# An Unusual Co-ordination of Thallium in the Crystal Structure of Dimethyl-1,10-phenanthrolinethallium Perchlorate

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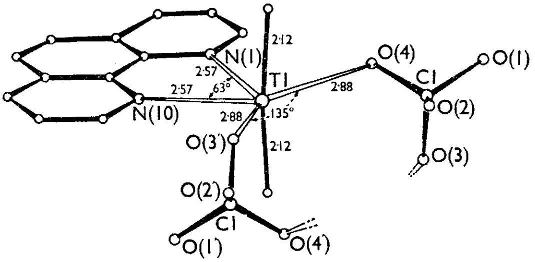
COMPLEXES of the dimethylthallium ion[1] have been known for some time,[2] but their effective co-ordination and thus the geometry of the thallium–dimethyl system have been disputed.[3,4,5] The early crystal structure[3] determination of a $\beta$-diketone adduct with the ion indicated that the co-ordination of thallium is probably tetrahedral, while infrared and Raman data of pyridine and 1,10-phenanthroline complexes[4] suggested that in these cases the thallium dimethyl system is only slightly bent. We report here the crystal structure of dimethyl-1,10-phenanthrolinethallium perchlorate, which has a slightly bent thallium-dimethyl group. The effective co-ordination of six is best described as a distorted pentagonal bipyramid with one equatorial position vacant.

The complex $TlMe_2$1,10-phen,$ClO_4$ crystallises in space group $P2_1/c$ with $a = 7{\cdot}50$, $b = 9{\cdot}11$, $c = 23{\cdot}54$, $\beta = 94{\cdot}4°$, $Z = 4$. The present reliability factor for 1527 photographically observed reflections (Cu-$K_\alpha$ radiation) is 8·8%.

The structure of the complex is shown in the Figure. The average values of the standard deviations for the bond lengths given are 0·03 Å (Tl–C, Tl–O) and 0·027 Å (Tl–N). The plane of the phenanthroline bisects the angle of 168° (e.s.d. = 1·0°) made at the thallium atom by the methyl carbons, which are bent away from the phenanthroline. Two oxygen atoms from perchlorate groups occupy positions in the plane of the phenanthroline and thallium, so that the angle subtended by the oxygen at the thallium atom is 135° (1·0°). There is a non-crystallographic mirror plane containing the thallium and the methyl carbon atoms, and bisecting the phenanthroline. The weakly co-ordinating bidentate perchlorate groups bridge two thallium atoms. This results in a helical structure which has its units related by a two-fold screw axis.

All atoms surrounding thallium at a distance of less than the sum of the van der Waals radii are considered to belong to the thallium co-ordination sphere (after Grdenic).[6] The radius of the thallium[1] in the thallium dimethyl ion is taken as 1·22 Å and values of van der Waals radii are those of Pauling.[7] The effective co-ordination of six consists of two covalent thallium to carbon bonds and four essentially electrostatic bonds between the thallium and the two oxygens and the two nitrogens. The thallium to oxygen distances (2·88 Å) are longer than is expected for an ion–dipole contact between a dimethylthallium ion and a lone pair of a perchlorate oxygen which would be about 2·62 Å. However, the observed thallium to nitrogen distances of 2·57 Å are significantly shorter than 2·72 Å, the sum of the dimethylthallium ion radius and the van der Waals radius of nitrogen. This may be due to a partial covalent character of these bonds.

The angle between the thallium to nitrogen bonds is restricted by the geometry of the phenanthroline group. As a result, the O–Tl–O angle can be much greater than a right angle so that the perchlorate groups can be related by a twofold screw axis. Most probably packing requirements in the crystal determine the direction of the thallium to oxygen vectors. However, it is interesting that the N(1)–Tl–O(4) and N(10)–Tl–O(3′) angles are both 81° (e.s.d. = 0·95°), and that the oxygens, nitrogens, and thallium are so closely coplanar.



A further oxygen, O(2), from a perchlorate group occupies a position between the two co-ordinating oxygens outside the co-ordination sphere (as defined above) at 3·6 Å from the thallium atom.

The observed co-ordination emphasises the difficulty of forming more than two covalent bonds with thallium(III). This may be considered a consequence of the large *s*–*p* separation in this part of the Periodic Table.[8] The distortion of the dimethylthallium system from linearity may be due to repulsion between the electron pairs of the covalent thallium to carbon bonds and the small amount of electron density in the thallium to nitrogen bonds. This departure from linearity of 12° is greater than in any organomercury complex, where the largest distortion of 4° occurs in mercury diethylene oxide.

This complex provides an unusual example of six co-ordination which certainly cannot be described as octahedral.

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