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## Structure of *mer*-Trichlorotris(*N*-methylimidazole)thallium(III)

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**Abstract.** [TlCl<sub>3</sub>(C<sub>4</sub>H<sub>6</sub>N<sub>2</sub>)<sub>3</sub>], *M<sub>r</sub>* = 557.05, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 7.428 (6), *b* = 8.748 (2), *c* = 28.588 (4) Å, β = 93.28 (4)°, *V* = 1854.5 (3) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.995 g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71073 Å, μ = 92.391 cm<sup>-1</sup>, *F*(000) = 1056, *T* = 293 K, *R* = 0.031 for 2108 observed reflections. The structure consists of discrete units of [TlCl<sub>3</sub>(C<sub>4</sub>H<sub>6</sub>N<sub>2</sub>)<sub>3</sub>]. The Tl atom is surrounded by three Cl ions and three N atoms in a *mer*-distorted octahedral geometry.

**Introduction.** Thallium trihalide complexes with stoichiometry TlX<sub>3</sub>.*L* or TlX<sub>3</sub>.2*L* are generally well known, being monomeric or polymeric species, where the coordination around the Tl atom is distorted trigonal bipyramidal with halogen atoms occupying equatorial positions and the donor atom of the ligand molecules in axial positions (Jeffs, Small & Worrall, 1984*a*; Bermejo, Castiñeiras, Gayoso, Hiller, Englert & Strähle, 1984; Bermejo, Castiñeiras, García-Vázquez, Hiller & Strähle, 1991; Hiller, García-Fernández, Bermejo & Castaño, 1986; Hiller, Castiñeiras, Bermejo, García-Fernández, Bravo & Sánchez, 1988). However, there are only a few examples of the stoichiometry of TlX<sub>3</sub>.3*L*, which are six-coordinate thallium(III) halide complexes, rather than five-coordinate, with an additional ligand solvate molecule (Jeffs, Small & Worrall, 1984*b,c*).

Continuing our studies on the coordination of thallium(III) halides and mixed halides, this paper gives the results of the structural investigations of TlCl<sub>3</sub>(C<sub>4</sub>H<sub>6</sub>N<sub>2</sub>)<sub>3</sub>, a new octahedral complex.

**Experimental.** Crystals of the title compound were obtained by slow cooling of a solution of TlCl<sub>3</sub>(C<sub>4</sub>H<sub>6</sub>N<sub>2</sub>)<sub>3</sub> in methyl cyanide. Enraf-Nonius CAD-4 four-circle single-crystal automatic diffractometer, Mo *K*α graphite-monochromated radiation, ω/θ scan method. Plate-like colourless crystal used, 0.04 × 0.12 × 0.52 mm. Accurate cell dimensions from least-squares procedure on 25 reflections (8 < θ < 12°). Empirical absorption correction applied (*DIFABS*; Walker & Stuart, 1983); max./min. and average absorption correction 1.280, 0.796 and 1.003, respectively. 3366 reflections (3 < θ < 24°) measured, 0 < *h* < 8, 0 < *k* < 9 and -32 < *l* < 32, 2848 reflections were unique, *R*<sub>int</sub> = 0.023, and 2108 reflections with *I* > 3σ(*I*). Intensities of three reference reflections (101̄4, 325̄, 318̄), measured every 3600 s of X-ray exposure time showed no significant variation. Structure solved from interpretation of Patterson map (*SHELXS86*; Sheldrick, 1986), full-matrix least-squares refinement of 200 parameters based on *F* (*SDP*; Frenz, 1978). Anisotropic thermal parameters applied to all non-H atoms; H-atom positions not calculated. At convergence *R* = 0.031, *wR* = 0.036, *w* = 1/σ<sup>2</sup>(*F*), *S* = 0.110, (Δ/σ)<sub>max</sub> = 0.01,

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Table 1. *Positional and equivalent isotropic thermal parameters* ( $\text{\AA}^2$ )

$U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	$U_{eq}$
Tl	0.22685 (5)	0.17970 (4)	0.37759 (1)	0.0313 (2)
Cl(1)	0.3998 (4)	0.4244 (3)	0.3811 (1)	0.054 (2)
Cl(2)	-0.0395 (3)	0.2939 (3)	0.32754 (9)	0.042 (1)
Cl(3)	0.4740 (4)	0.0401 (4)	0.4255 (1)	0.057 (2)
N(1)	0.355 (1)	0.103 (1)	0.3089 (3)	0.040 (5)
N(2)	0.074 (1)	-0.0538 (9)	0.3705 (3)	0.038 (4)
N(3)	0.067 (1)	0.227 (1)	0.4427 (3)	0.044 (5)
N(11)	0.565 (1)	0.032 (1)	0.2634 (3)	0.042 (5)
N(21)	-0.138 (1)	-0.221 (1)	0.3674 (4)	0.055 (6)
N(31)	-0.149 (1)	0.294 (1)	0.4876 (3)	0.059 (6)
C(1)	0.747 (2)	0.11 (2)	0.2452 (5)	0.087 (8)
C(2)	-0.322 (2)	-0.289 (2)	0.3681 (8)	0.12 (1)
C(3)	-0.324 (2)	0.351 (2)	0.5031 (5)	0.089 (8)
C(11)	0.530 (1)	0.104 (1)	0.3032 (4)	0.041 (6)
C(12)	0.402 (2)	-0.013 (1)	0.2416 (4)	0.052 (7)
C(13)	0.275 (1)	0.026 (2)	0.2703 (4)	0.052 (6)
C(21)	-0.102 (1)	-0.074 (1)	0.3750 (4)	0.044 (6)
C(22)	0.013 (2)	-0.301 (1)	0.3580 (5)	0.060 (7)
C(23)	0.148 (2)	-0.194 (1)	0.3614 (4)	0.052 (7)
C(31)	-0.096 (2)	0.289 (1)	0.4430 (4)	0.055 (7)
C(32)	-0.011 (2)	0.235 (2)	0.5154 (5)	0.11 (1)
C(33)	0.124 (2)	0.193 (2)	0.4877 (5)	0.094 (9)

Table 2. *Selected distances* ( $\text{\AA}$ ) *and angles* ( $^\circ$ ) *with e.s.d.'s*

Tl—Cl(1)	2.495 (3)	Tl—N(1)	2.329 (8)
Tl—Cl(2)	2.576 (3)	Tl—N(2)	2.340 (8)
Tl—Cl(3)	2.540 (4)	Tl—N(3)	2.303 (9)
Cl(1)—Tl—Cl(2)	93.84 (9)	Cl(1)—Tl—Cl(3)	92.1 (2)
Cl(1)—Tl—N(1)	92.7 (2)	Cl(1)—Tl—N(2)	176.6 (2)
Cl(1)—Tl—N(3)	96.0 (2)	Cl(2)—Tl—Cl(3)	174.0 (1)
Cl(2)—Tl—N(1)	89.0 (3)	Cl(2)—Tl—N(2)	86.4 (3)
Cl(2)—Tl—N(3)	87.9 (2)	Cl(3)—Tl—N(1)	89.9 (2)
Cl(3)—Tl—N(2)	87.7 (2)	Cl(3)—Tl—N(3)	92.4 (2)
N(1)—Tl—N(2)	83.9 (4)	N(1)—Tl—N(3)	171.0 (4)
N(2)—Tl—N(3)	87.4 (3)		

$\Delta\rho_{max} = 0.940 \text{ e \AA}^{-3}$ . Secondary-extinction coefficient  $2.8438 (1) \times 10^{-8}$  (Zachariasen, 1963). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2A). All calculations on MicroVAX II computer. Atomic parameters are given in Table 1,\* interatomic distances and bond angles in Table 2, the numbering scheme used is shown in Fig. 1 and a stereoview of the molecule in Fig. 2.

**Discussion.** In the crystal structure, the asymmetric unit contains discrete distorted octahedral molecules of  $\text{TlCl}_3(\text{C}_4\text{H}_6\text{N}_2)_3$  with *mer* geometry (Fig. 1) and is similar to that found in  $\text{TlCl}_3(\text{C}_5\text{H}_5\text{N})_3 \cdot \text{C}_5\text{H}_5\text{N}$  (Jeffs, Small & Worrall, 1984b) or in  $\text{TlBr}_3(\text{C}_5\text{H}_5\text{N})_3$  (Jeffs,

\* Lists of structure factors, anisotropic thermal parameters, full bond lengths and angles, torsion angles and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53869 (37 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Small & Worrall, 1984c). The main angular distortion is observed in the *trans* bond angle N(1)—Tl—N(3) of  $171.0 (4)^\circ$ , and consequently in the *cis* bond angles N(1)—Tl—N(2) and Cl(1)—Tl—N(3) of  $83.9 (4)$  and  $96.0 (2)^\circ$ , respectively. This distortion is greater than in the octahedral pyridine complex of  $\text{TlCl}_3$  (Jeffs, Small & Worrall, 1984b) [N(2)—Tl—N(2'),  $174.4 (3)^\circ$ ] and in its analogous  $\text{TlBr}_3$  complex (Jeffs, Small & Worrall, 1984c) [N(1)—Tl—N(2),  $173.0 (4)^\circ$ ], although in the latter the Br(1)—Tl—Br(2) bond angle of  $170.5 (1)^\circ$  is smaller than the respective Cl(2)—Tl—Cl(3) angle of  $174.0 (1)^\circ$  in the title compound.

The three Tl—Cl distances are significantly different and the Tl—Cl(1) bond distance *trans* to the ligand molecule of  $2.495 (3) \text{ \AA}$  is considerably smaller than the other Tl—Cl distances [ $2.576 (3)$ ,  $2.540 (4) \text{ \AA}$ ]. Furthermore, the Tl—Cl(2) bond length of  $2.576 (3) \text{ \AA}$  is longer than the  $2.48\text{--}2.54 \text{ \AA}$  observed in other six-coordinate thallium(III) compounds (Lee, 1971). The Tl—N distances of  $2.30\text{--}2.35 \text{ \AA}$  are smaller than those found in  $\text{TlCl}_3(\text{py})_3$  [ $2.38 (1)\text{--}2.48 (1) \text{ \AA}$ ] or in  $\text{TlBr}_3(\text{py})_3$  [ $2.43 (1)\text{--}2.51 (1) \text{ \AA}$ ] (Jeffs, Small & Worrall, 1984b,c) and this may be attributed to greater metal—ligand bond strengths in the title compound. The methylimidazole ligands are planar and their positions in the

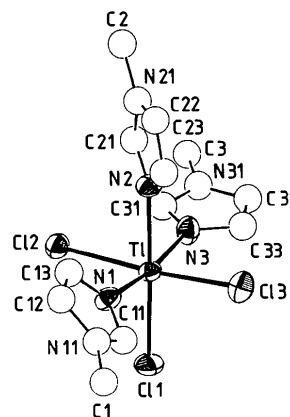


Fig. 1. Plot of the molecule showing the numbering scheme.

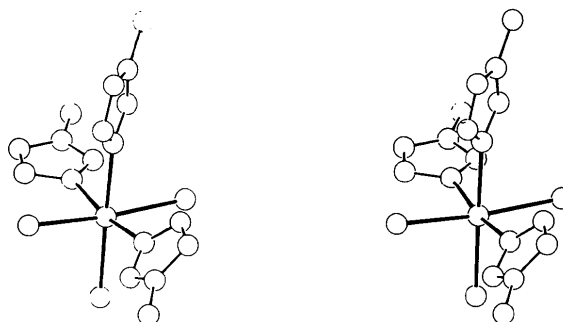


Fig. 2. Stereoscopic view.

molecule with respect to the Ti–Cl and Ti–N directions are different in the three rings (Fig. 2). The 1- and 2-methylimidazole ligands [rings containing atoms N(1) and N(2), respectively] are bisectors with angles of approximately 45°, while the third molecule is parallel [6(2)°]. The dihedral angle between the *trans* methylimidazole ligands is 135.9(5)° which differs from that in  $\text{TiCl}_3(\text{C}_5\text{H}_5\text{N})_3 \cdot \text{C}_5\text{H}_5\text{N}$ , where the planes of the *trans* pyridines are at 90° (Jeffs, Small & Worrall, 1984b), although this comparison is not ideal since the methyl group bonded to the imidazole ring, in the packing of the unit cell, may have a different effect to the additional solvate molecule in the pyridine complex.

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## Transition Metal Complexes with Hydrazides and Hydrazones. IV. Structure of *trans*-Diammine[2,3-butanedione bis(4-methoxybenzoylhydrazone)]cobalt(III) Nitrate Monohydrate

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**Abstract.**  $[\text{Co}(\text{C}_{20}\text{H}_{20}\text{N}_4\text{O}_4)(\text{NH}_3)_2]\text{NO}_3 \cdot \text{H}_2\text{O}$ ,  $M_r = 553.42$ , monoclinic,  $P2_1/n$ ,  $a = 15.820(2)$ ,  $b = 10.156(1)$ ,  $c = 17.127(1)$  Å,  $\beta = 117.41(1)^\circ$ ,  $V = 2442.8$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.504$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo K}\alpha) = 0.71073$  Å,  $\mu = 0.76$  mm<sup>-1</sup>,  $F(000) = 1152$ ,  $T = 293$  K, final  $R = 0.069$  for 2179 reflections with  $I > 2\sigma(I)$ . The coordination of the Co atom is distorted octahedral with *trans*-NH<sub>3</sub> groups. The quadri-dentate *N,N,O,O* ligand is equatorially disposed, forming three five-membered coplanar chelate rings. The O atoms of the NO<sub>3</sub> anion are disordered.

**Introduction.** Recent studies of hydrazones and their metal complexes are not only of theoretical but also

of practical importance. A great number of these compounds have found wide application in medicine, technology, analytical chemistry, etc. (Kitaev, 1977; Katyal & Dutt, 1975). The complexes with mono- and bishydrazones of diketones, such as diacetylhydrazones and acetylacetone hydrazones (Harrison & Nicholls, 1984; Khulbe, Kumar, Bhoon & Singh, 1984; James, McCleverty, McKenzie & Moore, 1985; Krimova, Ivanov & Ostankevich, 1986; Abu-El-Wafa, Gaber, Issa & Ismail, 1989) form a special class of compounds. In our previous work we described the structure of the square-planar Cu<sup>II</sup> complex with acetylacetone 1-naphthoylhydrazone (Fazlić, Divjaković, Leovac & Chundak, 1991).