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HIGH TEMPERATURE REFLECTANCE SPECTROSCOPY: APPLICATION TO THERMOCHROMIC COMPOUNDS*

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ABSTRACT

The thermochromic behavior of $Cu_2[HgI_4]$, $Ag_2[HgI_4]$, $Tl_2[HgI_4]$, $Pb[HgI_4]$, and $Hg[HgI_4]$ was investigated by the techniques of HTRS and DRS. The latter techniques are uniquely suitable for this type of study due to the dramatic color changes that the compounds exhibit during the thermochromic transitions.

INTRODUCTION

Two modes of investigation may be used for high temperature diffuse reflectance spectroscopy studies. The first is the measurement of the diffuse reflectance spectra of a sample at various fixed or isothermal temperatures. The sample is maintained at a given temperature and its spectrum obtained over the wavelength region of interest. The temperature is then changed to a new value and after a suitable equilibration period, the spectrum is again recorded. The procedure is repeated at a number of temperature intervals until the desired temperature range is covered. This mode of measurement is called *high temperature reflectance spectroscopy* (HTRS) and has been previously described by Wendlandt *et al.*[1-3] The second mode of measurement is to record the change in reflectance of the sample at a given wavelength as a function of temperature. The temperature of the sample is increased at a slow, linear rate. This mode is called *dynamic reflectance spectroscopy* (DRS)[4] and has been used to determine the structural changes of coordination compounds[2,3,5,7] and other studies[6].

The HTRS and DRS modes are illustrated in Fig. 1. In the HTRS mode a series of reflectance curves at various temperatures from 25–125°C are shown. With increasing temperature, the reflectance decreases in the wavelength region above 500 nm. If the exact temperature of the transition is desired, HTRS curves may be recorded at small temperature intervals. A more rapid method for determining the transition temperature or transition interval is by the DRS mode. Using a new sample, the change in its reflectance at 550 nm is recorded as the temperature is increased at some slow, uniform rate, say 2–4°C/min. The wavelength selected is generally in the

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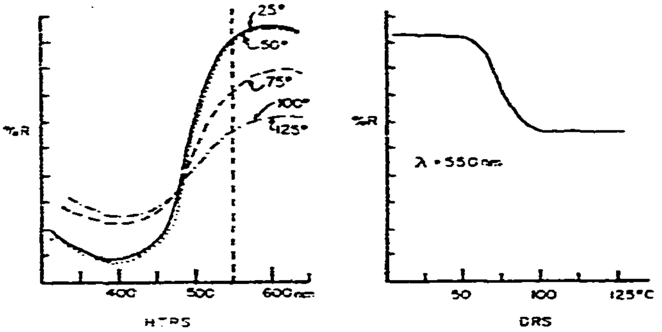


Fig. 1. Examples of the HTRS and DRS modes.

region of the greatest reflectance change of the sample. As can be seen from the DRS curve, the transition began at about 50 and was completed at 100 °C. The DRS curve (sometimes called *isolambdic curve*) thus indicates the temperature at which the transition began and ended. The transition temperatures obtained are, of course, procedural temperatures recorded under a dynamic temperature environment. Their interpretation is thus similar to those data obtained under similar conditions, such as TG, DTA, and so on. Unlike the latter techniques, DRS permits the elucidation of only one transition or reaction at a time.

The purpose of this investigation is to examine the thermochromic transitions of a number of $M_n[HgI_4]$ complexes by the HTRS and DRS techniques. Since thermochromism is defined as the reversible change in the color of a compound when it is heated or cooled[8], the color change is distinguished by being quite noticeable, often dramatic, and occurring over a small or sharp temperature interval. For inorganic compounds, the thermochromic transition is due to a crystalline phase change, to a change in solvation, or a change in the ligand geometry. In the case of the $M_n[HgI_4]$ complexes, an order–disorder change in the crystal lattice is used to explain the thermochromic behavior. Day has recently reviewed the thermochromism of both inorganic[8] and organic[9] compounds.

EXPERIMENTAL

Preparation of compounds

The $Ag_2[HgI_4]$ was prepared by the procedure of Meyer[10] while Walton's method[11] was used to prepare $Cu_2[HgI_4]$. The $Tl_2[HgI_4]$, $Pb[HgI_4]$, and $Hg[HgI_4]$ were prepared by a modification of the method used for the analogous silver(I) compound.

Reflectance measurement

The heated sample holder, previously described by Wendlandt and Dosch[12], was used for the HTRS and DRS studies. All measurements were made on a Beckman

Model DK-2A spectroreflectometer, using freshly prepared MgO as the reflectance standard. Heating rates employed for the DRS studies are given under each compound.

RESULTS AND DISCUSSION

The $M_n[HgI_4]$ complexes

The HTRS curves of the $M_n[HgI_4]$ complexes (M = Ag^I, Cu^I, Hg^{II}, Tl^I, and Pb^{II}) are given in Figs. 2–6.

$Ag_2[HgI_4]$. — The thermochromism of $Ag_2[HgI_4]$ has been of great interest since its first preparation by Caventou and Willm[13] in 1870. The transition was first investigated in a thorough manner by Ketelaar using specific heat, X-ray, and electrical conductivity techniques[14–17]. Additional information concerning the color changes[10,18,20,24], dilatometry[19,23], crystal structure[21,22], magnetic susceptibility[24], electrical conductivity[25,26], and thermal stability[27], of the compound has been reported. The compound has been proposed as a temperature indicator[20,28] and as a pigment for temperature indicator paints[28–30].

The thermochromism of $Ag_2[HgI_4]$ is due to an order–disorder transition which involves no less than three phases. According to Ketelaar[17], both the yellow low temperature β-modification and the red high temperature α-form contain iodide ions which are cubic close packed while the silver and mercury ions occupy some of the tetrahedral holes. The β-form has tetragonal symmetry with the mercury ion situated at the corners of a cubic unit cell and the silver ions at the mid-points of the vertical faces. As the temperature is increased it becomes possible for the silver and mercury ions to occupy each others lattice sites and also the two extra lattice sites (top and bottom face centers of the unit cube) which were unocupied at lower temperatures. Above 52°C, the mercury and silver ions are completely disordered. The α-modification has, therefore, averaged face centered cubic symmetry. More recently, magnetic[25] and dielectric polarization[21,25] measurements confirm the presence of a third phase, the β'-modification. With an increase in temperature, the silver ions become disordered occupying at random 2/3 of the face centered positions of the unit cube during the $\beta \rightarrow \beta'$ transition. During the $\beta' \rightarrow \alpha$ transition, the silver and mercury ions become further disordered occupying at random 3/4 of the corners plus face centers of the unit cell. The initially obtained β' crystalline phase has a tetragonal unit cell[21] corresponding to 2 cubic (but not isotropic) cells stacked one on top of the other. The Patterson function suggests that a portion of the silver atoms are disordered, having left sites surrounded tetrahedrally by iodide ions and appearing in interstitial (octahedrally occupied) sites. The interstitial silver ions would be expected to be rather labile, since the octahedral holes are large compared to those at the tetrahedral sites. This is also apparent from the low activation energy obtained[21] for the conduction process in β-$Ag_2[HgI_4]$, 12 kcal/mole below 20°C.

The reflectance curves for $Ag_2[HgI_4]$ from 23–100°C are shown in Fig. 2. The yellow β-form reflects rather strongly above 500 nm with the maximum shifting to higher wavelengths during the transition to the red α-form. The change in color is dependent upon the rate of heating. At 2.5°C/min the transition is completed at a somewhat lower temperature than at the 10°C/min heating rate. This heating rate is extremely rapid compared to the temperature rise of 5°C/*day* used by Neubert and Nichols[25] in their magnetic studies. The transition temperature found here was not very well defined in that the color change appeared to take place over the temperature range from 30 to about 60°C. Reported transition temperatures include 50.7±0.2, 51.2, 51, 50.5, and 52°C.

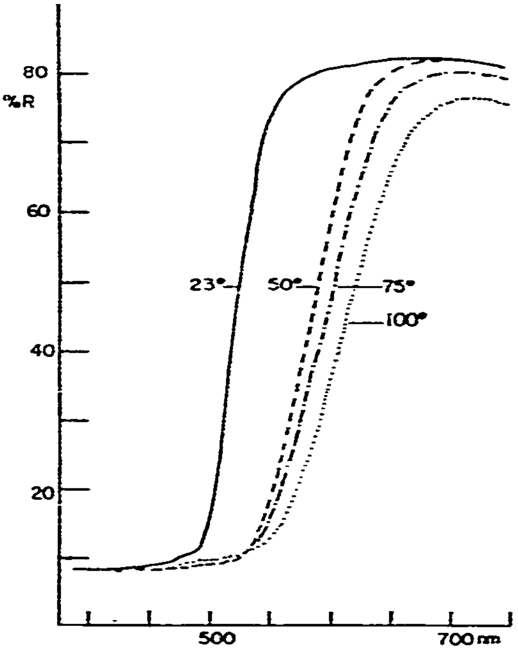


Fig. 2. HTRS curves of $Ag_2[HgI_4]$.

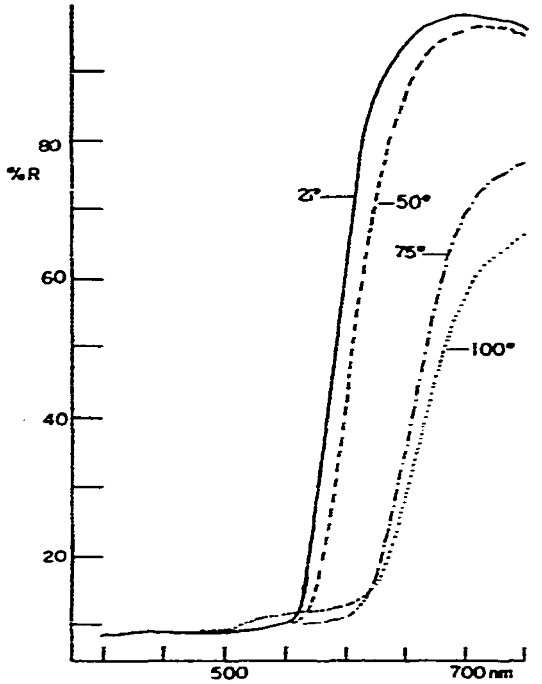
$Cu_2[HgI_4]$. — The thermochromism of this compound has not been as well investigated as that of the analogous silver complex. It can be concluded, however, that the same type of transition mechanism is involved, which will not be discussed in detail here. The transition temperature of the red β-modification to the brown-black α-modification has been reported to be 66.6, 71, 72, and 69.5°C.

The reflectance curves from 21–100°C for $Cu_2[HgI_4]$ are given in Fig. 3.

The red β-form reflects quite strongly above 600 nm. On going through the β→α transition, the reflectance maximum of the compound shifts to higher wavelengths and also decreases in magnitude. The HTRS curves are in agreement with those previously reported[6]. The DRS curve, obtained at a heating rate of 5°C/min, shows the same gradual type of transition in reflectance. It appears to take place between 50–75°C. Although not shown here, the transition was reversible.

The reflectance curves of $Hg[HgI_4]$ are given in Fig. 4.

This compound, according to Meyer[10], is photosensitive and darkens on exposure to light. It is reported to have several transitions, not as sharp as in the case of the other compounds, but becoming red above 160°C. It has a fairly definite



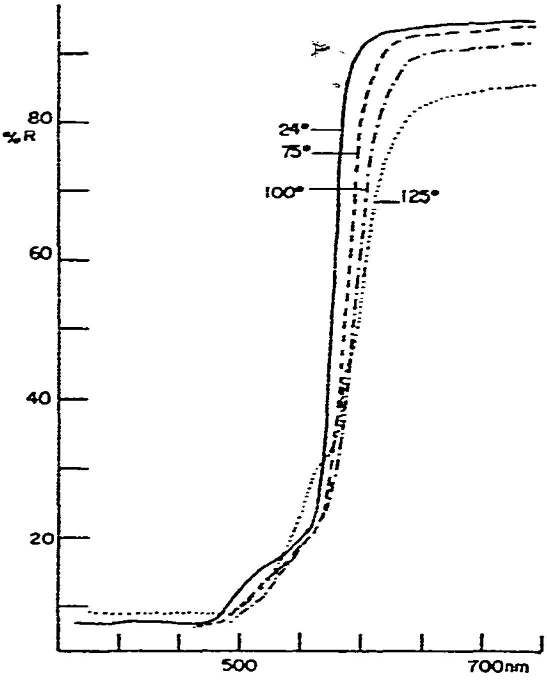


Fig. 3. HTRS curves of $Cu_2[HgI_4]$.

Fig. 4. HTRS curves of $Hg[HgI_4]$.

transition to orange-red at 172.6, deep red at 220.1, and melts quite sharply to a red mass at 224.4°C[10].

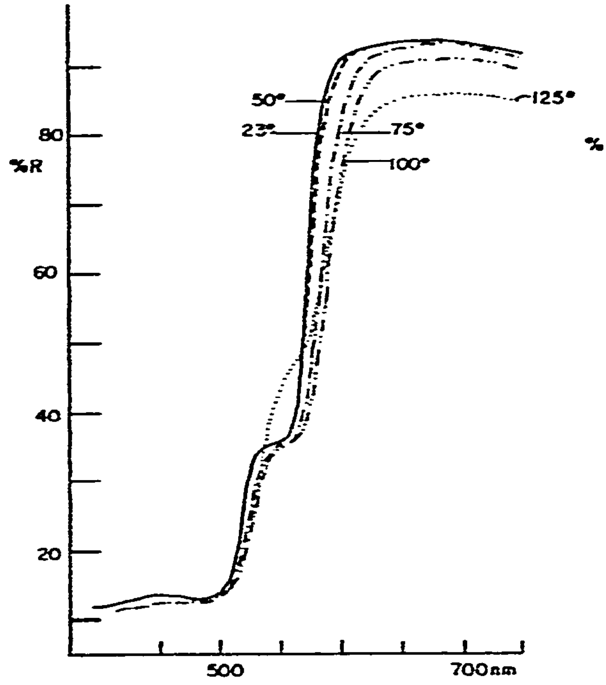
The HTRS curves, from 24–125°C, indicate a slight shift to higher wavelength values on heating. A shoulder peak is present at about 500 nm and this also shifts to higher wavelength values as the temperature is increased. The DRS curve indicates that the transition from a yellow-orange to a red color is quite gradual but the rate of transition becomes more rapid above 100°C. The transition is reversible.

$Pb[HgI_4]$. — The HTRS curves of this compound are given in Fig. 5. The reflectance curves for the orange-red colored compound were similar to those found for $Hg[HgI_4]$. The compound darkens to a red color, as shown by the HTRS curves, as it is heated above 100°C.

$Tl_2[HgI_4]$. — The HTRS curves of this compound are shown in Fig. 6.

This compound was first reported by Gallais[31] while the thermochromic transition temperature was reported as 116.5°C[24]. The transition temperature from yellow to red, in the temperature range from 23–150°C, is gradual, as can be seen by the DRS curve. The transition, like the others reported here, was reversible.

The DRS curves of the $M_x[HgI_4]$ complexes are given in Fig. 7. All of the compounds exhibit a rather sharp thermochromic transition with the exception of $Tl_2[HgI_4]$. The latter compound is reported to have a transition at 116.5°C[24]; however, it is not evident from the DRS curve. The change in reflectance of the compound appears to decrease linearly with temperature.



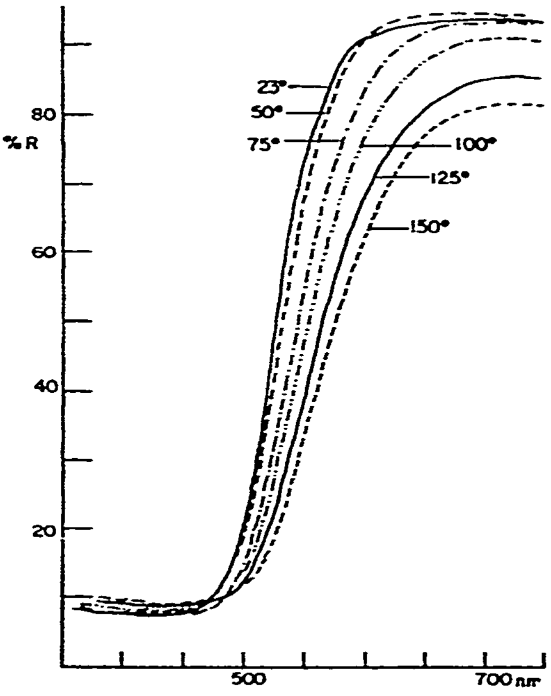


Fig. 5. HTRS curves of Pb[HgI_4].

Fig. 6. HTRS curves of Tl_2[HgI_4].

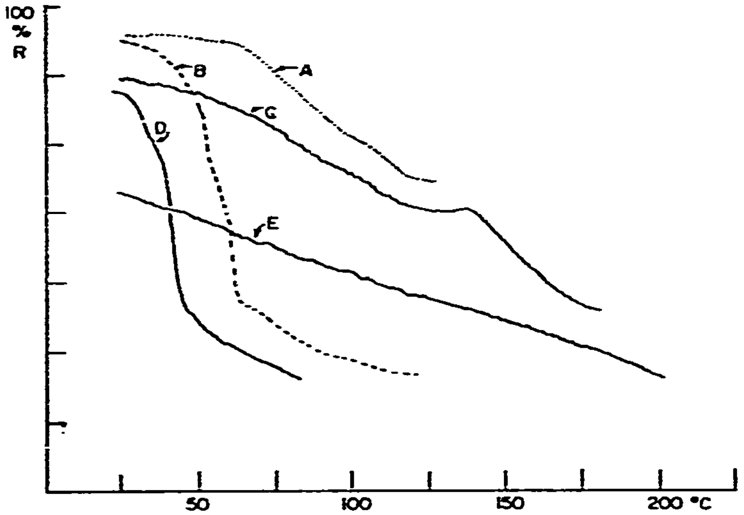


Fig. 7. DRS curves of complexes (5°C/min): (A) Pb[HgI_4], 585 nm; (B) Cu_2[HgI_4], 650 nm; (C)Hg[HgI_4], 600 nm; (D) Ag_2[HgI_4], 575 nm; (E) Tl_2[HgI_4], 550 nm.

General

The techniques of HTRS and DRS are very useful in the elucidation of thermochromic transitions in complexes of this type as well as for other inorganic and organic compounds. Generally, the ΔH of transition of these complexes is quite small which would preclude the use of DTA or DSC for studies of this type. Since there are no mass losses for the transitions, TG could not be employed. Thus, HTRS and DRS are uniquely suitable for the determination of thermochromic transitions.

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