Crystal Structure of Salicylato-(1,10-phenanthroline)thallium(I)

By **David L. Hughes** and **Mary R. Truter,*** A.R.C. Unit of Structural Chemistry (University College London), Inveresk House, 346 Strand, London WC2R 0HG

A three-dimensional X-ray crystal structure analysis has shown that the title compound exists as a dimeric entity, the two halves related by a two-fold axis. The five atoms of the thallium co-ordination sphere form the base of a shallow, irregular pentagonal pyramid which has the thallium ion at its apex. The phenanthroline ligand co-ordinates to the Tl^+ ion through both nitrogen atoms, with Tl · · · N 2·65 and 2·71 Å. The salicylate ion forms an asymmetrical bidentate co-ordination with one Tl^+ through the two oxygen atoms of the carboxylate group, Tl · · · O 2·65 and 2·98 Å; the first oxygen also has a weak ' bridging ' interaction with the other thallium of the dimer, Tl · · · O 3·00 Å. The second oxygen atom of the carboxylate group is hydrogen-bonded to the phenolic group, O · · · O 2·52 Å.

Crystals are colourless needles, orthorhombic, space group $Pbcn$, with a = 22·769, b = 10·273, c = 14·204 Å. The structure was determined from diffractometer observations, by the heavy-atom method, and refined (the thallium ion anisotropically) by least-squares methods to R 0·101 for 1599 reflections.

IN the course of studies of alkali-metal complexes, comparable complexes of thallium(I) have also been prepared and examined.[1] We now report the results of the crystal structure analysis of one of these complexes, salicylato-(1,10-phenanthroline)thallium(I).

EXPERIMENTAL

Samples of salicylato-(1,10-phenanthroline)thallium(I) and of salicylato-(2,9-dimethyl-1,10-phenanthroline)thallium(I) were prepared as described in ref. 1. Crystals of both complexes are colourless needles.

The crystal selected for structure analysis was taken from the latter (the 2,9-dimethyl-1,10-phenanthroline sample), as one of several good crystals having a distinct diamond-shaped cross-section. It was shown in the course of the X-ray analysis that these crystals were impurities in that sample, apparently produced from impurities of 1,10-phenanthroline in the reagent used. The smaller, less well-formed needles with more rectangular cross-section were the expected product of the reaction and their unit-cell dimensions are recorded below. Crystals of the complex prepared from pure 1,10-phenanthroline have the same space group, cell dimensions, and diffraction pattern as those of the crystal we used, but they differ in habit, having a rectangular cross-section with the b axis as their needle axis (not the c axis of our crystal).

The crystal used in the intensity data collection was cut down to length 0·44 mm and triangular cross-section of height (along a axis) 0·16 mm and base (b axis) 0·13 mm.

Crystal Data.—(i) *Salicylato*(2,9-*dimethyl*-1,10-*phenanthroline*)*thallium*(I). $C_{21}H_{17}N_2O_3Tl$, M = 549·7, Monoclinic, a = 23·756(3), b = 10·305(2), c(needle axis) = 7·897(2) Å, β = 101·61(2)°, U = 1893·7 Å^3, D_m = 1·93, Z = 4, D_c = 1·928, $F(000)$ = 1048. Space group $P2_1/a$ from absent spectra. Cu-K_α radiation (λ = 1·5418 Å). Oscillation, Weissenberg, and Guinier powder photographs.

(ii) *Salicylato*(1,10-*phenanthroline*)*thallium*(I). $C_{19}H_{13}N_2O_3Tl$, M = 521·70, Orthorhombic, a = 22·769(14), b = 10·273(5), c = 14·204(17) Å, U = 3322·3 Å^3, D_m (by flotation) = 2·08, Z = 8, D_c = 2·086, $F(000)$ = 1968. Space group $Pbcn$, from absent spectra. Mo-K_α radiation, λ = 0·70926 Å (1 Å $\equiv$ 10^{-10}m); μ(Mo-K_α) = 98·0 cm^{-1}. Four-circle diffractometer observations.

Preliminary photographs from Weissenberg and precession cameras indicated the space group and systematically strong and weak reflection intensities from which the thallium ion was estimated to lie at *ca.* (0, 0·125, 0·11). Consequently, intensities measured on a Picker four-circle automatic diffractometer (Mo-K_α radiation, with Zr-filter and pulse-height analyser) were collected in two portions: the ' strong data ' for which a 2θ—θ scan rate of $\frac{1}{2}$° min^{-1} was used, and the ' weak data ' for which the scan rate was $\frac{1}{4}$° min^{-1}. The latter comprised measurements of reflections of indices hkl with (i) $h + k$ odd, (ii) $(k/2) + l$ odd, or (iii) l = 2 or 5.

Data for $2\theta \leqslant 40·0°$ were collected, 1022 ' weak ' plus 577 ' strong ' reflections, totalling 1599. Of the former, 510 reflections (*i.e.* 50%) were considered ' unobserved ', having $I < \sigma_I$ [where $\sigma_I^2 = T + (b_1 + b_2) . (T_s/50)^2$, T = scan count, b_1 and b_2 are background counts, each for 25s, and T_s = scan time]. Of the ' strong ' data, 23 (4·0%) had $I < 2\sigma_I$ and were considered ' unobserved '.

Lorentz and polarisation factors were applied, but no absorption corrections were made. Structure amplitudes were calculated and the two sets of observations placed on the same scale by comparison of three standard reflections (indices 710, 240, 423), measured throughout the data collection. There was no apparent decomposition of the crystal during the exposure.

Structure Analysis.—The estimated co-ordinates of the thallium ion were refined by least-squares methods (maintaining the temperature factor, B, constant at 4·0 Å^2) to R 0·27 and these parameters were used for a Fourier difference synthesis, with all the observed data (1066 reflections). The salicylate ion appeared clearly in this map. A further difference-Fourier synthesis, on the thallium and salicylate ions, with the observed ' weak ' data only, indicated all the atoms of the phenanthroline molecule.

Initially, the structure was refined with only the ' weak ' data (to which there was little contribution from the thallium ion), but later cycles of refinement used all the observed data, and the final cycles employed all data. Refinement was by minimisation of $\Sigma w(|F_o| - |F_c|)^2$ (= $\Sigma w\Delta^2$) and in the preliminary stages w was taken from the diffractometer measurements: $w_c = 1/\sigma_c^2$, where $\sigma_c^2 = \sigma_I^2/4 . I . Lp$ (Lp is the Lorentz–polarisation factor). Later, Cruickshank-type weighting schemes [2] (determined from the least-squares fitting of curves to mean values of $w_c\Delta^2$ according to ranges of $|F_o|$ values) were found more suitable. For the ' weak ' data: $w = 1/\sigma^2$, where, for $F_o \leqslant 10·0$, $\sigma^2 = 0·15\,\sigma_c^2$, for $F_o > 10·0$, $\sigma^2 = \sigma_c^2(-0·433 + 0·143|F_o| - 0·00669|F_o|^2 + 0·000143|F_o|^3)$; for the ' strong ' data: $\sigma^2 = \sigma_c^2 . 10^{-4} (940 + 548 . |F_o| - 8·04F_o^2 + 0·0359F_o^3)$.

---

[1] N. S. Poonia and M. R. Truter, *J.C.S. Dalton*, 1972, 1791.

[2] D. W. J. Cruickshank in ' Computing Methods in Crystallography,' Pergamon Press, Oxford, 1965, p. 114.

Amongst the smallest observations there were 186 reflections, mostly from the ' weak ' set, which showed very poor agreement of observed and calculated structure amplitudes; these ' worst ' reflections, having $|F_c| < 5{\cdot}0$ and $|F_o/F_c| \geqslant 4{\cdot}0$, or $|F_c| < 10{\cdot}0$ and $|F_o/F_c| \geqslant 2{\cdot}5$, were given a weight, w, of zero and were thus excluded from the refinement and the (weighted) R' calculations.

In the structure refinement, which was initially by block-diagonal and finally by full-matrix least-squares methods, the thermal parameters of the thallium ion were refined anisotropically; the other atoms were treated isotropically. The scattering factors for thallium ion, carbon, nitrogen, and oxygen were taken from ref. 3, those for thallium being corrected for anomalous dispersion.

At the completion of the refinement, R and R' factors for various portions of the data were calculated:

	R	R'
All data	0·101	0·070
Strong, obs. data	0·042	0·049
Weak, obs. data	0·227	0·201
Weak, obs. data, excluding 87 ' worst ' reflections	0·158	

A difference-Fourier synthesis, based on the final atomic parameters and all the data except the 186 ' worst ' reflections, showed peaks, 0·4—0·7 eÅ^{-3}, in some positions where hydrogen atoms would be expected; there were other, spurious peaks of the same height in the map, and larger peaks (maximum 1·6 eÅ^{-3}) about the thallium ion. Hydrogen atoms were not included in any calculations.

TABLE 1

Fractional atomic co-ordinates ($\times 10^4$) and isotropic temperature factors B (Å^2) from the expression $\exp[-B(\sin^2\theta)/\lambda^2]$; for the thallium ion, anisotropic vibration parameters (Å^2) are in the form $\exp[-2\pi^2 . 10^{-4}(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. Standard deviations are in parentheses

	x/a	y/b	z/c	B
Tl	5(1)	1242(1)	1051(1)	*
N(1)	654(8)	3382(17)	932(11)	3·77(39)
C(2)	1179(11)	3281(25)	679(18)	5·50(58)
C(3)	1564(10)	4372(24)	526(16)	4·74(55)
C(4)	1355(10)	5631(22)	638(16)	4·38(51)
C(5)	500(11)	6979(25)	1009(16)	5·68(62)
C(6)	−93(9)	7100(20)	1275(14)	3·59(47)
C(7)	−1003(10)	5978(22)	1763(17)	4·82(55)
C(8)	−1325(10)	4823(21)	1940(16)	3·91(47)
C(9)	−1035(10)	3648(22)	1825(17)	4·48(50)
N(10)	−489(7)	3559(16)	1510(12)	3·63(36)
C(11)	−191(7)	4633(18)	1317(12)	2·19(39)
C(12)	422(8)	4538(18)	1030(13)	2·64(38)
C(13)	750(10)	5719(22)	875(15)	3·99(50)
C(14)	−426(8)	5910(17)	1496(13)	2·43(39)
C(21)	1626(10)	−671(23)	2409(17)	4·52(50)
C(22)	1998(11)	−1516(24)	1967(19)	5·17(56)
C(23)	2411(12)	−2319(29)	2464(21)	6·54(66)
C(24)	2427(11)	−2156(26)	3429(20)	6·30(67)
C(25)	2048(12)	−1354(27)	3921(19)	6·65(68)
C(26)	1680(11)	−569(25)	3443(18)	5·52(58)
C(27)	1201(12)	58(23)	1929(19)	5·07(54)
O(28)	812(8)	711(19)	2337(12)	6·96(43)
O(29)	1201(7)	74(16)	1048(12)	6·21(39)
O(30)	2017(7)	−1578(16)	1018(12)	6·55(42)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
* Tl	917(8)	483(6)	560(6)	28(7)	62(7)	−46(5)

The final atomic parameters are in Table 1. Measured and calculated structure factors are listed in Supplementary Publication No. SUP 20472 (12 pp., 1 microfiche).†

Computing.—The determination of the orientation matrix for the Picker diffractometer and the unit-cell dimensions, data reduction, Patterson and Fourier syntheses, block-diagonal least-squares refinement, and calculation of planes through various groups of atoms and interatomic distances were computed on an IBM 1130.[4] Full-matrix least-squares and calculation of bond lengths and angles with standard deviations from a full correlation matrix were carried out on the University College IBM 360/H65 computer.[5]

DISCUSSION

Figure 1 indicates the atom numbering scheme used in the structure analysis and the bond lengths and valence angles of the phenanthroline and salicylate moieties of the complex. Details of the co-ordination arrangement about the thallium ion are in Figure 2 and Table 2.‡ The equations of several mean planes through the complex, and the angles between the planes are in Table 3.

TABLE 2

Angles (deg.) $i \cdots \mathrm{Tl} \cdots j$ subtended by co-ordinated atoms at the thallium ion. Mean estimated standard deviation in the angles is 0·51°

i	j	Angle
N(1)	N(10)	61·3
N(1)	O(28)	80·1
N(1)	O(29)	79·9
N(1)	O(28$^{\mathrm{I}}$)	123·0
N(10)	O(28)	107·6
N(10)	O(29)	137·2
N(10)	O(28$^{\mathrm{I}}$)	73·7
O(28)	O(29)	44·2
O(28)	O(28$^{\mathrm{I}}$)	82·4
O(29)	O(28$^{\mathrm{I}}$)	119·7

The Dimer.—Salicylato-(1,10-phenanthroline)thallium(I) is dimeric in the crystal; the two halves are related by a crystallographic two-fold axis. A phenanthroline molecule is co-ordinated through both its nitrogen atoms to each thallium ion. The carboxylate group of the salicylate ion forms asymmetrical bidentate co-ordination with the thallium ion [Tl $\cdots$ O(28) 2·65, Tl $\cdots$ O(29) 2·98 Å]. The oxygen atom O(28) also has a weaker interaction with a second thallium ion, [Tl$^{\mathrm{I}}$ $\cdots$ O(28) 3·00 Å];

---

† For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

‡ Roman numeral superscripts refer to symmetry-related molecules: I $\bar{x}, y, \frac{1}{2} - z$, II $\bar{x}, 1 - y, \bar{z}$.

[3] ' International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, p. 202.

[4] *X*-RAY ARC: IBM 1130 Program System for Crystallography, compiled by B. L. Vickery, D. Bright, and P. R. Mallinson. This includes least-squares program BLOK by B. L. Vickery; Fourier program FODAP by A. Zalkin and D. Bright; Picker setting program PICK 3 by W. C. Hamilton and D. Bright; data reduction program PRED by B. L. Vickery and P. R. Mallinson; mean planes program MPLN (NRC 22) by M. E. Pippy and F. R. Ahmed; and intermolecular contacts program BANGL by D. Bright.

[5] IBM 360 programs: full-matrix least-squares program NUCLS by R. J. Doedens and J. A. Ibers; interatomic distances and errors program ORFFE by W. R. Busing, K. O. Martin, and H. A. Levy.

the two thallium ions of the dimer are thus ' bridged ' by carboxylate oxygen atoms.

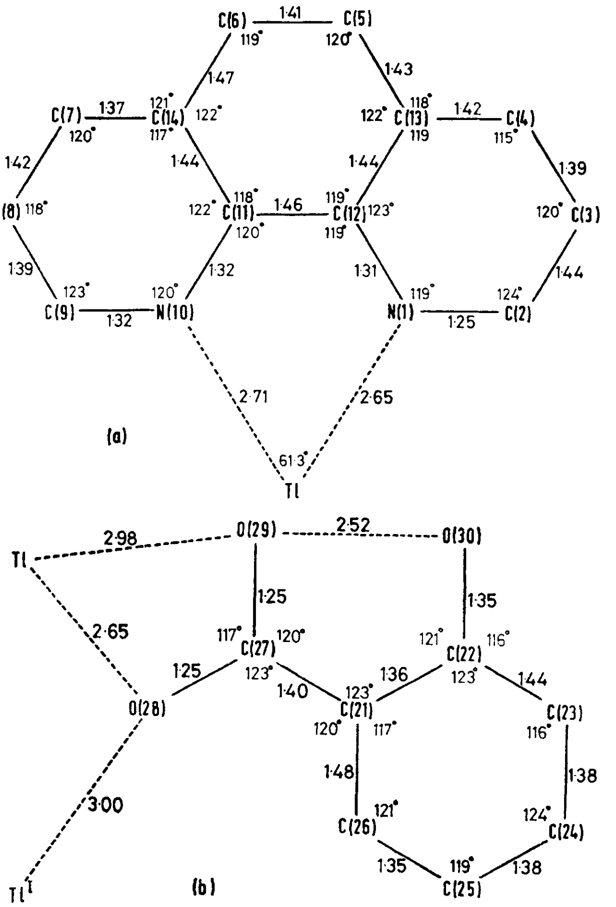


FIGURE 1 The designations of the atoms, bond lengths (Å), and bond angles (°), in (a) the 1,10-phenanthroline molecule and (b) the salicylate anion. Mean estimated standard deviations are: in (a), Tl · · · N 0·017, C–C 0·028, C–N 0·024 Å, and 1·9° in the angles within the molecules; in (b) Tl · · · O 0·018, C–C 0·032, C–O 0·027 Å, and 2·5° in the angles. The broken line indicates a hydrogen bond

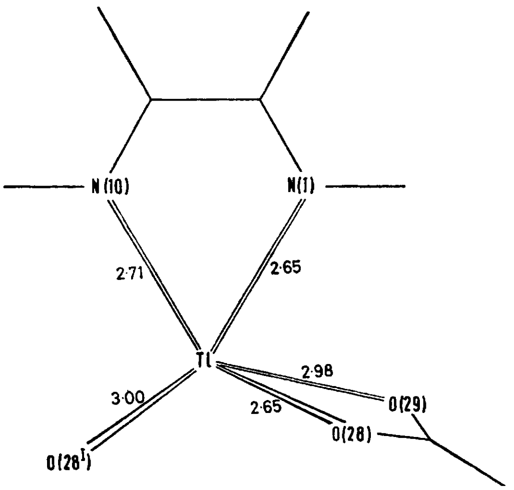


FIGURE 2 Environment of the thallium ion. Mean estimated standard deviation in the distances shown is 0·018 Å

TABLE 3

Mean planes

(*a*) Equation of mean planes, in the form: $lX + mY + nZ = p$, where X, Y, and Z are co-ordinates (Å), referred to the *a*, *b*, and *c* axes

Plane	Atoms	l	m	n	p
(*A*)	Five co-ordination atoms	0·3906	0·3926	0·8325	2·9060
(*B*)	Phenanthroline molecule	0·2958	0·0050	0·9552	1·7395
(*C*)	Central ring	0·2799	−0·0043	0·9600	1·6521
(*D*)	Outer ring I	0·2632	−0·0033	0·9647	1·6471
(*E*)	Outer ring II	0·3308	0·0255	0·9433	1·7481
(*F*)	Phenyl ring, C(21)—(26)	0·6879	0·7208	−0·0849	1·7686
(*G*)	C(21), C(22), C(26), C(27)	0·6626	0·7400	−0·1149	1·5430
(*H*)	C(21), C(27), O(28) O(29)	0·6079	0·7938	0·0105	1·7391

(*b*) Deviations (Å) of atoms from the planes. An asterisk indicates atoms included in the mean plane calculations

Plane (*A*):

Tl 1·157, N(1) −0·141,* N(10) 0·119,* O(28) −0·867,* O(29) 0·569,* O(28$^{\rm I}$) 0·193 *

Plane (*B*):

Tl −0·303, N(1) −0·017 * C(2) −0·007,* C(3) 0·051,* C(4) 0·069,* C(5) 0·001,* C(6) −0·036,* C(7) 0·007,* C(8) 0·025,* C(9) 0·058,* N(10) −0·001,* C(11) −0·057,* C(12) −0·035,* C(13) −0·017,* C(14) 0·034 *

Plane (*C*):

Tl −0·221, N(1) 0·020, C(2) 0·010, C(3) 0·043, C(4) 0·057, C(5) 0·011,* C(6) −0·004,* C(7) 0·085, C(8) 0·127, C(9) 0·160, N(10) 0·080, C(11) 0·001,* C(12) 0·000,* C(13) −0·006,* C(14) 0·090

Plane (*D*):

Tl −0·208, N(1) 0·010,* C(2) −0·022,* C(3) −0·004,* C(4) 0·021,* C(5) 0·010, C(6) 0·020, C(7) 0·147, C(8) 0·200, C(9) 0·220, N(10) 0·117, C(11) 0·027, C(12) 0·001,* C(13) −0·018,* C(14) 0·127

Plane (*E*):

Tl −0·303, N(1) 0·082, C(2) 0·136, C(3) 0·250, C(4) 0·276, C(5) 0·163, C(6) 0·077, C(7) 0·015,* C(8) −0·020,* C(9) 0·013,* N(10) 0·001,* C(11) −0·005,* C(12) 0·068, C(13) 0·140, C(14) 0·091

Plane (*F*):

Tl −0·967, C(21) −0·010,* C(22) 0·001,* C(23) −0·006,* C(24) 0·023,* C(25) −0·037,* C(26) 0·027,* C(27) −0·078, O(28) −0·252, O(29) 0·042, O(30) 0·099

Plane (*G*):

Tl −0·762, C(21) 0·006,* C(22) −0·003,* C(26) −0·002,* C(27) −0·003,* O(28) −0·158, O(29) 0·155

Plane (*H*):

Tl −0·703, C(21) 0·000,* C(22) −0·180, C(26) 0·175, C(27) −0·001,* O(28) 0·000,* O(29) 0·000 *

(*c*) Angles (deg.) between the normals to the planes

(*B*)–(*C*)	1·1	(*C*)–(*E*)	3·5	(*F*)–(*G*)	2·5
(*B*)–(*D*)	2·0	(*D*)–(*E*)	4·4	(*F*)–(*H*)	8·3
(*B*)–(*E*)	2·4			(*G*)–(*H*)	8·4
(*C*)–(*D*)	1·0	(*B*)–(*F*)	82·8		

The phenanthroline molecules lie perpendicular to the (010) plane, and the salicylate ions are roughly perpendicular to the (001) plane. Figure 3 shows a dimer pair in projection down the *a* axis.

Co-ordination of the Thallium Ion.—The thallium ion is co-ordinated strongly to three atoms, N(1), N(10), and O(28); there are weaker interactions Tl · · · O(29) and

$\mathrm{Tl}\cdots\mathrm{O}(28^{\mathrm{I}})$. The closest atoms to the thallium ion on the outer side of the dimer are $\mathrm{C}(5^{\mathrm{II}})$ and $\mathrm{C}(6^{\mathrm{II}})$, 3·64 and 3·72 Å respectively from the thallium ion, *i.e.* outside the co-ordination sphere.

Plane (*A*) of Table **3** is the mean plane through the five co-ordinated atoms. The maximum displacement of any of these atoms from that plane is —0·87 Å, and the Tl^+ ion is +1·16 Å from it. The arrangement of atoms within the co-ordination sphere may thus be described as a shallow, irregular pentagonal pyramid in which the Tl^+ ion forms the apex.

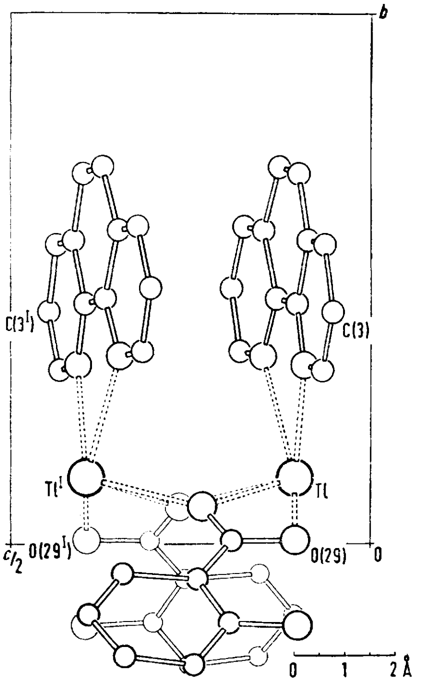
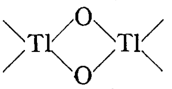


FIGURE 3 Projection of one dimeric unit down the *a* axis; the halves of the dimer are related by a two-fold axis parallel to *b* at $x = 0$, $z = \frac{1}{4}$

This co-ordination arrangement shows a major contrast between this thallium(I) complex and alkali-metal complexes. In the latter the metal is always surrounded by co-ordinated atoms whereas the Tl^+ ion has a large region free from co-ordination. This results from the electronic configurations of the different metal ions; the $6s^2$ electrons of Tl^+ are a stereochemically active lone pair which restrict, in complexes, the extent of co-ordination and occupy a large portion of the co-ordination sphere.

Our thallium co-ordination distances may be but cautiously compared with those of previous similar analyses. Of direct comparison are the results for thallium tetrametaphosphate,[6] thallium(I) acetylacetonate,[7] and the thallium salt of grisorixin;[8] these have $\mathrm{Tl}\cdots\mathrm{O}$ separations 2·70—2·85 (mean of three 2·77), 2·43—3·39 (mean of six, 2·97), and five in the range 2·6—3·0 Å, compared with a range 2·65—3·00 Å (mean of three, 2·87) in our example. Other bond lengths have been measured in $(\mathrm{R_2Tl^{III}})^+$ ionic complexes. In dimethyl-(1,10-phenanthroline)thallium(III) perchlorate,[9] the $\mathrm{Tl}\cdots\mathrm{N}$ distances are both 2·57 Å and, as expected from the electronic state of the $\mathrm{Tl^{III}}$ ion, slightly shorter than in our complex (2·65 and 2·71 Å). Similarly in hydroxobis(pentafluorophenyl)thallium(III)[10] and diethyl(salicylaldehydato)thallium(III),[11] the $\mathrm{Tl}\cdots\mathrm{O}$ interactions, connecting the thallium ions in polymeric  chains are, in general, shorter than in our complex.

By comparison, $\mathrm{M}\cdots\mathrm{O}$ distances for alkali metals have similar ranges of values, *e.g.* $\mathrm{K}\cdots\mathrm{O}$ distances[12-24] are 2·63—3·23, (mean 2·83), $\mathrm{Rb}\cdots\mathrm{O}$ 2·84—3·25 Å (mean 3·00).[25-29] Few $\mathrm{M}\cdots\mathrm{N}$ distances have been reported, but $\mathrm{K}\cdots\mathrm{N}$ distances have been found in the range 2·84—2·91,[22,23] and $\mathrm{Rb}\cdots\mathrm{N}$ 2·94—3·10 Å.[27-29] Thus there are indications that thallium(I) differs from the alkali metals in allowing, in general, nitrogen donor ligands to approach the cation more closely than oxygen donors, whereas the radius of nitrogen in simple covalent compounds is *ca.* 0·05 Å greater than that of oxygen.

The Salicylate Ion.—The salicylate ion, in its several salts,[30-33] does not show a characteristic co-ordination pattern, and our result (diagrammatically as Figure 4) is different from any of those found previously. This ion appears subordinate to the demands of the cation; certainly the thallium–thallium distance of 4·116 Å of

---

[6] J. K. Fawcett, V. Kocman, S. C. Nyburg, and R. J. O'Brien, *Chem. Comm.*, 1970, 1213.

[7] N. C. Webb, personal communication.

[8] M. Alleaume and D. Hickel, *J.C.S. Chem. Comm.*, 1972, 175.

[9] T. L. Blundell and H. M. Powell, *Chem. Comm.*, 1967, 54.

[10] H. Luth and M. R. Truter, *J. Chem. Soc.* (*A*), 1970, 1287.

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

[12] Y. Okaya, *Acta Cryst.*, 1965, **19**, 879.

[13] D. van der Helm, J. P. Glusker, C. K. Johnson, J. A. Minkin, N. E. Burow, and A. L. Patterson, *Acta Cryst.*, 1968, **B24**, 578.

[14] H. Ringertz, *Acta Cryst.*, 1968, **B24**, 1686.

[15] E. L. V. Lewis and T. R. Lomer, *Acta Cryst.*, 1969, **B25**, 702.

[16] H. C. Freeman, J. E. W. L. Smith, and J. C. Taylor, *Acta Cryst.*, 1961, **14**, 407.

[17] D. R. McGregor and J. C. Speakman, *J. Chem. Soc.* (*A*), 1968, 2106.

[18] L. Manojlovic and J. C. Speakman, *J. Chem. Soc.* (*A*), 1967, 971.

[19] L. Manojlovic and J. C. Speakman, *Acta Cryst.*, 1968, **B24**, 323.

[20] K. Maartmann-Moe, *Acta Cryst.*, 1969, **B25**, 1452.

[21] D. M. Liebig and J. H. Robertson, *J. Chem. Soc.*, 1965, 5801.

[22] M. A. Bush, H. Luth, and M. R. Truter, *J. Chem. Soc.* (*A*), 1971, 740.

[23] M. A. Bush and M. R. Truter, *J. Chem. Soc.* (*A*), 1971, 745.

[24] M. A. Bush and M. R. Truter, *J.C.S. Perkin II*, 1972, 345.

[25] C. E. Nordman, A. S. Weldon, and A. L. Patterson, *Acta Cryst.*, 1960, **13**, 414.

[26] S. Grimvall and R. F. Wengelin, *J. Chem. Soc.* (*A*), 1967, 968.

[27] B. Metz, D. Moras, and R. Weiss, *Chem. Comm.*, 1970, 217.

[28] D. Bright and M. R. Truter, *J. Chem. Soc.* (*B*), 1970, 1544.

[29] D. L. Hughes, unpublished work.

[30] F. Hanic and J. Michalov, *Acta Cryst.*, 1960, **13**, 299.

[31] H. P. Klug, L. E. Alexander, and G. G. Summer, *Acta Cryst.*, 1958, **11**, 41.

[32] T. C. Downie and J. C. Speakman, *J. Chem. Soc.*, 1954, 787.

[33] H. S. Kim and G. A. Jeffrey, *Acta Cryst.*, 1971, **B27**, 1123.

our dimer is characteristic of several complexes in which thallium ions are bridged in pairs or in chains.[10,11,34,35]

The bond lengths and valence angles within the salicylate ion are, in general, of the same order as in similar compounds, although C(21)–C(26) and C(21)–C(27) appear somewhat long and short respectively. The O(29) · · · O(30) distance (2·52 Å) indicates the strong hydrogen bond usually found in salicylate ions.

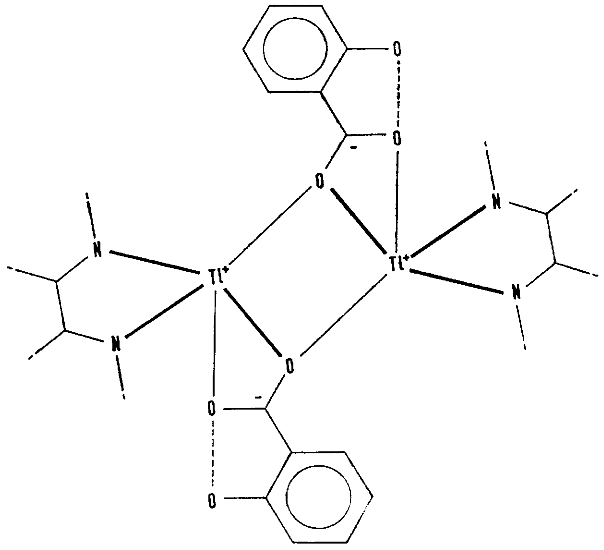


FIGURE 4 Diagramatic representation of a dimer showing Tl · · · O · · · Tl bridging; the internal hydrogen bond is shown by a broken line

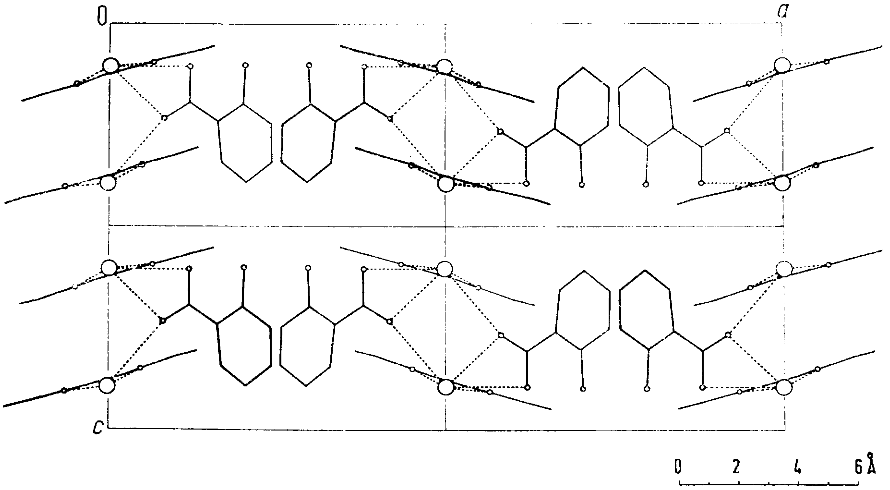


FIGURE 5 Projection of the structure down the *b* axis; the plane of the 1,10-phenanthroline ring is perpendicular to that of the projection

The mean plane [plane (*F*) in Table 3] through the carbon atoms of the phenyl ring of the salicylate ion shows that ring to be planar (maximum displacement from the plane is 0·037 Å, *i.e.* 1·3σ). The atoms C(27) and O(30) are displaced (by 0·078 and 0·099 Å) on opposite sides of this plane. The carboxylate group is rotated by 8·4° about the C(21)–C(27) bond [from consideration of the four-atom planes (*G*) and (*H*)]. This rotation and the displacement of C(27) out of the ring plane have the effect of bringing the atom O(28) closer to the thallium ions.

The Phenanthroline Molecule.—The phenanthroline molecule is roughly planar [plane (*B*)] and lies perpendicular to the (010) plane. Its dimensions are as expected.[36-41] C(14) appears displaced by 0·09 Å (5σ) from the mean planes [(*C*) and (*E*)] of rings of the molecule; otherwise, each of the three rings is planar and the outer rings appear bent from the central ring by 1·0 and 3·5°, both in directions away from the thallium ion. As in several other phenanthroline complexes,[36-38] the thallium ion is displaced from the plane of the molecule, here by 0·30 Å.

Molecular Packing.—The equation of the mean plane (*C*) through the central ring of the phenanthroline molecule was used in calculations of distances between neighbouring phenanthroline molecules. The distance between this plane and the like plane in molecule (II) is 3·35 Å; the minimum interatomic distance between the corresponding phenanthroline molecules is 3·38 Å for C(11) · · · C(13$^{\text{II}}$). Similarly, the two molecules of the dimer are *ca.* 3·46 Å apart but the minimum interatomic distance N(1) · · · C(9$^{\text{I}}$) is 3·31 Å. These are

---

[34] L. H. W. Verhoeff and J. C. A. Boeyens, *Acta Cryst.*, 1968, **B24**, 1262.

[35] L. H. W. Verhoeff and J. C. A. Boeyens, *Acta Cryst.*, 1969, **B25**, 607.

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

[37] R. C. Elder, J. Halpern, and J. S. Pond, *J. Amer. Chem. Soc.*, 1967, **89**, 6877.

[38] K. R. Butler and M. R. Snow, *J. Chem. Soc.* (*A*), 1971, 565.

[39] G. Mathern, R. Weiss, and R. Rohmer, *Chem. Comm.*, 1970, 153.

[40] D. C. Craig, E. T. Pallister, and N. C. Stephenson, *Acta Cryst.*, 1971, **B27**, 1163.

[41] B. A. Frenz and J. A. Ibers, *Inorg. Chem.*, 1972, **11**, 1109.

characteristic of distances between neighbouring aromatic rings.

The closest intermolecular contacts are (i) within each dimer unit, C(9) · · · O(28) 3·28 Å, and (ii) between units C(4) · · · O(30), also 3·28 Å; both of these are slightly, but not significantly, less than the expected van der Waals' distances. Figure 5 shows the packing arrangement of the dimer units in the crystal.

We thank Dr. N. S. Poonia for the crystals, C. Nave for powder photographic investigation, Dr. D. E. Fenton for discussion, Dr. P. R. Mallinson and other authors[4,5] for use of their programmes, the Director of the University College Computer Centre for facilities, and the Royal Society for some of the equipment.

[2/934 *Received, 27th April,* 1972]