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Metal Halide Complexes of 1,3-dioxan

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1,3-dioxan (mdx) forms 1:1 complexes with MX_2 (M is Mn, Co, Ni, Cu; X is Cl, Br). The copper complexes lose mdx at room temperature to yield $(CuX_2)_3$, 2 mdx. The spectra of all the compounds (40-45000 cm^{-1}) are reported and interpreted as consistent with polymeric pseudo-octahedral structures with bridging mdx (Mn, Co, Ni) or terminal mdx (Cu). Very similar structures have been found with 1,4-dioxan (pdx). The thermal decomposition behaviour of the mdx compounds is reported.

No mixed complexes were isolated from the systems MX_2-mdx-H_2O whereas pdx forms mixed solvates readily. The role of pdx in these compounds is to link hydrated metal ions by hydrogen bonding.

Introduction

The ratio of the number of crystalline metal complexes reported for 1,3-dioxan (mdx) to those reported for 1,4-dioxan (pdx) is more of an indication of the relative cost of the ligands (mdx 30 pence g^{-1}, pdx pence g^{-1}).than of their complexing ability. In reports of $HgCl_2$,mdx; $TiCl_3$,3mdx; $(CdCl_2)_3$,2mdx; $CdBr_2$,mdx and CdI_2,mdx vibrational and electronic spectra have been interpreted as indicating very similar structures to the corresponding pdx complexes,[1,2,3] with terminal mdx molecules in $TiCl_3$, 3mdx and possibly in the cadmium complexes but bridging mdx in $HgCl_2$,mdx. (Neither mdx nor pdx can chelate). When either dioxan occurs as a terminal ligand the complexes will be similar to those of the monofunctional ethers tetrahydrofuran (thf) and tetrahydropyran (thp). There is no reason to expect significant differences between mdx and pdx in this role. However, as bridging ligands, differences of structure and of free energy of complex formation would be expected because of the lower symmetry and the shorter O...O distance in mdx. These factors suggest that mdx might be less satisfactory as a bridging ligand than pdx.

The solid pdx complexes of MX_2 (M is Mn, Co, Ni, X is Cl, Br) are believed to be polymeric with bridging pdx.[4] $(CuX_2)_3$,2pdx (X = Cl, Br) contain terminal pdx molecules.[4,5] In the present paper the mdx analogues of these complexes, previously unknown, have been examined by spectroscopic and thermoanalytical methods. The results are compared with those obtained elsewhere for the pdx complexes. Both series of complexes exist only in the solid state. Metal halides MX_2 also form crystalline, hydrated, pdx complexes such as $CoCl_2$, pdx, $2H_2O$,[6,7] and attempts have been made to prepare similar compounds using mdx.

Experimental Section

1,3-dioxan (K and K Inc.) was distilled before use. Complexes were prepared by two routes:

(a) The hydrated metal halide was dehydrated by refluxing in ethanol with triethyl orthoformate. The addition of mdx to the cold solution precipitated the complex.

(b) The anhydrous metal halide was exposed to an atmosphere of mdx vapour at room temperature. Conversion to the complex required up to a week after which the sample weight became constant. The small excess of adsorbed mdx was removed under vacuum.

The previously unreported $CuCl_2$. thp and $CuBr_2$ thp were prepared by method (a).

Two methods were employed in the investigation of the MX_2-mdx-H_2O system. Hydrated pdx complexes can be obtained by either route.

(c) Anhydrous MX_2,mdx was exposed to 1-5 Torr of water vapour. With each compound all the mdx was lost with formation of the hydrate appropriate to the vapour pressure of water.

(d) When mdx was added to solutions of the hydrated metal halide in ethanol, crystals of the original hydrate were obtained.

Samples of $Co(ClO_4)_2$,5pdx, $6H_2O$ and $Ni(ClO_4)_2$, 5pdx, $6H_2O$ were prepared by the literature method.[8]

Spectra and thermal decomposition data were obtained as described previously.[6,7] Decomposition products were identified by thermogravimetry and by analyses. Far infrared spectra were recorded in wax discs by the Physico-Chemical Measurement Unit (Harwell, U.K.).

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(1) P.A. Laurent and P. Tarte, *Bull. Soc. Chim. Fr.*, 618, (1958).
(2) E.C. Alyea and E.G. Torrible, *Can. J. Chem.*, *43*, 3468, (1965).
(3) J.C. Barnes and C.S. Duncan, *J. Chem. Soc.*, (*A*), 1746 (1969).
(4) G.W.A. Fowles, D.A. Rice, and R.A. Walton, *J. Chem. Soc.* (*A*), 1842 (1968).
(5) J.C. Barnes, *J. Inorg. Nuclear Chem.*, *31*, 95 (1969).
(6) J.C. Barnes and C.S. Duncan, *J. Chem. Soc.* (*A*), 1442 (1970).
(7) J.C. Barnes and C.S. Duncan, *J. Chem. Soc.*, *Dalton Trans.*, 923 (1972).
(8) G. Vicentini, M. Perrier, and E. Giesbrecht, *Bericte*, *94*, 1153 (1961).

Table I. Electronic spectra of cyclic ether complexes [a].

	Band positions × 10^{-3} cm^{-1}	
	Charge transfer region	(*d-d*) region
$MnCl_2$,mdx	42.4, (38.5), 36.7	30.3 ^4E_g, 28.3, 27.2 $^4T_{2g}$
(v. pale pink)		24.2 ^4E_g, $^4A_{1g}$, 22.5 $^4T_{2g}$; 18.8 $^4T_{1g}$
$MnBr_2$,mdx	41.3, 38.0, (37.0)	30.2, 28.3, 27.1, 24.0
(v. pale pink)		22.5, 18.8
$CoCl_2$,mdx	44.0, 38.8, 36.0	(26.0); 24.0; 22.1; (18.8),
(pale blue)		17.5 $^4T_{1g}$; 11.3 $^4A_{2g}$; 6.2 $^4T_{2g}$
$CoBr_2$, mdx	45.0, 38.0, 35.2	(25.4), 23.4, 21.0, (18.9)
(pale blue)		16.1, (13.1), 11.0, 6.3
$NiCl_2$,mdx	45.3, 37.2, (30.1)	22.2 $^3T_{1g}$; (19.0), (13.0), $^3T_{1g}$
(orange)		11.6 ^1E_g; 6.8 $^3T_{2g}$
$NiBr_2$,mdx	45.2, 36.5, 29.0	(23.0), 21.0, (18.8), (12.2)
(brown)		10.9, 7.0
$CuCl_2$,mdx	45.0, 35.2, 32.2 (25.6)	12.0, (7.5) (6.0) $^2T_{2g}$
(orange)	(18)	
$CuBr_2$,mdx	38.5, 29.0, 18.5	12.0, (8.0)
(black)		12.0 (7.6)
$CuCl_2$,thp	45.2, (35), 32.0 (26.5) (18.0)	12.2, (8.0)
		(21.4), 19.3 $^4T_{1g}$, (15.5) $^4A_{2g}$, (11.3); 8.1 $^4T_{2g}$
$CuBr_2$,thp	38.3, 29.2, 18.3	
$Co(ClO_4)_2$.5pdx,$6H_2O$	N.R.	
$Ni(ClO_4)_2$.5pdx,$6H_2O$	N.R.	24.8 $^3T_{1g}$, (21.4) $^1T_{1g}$, (18.7);
		15.0 ^1E_g, 13.5 $^3T_{1g}$; 8.3 $^3T_{2g}$

[a] Excited states are designated for the major bands in the chloride and perchlorate spectra, assignments for the bromides follow immediately from those of the chlorides. N.R. signifies « region not recorded », bands in parentheses appear as shoulders.

Table II. Infrared Spectra 1350 - 400 cm^{-1}.

mdx	(1305), 1288m, 1228s, (1195), 1185s, 1150s, (1138), 1088s, 1050s, 1010s, 988m, 900s, 880s, 832s, 650s, 490m 460m, 440m
$CoCl_2$, mdx [a]	1305m, 1228s, 1197s, 1190m, 1154s, 1138s, 1090m, 1077s, 1052m, 1012s, (990), 978s, 905s, 896s 865s, 835w, 826s, 807w, 724m, 675m, 654m 615m, 526m, 503m, 482m, (473), (462)
$(CuCl_2)_3$, 2mdx [b]	1308w, 1292m, 1230s, 1187s, 1148s, 1136s, 1080s 1048m, 1002s, (995), 970(s), 913m, 900m, 869s 826s, 808w, 724m, 660m, 492w, 475s, 440m

[a] Typical of MX_2, mdx spectra (M = Mn, Co, Ni, X = Cl, Br).
[b] Identical to spectrum of $(CuBr_2)_3$, 2mdx. Shoulders in parentheses.

Analyses. $C_8H_{15}O_4Cl_6Cu_3$ requires C, 16.57; H, 2.76; Cl, 36.71%. Found C, 16.7; H, 2.0; Cl, 36.9%. $C_4H_8O_2Br_2Cu$ requires C, 15.41; H, 2.56; Br, 51.32%. Found C, 15.2; H, 2.8; Br, 51.4%. $C_4H_8O_2Cl_2Mn$ requires C, 22.43; H, 3.37; Cl, 33.13%. Found C, 22.2; H, 3.5; Cl, 33.2%. $C_4H_8O_2Br_2Mn$ requires C, 15.84; H, 2.64; Br, 52.76%. Found C, 15.7; H, 2.7; Br, 52.8%.

Results

A series of 1:1 complexes were isolated for mdx with MX_2 (M is Mn, Co, Ni, Cu and X is Cl, Br). No evidence was found for higher complexes with any of these salts, although preparative method b (above) is particularly sensitive to the detection of higher complexes. All the complexes are insoluble in mdx but soluble in water or ethanol with decomposition. The complexes of manganese, cobalt and nickel are stable in dry air at 298 K. Under these conditions CuX_2mdx loses mdx to form the stable $(CuX_2)_3$,2mdx. The colours of the complexes and their electronic spectra are given in Table I. Table II and III contain the infrared spectra (1350-40 cm^{-1}). Table III includes some data on pdx complexes which have not been studied previously below 200 cm^{-1}. The results of differential enthalpic analysis (d.e.a.) and thermogravimetry (t.g.) are given in Table IV. Each compound decomposes without melting.

On exposure to water vapour, ligand exchange occurs with the loss of all the mdx and the formation of hydrates of MX_2. No evidence was obtained for the existence of complexes containing both water and mdx. The (d–d) spectra of $M(ClO_4)_2$,5pdx, $6H_2O$ (M is Co, Ni) have been recorded, Table I.

Discussion

Copper halide complexes. CuX_2,mdx and $(CuX_2)_3$, 2mdx closely resemble other members of the series $(CuX_2)_n$,2L ($n \geqslant 2$). (Table V). In each case the chloride compounds are orange-brown and the bromides black. The crystal structures of several of these complexes show fragments of the parent $CuCl_2$ chain terminated by *trans* ligands.[9,10]

With both pdx[5] and mdx the infrared spectra (2000-400 cm^{-1}) of the complexes are those of the liquid ligands with minor splittings and shifts which may be associated with localised Cu-O interactions but which are better considered as factor group splittings of the ligand fundamentals in the crystal lattice. Since the space groups etc. of the complexes are not known a detailed discussion of these spectra is not

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(9) R.D. Willett and R.E. Rundle, *J. Chem. Phys.*, *40*, 835 (1964).
(10) C.C. Houk and K. Emerson, *J. Inorg. Nuc. Chem.*, *30*, 1493 (1968).

Table III. Far Infrared Spectra of Cyclic Ether Complexes (400-40 cm^{-1}).

	Ring modes of ligand	ν(M-X)	ν(M-O)	Unassigned including lattice modes
$MnCl_2$, mdx	298	235, 210	142	(124), 99
$CoCl_2$, mdx	310, 290	250, 216	160	(145), 115, 84
$NiCl_2$, mdx	(330), 310	264, 234	172	146, 121, 89
$NiCl_2$, pdx	329, 321, 303	257, 229	188, 174, 167	147, 119, (83)
$(CuCl_2)_3$, 2mdx	302, (292), (285)	332 [a], 265 [b]	188, 162	138, (126), 103, (82)
$(CuBr_2)_3$, 2mdx	286	253 [a], 224 [b]	88	(170), (126)
$(CuCl_2)_3$, 2 pdx	287	311 [a], 265 [b]	184, 161	133, 116, (83)
$(CuBr_2)_3$, 2pdx	289	243 [a], 218 [b]	114, 105	168, 126, (88)
$CuCl_2$, thp		315 [a], 264 [b]	183, 156	104
$CuBr_2$, thp	272, 288	254 [a], 226 [b]	89	(170)

[a] ν(Cu-X) terminal. [b] ν(Cu-X) brindging. Shoulders in parentheses.

Table IV. Endothermic decomposition reactions of 1,3-dioxan complexes.

	T_1/K	T_2/K	ΔH_{T2}/kJ mol^{-1}	Δw_{obs}%	Δw_{Th}%
$MnCl_2$, mdx	473	505	61.7±1.2	39.4±0.2	41.14
$MnBr_2$, mdx	447	484	60.9±0.8	29.8±0.3	29.10
$CoCl_2$, mdx	443	468	44.3±5	18.2±1.0	20.21 [a]
	493	526		37.3±0.5	40.42
$CoBr_2$, mdx	403	421	160±10	15.0±1.2	14.40 [a]
	[b]	468		26.2±0.5	28.69
$NiCl_2$, mdx	487	515	50.1±0.5	38.5±0.2	40.42
$NiBr_2$, mdx	380	396	9.5±2.0 [c]		
	422	465	50.9±0.8	27.6±0.4	28.73
$CuCl_2$, mdx	326	367	120.2±24.0	12.8±0.4	13.26 [d]
	385	426	135.2±6.8	32.4±0.3	30.56 [e]
$CuBr_2$, mdx	300	347 [d]	87.4±6.4	25.8±0.6	28.29
	[b]	360 [e]			
	467	517	29.3±3.0	49.5±0.8	53.94 [f]

[a] formation of $(CoX_2)_2$, mdx. [b] obscured by previous endotherm. [c] phase transition. [d] formation of $(CuX_2)_3$, 2 mdx. [e] decomposition of $(CuX_2)_3$, 2 mdx to CuX_2. [f] decomposition of $CuBr_2$ to CuBr.
These experiments were conducted by differential enthalpic analyses, increasing temperature by 8.33 K min^{-1}. T_1 is the minimum temperature at which decomposition was detected. T_2 is the peak temperature of the reaction. Δw_{Th} is the theoretical weight loss to MX_2 unless stated otherwise. The atmosphere over the sample was nitrogen at atmospheric pressure, flowing at 30 cm^3 min^{-1}.

Table V. $(CuCl_2)_n$, 2L complexes.

L	n	Ref.
CH_3CN	2,3,5	8
pdx	3	4,5
mdx	2,3	
thf	3,4	5
thp	2	
n-pentanol	5	8
2-pyridone	2	9

possible. With pdx the vibrations most affected by complexing are the ring stretching modes at 874 and 1120 cm^{-1} (infrared) and 834 and 1015 cm^{-1} (Raman).[11] The 834 cm^{-1} band appears very weakly in the infrared spectrum of $(CuCl_2)_3$,2pdx, consistent with slight relaxation of the symmetry of the ligand associated with monodentate Cu-pdx interaction.[11]

All vibrations of mdx are both infrared and Raman active. The spectrum has not been assigned completely but the ring stretching modes are probably those at 832, 901, 1015 and 1137 cm^{-1} since these are the most sensitive to complex formation (Table II).

Figure 1 shows the striking similarity between the far-infrared spectra of $(CuX_2)_3$,2mdx and $(CuX_2)_3$,2 pdx. For the chlorides this similarity includes the lattice modes below 100 cm^{-1} but the spectra of the bromides differ below 200 cm^{-1}, the spectrum of $(CuBr_2)$,2pdx shows four well resolved bands in this

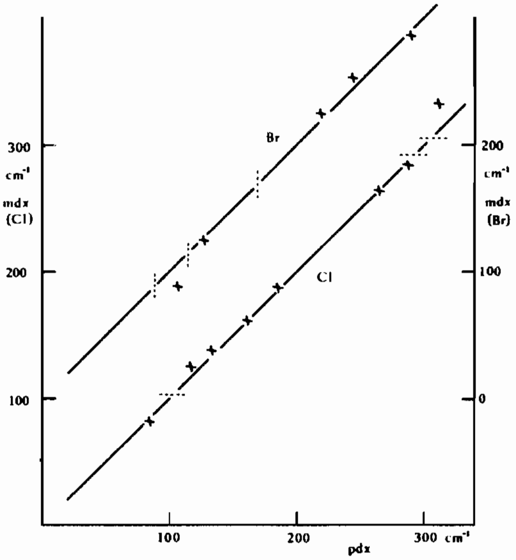

Figure 1. Correlation of the far-infrared spectra of $(CuX_2)_3$, 2pdx and $(CuX_2)_3$, 2mdx.

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(11) G.W.A. Fowles, D.A. Rice, and R.A. Walton, *Spectrochim. Acta, 26A*, 134, (1970).

region but $(CuBr_2)_3$,2mdx and $(CuBr_2)_2$,2thp each show two bands only. In each case both terminal and bridging ν(Cu-X) are observed. The ratios ν(Cu-Br)/ν(Cu-Cl) are essentially constant for the three ligands; 0.79±0.02 (terminal) and 0.85±0.02 (bridging).

The spectra show no bands above 200 cm^{-1} which might be assigned to ν(Cu-O). The $CuCl_2$ complexes of pdx, mdx and thp show strong bands at 186±3 and 159±3 cm^{-1} which do not appear in the $CuBr_2$ complexes. The latter have strong bands at 88 cm^{-1} (mdx and thp) and at 114 and 105 cm^{-1} (pdx). These are tentatively identified as ν(Cu-O). The energy difference for ν(Cu-O) between chloride and bromide is unexpectedly large. An alternative assignment in the bromide spectra would give ν(Cu-O) as the weak and ill-resolved feature about 170 cm^{-1}, in which case there is no obvious explanation of the strong features at lower energy, which have no counter part in the chloride spectra down to the experimental limit of 40 cm^{-1}. The only data available for comparison refer to HgX_2, pdx[12] where ν(Hg-O) was identified at 128 cm^{-1} (Cl), 108 cm^{-1} (Br) and 94 cm^{-1} (I) and ν(Hg-X) at 348 cm^{-1} (Cl), 249 cm^{-1} (Br) and 204 cm^{-1} (I).

The electronic spectra of $(CuX_2)_2$,2mdx and $(CuX_2)_2$, 2thp are very similar. They are identical to those of CuX_2 and of the other $(CuX_2)_n$,2L complexes.[4,5,9] The spectra are consistent with distorted six-coordination by an environment which is mostly halide.

D.e.a. and t.g. show that $(CuX_2)_2$,2mdx decomposes first into $(CuX_2)_3$,2mdx and then into CuX_2. Decomposition via higher members of the $(CuX_2)_n$,2L series also occurs with thf and CH_3CN but not with pdx. The enthalpies of decomposition for all these compounds are similar.

Complexes of $MnCl_2$, $CoCl_2$ and $NiCl_2$. The series of compounds MCl_2,mdx resemble MCl_2 . pdx very closely. For any metal the (d-d) spectra are almost indistinguishable, Table I, showing that there can be little difference in crystal field or in nephelauxetic effect. The far-infrared spectra of $NiCl_2$,mdx and $NiCl_2$,pdx show marked similarities (Table III). Additional splittings appear in both the ring stretching and ν(Ni-O) regions in the pdx compounds. ν(M-Cl) occur at very similar energies in MCl_2,mdx to those identified in MCl_2,pdx.[4] ν(M-O) have not been reported previously. These are now assigned to the bands at 142 cm^{-1} (Mn), 160 cm^{-1} (Co) and 173 cm^{-1} (Ni). ν(M-O) has been identified at 311 cm^{-1} (Mn), 331 cm^{-1} (Co) and 342 cm^{-1} (Ni) in pyridine-N-oxide complexes $M(PyNO)_6$, $(ClO_4)_2$.[13] The ratio ν(M-O_{PyNO}/ν(M-O)$_{mdx}$ is constant at 2.1±0.1. MCl_2,mdx show two low frequency modes ~90 and. ~120 cm^{-1} which can be assigned to lattice vibrations. These are also seen in $NiCl_2$,pdx. The spectra of $CoCl_2$,pdx and $MnCl_2$,pdx have not been measured below 200 cm^{-1}.

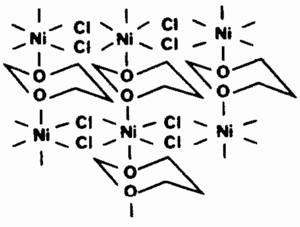
D.e.a. and t.g. measurements show that $MnCl_2$,mdx and $NiCl_2$,mdx decompose in a single endothermic step to MCl_2. This reaction occurs at slightly higher temperatures than in MCl_2,pdx[6] but the enthalpy of decomposition is 24% smaller so that the entropy of decomposition must be at least 25% less for the mdx complexes. $CoCl_2$,mdx decomposes in two steps forming an intermediate, $(CoCl_2)_2$,mdx whereas $CoCl_2$, pdx goes directly to $CoCl_2$.

All the evidence suggests very similar structures for MCl_2,pdx and MCl_2,mdx. Structure I is proposed for the mdx compound, as the analogue of the structure proposed by Fowles, Rice, and Walton[4] for MCl_2,pdx.

Complexes of $MnBr_2$, $CoBr_2$ and $NiBr_2$. mdx forms only a series of 1:1 complexes with MBr_2. pdx forms both 1:1 and 1:2 complexes with $CoBr_2$ and $NiBr_2$ but only the 1:2 complex with $MnBr_2$.[4] The absence of $MnBr_2$,pdx has been associated with the very high enthalpy of formation of $MnBr_2$,2pdx from $MnBr_2$ (462 kJ mol^{-1}).[7]

The thermal decomposition of MBr_2,mdx follows the pattern of MCl_2,mdx very closely. The intermediate $(CoBr_2)_2$,mdx was observed whereas $CoBr_2$.pdx decomposes in a single step.

The spectra of MBr_2,mdx are very similar to those of MBr_2,pdx. The near-identity of energy for the first charge transfer bands indicates that the number of coordinated bromide ions must be the same in the two series. These bands move to higher energy in the sequence MBr_2 . < MBr_2,pdx < MBr_2,2pdx, suggesting four Br^- coordinated in MBr_2,pdx and MBr_2, mdx and two Br^- coordinated in MBr_2,2pdx. MBr_2, mdx probably has a structure similar to structure I. Structure II is proposed for MBr_2,2pdx.



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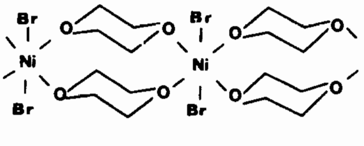

II

An examination of these structures does not suggest an explanation for the formation of structure I by MCl_2 or MBr_2 with either pdx or mdx whereas structure II occurs only with MBr_2 and pdx. Interlayer contacts are not worsened by the substitution of either Cl or mdx into structure II. The intralayer effects of these substitutions are similar to those in structure I.

Ternary sysems MX_2-dx-H_2O. The most striking difference between the behaviour of pdx and mdx as ligands lies in the behaviour of the ternary systems

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(12) Y. Mikaura, R.J. Jakobsen, and J.W. Brasch, *J. Chem. Phys.*, *45*, 4528 (1966).

(13) Y. Kakiuti, S. Kida, and J.V. Quagliano, *Spectrochim. Acta*, *119*, 201, (1963).

MX_2-dx-H_2O. With pdx hydrated complexes such as MCl_2,pdx, $2H_2O$;[6] MBr_2,2pdx, $4H_2O$[7] and $M(ClO_4)_2$, 5pdx,. $6H_2O$[13] are formed readily. Phase diagrams have been reported for a number of these systems at 298K.[14,15] Repeated attempts have failed to yield any mixed solvates from the systems MX_2-mdx-H_2O. Only simple hydrates were obtained.

The (d-d) spectra of MCl_2,pdx,$2H_2O$; and MBr_2,2 pdx,$4H_2O$ suggest that pdx is not found in the inner coordination sphere in these complexes, the chromophores being M(4Cl, $2H_2O$),[6] and M(2Br, $4H_2O$).[7] Similarly the spectra of $M(ClO_4)_2$,5pdx, $6H_2O$, Table I, are identical with those of compounds known to contain $M(H_2O)_6^{2+}$. The dioxan molecules of solvation probably link the coordinated water molecules into a hydrogen bonded network. The absence of hydrated mdx complexes suggests that the reduction in the O...O distance from pdx and the lower symmetry prevent stable hydrogen bond formation. N.m.r. studies in 50% aqueous pdx indicated that the metal ions were coordinated by water but not by pdx.[16]

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(14) J.A. Weicksel and C.C. Lynch, *J. Amer. Chem. Soc.*, *72*, 2632, (1950).

(15) H. Schott and C.C. Lynch, *J. Chem. Eng. Data*, *11*, 215 (1966).

(16) A. Fratiello and D.C. Douglas, *J. Chem. Phys.* *39*, 2017 (1963).