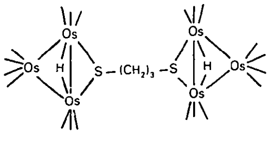
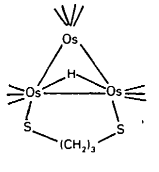
although the X-ray work did not locate the H atoms directly.

Geometries about the S atoms are unexceptional, the Os—S bond lengths of S(1)—Os(1) 2·406 (9), S(1)—Os(3) 2·403 (8), S(2)—Os(4) 2·419 (9), S(2)—Os(6) 2·403 (10) Å being entirely similar to those in compounds reviewed briefly in the preceding paper (Holden *et al.*, 1983*b*). S(1) lies 1·88 (2) Å below the plane of Os(1)Os(2)Os(3), and S(2) 1·90 (2) Å from that described by Os(4)Os(5)Os(6). The dihedral angle between these two planes of Os atoms is 78·9 (10)° (see Table 3). The —(C_3H_6)— link showed no evidence for conformational disorder in the crystal.

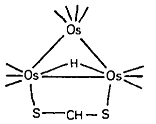
The structure determination shows the compound is (I) rather than (II), which had been strongly suggested on the basis of mass-spectral evidence. Adams & Selegue (1980) have reported the structural investigations of (III) and (IV) which have the bidentate dithioformato ligands chelating to give monomers. In (III), the (μ-H) Os—Os distance is 2·973 (1) Å (average) whilst the corresponding (μ-S_2CH) Os—Os in (IV) is 2·854 (1) Å.



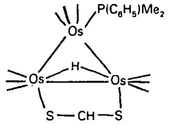
(I)



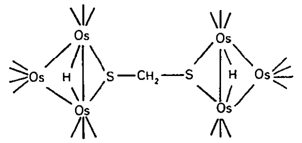
(II)



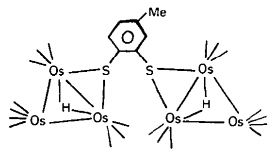
(III)



(IV)



(V)



(VI)

Table 3. *Least-squares planes and atom distances from plane* (Å × 10^2)

Plane (1): Os(1), Os(2), Os(3)

$-5{\cdot}453x + 7{\cdot}961y + 13{\cdot}358z - 1{\cdot}692 = 0$

S(1)	−188 (2)	C(3)	−394 (4)
S(2)	−550 (2)	Os(4)	−504 (1)
C(1)	−228 (4)	Os(5)	−781 (1)
C(2)	−340 (4)	Os(6)	−598 (1)

Plane (2): Os(4), Os(5), Os(6)

$11{\cdot}084x + 9{\cdot}067y + 2{\cdot}046z + 10{\cdot}662 = 0$

S(2)	−190 (2)	C(3)	−227 (4)
S(1)	−515 (2)	Os(1)	−592 (1)
C(1)	−379 (4)	Os(2)	−717 (1)
C(2)	−324 (4)	Os(3)	−439 (1)

The dihedral angle between the planes is 78·9 (10)°.

Other examples of dimerization have been noted. (V) is formed by reaction of $H_2Os_3(CO)_{10}$ with CS_2 (Adams & Golembseki, 1979; Adams, Golembeski & Selegue, 1981), and our work has shown that 3,4-toluenedithiol reacts with $Os_3(CO)_{10}(MeCN)_2$ to give the analogous dimer (VI) (Holden & Uden, 1982, unpublished results). This compound crystallizes in the orthorhombic space group *Pbca*; all non-H atoms have been located, but the refinement converged at the high *R* value of *ca* 0·100, presumably because of problems with absorption corrections.

References

Adams, R. D. & Golembeski, N. M. (1979). *J. Am. Chem. Soc.* **101**, 1306–1307.

Adams, R. D., Golembeski, N. M. & Selegue, J. P. (1981). *J. Am. Chem. Soc.* **103**, 546–555.

Adams, R. D. & Selegue, J. P. (1980). *J. Organomet. Chem.* **195**, 223–238.

Holden, H. D., Johnson, B. F. G., Lewis, J., Raithby, P. R. & Uden, G. (1983*a*). *Acta Cryst.* C**39**, 1197–1200.

Holden, H. D., Johnson, B. F. G., Lewis, J., Raithby, P. R. & Uden, G. (1983*b*). *Acta Cryst.* C**39**, 1200–1203.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

Uden, G. (1982). PhD Thesis, Univ. of Cambridge, England.

Acta Cryst. (1983). C**39**, 1205–1207

The Structure of (1,4-Dioxane)thallium(I) Tetrabromothallate(III), $Tl(C_4H_8O_2)^+.TlBr_4^-$

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Abstract. $M_r = 816{\cdot}4$, orthorhombic, $Cmc2_1$, $a = 10{\cdot}31$ (1), $b = 8{\cdot}560$ (5), $c = 15{\cdot}55$ (2) Å, $V = 1372{\cdot}3$ Å^3, $Z = 4$, $D_x = 3{\cdot}95$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 33{\cdot}98$ mm^{-1}, $F(000) = 1400$, $T = 293$ K, $R = 0{\cdot}057$ for 604 reflections. The structure consists of tetrahedral $TlBr_4^-$ ions and chains of Tl^+ ions bridged by 1,4-dioxane molecules; the geometry around eight-coordinate Tl^+ is a distorted dodecahedron.

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Introduction. We have recently shown that many of the addition complexes formed by the ionic 'dihalides' of gallium and indium (Ga_2X_4, In_2X_4) are neutral and contain metal–metal bonds; *e.g.* Ga_2Cl_4.2dioxane (Beamish, Small & Worrall, 1979) and In_2Cl_4.2dioxane (Sinclair & Worrall, 1982). There are no reports of analogous thallium compounds in the literature, and the present work was carried out as part of a study of the coordination chemistry of the mixed-oxidation-state thallium halides $Tl^+.TlX_4^-$. We here describe the crystal structure of Tl_2Br_4.dioxane.

Experimental. Prepared by refluxing a solution of thallium(III) bromide in dry dioxane for 12 h, needle crystals obtained upon cooling, satisfactory crystals transferred to Lindemann tubes in a nitrogen-filled dry box. Analysis: found Tl 50·05%; calculated, for Tl_2Br_4.dioxane, Tl 50·06%. Crystal data from Weissenberg, de Jong–Bouman and Buerger precession photographs, Cu*Kα* radiation ($\lambda = 1·542$ Å); systematic absences indicated *Cmc*2$_1$ or *Cmcm*, former proved more satisfactory; Stoe STADI-2 two-circle automatic diffractometer, graphite-monochromatized Mo *Kα*, *h* 0–13, *k* 0–9, *l* 0–20, $2\theta < 55°$, crystal 0·078 × 0·434 × 0·043 mm, absorption corrections (max. 0·0919, min. 0·0080) and scaling of data carried out with *SHELX*76 (Sheldrick, 1976), standards measured by each *k* layer, checked every 10 reflections, variation 1%, 866 reflections measured, 604 unique observed reflections [$I > 3\sigma(I)$]; *SHELX*76 used for all other calculations; thallium atom positions, obtained from Patterson maps, used to phase ($F_o - F_c$) maps to give positions of remaining non-hydrogen atoms; unit weights, full-matrix least-squares refinement on F of all atomic positions, anisotropic U_{ij} for Tl and Br, isotropic U for remaining non-H atoms, $R = 0·057$. As the space group is without a centre of symmetry, the enantiomorphous structure was also refined but no significant changes were observed in either R or structural parameters; max. shift/e.s.d. = 0·03 for heavy atoms, 1·511 for O(1) (see *Discussion*), max. and min. height in final difference synthesis 3·6 and $-1·8$ e Å^{-3}, atomic scattering factors, including anomalous scattering, from Cromer & Mann (1968) and Cromer & Liberman (1970).*

Discussion. Final coordinates and equivalent isotropic ($U_{\rm eq}$) values for Tl and Br and isotropic thermal parameters for C and O are given in Table 1. The structure is composed of tetrahedral $TlBr_4^-$ ions and $Tl(\rm dioxane)^+$ ions and is the first reported complex of

Table 1. *Fractional atomic coordinates* (×10^4 *for* Tl, Br, ×10^3 *for* O, C) *and isotropic thermal parameters* (Å^2 ×10^4 *for* Tl, ×10^3 *for* Br, O, C)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}/U$
Tl(1)	5000*	3243 (3)	1858*	409 (12)
Tl(2)	5000*	8258 (3)	1859 (8)	504 (13)
Br(1)	5000*	4919 (22)	3234 (10)	70 (9)
Br(2)	5000*	4876 (23)	527 (11)	53 (8)
Br(3)	2990 (4)	1484 (6)	1940 (15)	66 (4)
O(1)	500*	1002 (27)	373 (13)	169 (95)
C(1)	635 (8)	973 (11)	407 (5)	85 (27)
C(2)	614 (5)	79 (6)	465 (3)	36 (10)
O(2)	500*	924 (8)	20 (4)	51 (14)

* Constrained.

Table 2. *Bond distances* (Å) *and angles* (°)

Tl(1)–Br(1)	2·576 (17)	Tl(1)–Br(2)	2·498 (18)
Tl(1)–Br(3)	2·564 (5)	Tl(2)–Br(3^{ii})	3·439 (5)
Tl(2)–Br(1)	3·570 (18)	Tl(2)–Br(2)	3·559 (20)
Tl(2)–Br(3^{iv})	3·454 (6)	Tl(2)–O(2)	2·71 (6)
Tl(2)–O(1)	3·28 (22)		

Br(1)–Tl(1)–Br(2)	112·1 (2)	Br(1)–Tl(1)–Br(3)	106·6 (5)
Br(2)–Tl(1)–Br(3)	111·7 (5)	Br(3)–Tl(1)–Br(3^{i})	107·8 (2)
Br(2)–Tl(2)–Br(1)	72·4 (1)	Br(3^{ii})–Tl(2)–Br(2)	70·3 (2)
Br(3^{ii})–Tl(2)–Br(1)	67·9 (3)	Br(3^{ii})–Tl(2)–Br(3^{iii})	127·4 (2)
Br(3^{iv})–Tl(2)–Br(3^{v})	73·7 (2)	O(1)–Tl(2)–Br(1)	80 (4)
O(1)–Tl(2)–Br(2)	153 (4)	O(1)–Tl(2)–Br(3^{ii})	100 (2)
O(2)–Tl(2)–Br(1)	145 (2)	O(2)–Tl(2)–Br(2)	72 (1)
O(2)–Tl(2)–Br(3^{ii})	100 (1)	O(1)–Tl(2)–Br(3^{iv})	66 (4)
O(2)–Tl(2)–Br(3^{iv})	78 (1)	O(1)–Tl(2)–O(2)	135 (3)

Symmetry code

(i) $1-x, y, z$ (ii) $\tfrac{1}{2}+x, \tfrac{1}{2}+y, z$ (iii) $\tfrac{1}{2}-x, \tfrac{1}{2}+y, z$

(iv) $x, 1+y, z$ (v) $1-x, 1+y, z$ (vi) $x, 2-y, \tfrac{1}{2}+z$.

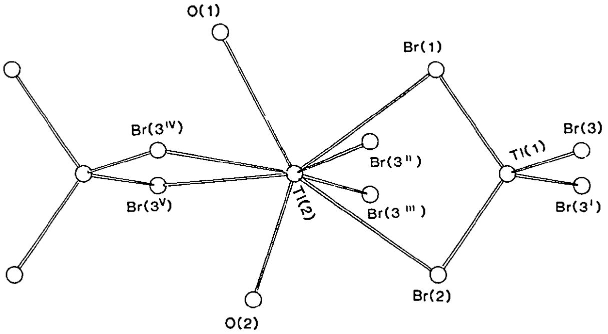

Fig. 1. Coordination around Tl atoms.

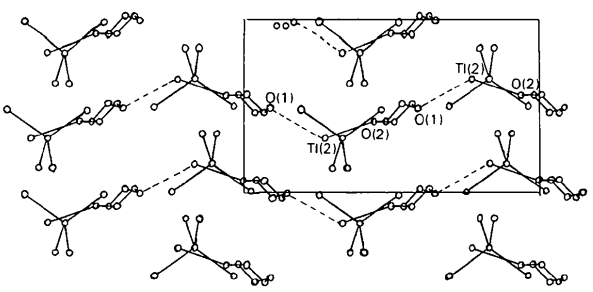

Fig. 2. Tl_2Br_4.dioxane.

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* Lists of structure factors, anisotropic thermal parameters, bond distances and angles involving C and O have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38631 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Tl_2Br_4. It is quite different from the dioxane complexes formed by the analogous gallium (Beamish, Small & Worrall, 1979) and indium dihalides (Sinclair & Worrall, 1982). Bond distances and angles are given in Table 2; tetrahedral distances [Tl(1)—Br] are similar to those observed in the parent halide [mean distance 2·51 (3) Å, Hazell, 1963]. The Tl^+ ion [Tl(2)] is at the centre of a distorted dodecahedron (Fig. 1) and is surrounded by six Br atoms (from four different tetrahedra) and two O atoms; the Tl(2)—Br distances are similar to other ionic eight-coordinate Tl^+—Br distances, *e.g.* 3·46 Å in Tl_2Br_4 where Tl^+ is at the centre of a distorted dodecahedron (Hazell, 1963), and 3·44 Å in TlBr which has a CsCl structure (Lee, 1971). The Tl^+ ions are bridged by weakly attached dioxane molecules in the chair conformation to form chains parallel to the *c* axis (Fig. 2). The Tl(2)—O distances, which have high e.s.d.'s, are similar to those observed in other ionic Tl^I complexes, *e.g.* Tl_3FCO_3, Tl—O 2·89 (6) Å (Alcock, 1973); $Tl.C_6H_2N_3O_7$, Tl—O 2·83–3·22 (2) Å (Herbstein, Kapon & Wielinski, 1977). We attribute these high e.s.d.'s to the mobility of the ligand due to its weak attachment; it is well known that Tl^+ is a very weak acceptor for 'hard' ligands such as oxygen (Lee, 1971); complexes of Tl^I which have been reported and which give more precise Tl—O distances are in the main those which contain negatively charged ions, *e.g.* acetate (Brown & Faggiani, 1980), salicylate (Hughes & Truter, 1972) and picrate (Herbstein, Kapon & Wielinski, 1977). The interaction between the charged ions will be stronger than the ion-dipole of a neutral ligand such as dioxane.

The fairly regular coordination around Tl^I suggests that the $6s^2$ lone pair of electrons is stereochemically inactive. This effect has been recently discussed (Brown & Faggiani, 1980).

References

ALCOCK, N. W. (1973). *Acta Cryst.* B**29**, 498–502.

BEAMISH, J. C., SMALL, R. W. H. & WORRALL, I. J. (1979). *Inorg. Chem.* **18**, 220–223.

BROWN, I. D. & FAGGIANI, R. (1980). *Acta Cryst.* B**36**, 1802–1806.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

HAZELL, A. C. (1963). *J. Chem. Soc.* p. 3459.

HERBSTEIN, F. H., KAPON, M. & WIELINSKI, S. (1977). *Acta Cryst.* B**33**, 649–654.

HUGHES, D. L. & TRUTER, M. R. (1972). *J. Chem. Soc. Dalton Trans.* pp. 2214–2218.

LEE, A. G. (1971). *The Chemistry of Thallium*, pp. 25–36. London: Elsevier.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

SINCLAIR, I. & WORRALL, I. J. (1982). *Can. J. Chem.* **60**, 695–698.

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catena-Di-μ-thiocyanato-*N*,*S*-bis(1*H*-1,2,4-triazole-*N*^{4})cadmium, $[Cd(C_2H_3N_3)_2(NCS)_2]$; a Third Structure Type of Composition *M*$(NCS)_2$(1,2,4-triazole)$_2$

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Abstract. $M_r = 366{\cdot}70$, triclinic, $P\bar{1}$, $a = 5{\cdot}717\ (2)$, $b = 7{\cdot}573\ (2)$, $c = 7{\cdot}683\ (2)$ Å, $\alpha = 79{\cdot}54\ (2)$, $\beta = 68{\cdot}70\ (2)$, $\gamma = 89{\cdot}36\ (2)°$, $V = 304{\cdot}2$ Å^3, $Z = 1$, $D_m = 1{\cdot}99\ (1)$, $D_x = 2{\cdot}00$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 2{\cdot}11$ mm^{-1}, $F(000) = 174{\cdot}94$, room temperature, $R = 0{\cdot}019$ for 1722 independent reflections. The compound was crystallized from an aqueous solution of cadmium thiocyanate and 1,2,4-triazole. Cd^{2+} is octahedrally coordinated by two monodentate N(4)-bonded 1,2,4-triazole ligands (*trans* oriented) with Cd—N = 2·317 (1) Å, two (*trans*) thiocyanate N atoms, Cd—N = 2·330 (2) Å, and two thiocyanate S atoms, Cd—S = 2·754 (1) Å. The thiocyanate ions constitute double bridges, thereby building infinite linear chains of thiocyanate-linked Cd^{2+} ions running parallel in one direction in the crystal. The structure differs from previous compounds of composition *M*$(NCS)_2$(1,2,4-triazole)$_2$ that contain bidentate 1,2,4-triazole ligands and N-bonded thiocyanate anions.

Introduction. Thiocyanates of divalent first-row transition metals are known to form either linear trinuclear, or two-dimensional layered compounds with 1,2,4-triazole (trz) as ligands. The overall composition is *M*$(NCS)_2(trz)_2$ (Haasnoot & Groeneveld, 1977). These types of compounds are easily distinguished by their

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