Role of 1,4-Dioxan in Solid Adducts of Hydrated Metal Halides.   Crystal Structures of Hexa-aquadichloromagnesium–1,4-Dioxan(1/1), trans-Tetra-aquadibromonickel(II)–1,4-Dioxan(1/2), and cis-Diaquatetrabromotin(IV)–1,4-Dioxan(1/2)

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In each of the title compounds 1,4-dioxan forms extended hydrogen-bond networks between water molecules co-ordinated to the metal atoms. $MgCl_2 \cdot 6H_2O \cdot C_4H_8O_2$, (I), space group $P2_1/n$, $a = 12.15$, $b = 7.96$, $c = 6.86$ Å, $\beta = 91.23°$, $Z = 2$; R 0.061 for 775 reflections. $NiBr_2 \cdot 4H_2O \cdot 2(C_4H_8O_2)$, (II), space group $I4_1/a$, $a = 9.189$, $c = 19.22$ Å, $Z = 4$; R 0.069 for 344 reflections. $SnBr_4 \cdot 2H_2O \cdot 2(C_4H_8O_2)$, (III), space group $Fdd2$, $a = 26.12$, $b = 19.07$, $c = 7.486$ Å; R 0.064 for 657 reflections. Unit-cell and space group measurements suggest that $CoBr_2 \cdot 4H_2O \cdot 2(C_4H_8O_2)$, (IV) ($I4_1/a$, $a = 9.19$, $c = 19.18$ Å), and $SnCl_4 \cdot 2H_2O \cdot 2(C_4H_8O_2)$, (V) ($Fdd2$, $a = 25.92$, $b = 18.67$, $c = 7.19$ Å), are isomorphous with (II) and (III) respectively.

NEITHER complex formation nor crystal-packing forces suffice to convert 1,4-dioxan (dx) from the chair conformation into a boat form. The chair form is frequently found bridging two metal ions giving either dimeric complexes [1] or extended polymers.[2–4] Only a few of these complexes can be recrystallised from aqueous dioxan; [5,6] the majority are converted into hydrates. Analysis of the spectra of some transition-metal halide–water–dioxan species [7] suggested that the dioxan is not co-ordinated to the metal but forms hydrogen-bonded bridges between water molecules co-ordinated to different metal atoms.

To investigate the role of dioxan in hydrated compounds of elements from different parts of the Periodic Table the structures of $MgCl_2 \cdot 6H_2O \cdot dx$ (I), $NiBr_2 \cdot 4H_2O \cdot 2dx$ (II), and $SnBr_4 \cdot 2H_2O \cdot 2dx$ (III) have been determined. In addition, unit cell and space group determination showed that $CoBr_2 \cdot 4H_2O \cdot 2dx$ is isomorphous with (II) and $SnCl_4 \cdot 2H_2O \cdot 2dx$ with (III).

(I) was reported by Weicksel and Lynch [8] to be the only ternary compound in the $MgCl_2$–H_2O–dx system at 25 °C. Its chemistry and that of $NiBr_2 \cdot 4H_2O \cdot 2dx$ (II) has been investigated.[7,9] $SnBr_4 \cdot 2H_2O \cdot 2dx$ has not been reported previously, although the inadequately characterised chloride has.[10] All three complexes are unstable in moist air at room temperature.

Some of this work has been included in a preliminary report.[4]

EXPERIMENTAL

Crystal Data and Structure Analyses.—*Hexa-aquadichloromagnesium*–1,4-*dioxan*(1/1),   (I), $MgCl_2 \cdot 6H_2O \cdot C_4H_8O_2$, $C_4H_{20}Cl_2MgO_8$, Monoclinic, $a = 12.15(3)$, $b = 7.96(2)$, $c = 6.86(2)$ Å, $\beta = 91.23°(15)$, $U = 663.31$ Å³, $D_m = 1.50(3)$, $Z = 2$, $D_c = 1.46$. Space group $P2_1/n$ (an alternative setting of No. 14), Cu-K_α radiation $\lambda = 1.5418$ Å; μ(Cu-K_α) = 49 cm⁻¹.

Crystallisation of $MgCl_2 \cdot 6H_2O$ from dioxan gave well

formed colourless crystals which were removed from the syrupy mother liquor as required and immediately sealed into Lindemann glass capillaries. The unit cell and space group were determined from rotation and Weissenberg photographs, calibrated with NaCl powder. Refinement of the unit-cell parameters and intensity measurements was carried out [11] from a (h 0—3) and c axis (l 0—5) equi-inclination Weissenberg photographs.   775 Reflections were considered significantly above the background. Lorentz and polarisation corrections were applied but absorption and anomalous dispersion corrections were not made.

Symmetry requirements place the magnesium atom and the centre of the dioxan ring at centres of inversion. A Patterson synthesis gave the co-ordinates of the chlorine relative to magnesium at the origin. A Fourier map phased on these atoms showed all the remaining non-hydrogen atoms.

The structure was refined by use of the local block-diagonal least-squares program to R 0.090 with isotropic thermal parameters. Subsequently the full-matrix SHELX program [12] was employed with anisotropic thermal parameters and a correction for secondary extinction. At R 0.070 the protons of the dioxan ring were introduced in calculated positions riding on the carbon atoms. A difference-Fourier map then revealed all the water proton positions, the positions and thermal parameters of which were allowed to refine freely. Convergence was obtained at R 0.061. Atomic scattering factors were taken from ref. 13. Atomic co-ordinates are given in Table 1 and bond lengths and bond angles in Table 2. Structure factors, and anisotropic thermal parameters for compounds (I)—(III) are listed in Supplementary Publication SUP No. 21760 (15 pp., 1 microfiche).*

trans-*Tetra-aquadibromonickel*(II)–1,4-*dioxan*(1/2),   (II). $NiBr_2 \cdot 4H_2O \cdot 2C_4H_8O_2$, $C_8H_{23}Br_2NiO_8$, Tetragonal, $a = 9.189(5)$, $c = 19.22(1)$ Å, $U = 1\ 622.89$ Å³, $D_m = 1.85$, $Z = 4$, $D_c = 1.91$. Space group $I4_1/a$ (No. 88).   Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) = 64 cm⁻¹.

Elongated green octahedra were prepared as described previously,[8] and stored under mother liquor before being transferred to Lindemann glass capillaries. Unit-cell and space-group data were determined from rotation and Weis-

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

[1] W. S. Dickmann, G. Hamer, S. C. Nyburg, and W. F. Reynolds, *Chem. Comm.*, 1970, 1295.
[2] M. Frey, *Acta Cryst.*, 1971, **27**, 2487.
[3] V. I. Kulishov, N. G. Bokii, T. Struchkov, O. M. Nefedov, S. P. Kolesnikov, and B. M. Perl'mutter, *Zhur. strukt. Khim.*, 1970, **11**, 71.
[4] J. C. Barnes and L. J. Sesay, *Acta Cryst.*, 1975, **A31**, 5144.
[5] J. C. Barnes and C. S. Duncan, *J. Chem. Soc. (A)*, 1969, 1746.

[6] J. C. Barnes and C. S. Duncan, *J.C.S. Dalton*, 1972, 1732.
[7] J. C. Barnes and C. S. Duncan, *J.C.S. Dalton*, 1972, 923.
[8] J. A. Weicksel and C. C. Lynch, *J. Amer. Chem. Soc.*, 1950, **72**, 2632.
[9] J. C. Barnes, *Inorg. Nuclear Chem. Letters*, 1976, **12**, 89,
[10] F. Rieff, *Z. anorg. Chem.*, 1932, **208**, 321.
[11] M. Elder and P. A. Machin, S.R.C. Microdensitometer Service, Atlas Laboratory, Chilton, Berkshire, 1974.
[12] G. M. Sheldrick, SHELX, Program for Crystal Structure Determination, Cambridge, 1975.

senberg photographs (Cu-K_α radiation), cell dimensions being refined on a Hilger and Watts linear diffractometer, which

corrected for Lorentz factors and polarisation, but not for absorption or anomalous dispersion. Ref. 13 gives alternative origin positions for space group $I4_1/a$. The origin was chosen to be a centre of symmetry. A Patterson map revealed the nickel and bromine, and water oxygen atom positions. A difference-Fourier map phased by these atoms revealed the remaining non-hydrogen atom positions. The nickel and bromine atoms lie on special positions (4a) and (8e) respectively. All other atoms occupy general positions, with the dioxan molecule centred on (8d).

The structure was refined as before with isotropic thermal parameters to $R = 0.097$, when a separate scale factor was calculated for each observed layer by making $k\Sigma(F_o) = \Sigma|F_c|$.

Refinement was continued with anisotropic thermal parameters for bromine, carbon, and oxygen. The necessary constraints for anisotropic thermal parameters at the (4a) position [14] could not be used in the available least-squares program. After convergence at R 0.069 positions of the hydrogen atoms of the dioxan molecule were calculated. Peaks were found in these positions on a final difference-Fourier map, which also indicated the hydrogen-bonded hydrogen atom of the water molecule. The remaining water hydrogen atom was not located. No other peaks on the map exceeded 0.5 eA^{-3}. A structure-factor calculation showed that all the unobserved reflections had $F_c \leqslant$ background. All planes were given unit weight since other weighing schemes showed no improvement.

Atomic co-ordinates and thermal parameters are given in Table 3, bond lengths and bond angles in Table 4.

TABLE 1

Atomic co-ordinates and isotropic thermal parameters for $MgCl_2 \cdot 6H_2O \cdot dx$, (I)

(a) Non-hydrogen atoms

	x/a	y/b	z/c
Mg	0.0	0.0	0.0
Cl	0.265 2(1)	−0.009 5(1)	0.466 7(2)
O(1)	−0.060 0(3)	0.040 5(5)	0.273 9(6)
O(2)	−0.064 7(3)	0.221 1(5)	−0.114 8(6)
O(3)	0.141 0(3)	0.122 7(5)	0.090 7(6)
O(4)	−0.011 4(3)	0.323 9(5)	0.502 9(6)
C(1)	−0.080 7(5)	0.425 7(8)	0.382 9(9)
C(2)	−0.094 7(5)	0.598 5(7)	0.470 1(9)

(b) Hydrogen atoms in order of the O and C atoms to which they are attached

	x/a	y/b	z/c	U
H[O(11)]	−0.130(12)	0.022(11)	0.320(21)	0.133(42)
H[O(12)]	−0.026(10)	0.132(14)	0.402(18)	0.095(32)
H[O(21)]	−0.137(10)	0.252(13)	−0.047(19)	0.105(40)
H[O(22)]	−0.025(13)	0.230(16)	−0.196(25)	0.173(53)
H[O(31)]	0.208(10)	0.089(14)	0.160(18)	0.090(33)
H[O(32)]	0.165(11)	0.229(15)	0.036(20)	0.062(38)
H[C(11)]	−0.044 6(6)	0.438 3(8)	0.243 2(11)	0.043(14)
H[C(12)]	−0.160 4(6)	0.367 0(8)	0.370 1(11)	0.055(15)
H[C(21)]	−0.050 3(6)	0.707 5(8)	0.420 8(11)	0.090(15)
H[C(22)]	−0.166 1(6)	0.636 2(8)	0.547 6(11)	0.123(15)

TABLE 2

Interatomic distances (Å) and angles (°) in (I)

(a) Distances

$[Mg(H_2O)_6]^{2+}$

| Mg–O(1) | 2.057(4) | Mg–O(3) | 2.060(4) |
| Mg–O(2) | 2.073(4) | | |

Other contacts to Cl (<3.5 Å)

| Cl $\cdots$ O(2^{II}) | 3.150(5) | Cl $\cdots$ C(1^{II}) | 3.458(5) |

Dioxan ring

| C(1)–C(2) | 1.494(8) | O(4′)–C(2) | 1.435(7) |
| C(1)–O(4) | 1.405(7) | | |

Hydrogen bonds

O(4)–O(1)	2.795(4)	Cl–O(3)	3.144(4)
O(4)–O(2*)	2.842(4)	Cl–O(3^{III})	3.162(5)
O(4)–H[O(12)]	1.69(12)	Cl–H[O(11)]	2.22(12)
O(4)–H[O(22*)]	1.75(14)	Cl–H[O(31)]	2.33(12)
Cl–O(1)	3.106(5)	Cl–H[O(32^{III})]	2.24(12)

(b) Angles

$[Mg(H_2O)_6]^{2+}$

| O(1)–Mg–O(2) | 94.1(2) | (O1)–Mg–O(3) | 87.4(2) |
| O(2)–Mg–O(3) | 90.9(2) | | |

Hydrogen bonds

Mg–O(1) $\cdots$ O(4)	124.3(2)	C(2′)–O(4) $\cdots$ O(2*)	103.2(8)
Mg*–O(2*) $\cdots$ O(4)	120.4(2)	C(1)–O(4) $\cdots$ O(2*)	124.0(7)
O(1) $\cdots$ O(4) $\cdots$ O(2*)	103.2(6)	C(2′)–O(4) $\cdots$ O(1)	91.5(6)
C(1)–O(4) $\cdots$ O(1)	91.6(8)	O(4)–O(1) $\cdots$ Cl	85.2(8)

Dioxan ring

| O(4)–C(1)–C(2) | 111.9(5) | C(1)–C(2)–O(4^I) | 110.6(5) |
| C(1)–O(4)–C(2^I) | 110.4(5) | | |

Symmetry relations: O(2), x, y, z; O(2^I), $-x$, $1-y$, $1-z$; O(2*), x, y, $1+z$; O(2^{II}), $x+\frac{1}{2}$, $\frac{1}{2}-y$, $\frac{1}{2}+z$; O(2^{III}), $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$.

was used to collect intensity data for layers $hk0$—10. Because of difficulties in manipulating the crystals in capillaries, data could only be collected about the c axis on two crystals each ca. $0.3 \times 0.3 \times 0.7$ mm; altogether, 344 independent reflections were considered above background. Data were

TABLE 3

Co-ordinates and isotropic thermal parameters for $NiBr_2 \cdot 4H_2O \cdot 2dx$

	x/a	y/b	z/c	$B/Å^2$
Ni^{2+}	0.0000	0.2500	0.1250	2.4(1)
Br$^-$	0.0000	0.2500	0.2576(3)	2.5
O(1)	0.0141(24)	0.4779(22)	0.1231(15)	3.3
O(2)	0.1913(32)	0.6457(27)	0.2050(20)	4.8
C(1)	0.2433(55)	0.7849(50)	0.1791(30)	5.6
C(2)	0.2282(63)	0.8958(47)	0.2345(33)	6.1
H[C(1)]	0.3595	0.7729	0.1645	1.5
H[C(1^I)]	0.1821	0.8154	0.1334	1.5
H[C(2)]	0.1168	0.9185	0.2449	1.5
H[C(2^I)]	0.2796	0.0010	0.2140	1.5
H[O(1)]	0.0384	0.5271	0.1500	1.5

Hydrogen positions and thermal parameters were not refined.

TABLE 4

Bond lengths (Å) and bond angles (°) in (II)

Ni–Br	2.548(7)	Br–Ni–O(1)	90.9(2)
Ni–O(1)	2.10(2)	C(2)–C(1)–O(2)	111.7(10)
O(2)–C(1)	1.45(5)	C(1)–O(2)–C(2^I)	111.7(10)
C(1)–C(2)	1.48(7)	O(2^I)–C(2)–C(1)	110.0(10)
O(2)–C(2^I)	1.46(6)	O(1)–O(2)–O(2^I)	164.6(15)
O(1)–O(2)	2.73(4)		

Symmetry relations:

O(2): x, y, z.
O(2^I): $\frac{1}{2}-x$, $\frac{1}{2}-y$, $\frac{1}{2}-z$.

Although the use of anisotropic thermal parameters in the final refinement produced an improvement in R which is significant by Hamilton's Test [15] the poor definition of the atoms of the dioxan molecule suggests that the thermal ellipsoids have little physical significance. Values are given

[13] 'International Tables for Crystallography,' vol. III, 1968, vol. IV, 1974, Kynoch Press, Birmingham.

[14] W. J. A. M. Peterse and J. H. Palm, Acta Cryst., 1966, **20**, 147.

[15] W. C. Hamilton, Acta Cryst., 1965, **18**, 502.

in the Supplementary data. The very high standard deviations of O(2), and especially C(1) and C(2) occur because of the high-symmetry space group with the heavy nickel and bromine atoms lying on special position. The light atoms in general positions could be defined precisely only if the weak reflections could be measured with high accuracy. This was not possible on the elderly diffractometer used. The refinement program did not allow the dioxan molecule to be treated as a rigid body of known dimensions.

trans-*Tetra-aquadibromocobalt*(II)–1,4-*dioxan*(1/2), (IV). $CoBr_2\cdot4H_2O\cdot2C_4H_8O_2$, $C_8H_{24}CoBr_2O_8$, Tetragonal, $a = 9.19(1)$, $c = 19.18(2)$ Å, $Z = 4$, $D_c = 1.91$. Space group $I4_1/a$ (No. 88).

The distribution of intensities on zero- and upper-layer Weissenberg photographs appeared very similar to those in (II). Because of the strong fluorescence of the Co atom no attempt was made to collect intensity data.

cis-*Diaquatetrabromotin*(IV)–1,4-*dioxan*(1/2), (III). $SnBr_4\cdot2H_2O\cdot2C_4H_8O_2$, $C_8H_{20}Br_4O_6Sn$, Orthorhombic, $a = 26.12(3)$, $b = 19.07(2)$, $c = 7.486(10)$ Å, $U = 3\,728$ Å^3, $D_m = 2.32$, $Z = 8$, $D_c = 2.32$. Space group $Fdd2$ (No. 43). Cu-K_α radiation, μ(Cu-K_α) $= 228$ cm^{-1}.

This compound was prepared accidentally. A sample of SnBr$_4$·2dx, prepared according to the literature,[16] was left
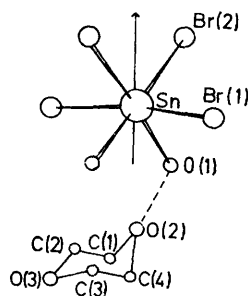

FIGURE 1 One SnBr$_4$(H$_2$O)$_2$ complex and one dioxan molecule, showing the numbering of the atoms in one asymmetric unit

at room temperature in a vial with a polyethylene stopper for *ca.* 5 years. During this time colourless crystals up to 2 mm on edge grew from the vapour in the upper part of the vial. The crystal structure determination established that these were the dihydrate. Equidimensional fragments (0.25 mm on edge) were cut under paraffin oil and sealed into Lindemann glass capillaries. Cell parameters and space group were determined from Weissenberg photographs as before.

Intensities were obtained [11] from equi-inclination Weissenberg photographs (*a* axis, *h* 0—4; *b* axis, *k* 0—10; *c* axis, *l* 0—5). Of *ca.* 1 100 independent reflections examined, 657 were considered observed. Lorentz, polarisation, and absorption corrections were applied before the data were scaled and combined.

The tin atoms occupy the special position 0,0,*z* (8*b*). The positions of the bromine atoms, relative to a tin atom at the origin were determined from a Patterson synthesis. After two cycles of refinement of the Sn and Br atoms from these positions (*R* 0.23), a Fourier synthesis showed the remaining non-hydrogen atom positions (Figure 1) (scattering factors for tin and bromine [13] were corrected for the real part of the anomalous dispersion). Block-diagonal least-squares refinement with individual isotropic thermal parameters for all atoms gave *R* 0.136 and refinement continued to

R 0.083 with anisotropic thermal parameters for the tin and bromine atoms. A difference synthesis at this point failed to show any hydrogen atom positions clearly, but in subsequent structure-factor calculations these were included at calculated positions, but not refined, their positions being adjusted as the parent atoms shifted. Refinement terminated at *R* 0.064. The weighting scheme used in the later stages was $w = 1/[1 + (|F_o| - 90)/120]^2$. A list of F_c values for unobserved reflections showed no anomalies.

Atomic co-ordinates and thermal parameters are given in Table 5, bond lengths and bond angles in Table 6.

TABLE 5

Fractional atomic co-ordinates and isotropic thermal parameters for SnBr$_4$·2H$_2$O·2dx, (III)

	x/a	y/b	z/c	$B/\text{Å}^2$
Sn	0.000 0(0)	0.000 0(0)	0.008 1(2)	
Br(1)	0.067 7(1)	−0.094 0(1)	−0.029 0(4)	
Br(2)	0.049 3(1)	0.073 5(1)	0.230 0(4)	
O(1)	0.037 1(6)	0.048 5(9)	−0.208 7(20)	4.8(3)
O(2)	0.042 5(6)	0.189 4(8)	−0.290 6(20)	4.5(3)
O(3)	0.123 7(6)	0.261 6(8)	−0.113 1(21)	5.0(3)
C(1)	0.091 3(9)	0.196 6(12)	−0.374 8(31)	4.5(4)
C(2)	0.133 1(10)	0.201 9(13)	−0.231 5(36)	5.1(5)
C(3)	0.076 6(10)	0.252 5(12)	−0.024 5(30)	4.8(5)
C(4)	0.033 9(9)	0.246 5(12)	−0.163 7(31)	4.4(4)

TABLE 6

Molecular geometry in (III)

(*a*) Bond lengths (Å)

Sn–Br(1)	2.534(2)	O(3)–C(3)	1.41(3)
Sn–Br(2)	2.527(3)	C(1)–C(2)	1.53(4)
Sn–O(1)	2.10(2)	C(3)–C(4)	1.53(3)
O(2)–C(1)	1.43(3)	O(1)–O(2)	2.76(2)
O(2)–C(4)	1.46(3)	O(1)–O(3*)	2.70(2)
O(3)–C(2)	1.46(3)		

(*b*) Interbond angles (°)

O(1)–Sn–O(1)	79.1(6)	C(1)–O(2)–C(4)	110.5(16)
O(1)–Sn–Br(1)	84.6(4)	C(2)–O(3)–C(3)	109.6(18)
O(1)–Sn–Br(1^I)	85.7(4)	O(2)–C(1)–C(2)	109.4(18)
O(1)–Sn–Br(2)	91.6(4)	C(1)–C(2)–O(3)	110.8(19)
Br(1)–Sn–Gr(2)	96.3(1)	O(3)–C(3)–C(4)	108.9(18)
Br(2)–Sn–Br(2^I)	97.8(1)	O(2)–C(4)–C(3)	112.8(19)
Br(1)–Sn–Br(2^I)	92.0(1)	Br(1)–Sn–Br(1^I)	167.4(1)

(*c*) Intramolecular non-bonded contacts (Å)

O(1) ⋯ O(1^I)	2.68(2)	Br(1) ⋯ Br(2)	3.769(4)
O(1) ⋯ Br(1)	3.13(2)	Br(1) ⋯ Br(2^I)	3.641(4)
O(1) ⋯ Br(1^I)	3.17(2)	Br(2) ⋯ Br(2^I)	3.807(4)
O(1) ⋯ Br(2)	3.33(2)		

Symmetry relations: O(1), x, y, z; O(1^I) $-x, -y, z$; O(1*), $\frac{1}{4} - x, \frac{3}{4} + y, \frac{3}{4} + z$.

cis-*Diaquatetrachlorotin*(IV)–1,4-*dioxan*(1/2), (V). $SnCl_4\cdot2H_2O\cdot2C_4H_8O_2$, $C_8H_{20}Cl_4O_6Sn$, Orthorhombic, $a = 25.92$, $b = 18.67$, $c = 7.19$ Å, $D_m = 1.81$, $Z = 8$, $D_c = 1.80$. Space group $Fdd2$.

This compound was prepared as large colourless crystals by cooling a solution of SnCl$_4$·5H$_2$O in hot dioxan. The unit cell and the general distribution of intensities on zero- and upper-layer Weissenberg photographs are very similar to those for (III).

DISCUSSION

Complex (I).—Figure 2 shows a projection of the structure. The dx molecule forms four hydrogen bonds each to a separate Mg(H$_2$O)$_6$ octahedron. The space group

[16] H. Rheinboldt and R. Rey, *J. prakt. Chem.*, 1931, **129**, 268.

imposes a centre of symmetry only on the octahedron. The $O(1) \cdots Mg$ vector is tilted by $3°$ from a normal to the $O(2)$, $O(3)$, Mg plane. The Mg–O distances (2.063 Å)
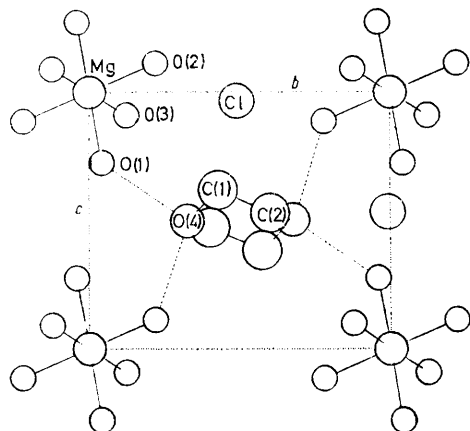

FIGURE 2   (I): a axis projection showing hydrogen bonds to dioxan; hydrogen bonds to chlorine are omitted

are comparable with those in $MgCl_2 \cdot 6H_2O$ (2.05 Å).[17] The Cl^- ion is linked into the structure by extensive hydrogen bonding and by van der Waals contacts.

Complex (III).—A projection of the structure of $SnBr_4 \cdot 2H_2O \cdot 2dx$ is shown in Figure 4.   Each cis-$SnBr_4(H_2O)_2$ octahedron is linked to its four glide-related neighbours by hydrogen bond sequences $Sn–O(H)H \cdots OC_4H_8O \cdots HO(H)–Sn$.   Each water molecule participates in two hydrogen bonds.

In all the SnX_4L_2 complexes so far examined where L involves an oxygen-donor atom only the cis-configuration has been observed [18-23] and the O–Sn–O angle is between 78 and $81°$.   The Sn–O distances range from 2.08 to 2.46 Å.   There are only three Sn–Br distances reported for octahedral compounds $(2.504, 2.516, \text{ and } 2.588 \text{ Å})$.   Sums of covalent radii suggest 2.14 for Sn–O and 2.54 Å for Sn–Br.

The values for (III) (Table 6) are consistent with these reports.

The Role of Dioxan.—Within the accuracy and precision of these determinations the dimensions of the dioxan molecules in (I)—(III) do not differ from those reported previously.   The hydrogen bonds to dioxan are summarised in Figure 5.   The pattern is different in each of the compounds.   In (I) each dioxan oxygen forms two hydrogen bonds, $103°$ apart.   The angle between the planes $O(1),(O4),O(2 *)$ and $C(1),O(4),C(2')$ is $69.9°$ so

FIGURE 3   (II): Partial cell contents showing hydrogen bonding

Complex (II).—Although $NiBr_2 \cdot 4H_2O \cdot 2dx$ is a hydrate the structure is reminiscent of those of $MgCl_2 \cdot 2dx$ (ref. 2) and $NiBr_2 \cdot 2dx$.[4]   All crystallise in tetragonal space groups with linear X–M–X units parallel to the c axis. The dx molecules lie in a four-fold symmetry about the metal ion.   In (II) the dioxan is separated from the metal by a co-ordinated water molecule to which it is hydrogen bonded (Figure 3).

The $Ni(H_2O)_4$ group is not required to be planar but is so within 2σ.   The Ni–Br and Ni–O bond lengths are close to literature values.

that the four bond-vectors from $O(4)$ form a distorted tetrahedron.

In (II) and (III) each dioxan oxygen forms only one hydrogen bond.   The angles between these hydrogen bonds and notional lone pairs of electrons lying $109.5°$ apart in a plane normal to the C–O–C plane are shown in Figure 5.   There is no suggestion that in (II) either lone-pair direction has over-riding influence on the direction of the hydrogen bond.   This is similar to the situations in $AgClO_4 \cdot 3dx$ (ref. 24) and $NiBr_2 \cdot 2dx$ (ref. 4) where the

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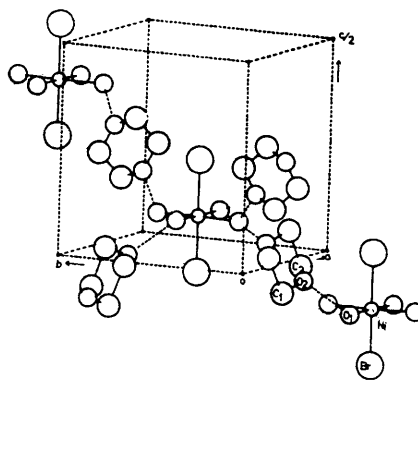[19] M. Yoshida, T. Veki, N. Yasuoka, N. Kassi, M. Kakudo, I. Omac, S. Kikkawn, and S. Matsuda, *Bull. Chem. Soc. Japan*, 1968, **41**, 1113.

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dioxan positions suggest that packing rather than speci-
fic metal–lone-pair bonding controls the structure. In
(III) however, the hydrogen bonds lie closer to the lone-
pair directions, with O(1) · · · (O2) approximately equa-
torial to the dioxan ring and O(1) · · · O(3*) approxi-
mately axial. The Sn, O(1), O(2), and O(3*) atoms are
almost coplanar.

The hydrogen bond values range from 2.70 to 2.84 Å,
typical for those between water molecules and oxygen
atoms in organic molecules.[25] The twin bonds in (I) are
just significantly longer than the single hydrogen-bonds in
(II) and (III).

These structures can be compared with those of three
recently reported hydrated metal-halide–dioxan sol-
vates. LiCl·H$_2$O·dx differs [26] from all the others in
having both water and dioxan co-ordinated to the metal.
The tetrahedrally co-ordinated Li atom is surrounded

FIGURE 5   Bond angles involving the hydrogen bonds to dioxan
in (I), (II), and (III). Calculated lone-pair directions from the
dioxan oxygen atom are shown by heavy dotted lines

tive affinity of lithium for water and dioxan is clearly
intermediate between that of sodium, for which NaI·3dx

and NaClO$_4$·3dx can be crystallised from aqueous solu-
tion, and of magnesium and the first-transition series
metals where dioxan cannot compete with water for
sites in the first co-ordination sphere.

In InCl$_3$·3H$_2$O·3dx (ref. 27) and [SnCl$_3$(OH)·H$_2$O]$_2$·3dx
(ref. 28) dioxan fulfils the same role of inter-complex
hydrogen bonding as in the present structures. The i.r.
spectra of both of these compounds would be of interest
since they contain dioxan molecules in the chair configura-
tion but lacking a centre of symmetry. [SnCl$_3$(OH)·
H$_2$O]$_2$·3dx is very different from (III), since it contains
dimeric tin octahedra sharing two water molecules.
These seem to be the only structures reported for hy-
drated tin(IV) halides. There is an interesting contrast
between the very ready hydrolysis of SnX$_4$ and the ex-
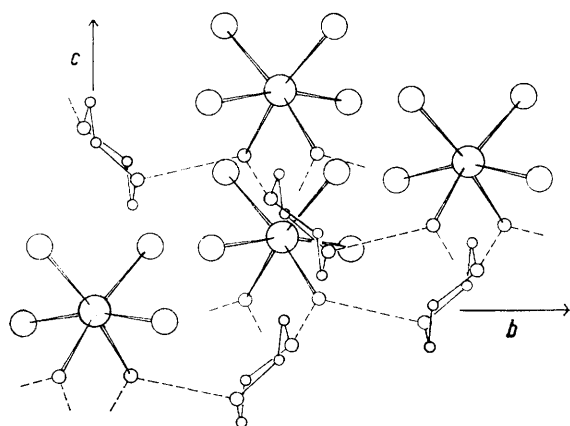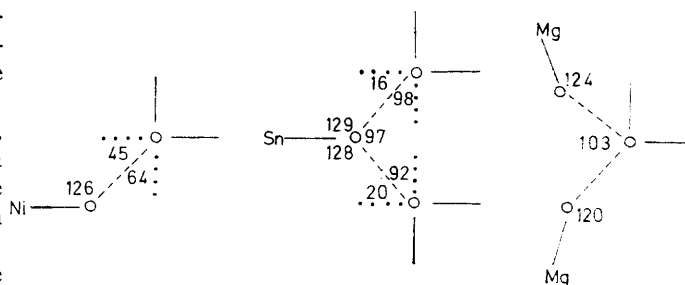istence of several crystalline hydrates.[29,30]

FIGURE 4   (III):   a axis projection of part of the unit cell,
showing hydrogen-bonded chains.   Dioxan molecules related
to those shown by C$_2$ (z) axes through Sn have been omitted
for clarity

by Cl, water, and two bridging dioxan molecules. The
dioxan is not involved in hydrogen bonding. The rela-

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