CONTRIBUTION FROM NATIONAL RESEARCH LABORATORY,
COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH, PRETORIA, REPUBLIC OF SOUTH AFRICA

# The Crystal and Molecular Structures of Thallium Trihalide Complexes. I. Trichloro(1,10-phenanthroline)thallium(III)

BY W. J. BAXTER AND G. GAFNER*

*Received May 10, 1971*

The crystal structure of $TlCl_3$(phen), where phen = 1,10-phenanthroline, has been determined from a three-dimensional single-crystal X-ray study using intensities obtained on a single-crystal diffractometer with Mo K$\alpha$ radiation at room temperature. The triclinic cell, space group $P\bar{1}$ with $a = 9.458 \pm 0.001$ Å, $b = 10.946 \pm 0.002$ Å, $c = 7.638 \pm 0.002$ Å, $\alpha = 97.94 \pm 0.02°$, $\beta = 96.84 \pm 0.02°$, and $\gamma = 115.9 \pm 0.02°$, contains two formula units. The atomic parameters were refined by full-matrix least-squares procedures using anisotropic thermal parameters to a conventional $R = 0.061$. The thallium atom has a distorted octahedral environment in which the basal plane is formed by the two nitrogen atoms of the chelating ligand and two chlorine atoms. The apex positions are occupied by two chlorine atoms. The interatomic distances between two centrosymmetrically-related molecules indicate weak dimer formation.

## Introduction

The compounds of thallium(III) halides with neutral ligands such as dimethyl sulfoxide, triphenylphosphine oxide, pyridine, 2,2′-bipyridyl, and 1,10-phenanthroline are all of the stoichiometric type $TlX_3L_2$, where L represents a unidentate or half of a bidentate ligand and X = Cl or Br. Conductivity[1-3] and molecular weight measurements have been carried out as indicators of the probable structure and stereochemistry of the complexes but have not led to unambiguous conclusions. In the absence of X-ray structure determinations, extensive spectroscopic studies have been made of the complexes of thallium(III) halides.[2,4-6] However, when the ligand is a molecule such as 2,2′-bipyridyl, the structures of the compounds $TlX_3L_2$ remain a matter of speculation. Hudman, *et al.*,[6] favor a polymeric structure as opposed to a dimeric structure for $TlX_3L_2$. The solid-state spectra of $TlX_3L_2$ compounds are difficult to interpret but are similar and imply similar solid-state structures.[5,6]

The available data indicate that the stereochemistries of thallium(III) halide complexes are probably varied, complicated, and certainly incompletely understood at present. It was thus decided to make a detailed study of trichloro(1,10-phenanthroline)thallium(III) using X-ray crystallographic methods.

## Experimental Section

**Preparative.**—$TlCl_3$(phen) where phen = 1,10-phenanthroline was prepared by Cotton's method.[1] Crystals were grown by slow cooling of a hot saturated solution of $TlCl_3$(phen) in methyl cyanide. Colorless needle-shaped crystals were obtained which were of satisfactory quality and gave oblique extinction in polarized light.

**Crystal data** for trichloro(1,10-phenanthroline)thallium are as follows: $a = 9.458$ (1) Å, $b = 10.946$ (2) Å, $c = 7.638$ (2) Å, cell volume 690 Å$^3$, $\alpha = 97.94$ (2)°, $\beta = 96.84$ (2)°, $\gamma = 115.90$ (2)°. [Figures in parentheses here and in Tables I and II are estimated standard deviations and refer to the least-significant digits. The unit cell esd's were obtained from least-squares fitting of $2\theta$ values of 12 high-angle reflections measured on the diffractometer.]

The density was determined by flotation methods, using a mixture of bromoform and xylol, to be 2.39, which agrees satisfactorily with the value of 2.40 g cm$^{-3}$ calculated for 2 mol per unit cell. The space group is $P1$ or $P\bar{1}$ and was assumed to be $P\bar{1}$. This choice was shown to be correct by the successful structural analysis.

Intensity data for the sphere with $\sin\theta/\lambda \leq 0.4822$ were collected on a Hilger and Watts single-crystal diffractometer using Zr-filtered Mo K$\alpha$ radiation. An $\omega$ scan mode was used, counting for a total of 300 sec per reflection. This was done in 50 steps of 0.02° and counting for 6 sec per step. Corrections for background were made by measuring the general background as a function of $\theta$ between two lattice rows and subtracting the scaled values from the measured integrated peak intensities. A total of 4250 reflections were measured; 384 of these were not significantly above the background. Periodic checks on the strong 0, 2, 0 and −1, −4, 2 reflections confirmed that no appreciable crystal decomposition occurred. Lorentz–polarization and absorption corrections were applied for a spherical crystal (as the crystal had been cut to this shape) with radius 0.0075 cm, $\mu R = 0.94$, using the computer program CORRECT by E. G. Boonstra.[7]

The structure was solved by the heavy-atom technique and successive Fourier syntheses. The trial parameters were refined by full-matrix least-squares with the program ORFLS of Busing, Martin, and Levy (1962) on an IBM 360/65 computer. The listing of observed and calculated factors may be found elsewhere.[8] Fractional atomic coordinates and isotropic individual temperature factors (Table I) were refined until the conventional $R$ factor reached 0.135. Anisotropic thermal parameters (Table II) were introduced and refinement with unitary weights was continued until all parameter shifts were less than 0.1 of the estimated standard deviations. At this stage $R = \Sigma|\Delta F|/\Sigma F_o = 0.062$ and the weighted $R_w = \{\Sigma w(\Delta F)^2/\Sigma WF_o^2\}^{1/2} = 0.069$. During further refinement a weighting scheme based on counting statistics[9] was introduced. The reflections were weighted in an inverse proportion to their variance obtained from counting statistics. This yielded $R = 0.066$ and $R_w = 0.061$. The estimated standard deviations were uniformly lower than before and no difference in the calculated bond lengths was observed. The results given here are based on the refinement made using the weighting scheme for all the observed reflections.

## Structure and Discussion

Interatomic distances and bond angles were calculated using the function and error program ORFFE of

---

[1] F. A. Cotton, B. F. G. Johnson, and R. M. Wing, *Inorg. Chem.*, **4**, 502 (1965).

[2] (a) F. Ya Kul'ba, V. E. Mironov, T. Chiny, and Z. Filipova, *Russ. J. Inorg. Chem.*, **8**, 341 (1963); (b) F. Ya. Kul'ba, V. E. Mironov, and O. S. Andreeva, *ibid.*, **8**, 1217 (1963).

[3] R. A. Walton, *Inorg. Chem.*, **7**, 640 (1968).

[4] A. J. Carty, *Coord. Chem. Rev.*, **4**, 29 (1969).

[5] W. R. McWhinnie, *J. Chem. Soc. A*, **89**, (1966).

[6] J. R. Hudman, M. Patel, and W. R. McWhinnie, *Inorg. Chim. Acta*, **4**, 161 (1970).

[7] Computer program CORRECT written by Dr. E. G. Boonstra fort he IBM 360/65 computer.

[8] A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D.C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

[9] G. H. Stout and L. H. Jensen, "X-ray Structure Determination," Macmillan, New York, N. Y., 1968, p 456.

TABLE I
ATOMIC FRACTIONAL COORDINATES AND THEIR STANDARD DEVIATIONS, ×10⁴

| | *X* | *Y* | *Z* |
|---|---|---|---|
| Tl | 1721 (1) | 1891 (1) | 2127 (1) |
| Cl(1) | 3326 (4) | 2721 (4) | 5214 (4) |
| Cl(2) | 0702 (4) | −0675 (3) | 1764 (5) |
| Cl(3) | 3697 (4) | 2416 (4) | 0190 (5) |
| N(1) | −0732 (10) | 1712 (9) | 2732 (12) |
| N(2) | 1657 (10) | 4017 (9) | 1921 (12) |
| C(1) | −1870 (14) | 0549 (12) | 3108 (17) |
| C(2) | −3343 (15) | 0500 (13) | 3482 (19) |
| C(3) | −3579 (15) | 1675 (13) | 3469 (17) |
| C(4) | −2351 (13) | 2893 (12) | 3120 (15) |
| C(5) | −2502 (14) | 4157 (13) | 3187 (16) |
| C(6) | −1276 (15) | 5327 (13) | 2882 (17) |
| C(7) | 0173 (14) | 5315 (11) | 2448 (16) |
| C(8) | 1505 (15) | 6504 (12) | 2135 (16) |
| C(9) | 2874 (16) | 6437 (12) | 1778 (18) |
| C(10) | 2906 (14) | 5159 (11) | 1676 (17) |
| C(11) | 0308 (12) | 4070 (11) | 2366 (15) |
| C(12) | −0951 (13) | 2859 (10) | 2728 (14) |

TABLE II
ANISOTROPIC TEMPERATURE FACTORS AND THEIR STANDARD DEVIATIONS, ×10⁴

| | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| Tl | 0116 (1) | 0078 (1) | 0164 (1) | 0068 (1) | 0042 (1) | 0032 (1) |
| Cl(1) | 0175 (5) | 0138 (4) | 0162 (7) | 0104 (4) | 0015 (5) | 0022 (5) |
| Cl(2) | 0213 (6) | 0092 (4) | 0239 (8) | 0101 (4) | 0043 (6) | 0042 (5) |
| Cl(3) | 0145 (5) | 0144 (5) | 0209 (8) | 0062 (4) | 0077 (6) | 0004 (5) |
| N(1) | 0117 (14) | 0076 (10) | 0161 (21) | 0066 (11) | 0033 (14) | 0033 (12) |
| N(2) | 0102 (14) | 0085 (11) | 0157 (21) | 0057 (10) | 0020 (14) | 0036 (12) |
| C(1) | 0119 (17) | 0081 (13) | 0174 (27) | 0029 (13) | 0034 (19) | 0014 (16) |
| C(2) | 0148 (22) | 0115 (16) | 0230 (33) | 0072 (16) | 0064 (22) | 0023 (19) |
| C(3) | 0148 (21) | 0109 (16) | 0167 (28) | 0059 (16) | 0034 (20) | 0018 (18) |
| C(4) | 0124 (18) | 0102 (14) | 0122 (23) | 0071 (14) | 0021 (17) | 0005 (15) |
| C(5) | 0159 (21) | 0119 (16) | 0136 (25) | 0104 (16) | 0013 (19) | 0003 (16) |
| C(6) | 0167 (22) | 0116 (16) | 0167 (27) | 0106 (17) | 0017 (20) | 0019 (17) |
| C(7) | 0150 (20) | 0075 (13) | 0162 (26) | 0073 (14) | 0018 (19) | 0022 (15) |
| C(8) | 0172 (23) | 0080 (14) | 0153 (26) | 0057 (15) | 0013 (20) | 0031 (16) |
| C(9) | 0180 (24) | 0089 (15) | 0197 (30) | 0064 (16) | 0027 (22) | 0034 (17) |
| C(10) | 0146 (20) | 0071 (13) | 0194 (29) | 0049 (14) | 0037 (20) | 0044 (16) |
| C(11) | 0107 (17) | 0076 (12) | 0150 (24) | 0055 (12) | 0017 (17) | 0027 (14) |
| C(12) | 0116 (17) | 0073 (12) | 0115 (21) | 0063 (12) | 0016 (16) | 0007 (13) |

Busing, Martin, and Levy. Bond lengths and angles in the $TlCl_3$(phen) molecule are shown in Figures 1 and 2 with their standard deviations. Figure 1 also gives the numbering scheme which was used.

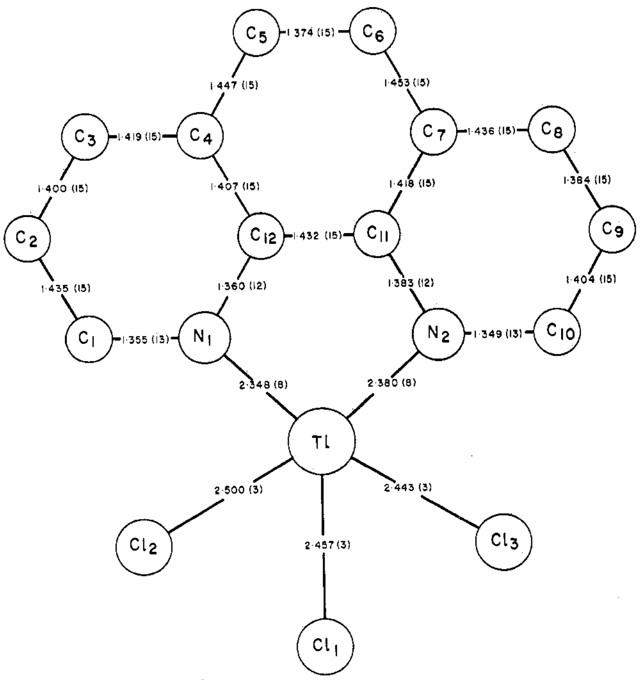

Figure 1.—Bond lengths (Å) and atomic nomenclature.

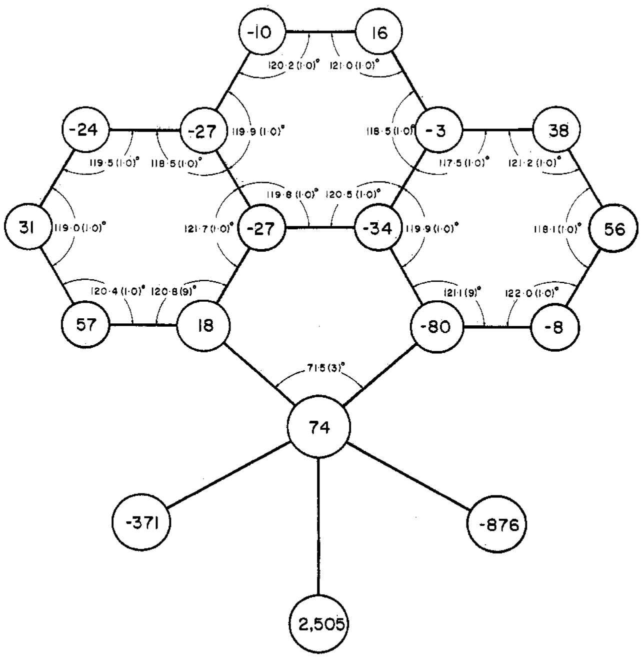

Figure 2.—Bond angles with displacements of atoms from least-squares plane. Displacements are given in the circles and are in units of $10^{-3}$ Å.

The phenanthroline molecule itself was found to be nearly planar; the best least-squares plane through the ligand is given by the equation (in orthogonalized coordinates ($X \| a^*$, $Y \| b^*$, $Z \perp a$ and $b^*$, origin unchanged))

$$0.20354X' + 0.09889Y' + 0.97496Z' = 1.71851$$

and Figure 2 shows the deviations (×10³ Å) from this plane.

The mean C–C and C–N bond lengths and their root-mean-square deviations were calculated for the ligand as 1.41 ± 0.02 and 1.36 ± 0.01 Å, respectively. These values are not significantly different from the values reported for dichloro(1,10-phenanthroline)-zinc(II) by Reimann, *et al.*[10] The thallium atom is bonded to the bidentate ligand through the two ring-nitrogen atoms. The two thallium–nitrogen distances are 2.348 (8) and 2.380 (8) Å and are significantly shorter than the 2.57 Å reported for dimethyl-1,10-phenanthroline perchlorate.[11] This difference in Tl–N bond length is due to the stronger covalent character of these bonds in the present compound. The mean distance of 2.466 ± 0.03 Å between the thallium and chlorine atoms is in good agreement with the value of 2.48 Å reported for the compound $Co(NH_3)_6TlCl_6$.[12] The $TlCl_3$(phen) unit has an almost square-pyramidal structure; the basal plane is formed by two chlorine atoms and the two nitrogen atoms with the thallium atom displaced from this basal plane toward the chlorine atom in the apical position (Figure 3).

The closest approach between molecules is between two which are related by the center of symmetry at the origin. Each arm of the double chlorine bridge which joins them consists of one short 2.502 (3) Å Tl–Cl(2)

---

[10] C. W. Reimann, S. Block, and A. Perloff, *Inorg. Chem.*, **5**, 1185 (1966).

[11] T. L. Blundell and H. M. Powell, *Chem. Commun.*, 55 (1967).

[12] T. Watanabe, M. Atoji, and C. Okazako, *Acta Crystallogr.*, **3**, 405 (1950).

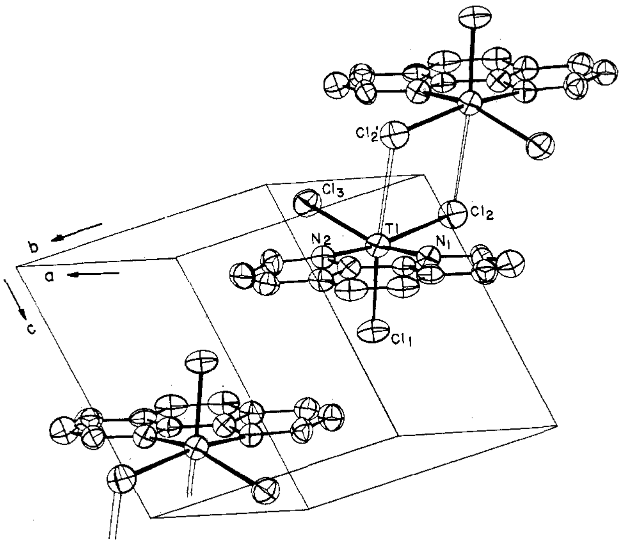

Figure 3.—A perspective view of the packing of the molecules in the unit cell, which is rotated so that the origin is at the top right-hand corner. In addition the bonding in the centrosymmetric dimer is shown. The thermal ellipsoids are scaled to include 50% probability.

bond and one long 3.236 (4) Å Tl–Cl(2′) bond. The length of the latter bond would seem to indicate that the pair forms a weak dimer. In the absence of a reliable value for the van der Waals radius of thallium in the present bonding arrangement, no well-founded opinion can, however, be given. If the values for the nonbonded radius of thallium (1.96 Å) and chlorine (1.75 Å) given by Bondi[13] are reliable, it is clear that the Tl···Cl approach of 3.236 (4) Å as found here is substantially shorter and that the description of the pair of molecules as a dimer, albeit a weak one, is justified. The structure is also consistent with the results obtained by Hudman, *et al.*,[6] when treating the complex with dimethylformamide (DMF). A single product forms during the reaction

$$(\mathrm{TlCl_3phen})_2 + 2\mathrm{DMF} \longrightarrow 2(\mathrm{TlCl_3phen\cdot DMF})$$

indicating the weakness of the dimeric association. Had the bridge bonds been of similar strength to the intramonomeric TlCl bonds, four isomers would have formed. What is certain is that the arrangement is centrosymmetric, in contrast to the conclusions drawn on the basis of infrared and Raman spectroscopy by Walton[14] and Hudman, Patel, and McWhinnie.[6] It is to be noted that the authors of both these papers have stressed the dependence of their conclusions on the tenuous assumptions made.

Figure 4 shows the arrangement of the atoms about the thallium atom together with their standard deviations ($\times 10^3$ Å) from the least-squares plane through the four basal ligands. The complex molecule has a distorted octahedral structure with the thallium atom, Cl(2), and N(2) slightly above this plane, and Cl(3) and N(1) below it with Cl(1) and Cl(2′) in the apical positions.

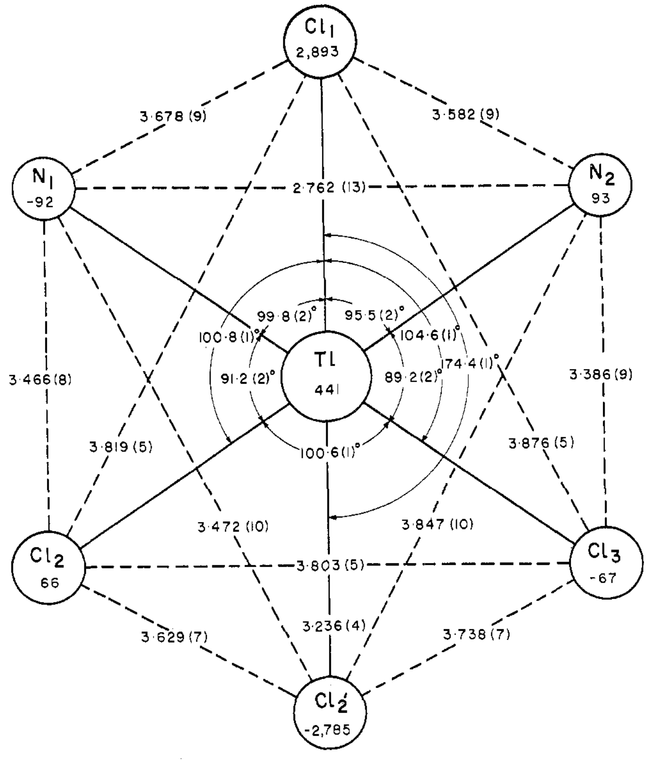

Figure 4.—Shows the distorted octahedral environment of the thallium atom. The equation of best least-squares plane passing through the Cl(2), Cl(3), N(1), and N(2) atoms is given in orthogonalized coordinates ($X||a^*$, $Y||b^*$, $z\perp a$ and $b^*$, origin unchanged) by $0.3990X' + 0.1006Y' + 0.9114Z' = 1.3591$.

Large differences, as found here for the Tl–Cl bonds, between the lengths of bridge bonds and chemically similar bonds within the monomer are common in thallium polymers. In diethyl(salicylaldehydato)thallium(II), Milburn and Truter[15] have found Tl–O bonds of 2.46, 2.65, 2.61, and 3.15 Å in the double oxygen bridge between thallium atoms. The quasi-tetrameric aggregate formed by trimethylthallium[16] has a shortest Tl–C intertetramer approach of 3.31 Å and a shortest Tl–C bond of 2.22 Å within the tetramer. In the polymer chains of hydroxobis(pentafluorophenyl)thallium(III) found by Luth and Truter[17] the Tl–O bond within the molecule is 2.23 Å long in contrast to 2.51 and 2.69 Å between molecules.

It is interesting to note that this appears to be the first neutral coordination complex of thallium(III) halides to have been found.

**Acknowledgment**.—The authors wish to thank Dr. J. P. R. de Villiers for his assistance in the collection of diffractometer data.

---

(13) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

(14) R. A. Walton, *J. Inorg. Nucl. Chem.*, **32**, 2875 (1970).

(15) G. H. W. Milburn and M. R. Truter, *J. Chem. Soc. A*, 648 (1967).

(16) G. M. Sheldrick and W. S. Sheldrick, *ibid.*, *A*, 28 (1970).

(17) H. Luth and M. R. Truter, *ibid.*, *A*, 1287 (1970).