The Magnetic Properties of the Thermochromic Compounds

Cu_2HgI_4, Ag_2HgI_4 and Tl_2HgI_4

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The magnetic susceptibilities of Cu_2HgI_4, Ag_2HgI_4 and Tl_2HgI_4 have been measured at varying temperatures: 90—403 °K, 88—335 °K and 84—403 °K, respectively. The compounds are diamagnetic at all temperatures in the intervals stated. The χ_g, T curves are nearly parallel to the T-axis. After correction for the diamagnetism of the electron systems of the ions it is shown that the corrected χ_M values represent a weak paramagnetism nearly independent of the temperature. No discontinuity is observed in any of the susceptibility curves at the colour transition temperatures. A colourimetric method for the determination of the colour transition temperatures has been worked out. The transition temperatures for Cu_2HgI_4, Ag_2HgI_4 and Tl_2HgI_4 are determined to be 69.5, 50.5 and 116.5 °C, respectively, for our preparations.

Silver(I)iodomercurate and copper(I)iodomercurate were prepared by Caventou and Willm[1], Mensel[2], Wegelius and Kilpi[3] and Popow[4]. Gallais[5] prepared the compounds mentioned and also the thallium(I)iodomercurate. The compounds are thermochromic having a low and a high temperature form of different colour. The two phases are usually designed β and α, respectively. Ketelaar[6,7] studied the crystal structures of the β and α forms of the silver and copper compound. The β forms are reported to be of pseudocubic tetragonal symmetry and the α phases cubic. Recently Hahn, Frank and Klingler[8] determined the structure of β-Cu_2HgI_4 and β-Ag_2HgI_4 with results differing from those of Ketelaar (compare also Suchow and Keck[9], Olsen and Harris[10] and Frevel and North[11]). Hoshino's[12] structure determination on α-Ag_2HgI_4 also differs from that of Ketelaar.

Furthermore, Ketelaar[13-15] measured the electric conductivity and the specific heat capacity of the different forms of the silver compound at varying

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temperatures. Ag_2HgI_4 has ionic conductivity [13],[15], which inreases rapidly just below the colour transition temperature. In the case of the copper compound an electronic conductivity is superimposed upon the ionic conductivity. Ketelaar has interpreted his experimental results in terms of an order-disorder mechanism. Suchow and Keck [9] investigated the system Cu_2HgI_4-Ag_2HgI_4 and report also Munsell colour specifications and reflectance measurements. Suchow and Pond [16] studied the temperature dependence of the electrical conductivity of the copper and the silver compound and their eutectoid.

Magnetic properties. Gallais [5] measured the magnetic susceptibilities of Cu_2HgI_4, Ag_2HgI_4 and Tl_2HgI_4 at room temperature. We considered it of value to study the magnetic properties of these compounds in a larger temperature interval covering the transition temperatures and the temperatures at which the electrical conductivities increase rapidly. The results of our measurements are given in the lower part of Fig. 1, where the diamagnetic gram susceptibilities measured are plotted against the absolute temperature. It is seen that the straight lines are nearly parallel to the temperature axis. If we correct the molar susceptibilities for the diamagnetism of the electron systems of Cu^+, Ag^+, Tl^+, Hg^{+2} and I^- (see experimental part) we obtain the small but paramagnetic susceptibilities, which are plotted against the absolute temperature in the upper part of Fig. 1. The vertical arrows indicate the position of the colour transition temperatures. The straight lines like those for χ_g are of course nearly parallel to the temperature axis.

The correction for diamagnetism has been performed under the assumption that the diamagnetic susceptibility of an ion is the same in the crystal as in the free state. The obvious and direct result of the calculation is that the total calculated molar diamagnetic susceptibility is numerically greater than the observed numerical value. The reason for the difference between the observed and the calculated diamagnetism may be that the ions are deformed in the crystal. The true diamagnetic susceptibility of the ions in the crystal may be numerically smaller than that in the free state because the mean square radii of the electrons in the ions are decreased. However, we must point out that the weak paramagnetism plotted in Fig. 1 may be a physical reality as a temperature independent paramagnetism, the general existence of which has been predicted by Van Vleck [17]. The presence of this paramagnetism has been verified experimentally in many deeply coloured substances (compare for instance Ballhausen and Asmussen [18]).

The magnetic measurements prove that no discontinuity in the magnetic properties occurs at the colour transition temperatures. This is so far in accordance with Ketelaar's order-disorder mechanism, since this does not involve a change in the electron configuration of the ions but a motion of metal ions to other positions during the continuous transformation process.

Colour transition temperatures. The colour transition temperatures were determined by means of reflectance measurements as described in the experimental part. In Fig. 2 the reflectances F are plotted against the temperature in °C. The black points represent measurements carried out during cooling of the preparation. Hysteresis phenomena were only observed when not quite pure preparations were used. The observations on Tl_2HgI_4 are of particular interest indicating that thermochromi is also a property of this substance.
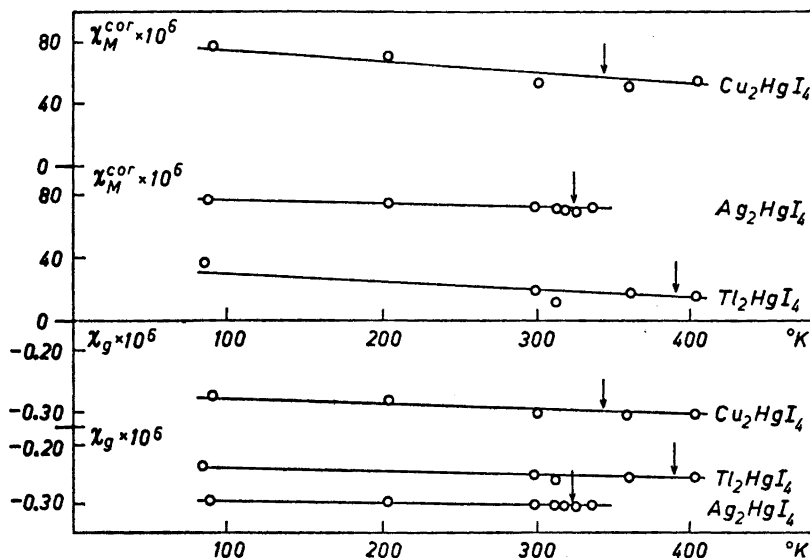
Fig. 1. Gram susceptibility and corrected molar susceptibility of Cu_2HgI_4, Ag_2HgI_4 and Tl_2HgI_4 plotted against the abs. temperature. The vertical arrows indicate the colour transition temperature.

The curves give the values 69.5, 50.5 and 116.5°C for the transition temperatures of Cu_2HgI_4, Ag_2HgI_4 and Tl_2HgI_4, respectively. In Table 1 is given a comparison between these observations and those of other authors.

Table 1. Colour transition temperatures.

Substance	Colour		Colour transition temperature, °C		
	β	α	Ketelaar [7]	Suchow and Pond [16]	Present paper
Cu_2HgI_4	ruby	darkbrown	70	66.6	69.5
Ag_2HgI_4	yellow	redorange	50.7	50.0	50.5
Tl_2HgI_4	orange	red			116.5

In Fig. 3 we report reflectance measurements on HgI_2. The red tetragonal crystal is transformed into a yellow rhombic form at 127 °C. The reflectance measurements show that the colour change occurs abruptly near 127 °C in contrast to the picture given in Fig. 2 of the colour change during the disordering process.

EXPERIMENTAL

Preparation and analysis of the compounds

Cu_2HgI_4 can be precipitated from a solution of K_2HgI_4 containing the equivalent amount of $CuSO_4$ (referred to the formula Cu_2HgI_4), by bubbling SO_2 through the solution.
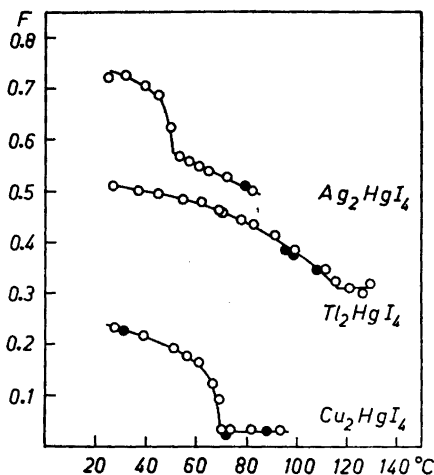
Fig. 2. Reflectance *F* of the compounds Cu_2HgI_4, Ag_2HgI_4 and Tl_2HgI_4 plotted against the Celsius temperature. The "black" points represent *F*-values measured at decreasing temperatures.

However, our experiences have shown that better developed and purer crystals can be obtained by a diffusion method. The preparations used for the magnetic and optical measurements were obtained as follows:

Two crystallizing dishes *A* and *B* of 7 cm diameter and 4.5 cm height were placed in a 21 × 11 × 11 cm glass vessel. The distance between *A* and *B* was 12 cm. *A* contained a 0.1 M aqueous solution of K_2HgI_4. *B* contained a saturated solution of CuCl in 20 % hydrochloric acid and a few pieces of copper turnings. *A* and *B* were completely filled with solutions. The junction liquid was 20 % hydrochloric acid saturated with SO_2. The glass vessel had an airtight glass lid. The first crystals were formed after 24 h. After 24 days the junction liquid was siphoned off and the crop of ruby crystals formed (mainly in *A*) was isolated, washed with water, and dried on filterpaper. A few larger crystal needles were also obtained. The yield was 50 %.
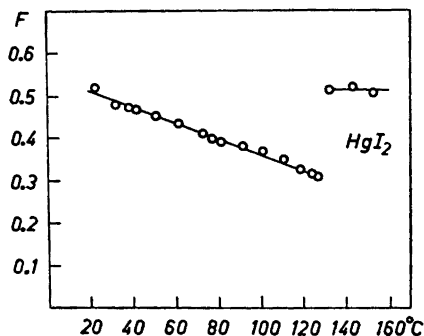

Fig. 3. Reflectance *F* of HgI_2 plotted against the Celsius temperature.

The amount of crystal needles could be increased by replacing A and B by two smaller dishes having a lesser diameter at the top part than at the bottom. The two dishes were covered with a piece of circular filterpaper. After 30 days a small crop of crystals was formed on the filterpaper upon A. The length of the needles was nearly 4 mm.

The quantitative analysis was carried out as follows: The sample was treated with conc. nitric acid in order to remove iodine and to convert Cu^{+1} to Cu^{+2}. The solution was evaporated (nearly to dryness). Nitrogen oxides were removed by boiling with dil. hydrochloric acid. Hg was determined by weighing as HgS, and Cu iodometrically. Iodine was determined by the iodate-method, the metals being eliminated by means of zinc.

$$\text{Found: Cu } 14.91 \%; \quad \text{calc. } 15.22 \%$$
$$\text{Found: Hg } 23.95 \%; \quad \text{calc. } 24.01 \%$$
$$\text{Found: I } \quad 60.71 \%; \quad \text{calc. } 60.77 \%$$

The copper determination gives values for per cent Cu, which are 2 % (relatively) lower than the theoretical value, when the analysis is carried out as described.

Ag_2HgI_4. Experiments were carried out in order to prepare this compound according to the diffusion method described above. The dish B contained a silver sulphate solution and the junction liquid was dil. sulphuric acid. We have, however, not succeeded in obtaining crystals of a purity sufficient for our purpose. The samples used for the physical measurements were prepared by precipitation as described by Henderson and Fernelius [19].

The quantitative analysis was confined to a determination of iodine by the iodate method after conversion of the metal ions to the metallic state (zinc-reductor).

$$\text{Found: I } 54.63 \%; \quad \text{calc. } 54.94 \%$$

Tl_2HgI_4. The diffusion method gives crystal mixtures containing yellow, red, and black crystals. No well defined preparation could be obtained. The samples used for the measurements were prepared according to Gallais [5]. X-Ray powder-photos prove that the substance is a well defined compound. The crystals are of orange colour. The compound is decomposed above 130°C.

Magnetic measurements

The magnetic susceptibilities were measured by means of the Gouy method similar to that of Asmussen and Soling [20]. The observed diamagnetic gram susceptibilities are plotted against the temperature in °K in the lower part of Fig. 1. In the upper part of Fig. 1 the corrected molar susceptibilities are plotted against $T°K$. It should be noticed that the ordinates for each curve are measured from a zero-point, the position of which is fixed for each curve. The corrections applied for the diamagnetism of the electron systems of the ions Hg^{+2}, Cu^+, Ag^+, Tl^+, and I^- are, respectively: 47.6×10^{-6}, -19.3×10^{-6}, -42.1×10^{-6}, -17.0×10^{-6}, and -55.3×10^{-6}.

Gallais [5] has measured the magnetic susceptibilities of Cu_2HgI_4, Ag_2HgI_4, and Tl_2HgI_4 at room temperature only and gives the following diamagnetic gram susceptibilities: -0.26×10^{-6}, -0.19×10^{-6}, and -0.24×10^{-6}, respectively. Gallais' value for Ag_2HgI_4 is 37 % lesser than our room temperature susceptibility.

Determination of the colour transition temperatures

The colour transition temperature is usually measured by immersing small glass tubes containing the substance in a water-bath. The temperature of the water-bath is slowly increased and the colour change is observed visually.

We considered it of value to carry out objective measurements of the colour change for the $\beta \rightarrow a$ transitions by means of the photoelectric tricolourimeter constructed by Buchmann-Olsen [21]. We have determined one coefficient only applying the filter OY 12, the transmission curves of which are given in the paper of Buchmann-Olsen [21] (page 82). This filter allows a recording of the reflections in a wavelength interval corresponding to that of visible light. In order to measure the reflectance at different temperatures a heating block of nickel plated brass (60 mm diameter and 85 mm height) was used. In the lower end of the block was a chamber, in which an incandescent lamp was mounted.

Regulation of the electric current through the filament allows to fix the temperature of the block. In the upper end of the block was a small chamber for the specimen powder (35 mm diameter and 0.5 mm deep). The block was thermally isolated from the surroundings by a brass tube covered with asbestos. A copper-constantan thermocouple was mounted in the specimen chamber through a drill sloping upwards so that the bead of the thermocouple was situated in the center of the bottom of the chamber. The temperature measured may be considered as a mean temperature of the surface of the specimen powder; the bead of the thermocouple being just covered with powder.

The photo-cell used in the tricolourimeter was a selenium photo-cell from Ewans Electro-selenium Ltd. The photo-current was measured with a Cambridge light spot galvanometer. The reflectance was measured as the ratio F of the readings on the galvanometer when light is reflected from the specimen powder and from a white standard. Each of the F values plotted in Figs. 2 and 3 are mean values of 3 measurements of F. The time necessary for these measurements was about 8 min. In this time interval the observed temperature did not vary more than 0.25 degrees. The F values were found to be reproducible within 1 %.

REFERENCES

1. Caventou, E. and Willm, E. *Bull. soc. chim. France II* **13** (1870) 194.
2. Mensel, E. *Ber.* **3** (1870) 123.
3. Wegelius, H. and Kilpi, S. *Z. anorg. allgem. Chem.* **61** (1909) 413.
4. Popow, P. G. *Ukraine Chem. J.* **11** (1936) 11; *Chem. Zentr.* **1936** II 448.
5. Gallais, F. *Ann. Chim. 11*, **10** (1938) 117.
6. Ketelaar, J. A. A. *Z. Krist. A* **80** (1931) 190.
7. Ketelaar, J. A. A. *Z. Krist. A* **87** (1934) 436.
8. Hahn, H., Frank, G. and Klingler, W. *Z. anorg. allgem. Chem.* **279** (1955) 271.
9. Suchow, L. and Keck, P. H. *J. Am. Chem. Soc.* **75** (1953) 518.
10. Olsen, C. E. and Harris, P. M. *Phys. Rev.* **286** (1952) 651.
11. Frevel, L. K. and North, P. P. *J. Appl. Phys.* **21** (1950) 1038.
12. Hoshino, S. *J. Phys. Soc. Japan* **10** (1955) 197.
13. Ketelaar, J. A. A. *Z. physik. Chem. B* **26** (1934) 327.
14. Ketelaar, J. A. A. *Z. physik. Chem. B* **30** (1935) 53.
15. Ketelaar, J. A. A. *Trans. Faraday Soc.* **34** (1938) 874.
16. Suchow, L. and Pond, G. R. *J. Am. Chem. Soc.* **75** (1953) 5242.
17. Van Vleck, J. H. *The Theory of Electric and Magnetic Susceptibilities.* Oxford University Press, Oxford, 1932.
18. Ballhausen, C. J. and Asmussen, R. W. *Acta Chem. Scand.* **11** (1957) 479.
19. Henderson, W. E. and Fernelius, W. C. *Inorganic Preparations* (1935) 149.
20. Asmussen, R. W. and Soling, H. *Acta Chem. Scand.* **8** (1954) 558, 563.
21. Buchmann-Olsen, B. *Trans. Danish Acad. Tech. Sci.* **1950** No. 4.