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Ethers as Ligands.
Part IV. Metal(II) 1,4-Dioxane Solvates

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A number of new coordination compounds have been obtained with 1,4-dioxane (DXN) as the ligand, viz. $M(DXN)_6(InCl_4)_2$ where M is Mg(II), Ca(II), Sr(II), Fe(II), Co(II), and Ni(II), $Zn(DXN)_6(InCl_4)_2(DXN)$, $Mn(DXN)_6(InCl_4)_2(DXN)_2$, and $Cu(DXN)_3(InCl_4)_2$. Physical measurements indicate the presence of regular octahedral species $(M(DXN)_6)^{2+}$ in the compounds, with the exception of the Cu(II) compound.

Introduction

In previous publications we reported the complex forming properties of dimethoxyethane [1] and tetrahydrofuran [2]. In this paper the syntheses and characterizations of solvates of another simple ether, *viz.* 1,4-dioxane (DXN), are reported. The common solvent dioxane has hitherto been reported to serve as a ligand mainly in adducts [3–13], *e.g.* $MCl_2 \cdot DXN$ where M is Mn(II), Fe(II), Co(II), Ni(II), Zn(II), Cd(II), and Hg(II); $3CuCl_2 \cdot 2DXN$; $FeCl_3 \cdot DXN$; $NiI_2 \cdot 2DXN$; and $M(DXN)_4(ClO_4)_2$ where M is Fe(II) and Cu(II). In these compounds dioxane functions both as a monodentate ligand as well as a bridging bidentate ligand, the coordination taking place of course, via one or both of its oxygen atoms. Dioxane itself possesses the chair conformation [14]. This conformation is retained in its complexes, possibly with only one exception, involving a chelating 1,4-dioxane ligand in the boat conformation in the yellow modification of $ZnCl_2 \cdot DXN$ [15].

Experimental

The ligand dioxane was used after storage over molecular sieve 3A. The complexes were prepared by stirring the anhydrous metal(II) chlorides with indium(III) chloride in the ratio 1:2 in 1,4-dioxane at room temperature for several days. The solid compounds, which are hardly soluble in the parent solvent, separated as finely divided powders. These were collected on a glass filter, washed with sodium-dried pentane and dried *in vacuo* at room temperature. The compounds are extremely sensitive towards moisture. All operations were therefore carried out in a P_2O_5-dried atmosphere. A Raman spectrum was recorded on a Jeol JRS-4000 laser-Raman spectrophotometer, equipped with a Coherent Radiation

TABLE I. Complexes of 1,4-dioxane (DXN), Their Analyses (% weight) and Colours.

Compound	Metal(II)		Indium(III)		Colour
	calc.	found	calc.	found	
$Mg(InCl_4)_2(DXN)_6$	2.28	2.35	21.5	22.2	white
$Ca(InCl_4)_2(DXN)_6$	3.70	3.65	21.2	20.9	white
$Sr(InCl_4)_2(DXN)_6$	–	–	20.3	20.3	white
$Mn(InCl_4)_2(DXN)_8$	4.31	4.43	18.0	18.5	white
$Fe(InCl_4)_2(DXN)_6$	5.09	5.10	20.9	21.0	white
$Co(InCl_4)_2(DXN)_6$	5.35	5.32	20.9	20.8	blue-purple
$Ni(InCl_4)_2(DXN)_6$	5.33	5.26	20.9	20.5	pale-yellow
$Cu(InCl_4)_2(DXN)_3$	7.55	7.57	27.3	27.4	orange
$Zn(InCl_4)_2(DXN)_7$	5.47	5.30	19.2	18.6	white

TABLE II. Some of the Infrared and Raman Absorption Bands (cm^{-1}) of 1,4-Dioxane (DXN) and the Compounds M(1,4-dioxane)$_n$(InCl$_4$)$_2$.

Assignment[a]	DXN[b]	DXN	Mg	Ca	Sr	Mn	Fe	Co	Ni	Cu	Zn	Raman DXN[a]	Mn
δ_{CH_2}	1296m	1290m	1301	1301	1301	1300	1302	1300	1300	1302	1300m	1334	1330vw
			1290	1291	1292	1292	1292	1290	1290	1290	1290m	1302	1317m
δ_{CH_2}	1265m	1265m	1257	1257	1256	1254	1258	1255	1255	1256	1256m	1216	1224w
	1258s											1127	1132w
ν_{ring}	1129sh	1123vs	1106	1107	1108	1106	1109	1105	1106	1106	1106s	1109	–
	1117vs											–	1071
ν_{ring}	1088m	1087m	1088	1086	–	1087	1090	1087	1087	1087	1088sh	1015	1024m
			1077	1077	1077	1072	1078	1074	1077	1076	1076m		
			1065	1064	1063	1065	1066	1065	1064	1063	1063m	946	–
ρ_{CH_2}	1052m	1050m	1047	1043	1046	1043	1047	1045	1046	1045	1047m	852	855vw
			1034	1034	1036	1035	1033	1035	1032	1033	1033w	834	830s
ρ_{CH_2}	894m	890m	896	895	894	896	898	897	897	895	897m	486	480m
			890	–	891	890	891	890	890	891	891m	433	425w
ν_{ring}	874sh	877s	873	878	872	869	870	872	876	872	– sh	422	–
	871s		855	856	855	860	856	860	856	856	854s		
δ_{ring}	610m	615m	621	619	619	621	622	622	620	621	620m		
			605	604	604	605	607	605	603	607	602m		
ν_{In-Cl}			327	327	327	329	330	329	327	326	326m		
δ_{ring}	276m	278m	294	291	291	290	291	291	291	288	287m		
				311		309				309	m		
ν_{M-O}			276	250	249		248	254	268	264	250m		

[a] Assignment and values after ref. 14. [b] Values of solid dioxane at –196 °C, after ref. 16.

CR-2 Argon gas-ion laser, at 488.0 nm. The other physical methods employed and the analytical methods have been described elsewhere [1].

Results and Discussion

In Table I nine new coordination compounds of 1,4-dioxane are listed with their colours and analytical data. From the stoichiometry and the colours of the compounds a first indication is gained that the metal ions, with the exception of the copper ion, are hexacoordinated by 1,4-dioxane molecules. The compounds possess no distinct melting point: gradually they fall apart upon heating as is shown by their discolouring.

In Table II some of the infrared absorption bands of 1,4-dioxane and its complexes have been listed. In the far infrared spectra of all compounds a strong absorption band is present at about 327 cm^{-1}. This band is due to the $\nu_3(T_2)$ vibration mode of the tetrahedral InCl$_4^-$ ion [17, 18].

On comparing the infrared spectra of the complexes with the infrared spectrum of liquid dioxane (see Table II), it is noticed that some bands are split. Some, although fewer, absorption bands are also split on solidification of dioxane [16]. The splitting of bands in the complexes is thus not only the consequence of 'solidification' – which one might call the matrix effect – but is caused also by ligand-to-metal bond formation. This 'extra' splitting of bands can be understood by realizing that upon coordination as a monodentate ligand the symmetry of dioxane is lowered.

Some of the infrared absorption bands of dioxane also shift upon coordination. The largest shifts are observed for the ring stretching vibrations. This phenomenon is in itself already proof of ligand-to-metal bond formation. The shifts are not metal dependent. In general, ligands are coordinated via a donor atom which is part of a distinct group of the ligand molecule, as for example with RR'C=O ligands [19]. The stretching and bending vibrations of such donor groups are coupled scarcely with other ligand vibration modes. As a consequence the magnitude of the inductive effect of metal ions on the ligand is reflected in a correspondingly large shift of the stretching and bending vibration bands of the distinct donor group. In this way a so called Irving–Williams sequence [20] of shift magnitudes is formed. In 1,4-dioxane, however, the donor atom is not part of a distinct group, and the C–O stretching and bending vibration modes are coupled strongly with other vibration modes. Differences in inductive effect on the ligand are thus not manifested in differences in shift magnitudes, as such differences are leveled out. 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, dimethoxyethane, and tetrahydro-

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

$Co(DXN)_6(InCl_4)_2$	6270	$^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$	Dq = 670 cm^{-1}
	14600	$^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$	B = 785 cm^{-1}
	16805	$^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$	Dq/B = 0.82
	18870 sh	$^2A_{1g}(G) \leftarrow {}^4T_{1g}(F)$	
$Ni(DXN)_6(InCl_4)_2$	7020	$^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$	Dq = 700 cm^{-1}
	11765	$^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$	B = 830 cm^{-1}
	22220	$^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$	Dq/B = 0.85

furan [1, 2, 21], which are in this respect comparable cases.

In the far infrared spectra of the complexes an absorption band is present which does not occur in free dioxane, and which does not stem from an anion vibration mode. The positions of this band in the various complexes – the copper complex excepted – follow the Irving–Williams order, while the position is highest in the Mg complex. These characteristics are typical for metal–ligand vibration modes. We therefore assign this absorption band to the metal–dioxane stretching vibration. The unusual low position of this band in the copper complex points to a different interaction between the metal ions and the ligand molecules than in the other complexes. The differences in the Raman spectra of liquid dioxane and of the Mn complex (see Table II) also indicate that dioxane functions as a monodentate ligand in our complexes [22].

The infrared spectra of the compounds, with the exception of the copper compound (see below), show the same pattern of bands and relative intensities. This implies that these compounds are structurally related. In the infrared spectra of the Mn- and Zn- compounds some extra absorption bands are present (not listed in Table II), which occur on the positions of free dioxane. This is indicative for the presence of un-coordinated ligand molecules in these complexes. These compounds should therefore be formulated as $\{Mn(DXN)_6\}(InCl_4)_2(DXN)_2$ and as $\{Zn(DXN)_6\}(InCl_4)_2(DXN)$.

The reflectance spectrum of the iron compounds shows one asymmetric absorption band at 8590 cm^{-1}. This band seems to consist of two component bands, which might well be caused by a Jahn–Teller splitting of the upper ^5E_g level [23]. The positions and the relative intensities of the absorption bands in the reflectance spectra of the cobalt and nickel compounds in the visible and near infrared region irrefutably point to a regular octahedral coordination of these metal ions. Assignments of the bands and calculations of the ligand field spectral parameters were made accordingly (see Table III) [24, 25]. The values for the spectrochemical parameter are in accord with corresponding values obtained from cobalt and nickel dioxane adducts [11]. The Dq values are very low [24, 25]: probably an effective overlap of metal- and ligand-orbitals is hindered, possibly for steric reasons.

The reflectance spectrum of the copper compound shows one asymmetric band at 11840 cm^{-1}, which points to a tetragonal environment of the copper ion. The EPR spectrum, which was recorded at room temperature, exhibited an asymmetric signal which rendered a g-averaged of 2.17. This also indicates a tetragonal environment for the copper ion. Hexa-coordination could only have occurred in this case when all dioxane molecules would have been coordinated via both oxygen atoms. However, the copper compound contains at least also monodentate dioxane molecules as can be inferred from the infrared spectrum which has some characteristics very similar to the infrared spectra of the other complexes. From these considerations and with regard to the stoichiometry of this compound, it seems justified to describe the copper compound as polynuclear. Two structures are possible: a dimer containing two bridging and four terminal dioxane molecules, or infinite chains of copper ions linked by dioxane molecules in such a way that one bridging and two end-on dioxane molecules per copper ion are present. In both cases each copper ion is surrounded by four dioxane molecules, the anions not taking part in the coordination.

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