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Crystal Structure of Pyridinium Pentachloro(Dimethylsulfoxide)thallate(III)

BRUCE D. JAMES*, MARY B. MILLIKAN and MAUREEN F. MACKAY

Department of Chemistry, La Trobe University, Bundoora, Vic. 3083, Australia

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Whilst thallium(III) is well known in the tetrahedral $TlCl_4^-$ ion, it is rather less familiar in $TlCl_5^{2-}$. The latter ion seems to be a fairly flexible entity, apparently being trigonal bipyramidal in (DMTEA)-$TlCl_5$ (where DMTEA = dimethyl quaternary ammonium ion of diazabicyclo [2,2,2]-octane) and square pyramidal in $[(C_2H_5)_4N]_2TlCl_5$ [1]. Since there have not been any reports of reactions performed with $TlCl_5^{2-}$, we explored the reaction with dimethylsulfoxide as part of our investigations into the pyridinium salt. In view of the relatively small formation constant for the $TlCl_5^{2-}$ ion [2], it was of interest to ascertain whether the coordination number around thallium had increased or, alternatively, whether a chloride ligand had been displaced to yield a double salt (or adduct) involving $TlCl_4^-$. In fact, a 1:1 adduct of formula $(C_5H_6N)_2TlCl_5 \cdot (CH_3)_2SO$ was obtained [3]. Here we report the crystal structure of this compound.

Experimental

The compound $(C_5H_6N)_2TlCl_5 \cdot (CH_3)_2SO$ was prepared by adding dimethylsulfoxide (8 cm^3) to an ethanol solution of $(C_5H_6N)_2TlCl_5$ (2.96 g) in a nitrogen-filled glovebox. The oily yellow layer which separated was collected and evaporated in an air stream until the white solid (mp 88C) crystallized out. *Anal.* Calcd. for $C_{12}H_{18}Cl_5N_2OSTl$: C, 23.25; H, 2.93; Cl, 28.59; O, 2.58; S, 5.17%. Found: C, 22.90; H, 2.92; Cl, 28.90; O, 3.9; S, 5.5%. (Australian Microanalytical Service, Division of AMDEL, Melbourne).

Although the compound was not moisture-sensitive, crystals were sealed in Lindemann glass capillaries for the X-ray analysis since they appeared to decompose in the X-ray beam when left in the air. Crystals are orthorhombic, space group *Pnma* (from systematic extinctions) with a = 17.793(1), b = 15.009(1), c = 7.420(1) Å; U = 1981.6(2) Å. The unit cell contains four $(C_5H_6N)_2TlCl_5 \cdot (CH_3)_2SO$ units; M = 620.0, D_m = 2.09, D_c = 2.078 g cm^{-3}, F(000) = 1176; μ(Cu Kα) = 216.2 cm^{-1}. Intensity data were measured at 290 K on a Rigaku-AFC diffractometer (graphite crystal monochromator) from a crystal of approximate dimensions 0.28 × 0.28 × 0.14 mm. The data were recorded by an ω–2θ scan with a scan rate 2° min^{-1} and 10 sec stationary background counts. Of the 1634 unique intensities measured to a 2θ maximum of 130°, the 1423 for which $|F_o| > 3\sigma|F_o|$ were used in the refinement. The intensities were corrected for Lorentz and polarization factors and for absorption. Neutral atom scattering factors were used [4] and anomalous-dispersion corrections were made with the values of Cromer and Liberman [5]. The sites of the Tl and Cl atoms were derived from the vector map and by direct methods, and the C, N, O and S atom sites were located on the subsequent difference map. Refinement with anisotropic temperature factors given to the atoms converged at R = 0.070 and R_w = 0.073. The function minimized in the least-squares refinement was $(\Sigma w|F_o| - |F_c|)^2$ with $w = \sigma^2|F_o| + 2 \times 10^{-4}|F_o|^2$, and the mean shift-to-error ratio at convergence was 0.005:1. Final atomic coordinates are given in Table I. The major calculations were carried out with the SHELX-76 program [6] while the Figures were obtained with the ORTEP program [7].

TABLE I. Atomic Fractional Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors.

	X/a	Y/b	Z/c	B_{eq}(Å^2)
Tl	1207(1)	2500	1326(1)	2.79(4)
Cl(1)	1101(3)	836(3)	1217(7)	3.6(2)
Cl(2)	300(4)	2500	4021(8)	3.8(3)
Cl(3)	2056(3)	2500	−1436(9)	3.3(3)
Cl(4)	2367(3)	2500	3535(9)	3.4(3)
S(1)	−623(4)	2500	−339(8)	3.2(3)
O(1)	190(10)	2500	−841(25)	4.4(10)
C(1)	−947(16)	1632(17)	−1686(54)	7.3(17)
C(2)	2061(12)	253(17)	5278(36)	5.4(12)
C(3)	1873(15)	−628(17)	5609(36)	5.6(13)
C(4)	1222(16)	−850(14)	6391(33)	5.2(10)
C(5)	699(14)	−186(22)	6861(32)	5.8(13)
C(6)	910(15)	696(19)	6587(32)	5.6(12)
N(1)	1564(12)	881(12)	5806(24)	4.8(9)

Results and Discussion

The structure consists of discrete pentachloro-(dimethylsulfoxide)thallate(III) anions and pyridinium cations as illustrated in Fig. 2. The complex anions have site symmetry m and the geometry about the Tl atom is distorted octahedral (see Table II and Fig. 1) with atoms Tl, Cl(2), Cl(3), Cl(4), O(1), S(1) lying on the crystallographic mirror plane. The Tl–Cl

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*Author to whom all correspondence should be addressed.

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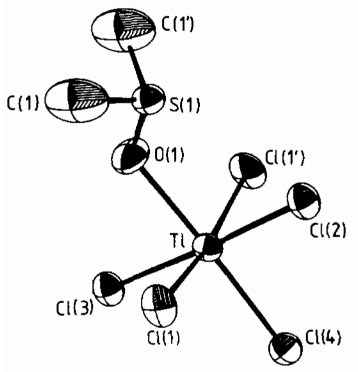

Fig. 1. The $[TlCl_5\cdot(CH_3)_2SO]^{2-}$ ion with thermal ellipsoids scaled to 40% probability.

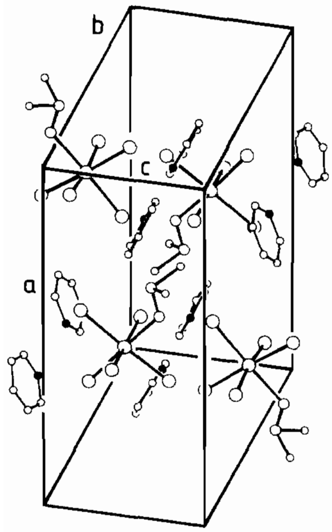

Fig. 2. The crystal packing.

TABLE II. Distances (Å) and Angles (°) in the $TlCl_5\cdot(CH_3)_2SO$ anion.

Tl–Cl(1)	2.506(6)	Cl(1)–Tl–Cl(1')	170.6(1)
Tl–Cl(2)	2.570(7)	Cl(1)–Tl–Cl(2)	88.7(1)
Tl–Cl(3)	2.546(6)	Cl(1)–Tl–Cl(3)	91.1(1)
Tl–Cl(4)	2.636(6)	Cl(1)–Tl–Cl(4)	94.5(1)
Tl–O(1)	2.42(2)	Cl(1)–Tl–O(1)	85.5(5)
O(1)–S(1)	1.49(2)	Cl(2)–Tl–Cl(3)	177.5(2)
S(1)–C(1)	1.74(3)	Cl(2)–Tl–Cl(4)	90.4(2)
Cl(1)····Cl(2)	3.549(8)	Cl(2)–Tl–O(1)	92.7(5)
Cl(1)····Cl(3)	3.605(7)	Cl(3)–Tl–Cl(4)	92.1(2)
Cl(1)····Cl(4)	3.778(7)	Cl(3)–Tl–O(1)	84.8(5)
Cl(2)····Cl(4)	3.695(8)	Cl(4)–Tl–O(1)	176.8(5)
Cl(3)····Cl(4)	3.730(7)	Tl–O(1)–S(1)	124(1)
Cl(1)····O(1)	3.35(1)	O(1)–S(1)–C(1)	100(1)
Cl(2)····O(1)	3.61(2)	C(1)–S(1)–C(1')	97(1)
Cl(3)····O(1)	3.35(1)	C–N–C	124(2)
C–C(mean)	1.38(4)	C–N–C–C(mean)	119(2)
C–N(mean)	1.34(3)		

bond lengths range in value from 2.506(6) to 2.636(6) Å and the intramolecular Cl·····Cl distances range from 3.549(8) to 3.778(7) Å. While the value 2.593(3) Å found for the Tl–Cl bond and the values 3.637(4) and 3.723(3) Å found for the Cl·····Cl distances in $Na_3TlCl_6\cdot 12H_2O$ [8] lie within the ranges quoted above, the smaller values 2.48 and 3.48, 3.54 Å were reported for the comparable lengths in an earlier determination of $[Co(NH_3)_6]\cdot TlCl_6$ [9].

Coordination of the sulfoxide ligand through the oxygen atom confirms the infrared data which showed a γ(CSO) vibration at 332 cm^{-1} (*cf.* 334 cm^{-1} in $TlCl_3\cdot 2DMSO$ [10]). The γ(CSO) vibration occurring in the 375–385 cm^{-1} region was shown recently to be diagnostic of S-coordinated DMSO, while O-coordination was indicated when this mode occurs in the 300–350 cm^{-1} range [11]. The complex ion is thus rather similar to $[TlCl_5\cdot H_2O]^{2-}$ although the Tl–O distance of 2.42(2) Å in the sulfoxide complex is significantly longer than the Tl–OH_2 distance (2.19 Å) observed in $Cs_2TlCl_5\cdot H_2O$ [12]. Also, whilst three Cl·····O contacts of 3.35(1) Å are similar to the mean value of 3.33 Å observed in $Cs_2TlCl_5\cdot H_2O$, the Cl(2)····O(1) distance of 3.61(2) Å is significantly longer.

The crystal packing is illustrated in Fig. 2. Each pyridinium ion makes a short contact with two complex anions. The distances N(1)·····Cl(3), [*x*, *y*, 1 + *z*] 3.30(2) Å and N(1)····Cl(4) [*x*, *y*, *z*] 3.28(2) Å are slightly longer than the sum of their van der Waals radii (3.2 Å) and so not close enough for hydrogen bonding (*cf.* N····Cl distances of 2.98(3) Å in the compounds $(C_5H_6N)_2FeCl_5\cdot\frac{1}{2}C_5H_6NCl$ [13] and 2.95 Å in C_5H_6NCl [14] where hydrogen bonding is present). There are no other N····Cl approaches less than 3.50 Å. This result is again in accordance with the infrared spectrum of the compound in which the ν(N–H) band for the pyridinium ion occurs as a relatively sharp feature near 3250 cm^{-1}. In contrast, the corresponding peak in C_5H_6NCl is extremely broad and spans at least the 3200–2400 range [15].

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