrofuran molecules. The melting points are better described as decomposition points. At the listed temperature the compound started to discolour, whereupon within one degree (in most cases) liquifying followed by evaporation of THF occurred.

In Table II some of the infrared absorption bands of tetrahydrofuran and its complexes have been listed. The assignment of the ligand bands is after Eyster and Prohofsky [14]. In the far infrared spectra of the 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 $(SbCl_6)^-$ ion [10, 12, 15].

In the far infrared spectra of the complexes (see Table II) a band appears which is not present in the infrared spectrum of the un-coordinated tetrahydrofuran. Neither does this band stem from an anion vibration mode. The positions of this band in the various complexes lie in the order of the Irving–Williams sequence [16], while the position is highest in the spectrum of the complex with the lightest metal ion, in this case in the Mg complex. These characteristics are typical for metal–ligand vibration modes. We therefore assign this band to the metal–ligand stretching vibration (ν_{M-O}).

The infrared spectra of the complexes are very much alike one another, but different from the infrared spectrum of liquid tetrahydrofuran and also different from the infrared spectrum of solid tetrahydrofuran (see Table II). One may assume that the spectra of the complexes lie in between the spectra of liquid and of solid tetrahydrofuran. Apart from the metal–ligand vibration band, there is no absorption band with a clear metal-dependent character. The only band which seems to have some Irving–Williams character is the band around 960 cm^{-1}. It is a general feature of coordination compounds that some of the absorption bands of the ligand shift upon complexing, whereby the magnitude of the shift depends in a certain manner on the metal ion. 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 or C=O in RR'CO ligands [17, 18]. The stretching and bending vibrations of such donor groups are coupled with other ligand modes only to a limited extent. The inductive effect of the metal ion is reflected in a corresponding shift of the stretching or bending frequency. An Irving–Williams sequence is then produced in the

TABLE III. Absorption Bands (kK) in the Visible and Near Infrared, Their Assignments, and the Calculated Ligand Field Parameters of the Cobalt and Nickel Compounds.[a]

$Co(THF)_6(SbCl_6)_2$	8.16	$^4T_{2g} \leftarrow {}^4T_{1g}(F)$	$Dq = 890\ cm^{-1}$
	14.8	$^4A_{2g} \leftarrow {}^4T_{1g}(F)$	$B = 795\ cm^{-1}$
	19.0	$^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$	$Dq/B = 1.12$
$Ni(THF)_6(SbCl_6)_2$	8.40	$^3T_{2g} \leftarrow {}^3A_{2g}$	$Dq = 840\ cm^{-1}$
	13.6	$^3T_{1g}(F) \leftarrow {}^3A_{2g}$	$B = 895\ cm^{-1}$
	14.8 sh	$^1E_g \leftarrow {}^3A_{2g}$	$Dq/B = 0.94$

[a] sh = shoulder.

case of a series of complexes of bivalent transition metal ions [1, 10–12, 16–18]. In tetrahydrofuran however the C–O stretching and bending vibration modes are strongly coupled with other skeletal modes, 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 [19] and dimethoxyethane [1].

The infrared spectra of the compounds $\{M(THF)_6\}(SbCl_6)_2$ all show the same pattern of bands and relative intensities. This implies that these solid compounds are largely isomorphous. The same pattern of bands and relative intensities is also encountered in the infrared spectra of the calcium and the copper compound. However, in the infrared spectra of both compounds a few, rather weak, extra bands are present. This is probably indicative of the presence of un-coordinated ligand molecules in these compounds [20]. These compounds should therefore be formulated as $\{Ca(THF)_6\}(SbCl_6)_2(THF)$ and $\{Cu(THF)_6\}SbCl_6)_2(THF)_2$.

The ligand field spectrum of the iron compound consists of one asymmetrical band at 10.0 kK, 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 [18, 21]. The reflectance spectra of the cobalt and the nickel compounds are typical of octahedral coordination. Accordingly, assignments of the bands and calculations of the ligand field parameters have been performed (see Table III). The values for the ligand field parameters lie in a range which is normal for oxygen donor ligands [22, 23]. The reflectance spectrum of the copper compound shows one strongly asymmetric band, with a maximum at 11.8 kK, denoting that the environment of the Cu(II) ion deviates from octahedral symmetry. To verify this an EPR measurement has been performed at room temperature. An asymmetric signal has been obtained from which the following Landé factors are calculated: $g_\parallel = 2.18$ and $g_\perp = 2.04$. These values indicate that the environment of the Cu(II) ion can be described as compressed octahedral [24].

Conclusions

The existence of metal(II) solvates with tetrahydrofuran as the ligand has been proved, their syntheses can easily be performed provided that 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 the metal ions (the Cu(II) ion excepted) are in a regular octahedral environment of six oxygen atoms.

References

1 M. den Heijer and W. L. Driessen, *Inorg. Chim. Acta, 26,* 227 (1978).

2 G. W. A. Fowles, D. A. Rice, and R. A. Walton, *J. Inorg. Nucl. Chem., 31,* 3119 (1969).

3 R. J. Kern, *J. Inorg. Nucl. Chem., 24,* 1105 (1962).

4 G. W. A. Fowles, T. E. Lester, and R. A. Walton, *J. Chem. Soc. A,* 1081 (1968).

5 B. E. Bridgland, G. W. A. Fowles, and R. A. Walton, *J. Inorg. Nucl. Chem., 27,* 383 (1965).

6 G. W. A. Fowles, P. T. Greene, and T. E. Lester, *J. Inorg. Nucl. Chem., 29,* 2365 (1967).

7 M. Frey, H. Leligny, and M. Ledésert, *Bull. Soc. France Mineral. Cristallog., 94,* 467 (1972).

8 R. Makhya, L. Pazdernik, and R. Rivest, *Can. J. Chem., 51,* 2987 (1973).

9 E. C. Ashby, R. D. Schwartz, and B. D. James, *Inorg. Chem., 9,* 325 (1970).

10 W. L. Driessen and W. L. Groeneveld, *Rec. Trav. Chim. 88,* 491 (1969).

11 W. L. Driessen and P. L. A. Everstijn, *Z. Naturforsch.,*

12 P. L. Verheydt, P. H. van der Voort, W. L. Groeneveld and W. L. Driessen, *Rec. Trav. Chim., 91,* 1201 (1972).

13 N. V. Makletsova, I. V. Epel'baum, B. A. Rozenberg, and E. B. Lyudwig, *Vysokomolekul Soedin, 7,* 70 (1965); C.A., 62, *13255b.*

14 J. M. Eyster and E. W. Prohofsky, *Spectrochim. Acta, 30A,* 2041 (1974).

15 I. R. Beattie and M. Webster, *J. Chem. Soc.,* 38 (1963).

16 H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 3192 (1953).
17 P. L. A. Everstijn, A. P. Zuur, and W. L. Driessen, *Inorg. Nucl. Chem. Letters 12,* 277 (1976).
18 W. L. Driessen and W. L. Groeneveld, *Rec. Trav. Chim., 88,* 977 (1969).
19 D. Knetsch, *Thesis,* Leiden (1975).
20 W. L. Driessen and W. L. Groeneveld, *Rec. Trav. Chim., 87,* 786 (1968).
21 A. D. Liehr and C. J. Ballhausen, *Ann. Phys., 3,* 304 (1958).
22 J. Reedijk, W. L. Driessen and W. L. Groeneveld, *Rec. Trav. Chim., 88,* 1095 (1969).
23 J. Reedijk, P. W. N. M. van Leeuwen, and W. L. Groeneveld, *Rec. Trav. Chim., 87,* 129 (1968).
24 B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev., 5,* 143 (1970).