Table 1. *Lattice parameters and properties of vanthoffites*

Composition	Lattice parameters[1]					Reference	Decomposition point (°C)	Colour
	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)			
$MgNa_6(SO_4)_4$	9·776	9·202	8·189	113·48	675·7	Calculated from Madsen (1966)	506	White
	9·797	9·217	8·199	113·50	679·0	Fischer & Hellner (1964)		
	9·779	9·190	8·196	113·55	675·2	Erd, 1973[2]		
$MnNa_6(SO_4)_4$	9·965	9·280	8·248	116·25	684·1	This paper	430	Pale pink
$FeNa_6(SO_4)_4$	9·94	9·41	8·24	116·2	691·5		?	Reddish brown[3]
$CoNa_6(SO_4)_4$	9·922	9·246	8·282	116·25	681·4		430	Purple
$NiNa_6(SO_4)_4$	9·883	9·176	8·207	115·41	672·3		420	Yellow
$ZnNa_6(SO_4)_4$	9·871	9·211	8·226	115·98	672·4		360	White
$ZnNa_6(SO_4)(CrO_4)_3$ [4]	10·13	9·54	8·38	116·5	724·8		?	Greenish brown[5]

(1) Mean standard deviation of lattice parameters is 0·005 Å; for $FeNa_6(SO_4)_4$ and for the chromate vanthoffite, 0·01 Å. (2) Private communication to K. L. Keester. (3) Colour probably due to some iron oxide present. (4) Approximate composition. (5) Some chromium oxide present.

even the substituted ions are similar in size. Correspondingly, the powder diagrams are closely related with respect to intensities and *d*-spacings.*

Because of experimental difficulties only partial replacement of SO_4 by CrO_4 was achieved. The large volume effect of this replacement is evident from Table 1. On the basis of crystal chemical considerations isostructural fluoroberyllates, tungstates, molybdates and selenates can be predicted to exist. Finally, it should be mentioned that Cu-vanthoffite could not be synthesized. The same applies to $ZrCa_6(SiO_4)_4$, which would have similar radius ratios, but doubled valencies.

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* Complete powder data have been submitted to the Joint Committee on Powder Diffraction Standards for publication in the powder data file.

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Dibromo(1,4-dioxan)tin(II): the crystal structure.

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A full refinement ($R = 0{\cdot}062$) of the title compound has been performed with diffractometer data and the positional parameters of the isostructural chloride. The crystal data are: space group $C2/c$, $a = 7{\cdot}840$ (1), $b = 12{\cdot}180$ (2), $c = 9{\cdot}363$ (1) Å, $\beta = 95{\cdot}65$ (1)°, $Z = 4$.

There is a complete lack of detailed information concerning the crystal structures of adducts of tin(II) bromide with neutral ligands other than water. We report here the results of a single-crystal X-ray structure determination of dibromo(1,4-dioxan)tin(II). This adduct was chosen in order to allow a direct comparison of the tin(II) environment and tin–halogen distances with those in the isostructural dichloro(1,4-dioxan)tin(II) reported recently (Hough & Nicholson, 1976).

The experimental procedure was identical with that described for the chloride. Crystal data in addition to those given above are: $D_m = 2{\cdot}7$ (flotation), $D_c = 2{\cdot}74$ g cm^{-3}, $F(000) = 672$, $M_r = 366{\cdot}6$, $\mu(\text{Mo } K\alpha) = 53{\cdot}7$ cm^{-1}, $R = 0{\cdot}062$ for 1225 measured reflexions (98 unobserved). The structure was refined to a conventional R of 0·062. The positional and thermal parameters are given in Table 1 and the interatomic distances and valence angles are contained in Table 2.*

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31974 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Positional and thermal parameters*

(*a*) Final positional parameters ($\times 10^5$ for Sn or 10^4 for other atoms) with estimated standard deviations in parentheses.

	x	y	z
Sn	0	103 (1)	2500
Br	182 (2)	1623 (1)	4519 (2)
O	3253 (11)	283 (8)	2694 (13)
C(1)	4025 (17)	1235 (13)	2137 (27)
C(2)	4072 (18)	−708 (11)	2122 (24)

(*b*) Anisotropic temperature factors, with standard deviations in parentheses. The values listed are $\times 10^3$ and the temperature factor has the form:

$$\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + U_{12}a^*b^*hk + U_{23}b^*c^*kl + U_{13}a^*c^*hl)].$$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn	22·9 (5)	31·5 (5)	29·0 (5)	0·0	− 9·1 (4)	0·0
Br	55·6 (9)	38·3 (8)	35·7 (7)	2·3 (6)	−8·3 (6)	6·2 (5)
O	19 (4)	38 (5)	89 (8)	8 (37)	−20 (4)	−6 (5)
C(1)	22 (6)	33 (8)	156 (20)	−3 (5)	−19 (9)	−14 (10)
C(2)	31 (7)	23 (6)	127 (17)	−2 (5)	−19 (8)	6 (8)

Table 2. *Bond distances* (Å) *and angles* (°) *with estimated standard deviations in parentheses*

(*a*) Tin coordination

Sn—Br	2·639 (2)	Sn—O	2·549 (9)
Br—Sn—Br′	90·96 (2)	O—Sn—O′	170·2 (3)
O—Sn—Br′	88·5 (3)	Br′—Sn—O′	84·6 (3)

(*b*) Dioxan groups

C(1)—O	1·43 (2)	C(1)—C(1)′	1·61 (2)
C(2)—O	1·49 (2)	C(2)—C(2)′	1·55 (2)
C(1)—O—C(2)	108 (1)	C(1)—C(1)′—O	105 (1)
C(2)—C(2)′—O	105 (1)	C(1)—O—Sn	120 (8)
C(2)—O—Sn	111·6 (7)		

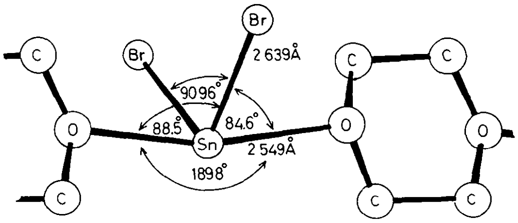

Fig. 1. Part of the polymeric array showing the tin environment (twofold axes through the tin atom and the dioxan molecule omitted).

Fig. 1 shows the twofold symmetric tin(II) environment and part of a polymeric $SnBr_2$—dioxan array. These arrays are connected by two long-range [3·508 (2) Å] Sn—Br interactions.

The coordination polyhedron about tin may be described as distorted five-coordinate with the fifth position evidently occupied by a stereochemically active lone pair. Hough & Nicholson have discussed the structure and bonding in the chloride complex in terms of tin 5*s* and 5*p* valence orbitals. In the latter compound the deviation (11°) of the OSnO angle from 180° is small and the Sn—O bonds are long and weak. This may be attributed to the polymeric nature of the complex which imposes a constraint on the OSnO bond angle. On comparing the present structure with the isostructural chloride it can be seen that substituting Cl by Br results in a marginal, but significant, decrease [1·7 (4)°] in the depression of the OSnO bonds from linearity. The constrained OSnO angle in both compounds means that the σ-antibonding contributions largely associated with the lone pair (*e.g.* Nicholson & Rademacher, 1974) to the Sn—O interactions cannot be reduced by further depression of the OSnO bonds. As a result they are rather long and weak. This conclusion is supported by the structure of the β-diketonate, bis(1-phenylbutane-1,3-dionato)tin(II) (Ewings, Harrison & King, 1975). The latter is particularly suited for comparison because it exhibits the same coordination number and point group for tin as the dioxan complexes, but is not polymeric. Hence, the constraint on the axial OSnO bonds is not present and they accordingly attain a bond angle of 150·6° and axial Sn—O bonds as short as 2·290 Å.

The slightly larger OSnO angle in the bromide should therefore be matched by slightly longer and weaker Sn—O bonds. However, the observed lengthening from 2·527 (5) to 2·549 (9) Å on going from the chloride to the bromide can only be described as possibly significant.

The halogen—tin—halogen bond angles in the units $SnCl_2$ and $SnBr_2$ are very close to 90°. The BrSnBr angle is only 0·44 (7)° larger than the corresponding angle in the chloride. Since the Sn—Cl bond lengths [2·474 (2) Å] have been shown to be normal, the Sn—Br distances should be representative of those in other tin(II) bromide adducts. In more crowded tin(II) environments such as in the tin(II) bromide hydrates (Andersson, 1972) the Sn—Br distances range from 2·77 to 3·79 Å

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