354. *The Stereochemistry of Quadricovalent Atoms : Thallium.*

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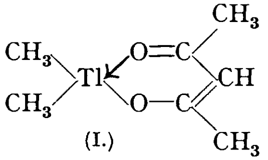
From the small separation of thallium atoms found by *X*-ray analysis of tetrakisthioureathallous nitrate and chloride it is inferred that if, as the chemical evidence indicates, these are typical 4-co-ordinated compounds of the type $[TlR_4]X$, then the four valencies of the thallous atom are coplanar. The data for dimethylthallic acetylacetone, which has also been studied, are less conclusive, but are in agreement with the view that the four valencies of tervalent thallium are distributed tetrahedrally.

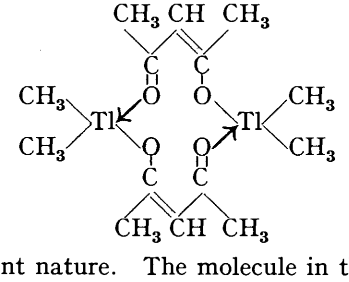
It has recently been shown for several metals that a change of principal valency is accompanied by a change in the configuration of quadricovalent derivatives; for example, in quadricovalent compounds of univalent copper the four bonds to the cuprous atom appear to have a tetrahedral distribution, whereas cupric co-ordination complexes exhibit a planar configuration. So far, no exception has been found to the rule that a tetrahedral valency distribution is shown by a metal atom whenever its effective atomic number in the complex is that of an inert gas, but the converse is not true, and no simple rule appears to be applicable to those cases in which the four metal valencies lie in a plane. (For a summary of previous results, see Cox and Wardlaw, *Science Progress*, 1938, **32**, 463).

This paper records the results from an investigation of some quadricovalent derivatives of thallium in its univalent and its tervalent state. The number of such compounds available is not large, and detailed *X*-ray studies are difficult on account of the high atomic number (81) of the thallium atom. Nevertheless, the present results show that in the thallous compounds studied the four metal valencies are coplanar (or approximately so). Further, as tervalent thallium in its 4-covalent derivatives has an effective atomic number of 86, *i.e.*, that of radon, it would be anticipated that the bond distribution would be tetrahedral, and the experimental results are fully consistent with this view.

The only thallous compounds found suitable for investigation were the thiourea derivatives $[Tl\ 4CS(NH_2)_2]X$ first prepared by Rosenheim and Löwenstamm (*Z. anorg. Chem.*, 1903, **34**, 72); of these, the nitrate and the chloride were examined. In neither case was a complete investigation possible on account of the small size of the crystals obtained, but it was found that in both substances the shortest distance of separation of thallium atoms was 4·2 A. If we assume, in accordance with all the chemical evidence, that in these compounds the typical quadricovalent complex $[Tl\ 4CS(NH_2)_2]^+$ exists, then this short distance of separation of thallium atoms completely excludes the possibility of a tetrahedral disposition of the thiourea groups around the central atom, and shows that the four thallium bonds must be coplanar (or very nearly so). It may be noted that the possibility of the intercalation of an anion between successive thallium atoms to give effectively an octahedral arrangement is also excluded. The effective atomic number of the thallous atom in these planar quadricovalent derivatives is 88, which is the same as that of bivalent lead in its planar co-ordination compounds (Cox, Shorter, and Wardlaw, *Nature*, 1937, **139**, 72).

As a typical quadricovalent thallic compound, dimethylthallic acetylacetone (I) was studied. This compound was first prepared by Menzies, Sidgwick, Cutcliffe, and Fox (J., 1928, 1288), who demonstrated its covalent nature. The molecule in the crystalline state is found to have a two-fold axis of symmetry, which is consistent with either a tetra-


(I.)


(II.)

hedral or a planar configuration (it being assumed that the acetylacetone group has a symmetrical resonance structure); a detailed analysis is not feasible, but considerations of the probable method of packing the molecules into the unit cell suggest that of the two possibilities the tetrahedral configuration is the more likely. A dimeric formulation (II), either planar or tetrahedral, is excluded.

It was thought that by replacing the methyl groups in (I) by the larger phenyl radicals a more favourable substance for distinguishing between the planar and tetrahedral possibilities would be obtained, and diphenylthallic acetylacetone was accordingly prepared, and examined crystallographically. It proved, however, to be much less symmetrical than the methyl derivative, and the results have not contributed to the solution of the problem.

It is interesting to contrast these results with those obtained from investigations on the stereochemistry of gold (see Gibson, Presidential Address to the British Association, Section B, 1938). This element, like thallium, is well known to occur in the univalent and the tervalent state, but whereas in the latter state it readily forms quadricovalent compounds, aurous gold seems unable to attain a higher co-ordination number than two. Moreover, whereas four-covalent auric gold has a planar distribution of valencies, it is in its univalent condition that thallium displays this same configuration. Although experimental data are as yet lacking, it may reasonably be assumed that aurous gold in the four-covalent state would have a tetrahedral configuration, since its effective atomic number would be 86, as is the case for thallium in its quadricovalent thallic derivatives.

Various interesting compounds of thallium are known which are normally formulated as containing the metal in both the univalent and the tervalent state, and which might thus afford the possibility of tetrahedral and planar co-ordination in the same structure, as, *e.g.*, $Tl[Tl(CN)_4]$. Investigations on this and similar substances are now in progress.

EXPERIMENTAL.

Tetrakisthioureathallous Nitrate.—This was prepared according to the method of Rosenheim and Löwenstamm (*loc. cit.*) by mixing hot aqueous solutions of the components in molecular proportions, felted aggregates of fine needles being deposited on cooling [Found: Tl, 36·0; N, 21·6. Calc. for $TlNO_3,4CS(NH_2)_2$: Tl, 35·8; N, 22·1%]. The crystals exhibit straight extinction with moderate birefringence. Single-crystal *X*-ray photographs show that the unit-cell dimension parallel to the direction of elongation is 8·40 A., and the almost complete absence of the odd layer lines in these photographs indicates a very marked pseudo-periodicity of 4·20 A. The other cell dimensions could not be determined owing to the small size of the crystals.

Tetrakisthioureathallous Chloride.—This substance was prepared similarly to the nitrate, and has similar properties, the crystals being even smaller. The periodicity along the needle axis was determined from *X*-ray measurements as 4·2 A., but it is possible that here also the true axis length is 8·4 A.

Dimethylthallic Acetylacetone.—This was prepared by the method of Menzies, Sidgwick, Cutcliffe, and Fox (*loc. cit.*) from thallous acetylacetone and dimethylthallic iodide. The waxy, needle-shaped, flexible crystals had an indistinct m. p. (decomp.) above 205° (Found: Tl, 61·0; C, 24·5; H, 3·2; *M*, micro-cryoscopic in benzene, 302. Calc. for $C_7H_{13}O_2Tl$: Tl, 61·3; C, 25·2; H, 3·9%; *M*, 333). The orthorhombic crystals have high birefringence ($\geqslant 0{\cdot}24$), the maximum refractive index being parallel to the direction of elongation (*b*-axis). From *X*-ray measurements, the dimensions of the unit cell, which contains four molecules, are $a = 14{\cdot}53$, $b = 8{\cdot}45$, and $c = 7{\cdot}87$ A., and the missing reflections are $\{hkl\}$ absent for $h + l$ odd, and $\{0k0\}$ absent for k odd. These are characteristic of the space-group $B22_12$ (Q^5, orthorhombic bisphenoidal), but the crystals do not show an appreciable pyroelectric effect, so the symmetry is possibly higher, *viz.*, C_{2v} or Q_h, although in such a case it would be necessary to regard the $\{0k0\}$ halving as accidental. The reflections from all planes with k odd tend to be weak, indicating a (not very marked) halving of the *b*-axis, which can only be due to the distribution of the thallium atoms at intervals of approximately $\frac{1}{2}b$. This circumstance, and the difficulty of fitting such a molecule into the unit cell in accordance with the symmetry requirements, exclude the possibility of the substance being dimeric in the solid state with the configuration (II). It seems probable that, in accordance with the symmetry of $B22_12$, the thallium atoms and the central carbon atoms of the four chelate groups in the unit cell lie on two-fold axes parallel to

[*a*], the co-ordinates of the Tl being $(x, 0, 0)$, $(\bar{x}, \frac{1}{2}, 0)$, $(\frac{1}{2} + x, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2} - x, \frac{1}{2}, \frac{1}{2})$ with x quite small. In addition, the cell dimensions and optical properties suggest that the carbon chains of the chelate groups are roughly parallel to the *b*-axis. Owing to their small scattering power compared with the remainder of the molecule, it is scarcely possible to determine the position of the methyl groups directly from *X*-ray data, but it seems that the packing together of the molecules in the unit cell is more satisfactory if it is assumed that the methyl groups lie in a plane perpendicular to that of the chelate groups, *i.e.*, if it is supposed that the thallium atoms have a tetrahedral distribution of valencies.

Diphenylthallic Acetylacetone.—This was prepared analogously to the methyl compound, from diphenylthallic bromide and thallous acetylacetone (Found: Tl, 43·8; C, 44·2; H, 3·9. Calc. for $C_{17}H_{17}O_2Tl$: Tl, 44·7; C, 42·9; H, 3·6%). The crystals, which are noticeably harder than those of the methyl derivative, are triclinic symmetric combinations of *a*{100}, {*b*010}, *c*{001} and *q*{0$\bar{1}$1}, tabular on *a*. The dimensions of the unit cell, which contains two molecules, are $a = 10·14$, $b = 8·14$, and $c = 9·50$ A.; $\alpha = 99°52'$, $\beta = 102°16'$, and $\gamma = 80°46'$ [*d* (calc.) = 2·02; *d* (obs.) = 1·98 g./c.c.]. The molecules are asymmetric; the available data give no indication of their orientation in the lattice, and a detailed analysis does not appear to be justified.

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