

Table 3. *Geometry of the hydrogen bonds*

O—H...O	O...O	O—H	H...O	O—H...O
O(3)—H(3)...O(5 ⁱ)	2.673 (4) Å	0.82 (4) Å	1.86 (4) Å	172 (4)°
O(6)—H(6)...O(2 ⁱⁱ)	2.640 (3)	0.85 (5)	1.80 (5)	175 (5)
O(7)—H(7)...O(2 ⁱⁱⁱ)	2.763 (4)	0.83 (5)	1.95 (5)	165 (4)
O(7)—H(72)...O(5 ^{iv})	2.669 (4)	0.90 (5)	1.78 (5)	169 (5)
O(8)—H(81)...O(1 ⁱⁱⁱ)	2.912 (4)	0.71 (6)	2.21 (6)	167 (6)
O(8)—H(82)...O(4 ⁱ)	2.762 (4)	0.99 (5)	1.79 (5)	164 (5)

Symmetry code: (i) $x - \frac{1}{2}, \frac{1}{2} - y, -z$; (ii) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $x - 1, y, z$; (iv) $\frac{1}{2} - x, -y, \frac{1}{2} + z$.

Table 4. *Analysis of the configuration of the lactate anions*

(a) Distances (Å) from planes through lactate anions (atoms used to define the planes are indicated by an asterisk)

O(1)*	0.001 (3)	O(4)*	0.001 (3)
O(2)*	0.001 (3)	O(5)*	0.002 (4)
C(1)*	-0.007 (4)	C(4)*	-0.007 (4)
C(2)*	0.002 (4)	C(5)*	0.002 (5)
O(3)	0.193 (3)	O(6)	-0.286 (3)
H(3)	0.18 (4)	H(6)	-0.71 (5)

(b) Conformational angles (°)

H(3)—O(3)—C(2)—C(1)	178 (3)
H(6)—O(6)—C(5)—C(4)	-148 (4)
O(3)—C(2)—C(1)—O(1)	-7.3 (4)
O(6)—C(5)—C(4)—O(4)	-12.8 (4)
O(3)—C(2)—C(1)—O(2)	171.5 (4)
O(6)—C(5)—C(4)—O(5)	168.4 (4)

Discussion. The Mn atom is octahedrally coordinated by one carboxylate O atom and one hydroxyl O atom from each L-lactate ligand and two water O atoms in

cis positions. The structure is built up from discrete molecules $[\text{Mn}(\text{C}_3\text{H}_5\text{O}_3)_2(\text{H}_2\text{O})_2]$ held together through hydrogen bonds. Hydrogen-bond data are given in Table 3.

The molecular structure of the title compound is similar to that of Mn^{II} glycolate dihydrate (Lis, 1980) but different from that of Mn^{II} DL-lactate trihydrate (Singh *et al.*, 1975), where the water molecules are in *trans* positions.

The bond lengths and angles (Table 2) are the normally expected values and comparable with those for Zn DL-lactate trihydrate (Singh *et al.*, 1975). The

configuration of the $\text{C}-\text{C}-\text{O}$ group of each ligand is planar (Table 4). There is also a tendency for the O(3) or O(6) hydroxy atoms to lie in this plane. Similar trends have been observed in most α -hydroxycarbonyl systems (Newton & Jeffrey, 1977; Lis, 1981).

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Structure of μ -[2,4,6-Tri(2-pyridyl)-1,3,5-triazine]-bis[bis(trifluoroacetato)mercury(II)]

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Abstract. $[\text{Hg}_2(\text{CF}_3\text{CO}_2)_4(\text{C}_{18}\text{H}_{12}\text{N}_6)]$, $\text{C}_{26}\text{H}_{12}\text{F}_{12}\text{Hg}_2\text{N}_6\text{O}_8$, triclinic, $P\bar{1}$, $a = 13.47$ (1), $b = 15.85$ (2), $c = 9.60$ (1) Å, $\alpha = 112.4$ (1), $\beta = 100.0$ (1), $\gamma = 110.3$ (1)°, $U = 1663$ Å³, $D_m = 2.360$, $Z = 2$, $D_x = 2.328$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 8.98$ mm⁻¹. $R = 0.055$ for 2062 diffractometer-measured intensities. The 2,4,6-tri(2-pyridyl)-1,3,5-triazine molecule acts as a bidentate

ligand to Hg(1) [Hg—N 2.17 (2), 2.61 (2) Å] and as a tridentate ligand towards Hg(2) [Hg—N 2.40 (2), 2.44 (2), 2.50 (2) Å]. The trifluoroacetate groups remain covalently attached to Hg [Hg(1)—O 2.13 (2), 2.86 (2), 2.35 (2), 2.63 (2) Å and Hg(2)—O 2.37 (2), 2.63 (2), 2.37 (2), 2.60 (3) Å]. Effectively, Hg(1) is six-coordinated and Hg(2) is seven-coordinated.

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Introduction. Mercury(II) trifluoroacetate is a useful reagent for the preparation of mercury(II) complexes. With pyridine it forms 1:2 and 1:3 complex cations (Halfpenny, Small & Thorpe, 1978; Halfpenny & Small, 1978) accompanied by the formation of tri-

fluoroacetate ions. It is of interest to examine the structures of further complexes with other nitrogen-donor ligands. Although 2,4,6-tri(2-pyridyl)-1,3,5-triazine (tpt) has been extensively used as a complexing agent, the structures of only a few crystalline derivatives have been determined and it has been argued on theoretical grounds that it cannot act simultaneously as a tri- and bidentate ligand. This ligand was found to form a complex with mercury(II) trifluoroacetate by recrystallization from a solution (1:1 molar) in dichloromethane. The crystals were oblique prisms with the forms {100}, {010}, {001}, {101}. Crystal data were obtained from Weissenberg photographs taken about **a**, **b**, **c** with Cu *K* α radiation ($\lambda = 1.542 \text{ \AA}$). Intensities were measured on a Stoe STADI-2 two-circle diffractometer with graphite-monochromatized Mo *K* α radiation ($\lambda = 0.7107 \text{ \AA}$). From a crystal $0.04 \times 0.24 \times 0.14 \text{ mm}$, 2986 unique intensity values for the layers $l = 0$ to 8 were measured; of these, 2062 [for which $I > 3\sigma(I)$] were used for the structure determination. After initial data reduction all subsequent computation was performed with *SHELX* (Sheldrick, 1976), including correction for absorption ($\mu = 8.98 \text{ mm}^{-1}$). The two independent Hg positions were obtained from the Patterson map and the remaining non-H atoms were located on ($F_o - F_c$) maps phased on the Hg atoms. Refinement of the positions of the non-H atoms with anisotropic U_{ij} for Hg and isotropic U for the remaining atoms proceeded by full-matrix least squares; at a later stage, separate scale factors for the data-collection layers $l = 0$ to 8 were refined. In the final cycles anisotropic U_{ij} for all F atoms were included and the refinement was concluded when the largest shift/e.s.d. ratio was 0.3 and R was 0.055. The ($F_o - F_c$) map showed no significant features. H atoms could not be located.

Atomic scattering factors for Hg, including anomalous scattering, were taken from Cromer & Mann (1968) and Cromer & Liberman (1970); those for all the other atoms were from *International Tables for X-ray Crystallography* (1962). Final atomic coordinates and isotropic temperature factors are listed in Table 1.*

Discussion. One structural unit is shown in Fig. 1; bond distances and angles involving Hg atoms are given in Table 2. In the ligand molecule, N(4), N(1) and N(5) are coordinated to Hg(2), and N(3) and N(6) to Hg(1); the latter coordination being by virtue of one long and one short Hg—N bond. The simultaneous bidentate and tridentate character of the tpt ligand is achieved only by appreciable distortion from planarity

Table 1. Fractional atomic coordinates ($\times 10^4$ for Hg; $\times 10^3$ for other atoms) and thermal parameters ($\times 10^3$)

	x	y	z	U_{eq}/U (\AA^2)
Hg(1)	10058 (1)	6357 (1)	5967 (1)	73 (1)†
Hg(2)	7710 (1)	9493 (1)	7627 (2)	95 (1)†
C(1)	948 (2)	850 (2)	778 (3)	49 (6)
C(2)	1021 (2)	987 (2)	743 (3)	54 (6)
C(3)	1097 (2)	876 (2)	697 (3)	64 (7)
C(4)	860 (2)	791 (2)	823 (3)	59 (7)
C(5)	862 (2)	711 (2)	855 (3)	75 (8)
C(6)	767 (2)	653 (2)	887 (3)	83 (8)
C(7)	680 (3)	676 (2)	886 (4)	95 (9)
C(8)	681 (3)	759 (2)	864 (4)	91 (9)
C(9)	1017 (2)	1079 (2)	736 (3)	66 (7)
C(10)	1101 (2)	1142 (2)	708 (3)	75 (8)
C(11)	1091 (3)	1232 (2)	706 (4)	90 (9)
C(12)	999 (2)	1243 (2)	736 (4)	87 (9)
C(13)	920 (2)	1177 (2)	766 (3)	89 (8)
C(14)	1178 (2)	843 (2)	634 (3)	58 (7)
C(15)	1273 (2)	912 (2)	621 (3)	73 (8)
C(16)	1344 (2)	873 (2)	561 (4)	88 (9)
C(17)	1317 (3)	771 (2)	506 (4)	90 (9)
C(18)	1224 (2)	709 (2)	525 (3)	80 (8)
C(19)	1081 (2)	568 (2)	828 (4)	79 (8)
C(20)	1153 (3)	566 (3)	971 (4)	90 (9)
C(21)	624 (3)	794 (3)	454 (5)	104 (10)
C(22)	558 (4)	712 (4)	280 (6)	141 (15)
C(23)	773 (3)	548 (2)	465 (4)	81 (8)
C(24)	649 (4)	474 (4)	398 (6)	119 (12)
C(25)	666 (3)	1064 (2)	887 (5)	103 (10)
C(26)	603 (4)	1126 (3)	951 (6)	123 (14)
N(1)	944 (2)	934 (1)	784 (2)	64 (5)
N(2)	1102 (2)	963 (1)	700 (2)	57 (5)
N(3)	1018 (2)	818 (1)	740 (2)	53 (5)
N(4)	772 (2)	817 (2)	833 (3)	79 (6)
N(5)	927 (2)	1091 (2)	761 (3)	80 (7)
N(6)	1154 (2)	744 (2)	588 (3)	72 (6)
O(1)	1080 (2)	646 (2)	846 (2)	97 (6)
O(2)	1028 (2)	483 (2)	705 (3)	129 (8)
O(3)	723 (2)	853 (2)	481 (3)	129 (8)
O(4)	577 (2)	794 (2)	551 (3)	136 (8)
O(5)	837 (2)	521 (1)	521 (2)	89 (6)
O(6)	796 (2)	624 (2)	446 (2)	100 (6)
O(7)	719 (2)	1044 (2)	968 (3)	100 (6)
O(8)	651 (2)	1046 (2)	748 (4)	146 (9)
F(1)	1099 (2)	483 (1)	991 (3)	158 (16)†
F(2)	1244 (2)	563 (2)	954 (3)	182 (18)†
F(3)	1180 (2)	642 (1)	1111 (2)	150 (15)†
F(4)	461 (2)	649 (3)	251 (4)	306 (33)†
F(5)	551 (3)	746 (3)	174 (4)	177 (20)†
F(6)	608 (2)	655 (2)	212 (3)	185 (21)†
F(7)	617 (2)	437 (3)	481 (5)	258 (27)†
F(8)	582 (2)	510 (2)	384 (6)	282 (30)†
F(9)	618 (2)	402 (3)	267 (4)	316 (32)†
F(10)	511 (2)	1101 (2)	880 (4)	218 (25)†
F(11)	608 (4)	1135 (4)	1084 (5)	368 (40)†
F(12)	659 (3)	1221 (2)	1002 (7)	334 (36)†

† U_{eq} values where $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36464 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

Symmetry code: (') 2 - x, 1 - y, 1 - z.

Hg(1)—N(3)	2.61 (2)	Hg(1)—N(6)	2.17 (2)
Hg(1)—O(1)	2.35 (2)	Hg(1)—O(2')	2.63 (2)
Hg(1)—O(5)	2.13 (2)	Hg(1)—O(6)	2.86 (2)
N(3)—Hg(1)—N(6)	71.7 (7)	O(5)—Hg(1)—O(1)	98.7 (7)
N(3)—Hg(1)—O(5)	110.4 (6)	N(3)—Hg(1)—O(1)	91.1 (6)
N(6)—Hg(1)—O(5)	159.8 (7)	N(6)—Hg(1)—O(1)	101.4 (7)
Hg(2)—N(4)	2.44 (2)	Hg(2)—N(1)	2.40 (2)
Hg(2)—N(5)	2.50 (2)	Hg(2)—O(3)	2.37 (2)
Hg(2)—O(4)	2.63 (2)	Hg(2)—O(7)	2.37 (2)
Hg(2)—O(8)	2.60 (3)		
N(4)—Hg(2)—N(5)	131.1 (7)	O(3)—Hg(2)—O(7)	145.5 (8)
O(3)—Hg(2)—N(4)	97.5 (8)	O(3)—Hg(2)—N(5)	88.3 (8)
O(7)—Hg(2)—N(4)	100.8 (7)	O(7)—Hg(2)—N(5)	100.9 (7)
Mean bond distances			
C—N	1.36	C—C(inter-ring)	1.49
C—C(ring)	1.40	C—C(trifluoroacetate)	1.53
C—O	1.22	C—F	1.26

Table 3. Distances of atoms (Å × 10²) from the least-squares plane defined by C(1)N(1)C(2)N(2)C(3)N(3) (triazine ring)

Equation of plane (relative to crystal axes)

$$3.798x - 0.228y + 7.058z = 8.897$$

C(1)	0 (1)	C(7)	-21 (1)	C(14)	-14 (1)
N(1)	0 (1)	C(8)	-39 (1)	C(15)	12 (1)
C(2)	0 (1)	N(4)	-27 (1)	C(16)	-4 (1)
N(2)	1 (1)	C(9)	-9 (1)	C(17)	-49 (1)
C(3)	-1 (1)	C(10)	2 (1)	C(18)	-71 (1)
N(3)	-1 (1)	C(11)	-6 (1)	N(6)	-54 (1)
C(4)	-1 (1)	C(12)	-20 (1)	Hg(1)	-101 (1)
C(5)	25 (1)	C(13)	-27 (1)	Hg(2)	-80 (1)
C(6)	12 (1)	N(5)	-2 (1)		

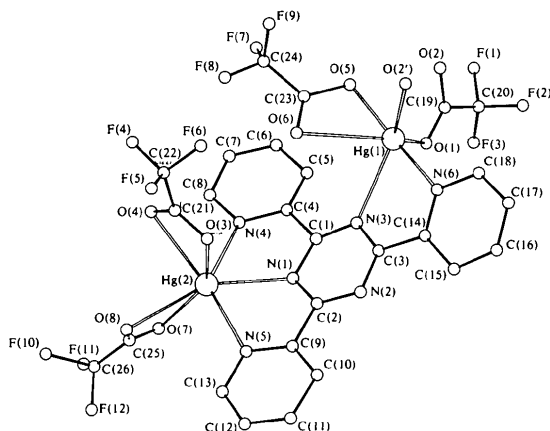


Fig. 1. The structure of the complex. Mercury atom Hg(1') (not shown) of a centrosymmetrically related complex molecule is weakly linked via O(1')—C(19')—O(2') and O(2)—C(19)—O(1) to Hg(1), where (') denotes (2 - x, 1 - y, 1 - z).

(Table 3). Each of the four rings is planar to within the limits of error. The axes of the pyridyl groups defined by the vectors C(4)—C(7), C(9)—C(12) and C(14)—C(17) are inclined respectively at angles of 4.0 (1.0), 2.4 (1.0) and 7.3 (1.0)° to the triazine ring to give a 'dish' shape. In addition there is rotation about these axes such that the pyridyl groups are inclined at 13.0 (1.0), 5.9 (1.0) and 17.6 (1.0)° respectively with respect to the triazine ring. The direction of these rotations is to move C(5) and its attached H atom away from Hg(1) which can thus effectively coordinate to N(3) as well as N(6). The original prediction (Durham, Frost & Hart, 1969) that tpt would not act as a bidentate and tridentate ligand simultaneously rested on the assumption that the molecule remained essentially planar.

Only two crystal structures involving a metal atom complexed to a tpt molecule have been reported (Barclay, Vagg & Watton, 1969, 1977, 1978). The Ni in triaqua[2,6-di(2-pyridyl)-4-(2-pyridinio)-1,3,5-triazine]nickel(II) bromide monohydrate is coordinated only at the tridentate site. In aquatetrachloro[2,4,6-tri(2-pyridyl)-1,3,5-triazine]dicobalt(II) monohydrate, two sites in the markedly non-planar ligand are occupied by Co atoms, the tridentate site being fully utilized in a symmetrical manner, but the Co—N distances in the bidentate site are so unsymmetrical, 1.99 and 2.75 Å, that only one bond is effectively formed. By comparison, in the present compound the bidentate site is more effectively coordinated, with the Hg—N distances closer in value.

Hg—O bonds complete the overall coordination of Hg(1) (sixfold) and Hg(2) (sevenfold). Each trifluoroacetate group forms two quite unequal Hg—O bonds; in all cases the shorter of the two falls within the range of covalent bonding. For one trifluoroacetate group, the longer bond, Hg(1)—O(2'), is towards a centrosymmetrically related molecule. Although three of the four trifluoroacetate groups behave as bidentate ligands towards Hg, the longer bond of each pair may be regarded as 'following' the shorter covalent bond.

The two shortest bonds to each Hg subtend the largest angle; this feature is common to many high-coordination Hg compounds and reflects the tendency for Hg to form two linear covalent bonds. The linearity is distorted when further bonds form unsymmetrically around the equatorial plane. The three principal bonds to Hg(1), *i.e.* those to O(5), N(6) and O(1), are very similar in distance and orientation to the three shortest bonds in tris(pyridine)mercury(II) trifluoroacetate (Halfpenny & Small, 1978). The coordination around Hg(2) is constrained by the rigidity of the tridentate ligand. Hg(2)—O(3) is approximately perpendicular [76 (1)°] to the plane through Hg(2)N(4)N(1)N(5) whereas Hg(2)—O(7) makes an angle of 139 (1)° with that plane such that O(7)—Hg(2)—O(3) deviates by almost 35° from linearity.

The U_{ij} values of all the F atoms are large; attention has already been drawn (Halfpenny & Small, 1981) to this feature which prevails in all mercury(II) trifluoroacetate structures investigated. In this structure the nearest intermolecular contacts of the F atoms are to other F atoms; all separations are in excess of the van der Waals values.

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Structure of the Adduct of Dimethyl Sulfoxide and 9-Methyladenine with Cadmium Chloride [*catena-Di-μ-chloro-(dimethyl sulfoxide)(9-methyladenine)cadmium(II)*]

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Abstract. C₈H₁₃CdCl₂N₅OS, $M_r = 410.4$, triclinic, $P\bar{1}$, $Z = 2$, $a = 6.955$ (3), $b = 8.774$ (3), $c = 11.937$ (6) Å, $\alpha = 97.69$ (3), $\beta = 102.52$ (3), $\gamma = 86.69$ (3)°, $V = 704$ (1) Å³, $D_x = 1.95$, $D_m = 1.99$ (3) g cm⁻³, $\lambda = 0.71073$ Å. Final $R = 0.031$ for 5526 non-zero reflections. The structure consists of approximately octahedrally coordinated Cd²⁺ species interconnected by chlorine bridges to form a one-dimensional polymer. The coordination polyhedron of the metal atom is made up of four Cl atoms, one O atom from dimethyl sulfoxide and an N atom, N(7), from the purine ring. The bonded distances are: Cd–Cl 2.611–2.653 (1); Cd–O 2.291 (2); Cd–N 2.357 (2) Å.

Introduction. ¹¹³Cd NMR spectroscopy with a demonstrated chemical shift range of ~850 p.p.m. has been shown in recent years to offer potential as a sensitive probe of metal-ion sites in a variety of compounds, including proteins and enzymes (Rodesiler, Griffith, Ellis & Amma, 1980, and references therein). It is not clear whether Cd has a specific site preference in nucleotides thereby imposing a limit to its application as a probe of polynucleotides. For example, in purine nucleotides crystal-structure evidence indicates that

Cd²⁺ binds to phosphate oxygen as well as purine bases to give a complicated three-dimensional structure (Goodgame, Jeeves, Reynolds & Skapski, 1975*a*; Clark & Orbell, 1975; Goodgame, Jeeves, Reynolds & Skapski, 1975*b*; Purnell, Estes & Hodgson, 1976). The Cd²⁺ interaction with nucleic acid bases and nucleotides has been reviewed along with the interactions of other metal ions (Hodgson, 1977; Marzilli, 1977; Lippard, 1978; Marzilli & Kistenmacher, 1977; Gellert & Bau, 1979; Martin & Miriam, 1979; Swaminathan & Sundaralingam, 1979; Pezzano & Podo, 1980). We have demonstrated that a relatively simple complex can be formed from 6-mercaptapurine and CdCl₂; Griffith & Amma (1979) have determined its crystal structure and observed its ¹¹³Cd NMR at 554 p.p.m. deshielded from the Cd(ClO₄)₂-water standard. The present compound is another compound in this series. Unfortunately, it has very low solubility in NMR solvents and the ¹¹³Cd NMR will have to be measured on solid samples. We report on the crystal structure at this time, and the structure-¹¹³Cd NMR correlation will be reported later.

To prepare the title compound, 0.03 g (0.002 mol) of 9-methyladenine (Cyclo Chemical) was dissolved in 30 ml of 1 *M* HCl and added to 0.43 g (0.002 mol) of CdCl₂·2½ H₂O (Baker & Adamson) dissolved in 20 ml

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