

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS**Coordination Compounds of Thallium(III)<sup>1</sup>**

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The preparation and partial structural characterization of some new complexes of the thallium(III) halides are described. From nonaqueous media the tetrahalothallate ions,  $[\text{TlX}_4]^-$ , for  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ , are readily obtained using large univalent cations such as quaternary ammonium and arsonium ions. For  $[(\text{C}_6\text{H}_5)_4\text{As}][\text{TlCl}_4]$ , the anion is shown to be tetrahedral. The  $[\text{TlI}_4]^-$  compounds provide the first direct evidence for the existence of  $\text{Tl}(\text{III})$  in the presence of  $\text{I}^-$ . The  $[\text{TlCl}_4]^-$  compounds are white, the  $[\text{TlBr}_4]^-$  compounds white or cream, and the  $[\text{TlI}_4]^-$  compounds orange in color. Compounds of  $\text{TlX}_3$  with neutral ligands such as DMSO, triphenylphosphine oxide, pyridine, and 1,10-phenanthroline have also been prepared; while with the exception of  $\text{TlI}_3[(\text{C}_6\text{H}_5)_3\text{PO}]_3$  they have the stoichiometry  $\text{TlX}_3\text{L}_2$ , it remains uncertain whether true five-coordinate species are present. Tris(diethylthiocarbamato)thallium(III) has also been prepared; it appears to be a normal, quasi-octahedral trichelate complex.

**Introduction**

Although a great deal of information is available on the existence and stabilities of tetrahalothallate(III) complexes in solution,<sup>2</sup> information on the isolation and characterization of crystalline complexes is generally lacking. Methods for the preparation of several compounds of the type  $\text{M}^+\text{TlX}_4$  have been described,<sup>3-8</sup> but details are incompletely reported and sometimes contradictory.<sup>6,7</sup> We describe here the preparation and properties of a series of salts of the  $[\text{TlCl}_4]^-$ ,  $[\text{TlBr}_4]^-$ , and  $[\text{TlI}_4]^-$  ions. Also described are a number of other complexes formed by addition of various neutral ligands, e.g., dimethyl sulfoxide, triphenylphosphine oxide, pyridine, *o*-phenanthroline, and *N,N*-diethylthiocarbamate, to the  $\text{Tl}(\text{III})$  halides.

**Experimental**

Thallous chloride and thallous bromide, purchased from Alpha Inorganics, Inc., and dimethyl sulfoxide, purchased from Matheson Coleman and Bell, were used as received. The tetraalkylammonium and tetraarylarsonium salts were used as received from Distillation Products and Aldrich Chemical Co., Inc. Triphenylphosphine oxide was prepared from triphenylphosphine and hydrogen peroxide in alcohol-water. The white crystalline product was recrystallized from alcohol-water (1:1).

Analytical data are the results of microanalyses by S. M. Nagy, M.I.T., and Galbraith Laboratories, Knoxville, Tenn.

**Preparation of Compounds:**  $(\text{C}_6\text{H}_5)_4\text{AsTlCl}_4$ .—Chlorine was passed briskly through a suspension of thallous chloride (1.2 g., 0.005 mole) in acetonitrile (30 ml.). After 30 min., when all the solid material had dissolved, tetraphenylarsonium chloride (2.1 g., 0.005 mole) was added. The solvent was then removed under vacuum, leaving white needles of  $(\text{C}_6\text{H}_5)_4\text{AsTlCl}_4$ . The crude product was recrystallized from acetone-alcohol (1:1); yield 3.5 g., 96%.

$(\text{CH}_3)_4\text{NTlCl}_4$ ,  $(\text{C}_2\text{H}_5)_4\text{NTlCl}_4$ , and  $(\text{C}_4\text{H}_9)_4\text{NTlCl}_4$ .—These complexes were prepared in almost quantitative yields following essentially the same procedure as that used for  $(\text{C}_6\text{H}_5)_4\text{AsTlCl}_4$ .

$(\text{CH}_3)_4\text{NTlBr}_4$ ,  $(\text{C}_2\text{H}_5)_4\text{NTlBr}_4$ , and  $(\text{C}_4\text{H}_9)_4\text{NTlBr}_4$ .—Excess bromine was added to a suspension of thallous bromide (1.4 g., 0.005 mole) in acetonitrile (30 ml.). The reaction mixture was stirred vigorously until all of the solid material had dissolved. To this solution was added the appropriate tetraalkylammonium bromide (0.005 mole) and then the solvent was removed under vacuum, leaving white needles of the product. The products were recrystallized from acetone-alcohol (1:1); yields ~ 95%.

$(\text{C}_6\text{H}_5)_4\text{AsTlI}_4$  and  $(\text{C}_4\text{H}_9)_4\text{NTlI}_4$ .—To a solution of  $(\text{C}_6\text{H}_5)_4\text{AsTlCl}_4$  (0.73 g., 0.001 mole) or  $(\text{C}_4\text{H}_9)_4\text{NTlCl}_4$  (0.59 g., 0.001 mole) in acetone (10 ml.) was added a solution of sodium iodide (0.6 g., 0.004 mole) in water (5 ml.). The solution immediately became red-orange in color. The solvent was then removed under vacuum. The residual red-orange solid was washed with water and alcohol and recrystallized from acetone-ether (1:1) as needles; yields: 1.0 g. of  $(\text{C}_6\text{H}_5)_4\text{AsTlI}_4$ , 93%; 0.86 g. of  $(\text{C}_4\text{H}_9)_4\text{NTlI}_4$ , 90%.

$(\text{C}_6\text{H}_5)_3\text{CH}_3\text{AsTlI}_4$ .—Chlorine was passed through a suspension of thallous chloride (1.2 g., 0.005 mole) in water (20 ml.) for 30 min. The excess chlorine was then removed in a fast stream of nitrogen and a solution of sodium iodide (2.25 g., 0.015 mole) and triphenylmethylarsonium iodide (2.24 g., 0.005 mole) in acetone-water (1:1) (20 ml.) added. The solution immediately became red-orange in color. The solvent was partially removed under vacuum when bright red-orange needles separated. The product was separated by filtration, washed with water and a little alcohol, and recrystallized from acetone; yield 4.2 g., 82%.

$\text{TlCl}_3 \cdot 2(\text{CH}_3)_2\text{SO}$ .—Chlorine was passed through a suspension of thallous chloride (1.2 g., 0.005 mole) in acetonitrile (30 ml.) for 30 min. The solvent and excess chlorine were then removed under vacuum, and the residual white solid was redissolved in dimethyl sulfoxide (10 ml.). The solvent was partially removed under vacuum at 25° and excess carbon tetrachloride added (100 ml.). On standing for 48 hr., a white solid separated. The product was removed by filtration and recrystallized from acetone; yield 1.5 g., 63%.

$\text{TlCl}_3 \cdot 2(\text{C}_6\text{H}_5)_3\text{PO}$ .—Triphenylphosphine oxide (2.8 g., 0.01 mole) in alcohol (20 ml.) was added to a freshly prepared solution of thallic chloride (1.55 g., 0.005 mole) in acetonitrile (30 ml.). On standing for 15 min., a white solid separated. The product was removed by filtration and was recrystallized from alcohol-water (1:1); yield 2.9 g., 67%.

$\text{TlBr}_3 \cdot 2(\text{C}_6\text{H}_5)_3\text{PO}$ .—This compound was prepared by essentially the same procedure as that for  $\text{TlCl}_3 \cdot 2(\text{C}_6\text{H}_5)_3\text{PO}$ .

$\text{TlI}_3 \cdot 3(\text{C}_6\text{H}_5)_3\text{PO}$ .—(1) Sodium iodide (0.28 g., 0.002 mole) in water (3 ml.) was added dropwise with stirring to a solution of  $\text{TlBr}_3 \cdot 2(\text{C}_6\text{H}_5)_3\text{PO}$  (0.5 g., 0.0005 mole) in acetone (10 ml.). The solution instantly became orange-yellow in color. The solvent was removed under vacuum when an orange-yellow solid precipitated. The product was separated by filtration and recrystallized from acetone.

(1) Supported by the National Science Foundation.

(2) See, for example, S. Ahrland, I. Grenthe, L. Johansson, and B. Noren, *Acta Chem. Scand.*, **17**, 1567 (1963).(3) R. J. Meyer, *Z. anorg. Chem.*, **24**, 321 (1900).(4) K. Renz, *Ber.*, **35**, 1110 (1902).(5) W. Krause and A. Grosse, *ibid.*, **59**, 1712 (1926).(6) G. J. Sutton, *Australian J. Chem.*, **11**, 120 (1958).(7) F. Ya. Kul'ba, V. E. Mironov, C. Ts'ung, and Z. G. Filippova, *Zh. Neorgan. Khim.*, **8**, 672 (1962).(8) F. Ya. Kul'ba, V. E. Mironov, V. I. Sazhina, and T. G. Ogibina, *ibid.*, **8**, 911 (1963).

TABLE I  
 ANALYTICAL DATA AND OTHER PROPERTIES OF SOME TETRAHALOTHALLIUM(III) COMPOUNDS

Compound	Color	M.p., °C.	C, %		H, %		Halogen, %		N, %		$\Delta m,^a$ ohm <sup>-1</sup> cm. <sup>2</sup> mole <sup>-1</sup>
			Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	
[(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> As][TiCl <sub>4</sub> ]	White	146–147	39.2	39.49	2.7	2.74	19.7	19.47	...	...	146
[(n-C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> N][TiCl <sub>4</sub> ]	White	115–116	32.7	32.60	6.09	6.11	24.2	24.11	2.40	2.38	148
[(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> N][TiCl <sub>4</sub> ]	White	253–254	20.4	20.19	4.29	4.21	29.7	29.86	3.05	2.94	157
[(CH <sub>3</sub> ) <sub>4</sub> N][TiCl <sub>4</sub> ]	White	>300	11.6	11.42	3.05	2.86	33.8	33.78	3.59	3.33	170
[(n-C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> N][TiBr <sub>4</sub> ]	White	127–128	25.2	25.05	4.74	4.70	...	...	1.84	1.79	141
[(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> N][TiBr <sub>4</sub> ]	White	254–259	14.8	14.68	3.05	3.06	...	...	2.30	2.14	153
[(CH <sub>3</sub> ) <sub>4</sub> N][TiBr <sub>4</sub> ]	Cream	247–249	8.89	8.03	2.30	2.01	...	...	2.48	2.34	170
[(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> As][TiI <sub>4</sub> ]	Red-orange	142–143	27.2	26.29	1.97	1.83	...	...	...	...	140
[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> CH <sub>3</sub> As][TiI <sub>4</sub> ]	Red-orange	141–142	22.7	22.08	1.89	1.74	...	...	...	...	131
[(n-C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> N][TiI <sub>4</sub> ]	Yellow-orange	117–118	20.4	20.17	3.91	3.78	...	...	1.62	1.47	166

<sup>a</sup> In acetonitrile.

(2) Sodium iodide (2.25 g., 0.015 mole) and triphenylphosphine oxide (2.8 g., 0.010 mole) in water-ethanol (1:10) (20 ml.) were added dropwise with stirring to a freshly prepared solution of thallic chloride (1.55 g., 0.005 mole) in acetonitrile (30 ml.). The solution immediately became orange-yellow in color. The solvent was removed under vacuum when orange-yellow TlI<sub>3</sub>·3-(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PO separated; yield 2.4 g., 27%.

**TlCl<sub>3</sub>·2C<sub>6</sub>H<sub>5</sub>N.**—Excess pyridine (10 ml.) was added to a freshly prepared solution of thallic chloride (1.55 g., 0.005 mole) in water (20 ml.). A white solid instantly separated. The product was separated by filtration, washed with ether, and recrystallized from alcohol-acetone (1:1); yield 1.83 g., 78%.

**Tl[(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NCS<sub>2</sub>]<sub>3</sub>.**—A solution of sodium diethyldithiocarbamate trihydrate (3.38 g., 0.015 mole) was added, dropwise with stirring, to a solution of thallic chloride (1.5 g., 0.005 mole) in acetonitrile (30 ml.). A bright yellow crystalline solid immediately precipitated. The product was separated by filtration, washed with several portions of water, and recrystallized from acetone; yield 2.66 g., 82%.

**Electrolytic Conductances.**—These were measured with a standard, commercial Wheatstone bridge. Solvents were of spectroscopic grade and the solutions were all approximately 10<sup>-3</sup> M.

**X-Ray Diffraction Data.**—Powder patterns were recorded using a General Electric rotating sample camera with Cu K $\alpha$  radiation. Single crystal photographs used to determine crystal classes and unit cell dimensions were taken with Cu K $\alpha$  radiation by the oscillation and Weissenberg methods.

**Molecular Weights.**—These were measured cryoscopically in sulfolane (tetramethylene sulfone) using the reported freezing point depression constant.<sup>9</sup>

## Results

**Salts of the [TiX<sub>4</sub>]<sup>-</sup> Ions.**—As shown in the Experimental section, salts, MTiX<sub>4</sub>, of the tetrahalothallate(III) ions with a variety of cations are easily prepared, usually in yields exceeding 90% by using approximately stoichiometric quantities of MX and TiX<sub>3</sub>, or by halogen exchange in nonaqueous media such as acetonitrile. Table I lists all the new tetrahalothallate compounds prepared and gives analytical and some other useful data for them. The salts of [TiCl<sub>4</sub>]<sup>-</sup> are all white, those of [TiBr<sub>4</sub>]<sup>-</sup> are white or cream, while those of [TiI<sub>4</sub>]<sup>-</sup> are red-orange or yellow-orange. Nearly all the compounds prepared here were obtained as well-defined needle crystals, readily soluble in acetonitrile, nitromethane, and acetone, but nearly insoluble in ethanol and quite insoluble in water, ether, and benzene. The formulations of all these compounds as uni-

valent electrolytes is substantiated by their molar electrolytic conductances in CH<sub>3</sub>CN, which are in the range 130–170 ohm<sup>-1</sup> cm.<sup>2</sup> mole<sup>-1</sup>. For the established, similar 1:1 electrolyte [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>As][FeCl<sub>4</sub>],<sup>10</sup> we find a value of 150 ohm<sup>-1</sup> cm.<sup>2</sup> mole<sup>-1</sup>, while for the 1:2 electrolytes, [As(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>]<sub>2</sub>[NiCl<sub>4</sub>] and [N(CH<sub>3</sub>)<sub>4</sub>]<sub>2</sub>[CoCl<sub>4</sub>], we have found values of 302 and 294 ohm<sup>-1</sup> cm.<sup>2</sup> mole<sup>-1</sup>, respectively, for ~10<sup>-3</sup> M solutions in CH<sub>3</sub>CN.

By means of X-ray studies, some structural features of the [TiX<sub>4</sub>]<sup>-</sup> complexes have been determined. Perhaps most significant is the demonstration that [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>As][TiCl<sub>4</sub>] is isomorphous with [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>As][FeCl<sub>4</sub>], since the latter is known, on the basis of a complete single crystal X-ray structure determination,<sup>10</sup> to contain tetrahedral [FeCl<sub>4</sub>]<sup>-</sup> ions. It is therefore extremely likely that the thallium compound contains tetrahedral [TiCl<sub>4</sub>]<sup>-</sup> ions.

From an oscillation photograph and Weissenberg photographs of the *hk0* and *hk1* layers, the crystal was found to be tetragonal with dimensions  $a = 13.3 \pm 0.1$  and  $c = 7.19 \pm 0.05$  Å. and reflections with  $h + k + l \neq 2n$  were systematically absent. The dimensions correspond very closely to those for [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>As][FeCl<sub>4</sub>], viz.,  $a = 13.16$  and  $c = 7.15$  Å., and the systematic absence is the same as for the iron compound. As a further check, a powder pattern for [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>As][TiCl<sub>4</sub>] was recorded and, as shown in Table II, all observed lines (out to a distance where they become so closely spaced as to be of little significance) can be satisfactorily indexed using the above cell dimensions and without violating the condition for systematic absences.

In addition, it has been shown that the two [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N][TiX<sub>4</sub>] compounds, with X = Cl and Br, are isomorphous. From oscillation and precession photographs, it was found that the bromo compound crystallizes in the orthorhombic system, with unit cell dimensions,  $a = 18.52$ ,  $b = 11.91$ , and  $c = 11.74$  Å. The following systematic extinctions were observed: for *hk0*,  $h \neq 2n$ , for *0kl*,  $k + l \neq 2n$ , for *h0l*,  $h + l \neq 2n$ . From these, the space group is uniquely identified as Pnna (No. 52). A rough density measurement, by flotation in iodoethane, gave  $1.93 \pm 0.05$  g. cm.<sup>-3</sup>, which indicates that there are four formula units per unit cell (calculated density 1.93 g. cm.<sup>-3</sup>).

(9) R. L. Burwell, Jr., and C. H. Langford, *J. Am. Chem. Soc.*, **81**, 3799 (1959).

(10) B. Zaslav and R. E. Rundle, *J. Phys. Chem.*, **61**, 490 (1957).

TABLE II  
 X-RAY POWDER DATA<sup>a</sup> FOR (C<sub>5</sub>H<sub>5</sub>)<sub>4</sub>AsTlCl<sub>4</sub>

<i>h</i>	<i>k</i>	<i>l</i> <sup>b</sup>	<i>I</i> <sup>c</sup>	<i>d</i> <sub>obsd</sub>	<i>d</i> <sub>calcd</sub> <sup>b</sup>	<i>h</i>	<i>k</i>	<i>l</i>	<i>I</i>	<i>d</i> <sub>obsd</sub>	<i>d</i> <sub>calcd</sub>
1	1	0	w	9.40	9.40	3	3	2	w	2.36	{ 2.36
2	0	0	s	6.66	6.66	1	0	3			
1	0	1	s	6.33	6.33	4	4	0	0	...	2.35
2	2	0	vw	4.72	4.70	5	2	1	w	2.34	2.34
1	2	1	vs	4.58	4.58	4	2	2	vw	2.29	{ 2.29
3	1	0	w	4.20	4.20	5	3	0			
3	0	1	w	3.77	3.76	2	1	3	w	2.22	2.22
0	0	2	0	...	3.59	6	0	0	0	...	2.21
1	1	2	vw	3.36	3.36	5	1	2	m	2.11	{ 2.11
4	0	0	0	...	3.32	3	0	3			
3	2	1	m	3.28	3.27	6	2	0	0	...	2.10
2	0	2	w	3.16	3.16	6	1	1	m	2.09	2.09
3	3	0	0	...	3.14	3	2	3	w	2.01	2.01
4	2	0	m, br	2.95	{ 2.98	5	4	1	w	2.00	2.00
4	1	1				{ 2.94	4	4	2	vw	1.96
2	2	2	w	2.86	2.86	5	3	2	m	1.93	{ 1.93
3	1	2	ms	2.74	2.74	4	1	3			
5	1	0	vw	2.61	2.61						
5	0	1	m	2.49	{ 2.49						
4	3	1				{ 2.49					
4	0	2	0	...	2.44						

<sup>a</sup> The body of the table lists all possible lines to a *d* value of 1.93. In addition to those lines listed the following weak ones were also found at still lower *d* values; possible indices for them are given in parentheses: 1.77 (503, 433), 1.75 (730), 1.72 (523), 1.67 (712, 552, 800), 1.61 (820, 811, 741), 1.57 (732, 543, 660). <sup>b</sup> Indices and *d*<sub>calcd</sub> values based on tetragonal cell with *a* = 13.30, *c* = 7.19 Å. <sup>c</sup> Relative intensities, visually estimated: v, very; s, strong; m, medium; w, weak; br, broad.

With these data, a powder photograph of [(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>-N][TlBr<sub>4</sub>] was completely indexed (Table III). It was then possible to index completely (Table III) a powder photograph of [(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N][TlCl<sub>4</sub>], using the same space group with unit cell dimensions, *a* = 18.25, *b* = 11.63, *c* = 11.40 Å. (The actual accuracy of these dimensions is probably only ±0.1 Å.) [(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N][TlI<sub>4</sub>] does not appear to be isomorphous with the corresponding chloro and bromo compounds, and its structure has not been further investigated.

**Complexes with Neutral Ligands.**—Those prepared are listed in Table IV together with analytical figures and some other characteristics. Many were obtained by addition of the neutral ligand to the appropriate thallium(III) halide in a nonaqueous medium, but for the pyridine compound the solvent was water.

From its formula and virtual lack of electrolytic conductance in CH<sub>3</sub>CN, the tris(diethyldithiocarbamate) compound appears to be a trichelate, octahedral complex, quite similar to those formed by many trivalent transition metal ions.<sup>11</sup>

Compounds of Tl(III) chloride with pyridine have long been known. Both Meyer<sup>3</sup> and Renz<sup>4</sup> reported the preparation of TlCl<sub>3</sub>(C<sub>5</sub>H<sub>5</sub>N)<sub>3</sub> by reaction of pyridine with aqueous thallic chloride. More recently, however, Kul'ba and co-workers<sup>8</sup> have claimed that the product of this reaction is in fact TlCl<sub>3</sub>(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub> and they have suggested on the basis of conductance data that it has an ionic structure such as [Tl(C<sub>5</sub>H<sub>5</sub>N)<sub>4</sub>Cl<sub>2</sub>][TlCl<sub>4</sub>] or [Tl(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>Cl<sub>2</sub>][TlCl<sub>4</sub>]. We have confirmed the stoichiometry found by Kul'ba, *et al.*; TlCl<sub>3</sub>(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub> is the only product we have obtained from this reaction. Moreover, the conductance, measured in aceto-

nitrile, also indicates that the compound may be ionic. The molar conductance of 107 ohm<sup>-1</sup> cm.<sup>2</sup> mole<sup>-1</sup> is somewhat low for the formula [Tl(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>Cl<sub>2</sub>][TlCl<sub>4</sub>] (*cf.* the range 130–170 ohm<sup>-1</sup> cm.<sup>2</sup> mole<sup>-1</sup> for the 1:1 electrolytes, M[TlX<sub>4</sub>]) but a little high for the formula [Tl(C<sub>5</sub>H<sub>5</sub>N)<sub>4</sub>Cl<sub>2</sub>][TlCl<sub>4</sub>], since on this basis the molar conductance is 214 ohm<sup>-1</sup> cm.<sup>2</sup> mole<sup>-1</sup>. Thus, like Kul'ba, *et al.*, we believe that the correct formula might be either of these two.

For comparison, we have also examined the compound TlCl<sub>3</sub>(phen), where phen represents 1,10-phenanthroline. This has been previously prepared by Sutton<sup>6</sup> and Kul'ba, *et al.*<sup>8</sup> We find that an approximately 10<sup>-3</sup> M solution in acetonitrile has a molar conductance of 52 ohm<sup>-1</sup> cm.<sup>2</sup> mole<sup>-1</sup> for the formula TlCl<sub>3</sub>(phen) or twice that for a dimer. The latter value, 104 ohm<sup>-1</sup> cm.<sup>2</sup> mole<sup>-1</sup>, is only a little bit low for the ionic formula [Tl(phen)<sub>2</sub>Cl<sub>2</sub>][TlCl<sub>4</sub>], whereas the former value is only about one-third of that which would be expected for [Tl(phen)Cl<sub>2</sub>][TlCl<sub>4</sub>].

Trichlorobis(dimethyl sulfoxide)thallium(III), TlCl<sub>3</sub>(DMSO)<sub>2</sub>, may be an authentic five-coordinate Tl(III) complex, but this is far from certain. Thus, the molar conductance in acetonitrile (Table IV) indicates negligible ionic dissociation and the molecular weight measured cryoscopically in sulfolane is 467 compared to 469 calculated for TlCl<sub>3</sub>(DMSO)<sub>2</sub>. The compound dissolves readily in a number of donor solvents, *e.g.*, ethanol, acetonitrile, acetone, dimethyl sulfoxide, and nitromethane, giving stable, colorless solutions, but it is quite insoluble in a variety of nondonor solvents, *e.g.*, carbon tetrachloride, chloroform, benzene, and aliphatic hydrocarbons. Thus, while dissociation to give a four-coordinate species in solution can be ruled out, it is possible, and perhaps even likely, that the species in solu-

(11) See, for example, F. A. Cotton and J. A. McCleverty, *Inorg. Chem.*, **3**, 1398 (1964), and prior references therein.

TABLE III  
 X-RAY POWDER DATA FOR  $[(n-C_4H_9)_4N][TlX_4]$  COMPOUNDS WITH X = Cl and Br

h	k	j <sup>a,b</sup>	X = Cl			X = Br		
			I <sup>c</sup>	d <sub>obsd</sub>	d <sub>calcd</sub> <sup>a</sup>	I <sup>c</sup>	d <sub>obsd</sub>	d <sub>calcd</sub>
1	0	1	vs	9.80	9.67	vs	9.99	9.91
2	0	0	w	9.07	9.13	w	9.33	9.25
1	1	1	vs	7.36	7.43	vs	7.67	7.62
2	1	0	mw	7.15	7.18	mw	7.34	7.31
2	1	1	0	...	6.07	vw	6.22	6.20
0	2	0	vs	5.79	5.81	m	5.93	5.95
3	0	1	s	5.33	5.37	w	5.48	5.46
1	2	1	0	...	4.98	vw	5.10	5.10
1	1	2	w	4.94	4.93	0	...	5.06
2	2	0	0	...	4.90	vw	5.02	5.01
2	0	2	w	4.82	4.83	0	...	4.96
4	0	0	vw	4.59	4.56	0	...	4.63
2	2	1	m	4.51	4.50	0	...	4.60
2	1	2	0	...	4.46	mw	4.58	4.58
4	1	0	w	4.24	4.25	vw	4.34	4.31
0	2	2	vw	4.06	4.07	vw	4.18	4.18
4	1	1	s	3.98	3.98	s	4.04	4.05
1	0	3	}	}	}	vw	3.83	3.83
2	2	2				w	3.72	0
0	3	1	0	...	3.67	vw	3.76	3.76
4	2	0	0	...	3.59	vw	3.66	3.65
4	0	2	}	}	}	0	...	3.63
2	3	0				m	3.56	0
2	3	0	}	}	}	0	...	3.65
2	3	1				vw	3.40	m
4	1	2	}	}	}	0	...	3.48
2	1	3				vw	3.35	0
1	2	3	}	}	}	w	3.22	3.22
3	3	1				0	...	3.14
3	1	3	vw	3.11	3.11	0	...	3.18
4	2	2	}	}	}	0	...	3.10
2	3	2				vw	3.03	vw
5	2	1	}	}	}	0	...	3.04
5	1	2				0	...	2.98
6	1	0	vw	2.94	2.94	0	...	2.99
3	3	2	}	}	}	0	...	2.90
4	1	3				vw	2.83	vw
6	1	1	}	}	}	0	...	2.90
						vw	2.85	vw

<sup>a</sup> Indices and  $d_{\text{calcd}}$  values for Cl compound based on orthorhombic cell with  $a = 18.26$ ,  $b = 11.63$ , and  $c = 11.40$  Å. <sup>b</sup> Indices and  $d_{\text{calcd}}$  values for Br compound based on orthorhombic cell with  $a = 18.52$ ,  $b = 11.91$ , and  $c = 11.74$  Å. <sup>c</sup> Relative intensities, visually estimated: v, very; s, strong; m, medium; w, weak.

 TABLE IV  
 ANALYTICAL DATA AND OTHER PROPERTIES OF SOME Tl(III) COMPOUNDS WITH NEUTRAL LIGANDS

Compound	Color	M.p., °C.	C, %		H, %		Halogen, %		Λ <sub>m</sub> , ohm <sup>-1</sup> cm. <sup>2</sup> mole <sup>-1</sup>	
			Found	Calcd.	Found	Calcd.	Found	Calcd.	CH <sub>3</sub> CN	CH <sub>3</sub> NO <sub>2</sub>
TlCl <sub>3</sub> ·2(CH <sub>3</sub> ) <sub>2</sub> SO	White	102	10.42	10.38	2.61	2.57	22.78	22.80	21.6	...
TlCl <sub>3</sub> ·2(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PO	White	196	49.71	49.77	3.41	3.46	12.36	12.27	20.3	...
TlBr <sub>3</sub> ·2(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PO	White	186	42.59	43.28	3.05	3.01	24.53	23.97	44.0	...
TlI <sub>3</sub> ·3(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PO	Yellow-orange	234-236	46.30	45.63	3.32	3.17	28.12	26.80	106	72
TlI <sub>3</sub> ·2(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PO <sup>a</sup>	...	...	...	38.74	...	2.63	...	33.38	...	...
TlCl <sub>3</sub> ·2C <sub>6</sub> H <sub>5</sub> N	White	160-162	26.41	25.60	2.25	2.13	21.69	21.59	97.0	...
TlCl <sub>3</sub> ·C <sub>12</sub> H <sub>8</sub> N <sub>2</sub>	White	303 dec.	29.89	29.34	1.69	1.63	20.29	21.69	52.0	...
Tl[(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NCS <sub>2</sub> ] <sub>3</sub>	Yellow	192 dec.	27.92	27.73	4.69	4.62	...	...	7.7	...

<sup>a</sup> Not prepared; analytical figures given for comparison with those for TlI<sub>3</sub>·3(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PO.

tion are six-coordinate molecules, [TlCl<sub>3</sub>(DMSO)<sub>2</sub>(solvent)]. As for the solid compound, the possibility of chlorine atom bridging to give a dimer in which each thallium atom has a coordination number of six cannot be ruled out on any evidence presently at hand. Probably only by X-ray structural work can the presence of five-coordinate monomers in the solid be proved or disproved.

The coordination of the DMSO to thallium through the oxygen is demonstrated by the infrared spectrum<sup>12</sup> of the solid, which shows the SO stretching mode shifted down to 930 cm.<sup>-1</sup>. This may be compared particularly with the frequency of 933 cm.<sup>-1</sup> found for FeCl<sub>3</sub>-

(DMSO)<sub>2</sub>, but it is typical for complexes containing O-coordinated DMSO.<sup>12</sup>

The preparation in analytical purity of  $\text{TlCl}_3[(\text{C}_6\text{H}_5)_3\text{PO}]_2$  has been reported before<sup>13</sup> but the compound was not further characterized. The molecular weight, measured cryoscopically in sulfolane, indicates that the compound is monomeric and undissociated in this solvent (found 908, calculated for monomer 868). In benzene, however, there is some dissociation since the molecular weight measured by vapor phase osmometry is only 642. Like the DMSO compound, this one also has a low conductivity in  $\text{CH}_3\text{CN}$ , indicating only slight ionic dissociation. Unlike the DMSO compound, however, it is soluble in benzene. It is also soluble in acetone and acetonitrile but insoluble in ether and alkanes. The infrared spectrum of the solid shows a lowering of the P-O stretching band by  $\sim 20 \text{ cm.}^{-1}$ , which is the characteristic result<sup>14</sup> of coordination of a phosphine oxide.

Tribromobis(triphenylphosphine oxide)thallium(III),  $\text{TlBr}_3[(\text{C}_6\text{H}_5)_3\text{PO}]_2$ , is somewhat different from the analogous chloro derivative. It is generally less soluble in organic media and it is highly dissociated in acetone and tetrahydrofuran. In both of these solvents, the molecular weight measured by vapor phase osmometry was 380 compared to 1000 for  $\text{TlBr}_3 \cdot 2 \cdot (\text{C}_6\text{H}_5)_3\text{PO}$ . It also shows a conductance in acetonitrile which is more than twice that of the chloro compound. While this conductance is below the range for a 1:1 electrolyte, even if the compound is formulated as  $\{\text{Tl}[(\text{C}_6\text{H}_5)_3\text{PO}]_4\text{Br}_2\} [\text{TlBr}_4]$ , it indicates appreciable ionic dissociation of some kind in  $\text{CH}_3\text{CN}$ .

Attempts to prepare  $\text{TlI}_3[(\text{C}_6\text{H}_5)_3\text{PO}]_2$  were unsuccessful, the product being, instead,  $\text{TlI}_3[(\text{C}_6\text{H}_5)_3\text{PO}]_3$ . This compound has molar conductances of  $106 \text{ ohm}^{-1} \text{ cm.}^2 \text{ mole}^{-1}$  in acetonitrile and  $72 \text{ ohm}^{-1} \text{ cm.}^2 \text{ mole}^{-1}$  in nitromethane. Both of these values are close to those typical of 1:1 electrolytes<sup>15</sup> on the basis of a dimeric molecular formula,  $\{\text{Tl}[(\text{C}_6\text{H}_5)_3\text{PO}]_4\text{I}_2\} \{\text{Tl}[(\text{C}_6\text{H}_5)_3\text{PO}]_4\text{I}_4\}$ .

### Discussion

Published data providing definitive structural information on thallium(III) complexes is very limited. The binuclear complex occurring in  $\text{Cs}_3\text{Tl}_2\text{Cl}_9$  was described by Hoard and Goldstein.<sup>16</sup> Hexahalothallate(III) ions with octahedral structures have been found in  $\text{K}_3\text{TlCl}_6 \cdot 2\text{H}_2\text{O}$ ,<sup>17</sup>  $\text{Rb}_3\text{TlBr}_6 \cdot 8/7\text{H}_2\text{O}$ ,<sup>17</sup>  $[\text{Co}(\text{NH}_3)_6]\text{TlCl}_6$ ,<sup>18</sup> and  $[\text{Co}(\text{NH}_3)_6]\text{TlBr}_6$ ,<sup>18</sup> and the octahedral  $[\text{TlCl}_5\text{H}_2\text{O}]^{2-}$  ion has been found in the cesium salt.<sup>19</sup> A tetrahedral tetrabromothallate(III) ion has recently

been shown<sup>20</sup> to exist in  $\text{TlBr}_2(\text{Tl}^{\text{I}}\text{Tl}^{\text{III}}\text{Br}_4)$ . Finally, it has been stated<sup>18,19,21</sup> that  $\text{CsTlBr}_4$  contains square  $[\text{TlBr}_4]^-$  ions and that structural studies have been made of  $(\text{NH}_4)\text{TlBr}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{KTlBr}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{RbTlBr}_4 \cdot \text{H}_2\text{O}$ ,  $\text{KTlI}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{RbTlI}_4 \cdot 2\text{H}_2\text{O}$ , and  $\text{CsTlI}_4$ , with at least one of them having been found to contain an octahedral *trans*- $[\text{TlBr}_4(\text{H}_2\text{O})_2]^-$  ion.

There appears to have been no comprehensive study of the preparation of salts of halothallate(III) ions reported since the investigation of Meyer<sup>3</sup>; his work, however, was limited entirely to aqueous media. Meyer found that from an aqueous solution of  $\text{TlCl}_3$  to which  $< 3$  moles of  $\text{KCl}$  was added, the only crystalline product was  $\text{K}_2\text{TlCl}_5 \cdot 2\text{H}_2\text{O}$ . This probably contains the  $[\text{TlCl}_5(\text{H}_2\text{O})]^{2-}$  ion found<sup>20</sup> in  $\text{Cs}_2\text{TlCl}_5 \cdot \text{H}_2\text{O}$ , which, however, is obtained<sup>19</sup> by evaporating an aqueous solution of  $\text{CsCl}$  and  $\text{TlCl}_3$  in a mole ratio of 10:1. Meyer further found that when the mole ratio  $\text{KCl}:\text{TlCl}_3$  was  $\geq 3$  the compound obtained was always  $\text{K}_3\text{TlCl}_6 \cdot 2\text{H}_2\text{O}$ , which contains<sup>17</sup> the  $[\text{TlCl}_6]^{3-}$  ion. With an excess of  $\text{NH}_4\text{Cl}$ , however, he obtained  $(\text{NH}_4)_3\text{TlCl}_6$ . With excess  $\text{KBr}$ , he obtained  $\text{KTlBr}_4 \cdot 2\text{H}_2\text{O}$ , while with only 1 mole of  $\text{KBr}$  per mole of  $\text{TlBr}_3$  he obtained  $\text{KTlBr}_4 \cdot \text{H}_2\text{O}$ . It is for these last two compounds that square-planar  $\text{TlBr}_4$  groups have been claimed.<sup>21</sup>

When the results outlined above are taken in conjunction with the observation<sup>2</sup> that  $\text{TlX}_n^{-n+3}$  species with  $n > 4$  apparently do not exist in equilibrium in aqueous solution, it seems evident that the nature of the compounds obtained from aqueous solution is determined by complicated *heterogeneous* equilibria and perhaps by certain kinetic factors, with these depending *inter alia* upon cation size. It was with these considerations in mind that the present studies were carried out largely in nonaqueous media, using relatively large quaternary cations. Our hope of thus finding somewhat simpler and more regular behavior has been fulfilled. Perhaps the most striking result is the prevalence of simple  $\text{M}[\text{TlX}_4]$  type compounds, in contrast to the virtual absence of such compounds among the products which have been obtained from aqueous systems.

The present study shows, first, that compounds of the stoichiometry  $\text{M}[\text{TlX}_4]$ , where  $\text{M}$  is a large quaternary ammonium or arsonium cation, are easy to prepare in pure, crystalline form, and that such compounds are 1:1 electrolytes in  $\text{CH}_3\text{CN}$ . No compounds of this class appear to have been reported prior to this. For the particular case of  $[(\text{C}_6\text{H}_5)_4\text{As}][\text{TlCl}_4]$ , it has been shown that the tetrachlorothallate ion is tetrahedral. The compounds  $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{TlX}_4]$  with  $\text{X} = \text{Cl}$  or  $\text{Br}$  are isomorphous and presumably isostructural, but there is no evidence regarding the symmetry of the  $[\text{TlX}_4]^-$  ions in these compounds. While it would seem likely that they are tetrahedral, the possibility that in some compounds the  $[\text{TlX}_4]^-$  ions may be planar cannot be ruled out in view of the claim<sup>21</sup> that the  $[\text{Tl}$

(13) M. J. Frazer, W. Gerrard, and R. Twaits, *J. Inorg. Nucl. Chem.*, **25**, 637 (1963).

(14) F. A. Cotton, R. Barnes, and E. Bannister, *J. Chem. Soc.*, 2199 (1960).

(15) For nitromethane the range is  $80\text{--}100 \text{ ohm}^{-1} \text{ cm.}^2$  at  $20\text{--}25^\circ$ . Cf. C. M. Harris, and T. N. Lockyer, *J. Chem. Soc.*, 3083 (1959); N. S. Gill and R. S. Nyholm, *ibid.*, 3997 (1959); J. E. Fergusson and R. S. Nyholm, International Conference on Coordination Chemistry, London, 1959, Paper No. 62.

(16) J. L. Hoard and L. Goldstein, *J. Chem. Phys.*, **3**, 199 (1935).

(17) J. L. Hoard and L. Goldstein, *ibid.*, **3**, 645 (1935).

(18) T. Watanabe, M. Atoji, and C. Okazaki, *Acta Cryst.*, **3**, 405 (1950).

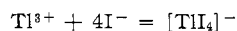
(19) T. Watanabe and M. Atoji, *J. Am. Chem. Soc.*, **72**, 3819 (1950).

(20) A. C. Hazell, *J. Chem. Soc.*, 3459 (1963).

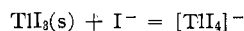
(21) T. Watanabe, Y. Sarto, R. Shiono, and M. Atoji, Abstracts, First Congress of the International Union of Crystallography, 1948, p. 30; see also *Structure Rept.*, **11**, 393 (1947-48).

$\text{Br}_4^-$  ion is planar in  $\text{CsTlBr}_4$ . It appears that a reinvestigation of the structure of  $\text{Cs}[\text{TlBr}_4]$  as well as complete structural studies of one or more of the other  $\text{M}[\text{TlX}_4]$  compounds would be worthwhile.

The  $\text{M}[\text{TlL}_4]$  compounds are of particular interest in connection with the question<sup>22</sup> of the nature of  $\text{TlI}_3$ . Sharpe<sup>22</sup> has proposed that, while  $\text{TlI}_3$  itself probably contains  $\text{Tl}^+$  and  $\text{I}_3^-$  ions, in the presence of excess  $\text{I}^-$  the thallium is in fact  $\text{Tl(III)}$ , the trivalent state being stabilized by complexation to form  $[\text{TlI}_4]^-$ . While there were some very old equilibrium data to indicate a large equilibrium constant for the reaction



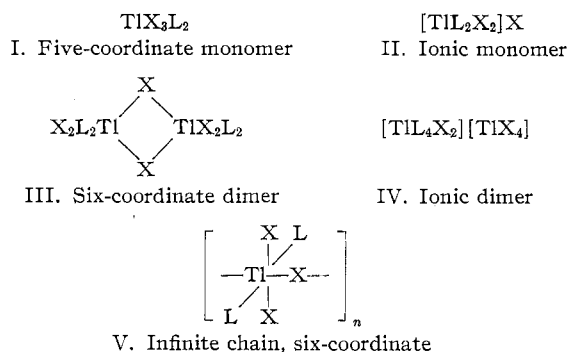
in aqueous solution, there has not, heretofore, been any direct proof of the existence of the  $[\text{TlI}_4]^-$  ion. The actual isolation of salts of this ion tends to substantiate Sharpe's view that the over-all reaction



actually occurs.

The group of compounds of the  $\text{Tl(III)}$  halides with the neutral ligands, dimethyl sulfoxide, triphenylphosphine oxide, pyridine, and 1,10-phenanthroline, pose some interesting problems in the assignment of structure. Unambiguous conclusions on the basis of the usual simple physical measurements are elusive, if not unattainable for several of them. With the exception of  $\text{TlI}_3[(\text{C}_6\text{H}_5)_3\text{PO}]_3$ , they are all of the stoichiometric type  $\text{TlX}_3\text{L}_2$ , where L represents a unidentate ligand or half of a bidentate one.

In general, five structural possibilities, I-V, appear reasonably plausible for these compounds. It should be kept in mind in the following discussion that conclu-



(22) A. G. Sharpe, *J. Chem. Soc.*, 2165 (1952).

sions regarding structures which occur in solvents such as sulfolane, acetonitrile, benzene, or nitromethane do not necessarily apply to the structures of the solid compounds.

For the compounds  $\text{TlX}_3(\text{C}_5\text{H}_5\text{N})_2$  and  $\text{TlCl}_3(\text{phen})$ , there seems little doubt that they have completely, or nearly completely, ionic structures in solution; for the former, either type II or IV, and for the phenanthroline compound, most likely type IV structures are suggested by conductance data.

For the compounds in which L represents DMSO or triphenylphosphine oxide, on the other hand, an essentially nonionic, monomeric structure, is indicated. This could be a genuine five-coordinate structure, type I, but might also be a six-coordinate, monomeric structure resulting from solvent coordination, namely,  $[\text{TlX}_3\text{L}_2(\text{solvent})]$ . There is also the possibility that in the solid there might be a six-coordinate dimer, III, or a chain polymer, V, which dissociates, either owing directly to the formation of  $[\text{TlX}_3\text{L}_2(\text{solvent})]$  species, or independently of this. For  $\text{TlCl}_3(\text{DMSO})_2$ , the solubility properties seem to indicate that the monomer in solution is  $[\text{TlCl}_3(\text{DMSO})_2(\text{solvent})]$ . There is little previous information to draw upon for comparison in this respect. There is a recent, brief report that the compound  $(\text{C}_6\text{F}_5)_2\text{TlBr}(\text{dipy})$ , dipy being 1,1'-dipyridyl, exists mainly as a monomer, possibly a genuine five-coordinate species of type I, in several solvents.<sup>23</sup> Direct evidence (*i.e.*, *via* X-ray diffraction) for five-coordination in compounds of  $\text{Tl(III)}$  or isoelectronic ones seems limited to that for  $(\text{CH}_3)_3\text{In}$ ,<sup>24</sup> which is rather atypical, and  $(\text{CH}_3)_3\text{SnCl}(\text{C}_5\text{H}_5\text{N})$ ,<sup>25</sup> in which a trigonal bipyramid was found.

Finally, the structures of the compounds  $\text{TlBr}_3[(\text{C}_6\text{H}_5)_3\text{PO}]_2$  and  $\text{TlI}_3[(\text{C}_6\text{H}_5)_3\text{PO}]_3$  remain quite uncertain on the available data.

In conclusion, the results of this study and data already in the literature suggest that the stereochemistry of thallium(III) is probably varied and complicated and certainly, at present, very incompletely understood. The need for X-ray structural work is in many instances quite evident.

(23) G. B. Deacon and R. S. Nyholm, *Chem. Ind. (London)*, 1808 (1963).

(24) E. L. Amma and R. E. Rundle, *J. Am. Chem. Soc.*, **80**, 4141 (1958).

(25) I. R. Beattie, G. P. McQuillan, and R. Hulme, *Chem. Ind. (London)*, 1439 (1962).