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Composition and Properties of Thallium Mercury Iodide

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Conflicting reports exist in the literature concerning the composition of thallium mercury iodide. Solid state synthesis with HgI_2 and TlI has been reported to give Tl_4HgI_6 while synthesis from solution has been reported to give Tl_2HgI_4. In this report we show that the "orange compound" precipitating from solution is actually a 1 : 1 mole ratio mixture of Tl_4HgI_6 and HgI_2. Pure Tl_4HgI_6, which is yellow, can be produced by heating the mixture at 100°C for several days to volatilize HgI_2 or more simply, by adding Tl(I) to a solution containing 2 : 1 KI : K_2HgI_4 to provide the additional iodide ions needed for Tl_4HgI_6. Tl_4HgI_6, unlike Ag_2HgI_4 and Cu_2HgI_4, has no sharp thermochromic changes and has no measurable ionic conductivity. This provides another example of the significant role the metal ion plans in determining structure and properties of metal mercury iodide compounds.

Silver and copper mercury tetraiodides have long been known to be both fast ion conductors (*1, 2*) and thermochromic pigments (*3, 4*). Because Ag_2HgI_4 and Cu_2HgI_4 have phase transitions in the 50–70° range involving color changes and large changes in ionic conductivity, these thermochromic materials have also been proposed for various sensors. Recently, the mechanism for the presence or absence of thermochromism in analogues of Ag_2HgI_4 above and below their phase transition temperature has been reported (*4*). The temperature-dependent thermochromism is due to changes in the charge transfer spectra arising from the donation of electron charge from the filled *p*-orbitals of the iodide ligands to the unfilled *d*-orbitals of the mercury atom. The phase transition is considered to be an order–disorder type. The low temperature, β, phases for Ag_2HgI_4 and Cu_2HgI_4 are both tetragonal but they differ in the placement of the M^+ cations and vacancy. In the high temperature, α, phases, the iodide sublattice is retained while cations are distributed randomly among all sites. Thus, they are isostructural in their α-phases. Clearly, then, the M^+ cation plays a role in the exact structure in the low temperature form and determines, for the most part, the conductivity, phase transition temperature, and thermochromic properties.

We have undertaken a study of the synthesis and properties of other analogues of

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Ag_2HgI_4 with the overall objective to fine-tune the electrochemical and optical properties of M_2HgI_4 compounds with the choice of M^+ and possible mixed M^+ substitutions to obtain materials useful for sensors and other electrochemical devices. Here we report the preparation of a thallium mercury iodide and reconcile the many conflicting reports in the literature concerning this compound.

A perusal of the literature shows that the chemistry of other metal(I)mercury halides may not be simple analogues of Ag_2HgI_4. For example, the smaller halides have been reported to form $MHgX_3$ and M_4HgX_6 compounds (*5, 6*) and the 4 : 1 metal : mercury ratio was also reported by two groups of investigators for Tl_4HgI_6 (*7a, b, 8*). On the other hand several other investigators have reported the compound to be Tl_2HgI_4 (*9–20*). A brief look at this history shows the conflicting evidence and paucity of evidence concerning thallium mercury iodide. Barlot and Pernot (*21*) in 1921 reported a double salt of TlI–HgI_2 and Gallais (*9*) in 1938 reported that a yellow–orange compound precipitated when an alcoholic solution of Tl_2SO_4 was added to an alcoholic solution of K_2HgI_4. The procedure was carried out as a conductometric titration and a sharp break was found at the 2 : 1 mole ratio. The only other evidence was an analysis for Tl content, which was found to be 35.86% compared to the theoretical value of 36.59%. Gallais found the product to be "phototropic" and rather unstable, yielding HgI_2 in cold ether. Twenty years later Asmussen and Andersen (*10*) measured the magnetic susceptibility of "Tl_2HgI_4" but gave no analyses, merely stating, "The samples used for the measurements were prepared according to Gallais." The compound was orange and decomposed above 130°C. A color transition from orange to red occurred at 116.5°C and was reversible after heating to ≤130°C.

Several recent workers have also assumed that the "orange compound" was Tl_2HgI_4 (*11–20*). For example, Adams and Hatton (*15*) in 1983 stated correctly that Ag_2HgI_4 was prepared from stoichiometric proportions of $AgNO_3$ and K_2HgI_4, and then continue, "The Tl(I) and Pb(II) complexes were obtained similarly." In 1988 Rosu and Negoiu reported (*16*) that Tl_2HgI_4 and $PbHgI_4$ were synthesized by the wet method utilized by Adams and Hatton, that is,

$$2Ag^+ + HgI_4^{2-} \rightarrow Ag_2HgI_4 \qquad (1)$$

$$2Tl^+ + HgI_4^{2-} \rightarrow Tl_2HgI_4. \qquad (2)$$

The analogy seemed so straightforward that Adams and Hatton (*15*) did not question the composition even though they noted, "The physical properties of Tl_2HgI_4 . . . are very different from those of the Cu and Ag analogues." Shriver *et al.* (*20*) also noted that "Tl_2HgI_4" does not undergo a phase transition to a more conductive state. Countering this statement, Halmos and Wendlandt (*11*), who prepared the compound using the procedure of Gallais (*9*), gave various thermochromic transition temperatures (23–150°C) for an orange-to-red color change. Wendlandt and Bradley (*13, 14*) reported reflectance curves as a function of temperature and noted sharp thermochromic transitions for all M_2HgI_4 *except* Tl_2HgI_4, for which a steady, linear decrease was observed at 550 nm. Contreras and Seguel (*19*) also employed the stoichiometric addition procedure and stated, "The analytical data agree well with the formulae M_2HgI_4 . . ." They gave the thermochromic transition temperature at 185.5°C.

Countering this evidence for Tl_2HgI_4, Huart and Durif (*7a*) reported the existence of Tl_4HgI_6 in 1963. They stated that when stoichiometric mixtures were used an excess of red HgI_2 was found. The excess HgI_2 could be removed by washing with a hot solution of KI or prolonged heating at 100°C to sublime HgI_2. A systemic study with stoichiometric ratios of TlI and HgI_2 in place of synthesis from solution ranging from 1 < $TlI/HgI_2 < 4.2$ showed that only TlI/HgI_2 = 4 gave pure product. However, no chemical analyses were given. The powder pattern was the same as that reported by Gallais (*9*). Crystals large enough for single crystal XRD were obtained by precipitation and the structure was found to be tetragonal with a_0 = 0.945_7 nm and c_0 = 0.927_1 nm and contained 2 units of Tl_4HgI_6 per unit cell.

More recently, the most definitive XRD work on the compound made by solid state reaction of TlI with HgI_2 was reported by Berthold *et al.* (*8*). Crystals large enough for XRD studies were obtained by recrystallization from hot water or directly from the melt (340°C) although they state that decomposition occurred above 200°C with loss of HgI_2. Again, no chemical analyses were given but their XRD results agreed closely to those of Huart and Durif.

Thus, everyone seems to agree that Tl^+ added to a solution of HgI_4^{2-} yields an orange product that is not highly stable and gives a distinctive XRD pattern. However, it is not clear whether the compound precipitated from solution is Tl_2HgI_4 or Tl_4HgI_6, although the solid state reaction definitely appears to give Tl_4HgI_6. We present here evidence to show the correct assignment as Tl_4HgI_6 and, hopefully, put to rest this conflict existing in the scientific literature. It should be noted that the present powder diffraction files (*22*) give the Pattern No. 16-212 as Tl_4HgI_6, based on the early report (a 2-page note) by Huart and Durif (*7a*) who prepared it as a solid state reaction.

Experimental

A total of 3.93 g K_2HgI_4 (0.005 mole) from Alpha Products was dissolved in 50 ml of hot water (70°C). A total of 2.66 g $TlNO_3$ (0.010 mole) was dissolved in 20 ml of water and added to the K_2HgI_4 solution. An orange precipitate formed and the mixture was stirred for 15 min, then filtered with a Buchner funnel. The filtrate was clear. The precipitate was gently dried in an oven at 115°C for about 30 min. The yield was 5.30 g, which was 95% of the theoretical yield based on Tl_2HgI_4. Chemuical analysis (Galbraith Laboratories) of one particular batch gave the following results: Found—Tl = 37.0%, Hg = 18.2%, I = 46.0%, Tl/Hg = 2.00. Calculated for Tl_2HgI_4—Tl = 36.59%, Hg = 17.96%, I = 45.44% (Calculated for Tl_4HgI_6—Tl = 45.94%, Hg = 11.27%, I = 42.79%). An independent check on another batch was carried out by XRF analysis (Carter Analytical Lab) with the following results: Found—Tl = 42%, Hg = 20%, I = 38%, Tl/Hg = 2.06. The analysis by XRF is not as accurate as the AAS method, but the Tl/Hg ratio certainly supports the hypothesis of a 2 : 1 stoichiometry.

The orange compound showed various color changes when heated but no sharp transitions were observed. At 75–80°C it became more red–orange, at 119–124° back to orange, at 124–126° to yellow, and in the range 148–200° back to orange and even appeared to show some signs of melting.

A procedure in which the Tl/Hg mole ratio was 4 was carried out, and again an orange precipitate formed. However, when the filtrate was treated with KI a precipitate of TlI formed, equivalent to 95% of the excess thallium present based on the Tl_2HgI_4 formula. The orange powder obtained from the 4/1 procedure was also sent for analysis and the results were Tl = 36.8%, Hg = 16.3%, I = 47.2%, Tl/Hg = 2.21.

The procedure was further modified, in light of the discussion below, by including additional KI in the K_2HgI_4 solution. A total of 1.57 g K_2HgI_4 (0.002 mole) and 0.66 g KI (0.004 mole) were dissolved in hot water (70°C). A total of 2.13 g $TlNO_3$ (0.008 mole) was dissolved in 20 ml of water and added to the K_2HgI_4–KI solution. A *yellow* precipitate formed. The mixture was stirred and filtered as described above. The product weighed 3.22 g. The filtrate was treated with

10% KI solution and no TlI formed although a small amount of Tl was detected by AAS. The yellow precipitate turned to orange around 130°C and returned to yellow on cooling, but the transition was gradual.

Chemical analysis (Galbraith Laboratories) of the "yellow compound" gave the following results: Found—Tl = 45.4%, Hg = 11.1%, I = 43.2%, Tl/Hg = 4.01. Calculated for Tl_4HgI_6—Tl = 45.94%, Hg = 11.27%, I = 42.79%.

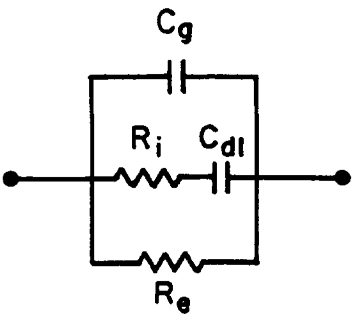
Differential scanning calorimetry was carried out with a DuPont 912 Thermal Analyzer System at a heating rate of 5°C/min from room temperature to 150°C. A second run with the "orange compound" after a heating/cooling cycle was carried out with virtually identical results. However, heating to 275° led to irreversible changes in the thermal properties. The "yellow compound" showed no DSC peaks up to 300°C.

X-ray powder diffraction was carried out with a fully automated Scintag diffractometer system.

Samples for conductivity measurements were prepared by pressing the powder into pellets uniaxially at ~6600 kg/cm^2. The pellets had a diameter of 0.48 cm, a weight of ~0.1–0.2 g, and thickness ranging from 0.06 to 0.14 cm.

Three types of electrodes were investigated initially: (i) platinum foil, (ii) pressed powder gold, and (iii) sputtered gold film. Our previous experience has been that sputtered gold produces an excellent solid–solid interface for conductivity studies, but some of the mercury compounds studied appeared to decompose when put under vacuum. Platinum foil was satisfactory but gave large contact resistance on occasion. Pressed powder gold, i.e., a pressed sandwich of powdered gold, powdered compound, powdered gold, gave excellent electrode contacts and was the technique of choice for this investigation.

Conductivity of each sample was determined using a Solartron 1174 Frequency Response Analyzer over a wide frequency range (1–10^6 Hz). Complex impedance diagrams obtained in this fashion were interpreted using a computer program developed in our laboratory and published previously (*23*). With blocking electrodes it was anticipated that the equivalent circuit for the cell would be



where C_g is the geometric capacitance (~10 pF), C_{dl} is the double layer capacitance (~10 μF), R_i is the ionic transport resistance, and R_e is the electronic transport resistance. The circuit will show a real axis intercept (~10^2–10^4 Hz) equal to R_i from which the ionic conductivity may be calculated provided the electronic conductivity is small. The existence of electronic conductivity can be detected by using low frequency measurements, in which case another real axis intercept will be observed equal to R_e. In the situation where there is predominantly electronic conductivity a single semicircle will be observed and the data at very low frequency (<10 Hz) will remain near the real axis at the value of R_e.

Results

The XRD powder pattern for the orange compound made under 2Tl : Hg stoichiometric conditions is given in Table I and compared to the pattern published by Huart and Durif (*7a*). The two are virtually identical, but four small lines could be assigned to a small amount of HgI_2 (shown in Table

TABLE I

XRD Results

hkl	d_{calcd}	Reported for Tl_4HgI_6 (*7a*)		Pattern for "orange compound"	
		d_{obsd}	*I*	d_{obsd}	*I*
110	6.69			6.693	5
101	6.61	6.62		6.618	5
				6.244^a	5
002	4.63	4.64	2	4.634	2
210	4.22	4.23	7	4.232	6
				4.129^a	10
112	3.80	3.81	1		
				3.585^a	10
220	3.34	3.34	17	3.342	10
212	3.12	3.12	100	3.123	100
310	3.00	2.99	79	2.991	60
103	2.93	2.93	6	2.933	7
311	2.84	2.86	<1		
113	2.79		0	2.770	4
320	2.62	2.62	3		
321	2.52	2.52	3		
312	2.51	2.51	4	2.512	4
213	2.490	2.491	4	2.492	6
400	2.358	2.361	6	2.363	5
004	2.315	2.313	9	2.317	13
322	2.278	2.278	6	2.280	5
330	2.229	2.225	8	2.227	7
114	2.226		0	2.230	7
303	2.202	2.204	2	2.195	8
				2.188^a	4
420	2.110	2.111	11	2.114	9
412	2.051	2.052	11	2.056	10
214	2.028	2.024	<1		
323	1.995	1.995	4	1.997	3
422	1.922		0	1.931	3
224	1.902	1.902	2	1.903	3
510	1.851	1.851	1		
413	1.838	1.837	3		
314	1.828	1.829	15	1.829	18
440	1.671		0	1.670	4
522	1.641		0	1.640	11
334	1.604		0	1.604	4
315	1.573		0	1.574	5
424	1.560		0	1.560	4
612	1.473		0	1.471	3
216	1.448		0	1.448	7
542	1.406		0	1.406	3

[a] These small intensity peaks are attributed to HgI_2 present in the sample and were not used for fitting purposes.

I) and were not used for fitting. The pattern fit well to a tetragonal system with a_0 = 0.94508 nm, c_0 = 0.92476 nm, and unit cell volume = 826 × 10^{-24} cm^3. The values reported by Huart and Durif (*7a*) were a_0 = 0.9457 nm, c_0 = 0.9271 nm, and unit cell volume = 829 × 10^{-24} cm^3. Space group was assigned to either $P4_2bc$ or $P4/mnc$. Values reported by Berthold *et al.* (*8*) were a_0 = 0.9446 nm, c_0 = 0.9260 nm, and tegragonal cell volume = 826 × 10^{-24} cm^3. Space group was assigned to $P4/mnc$. Measured density was 7.11 g/cm^3 which leads to a formula weight of 3535 g per mole of unit cell or two Tl_4HgI_6 (FW = 1780) per unit cell.

The "orange compound" precipitated from solution had a density of 6.8 g/cm^3 measured by immersion leading to a formula weight of 3381 g per mole of unit cell. Thus, if Tl_2HgI_4 (FW = 1117) were correct there would be 3 units per cell within experimental uncertainty.

As mentioned in the Experimental section, the "orange compound" showed several slight color changes in the range 75–200°C. Thermal analysis by DSC is shown in Fig. 1. Two endothermic transitions were seen with onsets at 140 ± 3°C and 146 ± 3°C which were reproducible if thermal cycling was kept below 170°C. However, a broad exothermic peak appeared near 250°C if a higher temperature cycle was undertaken, after which the lower temperature peaks decreased in size and eventually disappeared after three–four heating cycles.

The "yellow compound" precipitated from solutions containing K_2HgI_4 plus KI showed the same XRD pattern as the "orange compound" *but* showed no HgI_2 present. Its DSC spectrum (Fig. 1B) showed no transitions. The yellow compound gradually turned orange ~115°C and became red ~285°C. After heating to high temperature, the compound appeared more yellowish brown at room temperature.

Some preliminary results with the "or-

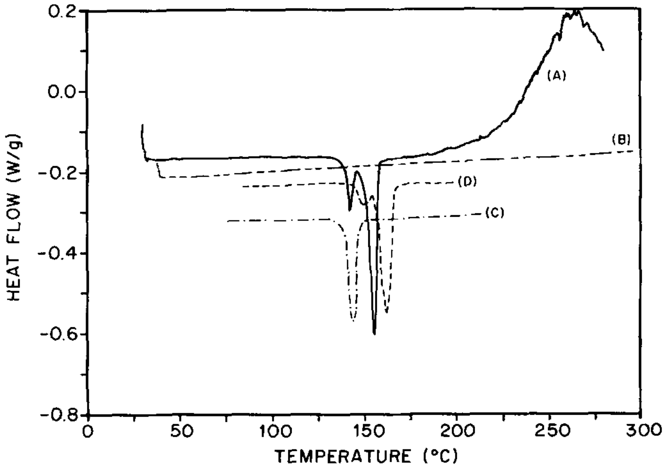


FIG. 1. DSC spectra at 5°/min. (A) "Orange compound," (B) "yellow compound" prepared by precipitation from a solution containing KI or by heating "orange compound" at 100°C for several days, (C) commercial HgI_2 (offset for clarity), and (D) 1 : 1 mixture of commercial HgI_2 and "yellow compound" assuming it is Tl_4HgI_6.

ange compound" exhibited low levels of conductivity as shown in Fig. 2A. However, when the compound was purified by heating at 100°C for several days the conductivity dropped to very low values (1.6×10^{-6} S/cm at 200°C) and were essentially the same as for the "yellow compound" as shown in Fig. 2B. Arrhenius plots for our measurements of Ag_2HgI_4 and Cu_2HgI_4 are shown for reference.

The resistance for the yellow compound was so high that only data above 150°C were judged reliable. Also, the nature of the low level of conductivity appeared to be electronic because only a single semicircle (Fig. 3) was observed even down to 1 Hz. The activation energy was 0.74 eV compared to

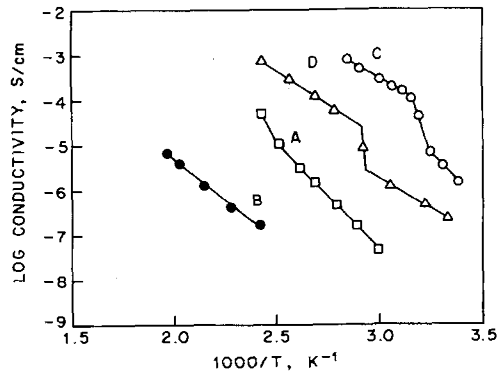


FIG. 2. Arrhenius plots for (A) "orange compound," (B) "yellow compound," (C) Ag_2HgI_4, and (D) Cu_2HgI_4. Pellet samples were Au/sample/Au.

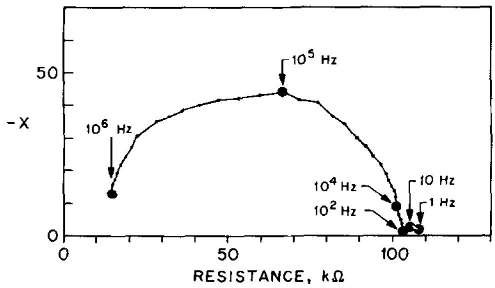


FIG. 3. Complex impedance plot for "yellow compound" from 1 to 10^6 Hz at 235°C. Real intercept (fitting from 10^2 to 10^6 Hz) was 1.04×10^5 Ω. Resistance at 1 Hz was 1.09×10^5 Ω. Imaginary component within experimental error of zero at all frequencies $< 6 \times 10^3$ Hz.

0.89 eV for β-Ag_2HgI_4. Conductivity at 25°C, calculated from the Arrhenius plot, was only 4×10^{-11} S/cm.

Discussion

At this point it is instructive to correlate all the results and to assign the composition of the "orange compound" precipitated from solution. The key to the puzzle is found in the observation that small peaks (10–20% of major peaks) attributed to HgI_2 were present. Rosu and Negoiu (*16*) also reported the presence of HgI_2 in their "Tl_2HgI_4" but did not try to explain its presence. When the orange compound was heated at 100°C for several days it slowly changed to a yellow color and HgI_2 peaks disappeared. However, no TlI was found that might indicate a decomposition had taken place.

Now if one assumes that Huart and Durif (*7a*) and Berthold *et al.* (*8*) are correct in their assignment as Tl_4HgI_6 reaction (2) would not occur but instead reaction (3) would take place:

$$2HgI_4^{2-} + 4Tl^+ \rightarrow Tl_4HgI_6(\text{yellow}) + HgI_2(\text{red}). \quad (3)$$

The 1 : 1 mole ratio mixture would appear orange since it consists of yellow Tl_4HgI_6 plus red HgI_2. When one considers the number of heavy atoms in Tl_4HgI_6 compared to HgI_2 it is not surprising that even for a 1 : 1 mole ratio HgI_2 XRD peaks would only be 10–20% as intense as Tl_4HgI_6 peaks. Based on the density reported by Berthold *et al.* (*8*) a 1 : 1 mole ratio mixture should have a density of 6.9 g/cm^3, within experimental error of the value of 6.8 reported here.

Final proof of this assignment was obtained by preparing the compound by precipitating from a solution containing additional KI as given in reaction (4)

$$HgI_4^{2-} + 2I^- + 4Tl^+ \rightarrow Tl_4HgI_6(\text{yellow}). \quad (4)$$

Previous workers using precipitation from solution had all used 2 moles of Tl^+ to 4 moles of iodide in the form of K_2HgI_4. Note that the mixture obtained from Eq. (3) will have a chemical analysis equivalent to Tl_2HgI_4.

One experimental result that needs to be considered is the chemical analysis for the "yellow compound." The same "yellow compound" was produced either by heating the "orange compound" at 100°C for several days or by precipitation from solution containing additional KI as given in Eq. (4). Chemical analysis as given in the Experimental section showed it to correspond closely to Tl_4HgI_6, with a Tl/Hg ratio = 4.01.

Equation (3) also explains why Gallais found a break at 2 : 1 Tl/Hg by conductometric titration. Addition of Tl_2SO_4 would precipitate all ions except K^+ and SO_4^{2-} until reaction (3) was complete and then conductivity would rise rapidly with further addition of Tl_2SO_4.

The DSC peaks reported here for the "orange compound" were also reported by Halmos and Wendlandt (*11*) using DTA. Subsequent thermal cycling showed that the lower peak (135–140°) slowly disappeared and can thus be assigned to HgI_2. DSC of commercial HgI_2 gave a single peak near 140°C (Fig. 1C). The "yellow compound" prepared by Eq. (4) gave no DSC peaks so there is still some question concerning the second DSC peak. It was observed that when the orange compound was purified by heating at 100°C for several days to eliminate HgI_2 completely no DSC peaks remained below 300°C. However, support for the 1 : 1 mole mixture assignment given in Eq. (3) was found from DSC measurements of a 1 : 1 mixture of commercial HgI_2 and the "yellow compound" assuming it to be Tl_4HgI_6. As seen in Fig. 1D it, too, showed two endothermic peaks reasonably close (145, 158°C) to the ones found for the "orange compound." These two peaks can then be attributed to HgI_2 in the presence of Tl_4 HgI_6 and disappear when HgI_2 is removed from the mixture by heating at 100°C for an extended period of time. Weight loss after heating was within experimental uncertainty of the amount expected from Eq. (3).

One more experimental observation fits the assignment of 1 : 1 $Tl_4HgI_6:HgI_2$, namely the possible melting at temperatures below 200°C. While Tl_4HgI_6 was reported to melt at 340°C (*8*), Huart (*7b*) gave a phase diagram showing mixtures of Tl_4HgI_6 and HgI_2 to melt as low as 149°C (eutectic) although the 1 : 1 composition melted at ~250°C. A heterogeneous mixture could, then, exhibit partial melting behavior in this temperature region.

Finally, some comments should be made concerning crystal structure assignment based on XRD powder patterns. It is usually necessary to begin fitting a tetragonal structure with some initial trial values. When one uses parameters near a = 0.9 nm, c = 0.9 nm as reported by Huart and Durif (*7a*) and Berthold *et al.* (*8*) fitting refines quickly to the values reported above. On the other hand, if one assumes that the "orange compound" is an analogue of Ag_2HgI_4 and would have cell dimensions slightly larger than the values for Ag_2HgI_4 (a = 0.63 nm, c = 1.26 nm) because Tl^+ is larger than Ag^+ fitting to a reasonable degree also occurs. In this way, Rosu and Negoiu (*16*) gave the values a_0 = 0.6450 nm, c_0 = 1.3140 nm for tetragonal "Tl_2HgI_4," having two units per unit cell. We have also used similar fitting routines and agree with those values but the fit is not nearly as close, with several lines being so far off that the computer program rejects them.

It might seem unexpected that the Tl^+ cation would change the coordination around Hg(II) from HgI_4^{2-} to HgI_6^{4-}. Although Tl^+ is bigger than Ag^+ or Cu^+ it is almost exactly the same size (0.140 nm ionic radius) as K^+ (0.133 nm ionic radius), which forms K_2HgI_4. However, as Berthold *et al.* (*8*) show the change is not as dramatic as it sounds. Four iodides are located near the mercury in a distorted tetrahedral arrangement with two Hg–I distances of 0.27 nm and two at 0.31–0.32 nm. The other two iodides are 0.37 nm away from the mercury atom. The latter distance is slightly greater than the sum of the ionic radii of Hg^{2+} and I^-, which is 0.34 nm. The authors (*8*) state, "the two longer distances . . . are so great that it may be assumed that the pertinent iodine atoms contribute only a little to the coordination of the mercury atom."

Thus, we may conclude that even though thallium mercury iodide does not possess a sharp thermochromic transition and exhibits very low conductivity compared to the silver and copper compounds, the metal cation again plays a strong role in determining the structure and properties. In the case of Tl^+, the "lone pair" is probably an important factor in determining the structure. The lesson to be learned is that this role is so important that even the composition cannot be assumed to be analogous to other members of this class of compounds.

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References

1. J. A. A. Ketelaar, *Z. Phys. Chem., B* **26,** 327 (1934).

2. J. A. A. Ketelaar, *Z. Kristallogr.* **87,** 436 (1934).

3. K. Funke, *Prog. Solid State Chem.* **11,** 345 (1976).

4. H.-R. C. Jaw, M. A. Mooney, T. Novinson, W. C. Kaska, and J. I. Zink, *Inorg. Chem.* **26,** 1387 (1987).

5. J. Huart, *Bull. Soc. Fr. Mineral. Cristallogr.* **88,** 66 (1965).

6. J. Huart, *Bull. Soc. Fr. Mineral. Cristallogr.* **88,** 699 (1965).

7. (a) J. Huart and A. Durif, *Acad. Sci. C. R.* **257,** 657 (1963); (b) J. Huart, *Bull. Soc. Fr. Miner. Cristallogr.* **89,** 23 (1966).

8. H. J. Berthold, D. Haas, R. Tamme, K. Brod-

ERSEN, K. P. JENSEN, D. MESSER, AND G. THIELE, *Z. Anorg. Allg. Chem.* **456,** 29 (1979).

9. F. GALLAIS, *Ann. Chim.* **10,** 117 (1938).
10. R. W. ASMUSSEN AND P. ANDERSEN, *Acta Chem. Scand.* **12,** 939 (1938).
11. Z. HALMOS AND W. W. WENDLANDT, *Thermochim. Acta* **7,** 113 (1973).
12. W. W. WENDLANDT AND T. W. GEORGE, *Chem. Anal.* **53,** 100 (1964).
13. W. W. WENDLANDT AND W. S. BRADLEY, *Thermochim. Acta* **1,** 529 (1970).
14. W. W. WENDLANDT, *Pure Appl. Chem.* **25,** 825 (1971).
15. D. M. ADAMS AND P. D. HATTON, *J. Raman Spectrosc.* **14,** 154 (1983).
16. T. ROSU AND D. NEGOIU, *Rev. Chim.* **39,** 170 (1988).
17. D. NEGOIU, T. ROSU, AND D. TODOR, *Rev. Chim.* **33,** 723 (1987).
18. T. ROSU, D. NEGOIU, AND A. BRADEANU, *Rev. Chim.* **39,** 334 (1988).
19. J. G. CONTRERAS AND G. V. SEGUEL, *Spectrosc. Lett.* **19,** 363 (1986).
20. D. F. SHRIVER, G. JOY III, AND D. GREIG, *J. Electrochem. Soc.* **123,** 588 (1976).
21. J. BARLOT AND J. PERNOT, *Acad. Sci. C. R.* **173,** 232 (1921).
22. JCPDS Powder Diffraction File (International Centre for Diffraction Data, Swarthmore, PA, 1986).
23. M. KLEITZ AND J. H. KENNEDY, *in* "Fast Ion Transport in Solids" (P. Vashishta, J. N. Mundy, and G. K. Shenoy, Eds.), p. 185, Elsevier/North-Holland, Amsterdam (1979).