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THERMOCHROMISM OF INORGANIC COMPOUNDS

JESSE H. DAY

Department of Chemistry, Ohio University, Athens, Ohio

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CONTENTS

I. INTRODUCTION

Thermochromism is the reversible change in the color of a compound when it is heated or cooled. The thermochromic color change is distinguished by being quite noticeable, often dramatic, and occurring over a small or sharp temperature interval. For inorganic compounds this transition is most often due to a change in crystalline phase, to a change in ligand geometry, or to a change in number of molecules of solvent in the coordination sphere. A lesser number of examples are due to equilibria between complexes in solution or to equilibria between different molecular structures in the case of organometallic compounds. The thermochromic transition temperature of a pure substance may be greatly changed by dispersing the compound in a solid matrix or by mixing it with other substances. Commonly used matrices include paint and lacquer vehicles, paraffin wax, and polymers such as poly(methyl methacrylate). In the solid matrix a hysteresis effect is common; the color transition may occur at a substantially lower temperature when the heated substance is cooled. Irreversible color transitions are due either to simple decomposition or to removal of one phase from a reversible transition. Reported transition temperatures are sometimes a function of the rate of heating.

This review covers the literature through 1967. Only one article before 1900 is reviewed, but the source of references for earlier work is noted in the body of this article. The thermochromism of organic compounds has been reviewed earlier.[1]

In the first systematic investigation of thermochromism (1871), Houston examined a number of solids by heating them on copper strips over a Bunsen burner and reported only those compounds whose color change was fully reversible.[2] Red or reddish compounds which darkened or turned black were copper ferrocyanide, antimony sulfide, iron oxide, copper subiodide, mercury sulfide, lead chromate, lead oxide, and potassium dichromate; orange compounds which turned to red or dark red were arsenic sulfide, mercury oxide, lead iodide, ferric oxalate; yellow compounds which turned to orange or orange-red were mercury sulfate, barium chromate, stannic sulfide, and arsenic sulfide; green compounds included silver iodide, which turned yellow then orange, and subiodide of mercury, which changed to orange then red then brownish red. Not entirely reversible changes were those of zinc oxide, which turned a light yellowish green, and tin oxide, which went from white to green and even to orange and red-orange, returning on cooling to a greenish white. The behavior of the copper iodide compound (dark red to brown-red, brown, brown-black, black) should be compared with the results of the extensive modern work with the copper bromide system.

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[1] J. H. Day, *Chem. Rev.*, **63**, 65 (1963).

[2] E. J. Houston, *Chem. News*, **24**, 177, 188 (1871).

Houston also attempted to discover the effect on the color of solid compounds and solutions when they are cooled. The only means then available to him to achieve a cooling effect was to evaporate a volatile liquid such as ether in the immediate vicinity of the sample which was painted on strips of paper. He recognized the possible effects of condensed moisture on the samples. He found that red mercury sulfide became bright red, stannic sulfide became lighter yellow, mercuric sulfate went from yellow to greenish, lead iodide changed from orange to a lighter orange, and lead chromate changed from yellow-orange to yellow-green.

II. SOLIDS

A. METALS

The temperature dependence of the reflectance spectrum has been studied for copper, silver, and gold.[3] The longer wavelength absorption for copper and gold has been assigned to a $[(n-1)d^{10}ns]$-$[(n-1)d^9ns^2]$ electronic transition, and the short-wavelength absorption band to a ns–np transition as in the case of silver. Because of the Fermi distribution of the metal electrons, the long-wavelength sides of the absorption curves show a striking temperature dependence. Thermal lattice expansion is a factor. A linear increase of absorption at higher temperatures is noted for the electronic transitions coupled to the lattice vibrations.

β-Brass-type alloys show reversible color changes with temperature.[4] The color changes are not primarily due either to disordering of the phase structure or to oxide formation but may be interpreted by the same mechanisms as given for Cu, Ag, and Au. Color effects are noted in Table I.

TABLE I

	−195°	Room temp
Copper–zinc	Yellow	Gold
Silver–zinc	Yellow	Pink
Gold–zinc	Red	Purple
Silver–cadmium	Red	Violet
Gold–cadmium	Gold	Gold

The β-copper–zinc alloy is copper red at about 300°; the other alloys are all gray. The color changes with temperature seem to be instantaneous.

B. CHROMIUM COMPOUNDS

Piezochromism (change in color with change in pressure) and thermochromism are believed to be general properties of solids containing the trivalent chromium ion. The continuous thermochromic transition is from red to violet to green as the temperature is raised. A study of the mixed oxides of trivalent chromium with aluminum, gallium, magnesium–aluminum, lanthanum–gallium, lanthanum–aluminum–gallium, and yttrium–aluminum led to the conclusion that the thermochromic transitions are a natural consequence of the lattice expansion that occurs on heating.[5]

Theoretical and paramagnetic resonance spectroscopy have shown that the chromium ion occupies octahedral or quasi-octahedral lattice sites exclusively and that the color changes depend on the distance to the neighboring central ions, such as Si, Be, S, or Mg.[6]

Mixed crystals of α-Al_2O_3 and Cr_2O_3 with up to 8 atom % of chromium are red at room temperature; above 8% the crystals are green.[7] The lattice constants are unchanged up to 8% chromium; then they increase linearly up to the values for Cr_2O_3; density increases linearly up to 8% and the magnetic susceptibility drops steeply; up to 30% there is a transition stage and above 30% a linear drop in magnetic susceptibility. The thermochromic properties change with the chromium content. The transition color occurs at 90°K for 58% Cr, 460°K for 8% Cr, 650°K for 2% Cr. All these properties are consistent with the corundum lattice structure.

C. MERCURY COMPOUNDS (TABLE II)

The structure of Ag_2HgI_4 has been studied as a function of temperature by means of X-ray diffraction, reflectance spectroscopy and dynamic reflectance spectroscopy, specific heat measurements, and determinations of electrical conductivity as well as by magnetic susceptibility and by visual color changes. The variation in these properties may be correlated with the thermochromic color transitions.

Ketellar[8-12] has found the low-temperature (β) forms of both Ag_2HgI_4 and Cu_2HgI_4 to be isomorphous and tetragonal (pseudo-cubic) and the α modifications to be cubic. Silver and mercury can occupy the same lattice points, but not all the lattice points are occupied. The silver ions are much more mobile than the mercury ions. Specific heats begin to show anomalies at 37° though the phase transition from the β to the α form is reported at 50.7 ± 0.2°. Ketellar proposes that a continuous order–disorder transition occurs over a considerable range of temperature, superimposed on the true phase transition. Electrical conductivity begins to increase rapidly at about 40°.

Dynamic reflectance spectroscopy (drs) has been used to measure the thermochromic transition tempera-

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(3) G. Joos and A. Klopfer, *Z. Physik.*, **138**, 251 (1954).

(4) L. Muldawer, *Phys. Rev.*, **127**, 1551 (1962).

(5) C. P. Poole, Jr., *J. Phys. Chem. Solids*, **25**, 1169 (1964).

(6) (a) A. Knappwost and W. Gunsser, *Z. Physik. Chem.* (Frankfurt), **21**, 305 (1959); (b) A. Neuhaus and W. Richartz, *Angew. Chem.*, **70**, 430 (1958).

(7) E. Thilo, J. Jander, H. Seeman, and R. Sauer, *Naturwiss.*, **37**, 399 (1950).

(8) J. A. A. Ketellar, *Z. Krist.*, **80**, 190 (1931).

(9) J. A. A. Ketellar, *ibid.*, **87**, 436 (1934).

(10) J. A. A. Ketellar, *Z. Physik. Chem.*, **B26**, 327 (1934).

(11) J. A. A. Ketallar, *ibid.*, **B30**, 53 (1935).

(12) J. A. A. Ketallar, *Trans. Faraday Soc.*, **34**, 874 (1938).

TABLE II

THERMOCHROMIC MERCURY COMPOUNDS

Compounds	Transition temp, °C	Color change on heating	Ref
HgI_2	127, 150[a]	Red (tetragonal) to yellow (rhombic)	14, *b*, *c*
(AgI)	(147)	(Yellow to red brown)	13, *b*
Ag_2HgI_4	50.7	Yellow to orange	9, 13–16, *c*, *d*
		Orange to yellow	18, *b*
Cu_2HgI_4	66.6, 67	Red to dark purple	15, 16
	25–85	Red to black	13
	69.5, 70	Red to dark brown	9, 17, 18, *b*
	71[a]	Red to brown-black	*c*, *d*
Ag_2HgI_4 (34%) and Cu_2HgI_4 (60%) in Lucite	70	Yellow-orange to red	18
Eutectoid of Ag_2HgI_4 and Cu_2HgI_4 (43 mole %)	34.2	Orange to red	15, 16
Tl_2HgI_4	116.5	Orange to red	14
$HgBr_2$ with HgS		Red to yellow or pink	*e*
HgI_2 with HgS		Red to orange	*e*

[a] Mixed with paraffin wax to make a crayon. [b] C. H. Bachman and J. B. Maginnis, *Am. J. Phys.*, **19**, 424 (1951). [c] F. G. Brickwedde, *Physica*, **24**, 128 (1958). [d] Z. Cimpl, F. Kosek, M. Stanek, and J. Klazar, *Strojirenstvi*, **15**, 543 (1965); *Chem. Abstr.*, **64**, 1673*g* (1966). [e] R. Harries, Clearinghouse for Federal Scientific Technical Information, Report AD-455014, 1961.

tures of Cu_2HgI_4, Ag_2HgI_4, and AgI.[13] The absorption at the most temperature-sensitive wavelength is recorded as the sample is heated at the rate of 5°/min. An inflection in the curve signals a change in phase or composition. Ag_2HgI_4 turns red as the temperature is increased from 25 to 155°. The color change is most pronounced from 25 to 55°, but darkening continues as the temperature is increased. Similarly for Cu_2HgI_4, the color change is from red to black in the 25–85° interval. For Ag_2HgI_4 there is no color change until 50°, above which there is a sudden decrease in reflectance, followed by a gradual decrease up to 150°. For AgI there is a minimum in the drs curve near 147°, corresponding to the reported transition temperature from β- to α-AgI.

Measurements of the magnetic susceptibility of Cu_2HgI_4, Ag_2HgI_4, and Tl_2HgI_4 show no discontinuity in magnetic properties at the thermochromic transition temperature.[14] This is consistent with an order–disorder mechanism involving a motion of metal ions during a continuous transformation process, with no change in electron configuration. Determinations of the color transition temperatures were made by locating the abrupt change in the amount of visible light reflected as shown on a plot of total reflectance against temperature. These workers also note that the red tetragonal form of HgI_2 is transformed into a yellow rhombic form at 127°, abruptly.

Suchow and Keck prepared solid solutions of Ag_2HgI_4 with Cu_2HgI_4.[15] X-Ray diffraction showed the formation of solid solutions, with a miscibility gap between 39 and 54 mole % of Cu_2HgI_4 at room temperature. They were able to prepare a phase diagram for the system by careful measurement of the visible transition temperatures of the solid solutions of various compositions. The powdered sample was held to a glass plate with a silicone lacquer and the plate placed on a temperature-gradient block; the temperature was measured at the color transition line. When heated, Ag_2HgI_4 changes sharply from yellow to orange and Cu_2HgI_4 equally sharply from red to dark red-purple. Mixtures with from 25 to 50 mole % of Cu_2HgI_4 also display very sharp color changes from orange to red, but at temperatures much lower than those of the parent compounds; upon cooling to room temperature these samples show a fairly sharp second step in a location which has been heated to a temperature above that of the first transition. This second dividing line is seen because the color in the area between the two positions fades gradually. The sample containing 42.7 mole % of the Cu_2HgI_4 showed only one sharp color change. With decreasing temperature the color changes were so gradual that it was difficult to determine their locations accurately. From the color transition data, the existence of a eutectoid with about 43 mole % of Cu_2HgI_4 is indicated. The results indicate that at all compositions copper, silver, and mercuric ions become disordered simultaneously; at the eutectoid composition the metal ions all go suddenly from an ordered to a disordered state with no variation in chemical composition.

Measurements of electrical conductivity of Ag_2HgI_4, Cu_2HgI_4, and their eutectoid show a sharp increase in conductivity at the transition point between the β and α structures corresponding to the thermochromic color changes. The temperature lag in color change during cooling was found to be about 8°, much less than previously reported when the powder was bound in a silicone lacquer for observation.[16]

Gallais prepared Ag_2HgI_4, Cu_2HgI_4, and Tl_2HgI_4 and reported their thermochromic properties and the results of magnetic measurements.[17] He also summarizes all of the earlier work and reports the references; for example, the silver salt was first prepared by Meusell in 1870 and its color change was noted on heating under

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(13) W. Wendlandt and T. W. George, *Chemist-Analyst*, **53**, 100 (1964).

(14) R. W. Asmussen and P. Andersen, *Acta Chem. Scand.*, **12**, 939 (1958).

(15) L. Suchow and P. H. Keck, *J. Am. Chem. Soc.*, **75**, 518 (1953).

(16) L. Suchow and G. R. Pond, *ibid.*, **75**, 5242 (1953).

(17) M. F. Gallais, *Ann. Chim.*, **10**, 117 (1938).

water. Gallais reports that the copper salt changes color reversibly, red below 50°, then brown, and nearly black by 70°.

A patent[18] covers the use of thermochromic materials layered over a pattern of Peltier junctions, such that each junction may be heated or cooled by changing the direction of current flow, resulting in formation of the desired image on the surface, which may be displayed, and then erased and the board reused. The thermochromic substances specifically mentioned are: an intimate mixture of 33.9% copper mercuric iodide and 60.1% silver mercuric iodide in a binder of Lucite 46, which is yellow-orange at room temperature but crimson red at 70°, then remains red even when cooled to room temperature but reverts to the original color on cooling to 10°. Copper mercuric iodide alone was found to change from a bright red to a deep brown or black on heating to about 70° and to return to its original color on cooling to about 58°. Silver mercuric iodide alone also exhibits this effect with color changes to yellow on heating to 47° and orange on cooling to 45°.

Mercuric bromide–mercuric sulfide (in the ratios 2:1, 1:1, and 1:2) mixtures are red, turning to yellow or pink when heated. The iodide–sulfide compounds (in the ratio 1:2 or 2:1) turn from red to orange.[19]

D. OTHER SOLIDS (TABLE III)

A dispersion of cadmium sulfoselenide in tetrafluoroethylene polymer shows a reversible color change from dark brown to black between the temperatures of 250 and about 400°F.[20]

TABLE III

Metal	Halogen	Color at room temp	Color at temp (°C) noted
Cu	Br	Green-blue	Green >350
Fe	Cl	Pale violet rose	Gray >115 Green >150
Fe	Br	Flesh	Gray-brown >190
Ni	Br	Golden brown	Green below −190
Ni	I	Dark green-brown	Green below −190

Topaz has the empirical formula $Al_2F_2SiO_4$. Some of the fluoride is usually replaced by hydroxyl, giving it a variable composition. Heat and irradiation have profound effects on the color of topaz. In general, colors are lost on heating from 400 to 750°. Blue topaz is completely bleached, whereas a pink tint remains in samples which were originally yellow. Irradiation tends to produce or intensify the color, which is lost on heating or exposure to sunlight. Blue topaz heated for half-hour periods at 100° intervals was completely bleached by 400°. The pink color produced by heating is caused by chromium. The colors are related to electronic defect centers.[21]

Boracites, $Me_3B_7O_{13}X$, in which Me is a divalent metal capable of other valencies, and where X is halogen, are thermochromic. No mechanism for the thermochromic transition was suggested.[22]

E. DISCUSSION

It seems apparent that there are two broad classes of thermochromic color change. The first is a gradual deepening in color with temperature rise for a great many substances. This is seldom noted, or at least is seldom reported. The second is a dramatic change in color, which for solids takes place either sharply or over a restricted temperature range. In the case of solids, the color changes and the sharpness observed may depend greatly on the heating rate as well as on the chemical composition. Unless there is a complete return to the equilibrium initial state, the thermochromic effects may be a function of the thermal history of the compound. This hysteresis effect, or lower transition temperature on cooling, would not exist if the cooling were infinitely slow. Dispersion of a powdered sample in a polymer film exaggerates the hysteresis effect.

The difficulty of preparing such compounds as Ag_2HgI_4, uncontaminated by AgI_2 and HgI_2, is manifest not only in the literature (see especially ref 15 and 17) but in the color changes reported in Table II, where at least two of the transitions reported correspond to that expected for HgI_2 itself.

III. SOLUTIONS

A. COBALT AND HEAVY METALS

The color changes of solutions of Co(II) compounds is an old problem. A recent paper[23] summarizes most of the points of view. The authors' findings fit well with almost all of the earlier work, particularly with the recent nmr work which seems to be conclusive. Solutions of $CoCl_2$ in water, methanol, ethanol, 1-propanol, 2-propanol, and acetone were studied spectrophotometrically at various temperatures. The spectrum shows a weak band at around 5500 Å and a strong band at about 6500 Å. The latter band is strongly sensitive both to solvent and to temperature, being most intense in the 2-propanol and acetone and weakest in water. The thermochromic effect is quite marked; the solutions are blue at the higher temperature and pink at the lower temperature, in the range from 25 to −80°. Small amounts of water suppress the thermochromic effect. Not only the nature of the ligand but the na-

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(18) F. A. Schwertz, U. S. Patent 3,219,993 (Oct 24, 1962).

(19) R. Harries, Clearinghouse for Federal Scientific Technical Information, Report AD-455014, 1961.

(20) Societe Anon. Tefal., British Patent 1,014,080 (1965); *Chem. Abstr.*, **64**, 11446 (1966).

(21) A. C. Dickinson and W. J. Moore, *J. Phys. Chem.*, **71**, 231 (1967).

(22) H. Schmid, *Phys. Chem. Solids*, **26**, 973 (1965).

(23) W. C. Nieuwpoort, G. A. Wesselink, and E. H. A. M. van der Wee, *Rec. Trav. Chim.*, **85**, 397 (1966).

ture of the negative ion is important; halide ion increases the thermochromic effect the most. The following interpretation is reached by comparison with solid-state spectra of these compounds and with the nmr structure data: the blue color is associated with the tetrahedrally surrounded cobalt ions and the color change on cooling points to a shift in the equilibrium concentrations to the octahedrally oriented solvation shell. Both solvent and negative ions take part in this "solvation shell." Thus, ultimately, many factors are responsible, as the size, kind, shape, and charge of the molecules and ions in the shell will determine whether it is tetrahedral or octahedral or some equilibrium mixture.

Gill and Nyholm noted that the green-to-blue transition is favored by increasing the temperature and they attribute this to

$$\mathrm{Co(H_2O)_6{}^{2+}(green) + 4Cl^-(solv) \rightleftharpoons CoCl_4{}^{2-}(blue) + 6H_2O}$$

a presumed decrease in the solvation of the chloride ion.[24]

Anhydrous salts of the types $[(C_2H_5)_4N]MX_4$ and $[(C_6H_5)_4As]_2MX_4$, as well as $CoCl_2$ in water, with added chloride ion give an octahedral species, which on heating give the intense blue color of the tetrahedral species.[25] Equilibria of the following type were studied.

$$\mathrm{X^- + [MX_2 \cdot 4solvent]_{octahedral} \rightleftharpoons [MX_3 \cdot solvent]^-{}_{tetrahedral}}$$

Optical density in the region of 700 mμ increases about eightfold over an approximate 40° range from room temperature to 70 or 80°.

The ultraviolet spectra of hexaphenyldilead and hexacyclohexyldilead in hexane follow Beer's law at -20 and 60° and show that their thermochromic behavior is not due to an equilibrium between the molecules and their free radicals.[26] When they are cooled in the solid state a reversible bleaching occurs. Examination by esr shows no radicals to be present. The authors explain the thermochromism in these words: "Broadening of ultraviolet bands of molecules with heavy atoms is well known. It is connected with the temperature-dependent distribution over vibrational levels; therefore it is not surprising that the band assigned to the lead–lead linkage at 2940 Å is sensitive to temperature." Thus the explanation is that of a broadening of an absorption band into the visible region, as first propounded in this connection by Grubb and Kistiakowsky. Similar phenomena are observed in the spectra of Ph_6Sn_2, $(Ph_3Sn)_4Sn$, $(Ph_3Pb)_4Sn$, and $(Ph_3Pb)_4Ge$.

A striking apparent thermochromism of liquid $VOCl_3$ is due to traces of water or even hydroxyl groups on the glass.[27] Carefully dried $VOCl_3$ (but residual water present) is yellow but at $-70°$ is bright red. A solution of the compound in methylene chloride is orange, again due to traces of water, and is thermochromic due to a tailing off of a strong absorption band which extends into the visible region. There are no distinct bands in the ultraviolet but continuously increasing absorption. The absorbing species is not known, but it is possibly a mixture of partially hydrolyzed products.

In a study of the hydrolysis of some thorium and uranium salts, one compound was found to be thermochromic, UO_2Cl_2; it is stable at 200°.[28]

B. THE COPPER BROMIDE SYSTEM

The thermochromic system consisting of copper(II) bromide, excess bromide ion, acid, and solvent (or binder) has been extensively studied with particular reference to its suitability for goggles designed to protect against flash-blindness.

Faye studied the copper(II) ion–bromide ion system in acetone solutions containing hydrobromic acid.[29] In this report he includes a critical summary of previous work. Plots of absorbance for each absorption peak against the bromide/copper ratio helped identify the absorbing species. The rapid reduction of Cu(II) to Cu(I) by bromide ion at bromide/copper ratios greater than 1 made only semiquantitative work possible. Faye reported the following species to be present: $[CuCr(OH_2)_3(acetone)_2]^+$ (distorted octahedron, d–d band about 835 mμ); $[CuBr_{2-4}(acetone)_2]^{0,1-,2-}$ (green, distorted octahedron, d–d band about 845–900 mμ); $CuBr_4^-$ (purple, distorted tetrahedron, d–d band about 1190 mμ, relatively stable toward reduction).

Barnes and Hume[30] had suggested earlier that the green solution contained $[CuBr_3^-(acetone)_2]$. They also noted that previous workers had considered the possibility of complexes containing five or six bromide ions (see also ref 31).

The effect of adding more bromide ion to the system is similar to the effect of heating the system, judging by the spectra. Addition of elementary bromine to the system does not make a notable difference.[32]

The part played by the solvent in the copper(II) bromide system is demonstrated in an interesting way when the system is dispersed in a partially hydrolyzed polyvinyl acetate polymer film.[33] The dry film is quite dark but becomes much more transparent when moistened simply by breathing on the film. It is believed that the acetate groups present in the poly-

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(24) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

(25) D. E. Scaife and K. P. Wood, *Inorg. Chem.*, **6**, 358 (1967).

(26) W. Drenth, L. C. Willemsens, and G. K. M. van der Kerk, *J. Organometal. Chem.*, **2**, 279 (1964).

(27) F. A. Miller and W. B. White, *Spectrochim. Acta*, **9**, 98 (1957).

(28) T. Katsurai, *Kolloid-Z.*, **170**, 57 (1960).

(29) G. H. Faye, *Can. J. Chem.*, **44**, 1643 (1966).

(30) J. C. Barnes and D. Hume, *Inorg. Chem.*, **2**, 444 (1963).

(31) C. Furlani and G. Mopurgo, *Theoret. Chim. Acta* (Berlin), **1**, 102 (1963).

(32) J. Goodman, S. Mook, and J. Steigman, Clearinghouse for Federal Scientific Technical Information, Report AD-47004, 1965.

(33) J. Goodman, S. Grand, and S. Mook, Clearinghouse for Federal Science Technical Information, Report AD-645539, 1966; *Chem. Abstr.*, **67**, 69419*u* (1967).

(vinyl acetate) may bind copper ion in the same way as a solvent molecule may. The precise role of phosphoric acid in this formulation is uncertain. Darkening of this film as the temperature is raised is increased by the effective loss of solvent from the system which has the effect of concentrating the dissolved complexes.

Solutions of copper bromide were studied in a number of solvents by comparison of optical absorbances over the entire visible band at room temperature and at 100°. The darkening of the solution was expressed as the ratio of absorbance at the higher temperature to the absorbance at room temperature. The largest value found was 4.4 for dimethyl sulfoxide as the solvent. No relationship between degree of darkening and the dielectric constant was apparent.[34]

Whereas addition of phosphoric acid to films containing copper bromide increased darkening and sometimes gave a reflective property to the film, it was found that this acid added to solutions of copper bromide resulted in only a slight increase in absorbance; it was concluded that no significant colored species are created or destroyed by the phosphoric acid. The addition of acids do not usually make any appreciable difference in the spectra.

Several patents[35-37] have been issued covering liquid and solid solutions of metal halides. Those mentioned include the halides of copper, silver, mercury, gold, cobalt, iron, nickel, and manganese; sensitivity is increased by adding the halide of a second metal. Most of the actual experimental work has been done with cupric chloride and cupric bromide. Cupric chloride or bromide darkens reversibly and in a fraction of a second when exposed to light. Darkening due to temperature rise alone has been given in terms of change in per cent transmittance for three different compositions; 22 to 0.9% transmittance for a temperature rise from 25 to 77°; 76 to 59% for 25 to 63°; 26 to 3% for 25 to 62°. The mechanism postulated is substantially as follows: in the original transparent state the cupric halide is attached to water as a ligand; initially the water splits away from the cupric halide and the metal salt associates with (in the case of a solid solution in a polymer) the polymer ligand at a higher energy level. At a still higher energy the cupric halide may dissociate to form cuprous halide and free *halogen;* at even higher energy input the cuprous halide may be reduced to the free metal. The patents cover energy input due to light, heat, electrical, and electromagnetic energy. The only color change described is from brown to blue black. One patent[36] notes that the presence of water in the phototropic films is important to the rate of opaquing and that heat increases the rate of opaquing. If the plastic film is stretched, the transmitted light is polarized.

C. DISCUSSION

It is obvious that there is a complex set of equilibria involving several species in the Cu(II)–halogen ion system, and that the number and relative amounts of the various species present depend on the halogen/copper ratio, the acidity, the temperature, possible reductions of the copper(II), the nature of the solvent, and perhaps whether atmospheric oxygen is immediately available to the system. There seems no doubt that the higher halide complexes are favored by higher halide concentrations and by higher temperatures.

Further evidence that the metal–bromide system is a thermochromic one comes from the study of copper salts used as photographic light-sensitive materials. Infrared radiation gave better images than shorter wavelength radiation.[38]

IV. METAL ORGANIC COMPOUNDS

The crystalline complex copper bistrifluoroacetylacetonate is slate blue but melts to deep green; it is possible that on melting the lattice collapses, allowing association to occur, and thus gives each copper atom a higher coordination number than in the crystal.[39] A more likely explanation is that the compound shows thermochromism, particularly in view of the marked reversible color changes observed on heating solutions of the compounds in xylene, chlorobenzene, or benzene; the royal blue cold solutions become green on boiling. The same changes are readily observed in solutions of bisacetylacetonatocopper(II) itself.

The perchlorate of bis(N,N-diethylethylenediamine)copper(II) is brick red at room temperature and blue above 44°. Seventeen different anions were checked, but only the perchlorate was thermochromic; even the N,N-di-*n*-butyl- or N,N-dimethylethylenediamine perchlorates were not thermochromic. A change in orientation of the ethyl groups or, more particularly, a conformational change in the ring would affect the nitrogen atoms and thus be much more effective in changing the ligand field; such conformational changes were deemed the most likely source of the thermochromism.[40] The maximum in the reflectance spectrum of the high-temperature form is shifted 30 μ to the red, from 490 to 520 μ, and is more intense at 50°

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(34) J. Goodman, S. Grand, and S. Mook, Nuclear Research Association Report No. 861 to Naval Air Systems Command, Dec 1967.

(35) C. G. Macarovici and M. Macarovici, *Bul. Univ. "V. Babes" "Bolyai" Cluj, Ser. Stiint Nat.*, **1**, 163 (1957); *Chem. bstr.*, **54**, 18414*e* (1960).

(36) A. M. Marks and M. M. Marks, British Patents 1,008,536, 1,008,537, and 1,008,538 (1965); *Chem. Abstr.*, **64**, 5270*d*, 9275*a* (1966).

(37) A. M. Marks and M. M. Marks, U. S. Patent 3,236,651 (1966).

(38) J. Wojtczak, *Roczniki Chem.*, **32**, 553 (1958) (English summary); *Chem. Abstr.*, **53**, 879*b* (1959).

(39) R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 5885 (1963).

(40) W. E. Hatfield, T. S. Piper, and U. Klabunde, *Inorg. Chem.*, **2**, 629 (1963).

than at 25°. The low-temperature triclinic crystal must be only very slightly different from the monoclinic form since the unit cell parameters change only very slightly. The seemingly drastic change in color is mainly an intensity effect; no large change in ligand field is entailed.

It was reported earlier that μ-dihydroxy-bis(N,N-diethyl-N′-methylethylenediamine)dicopper(II) perchlorate is blue at room temperature and turns to red between −100 and −120°.[41]

Solutions in decalin of the stearates of Cu, Co, Ni, and trivalent Cr and Fe were studied by spectroscopy.[42] It was noted that the colors in dry decalin solution of cobalt stearate with rising temperature were golden brown, gold, red, and red violet.

The perchlorate salts of the nickel ethylenediamine and propylenediamine complexes are yellow, but form blue solutions in alcohol.[43] These solutions turn yellow on heating and the change is reversible; aqueous solutions of sodium perchlorate and these compounds show similar behavior. Spectra show a band at about 4500 Å in the yellow solutions, which seems characteristic of planar, yellow complexes of nickel. The blue complexes are probably hydrates which lose two molecules of water on heating.

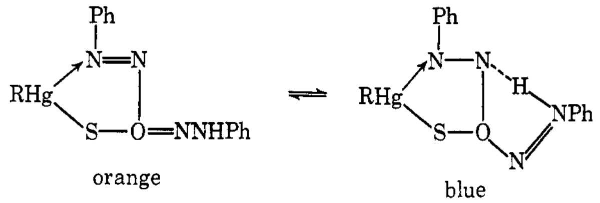
A solution of vanadium 8-quinolate alcohol in nitrobenzene is dark green at room temperature; above 130° it is the yellow color of the nitrobenzene alone.[44] This change is reversible and is attributed by the authors to dissociation. Addition of alcohol changes the color at room temperature from dark green to red-orange; this turns to yellow on heating but now the process is not reversible.

Silver allylthiourethan, $CH_2{=}CHCH_2{=}C(SAg)$-OEt, is a stable compound which gradually darkens in sunlight.[45] It shows marked thermochromism, being almost colorless at 0°, bright yellow at 15°, and lemon yellow at 30°, with little change above this temperature. If propyl or methyl groups replace the ethyl group, the compounds are thermochromic but to a lesser degree. The propyl compound, at about 70°, suddenly changes from light to dark yellow and no longer changes color on cooling. All three salts show a strong yellow color in solution but are not thermochromic. The corresponding salts of the thiourethans obtained from PhNCS and from $PhCH_2NCS$ are colorless and do not show thermochromism; hence this property in the allyl compounds probably depends on the presence of the C=C bond.

A unique and interesting method for determining the basicity of amines, the degree of hydrogen bonding in alcohols, and the effects of added diluents on hydrogen bonding was developed by Soloway and Mies.[46] Their determinations were based on the fact that a solution of ferric chloride, n-propyl gallate, and o-chloroaniline has a rather sharp thermochromic transition temperature from yellow to blue as the temperature is raised. The temperature of the transition is a function of the concentration, structure, and amount of the diluents or test substances. The thermochromic equilibrium is that between the chelate iron–gallate and the nonchelated materials.

The possibility of using the equilibrium as an indicator for pH determination and redox indication is also noted. The thermochromic transition temperatures for a series of amines range from 5 to 113°; for a series of alcohols from 50 to 99°. Ten to 15 repetitions of the thermochromic transition result in a lowering of the transition temperature; the transition temperature is lowered as much as 10° if the solution stands for several days. The effect of diluent is shown by the lowering of the thermochromic transition temperature of the 1-butanol solution from about 60 to less than 20°, depending on kind and amount of diluent. The thermochromic transition temperatures for aldehydes, ketones, esters, ether, and nitriles range from −92 to 15°. A wide variety of other types of compounds was tested as inhibitors of chelation. The use of properly prepared standard solutions as temperature indicators under certain conditions is an obvious potential use.

Mercury–organic dyes for nylon have been developed whose colors depend on light intensity and temperature; nylon dyed with p-aminophenylmercuric dithizonate and p-[(4,6-dichloro-s-triazin-2-yl)amino]-phenylmercuric dithizonate ranges from orange to blue.[47] The following equilibrium is suggested, based on infrared and kinetic data.



Certain spiropyrans having a chelating function at the 8′ position can form chelates with copper, cobalt, nickel, zinc, and chromium. Either in solution or in the solid form, the spiropyran forms the chelates when the pyran ring is opened by heat or light. The chelates themselves may also be thermochromic or photochromic.[48,49]

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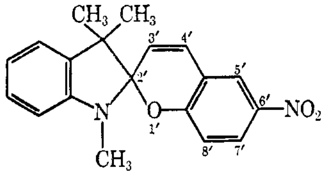
TABLE IV

"IRREVERSIBLE" COLOR CHANGES OF INORGANIC COMPOUNDS

Compound[a]	Color transition on heating	Transition temp, °C	Ref
$CoCl_2 \cdot 6H_2O$	Pink to blue	35	*b*
$CoCl_2 \cdot 2C_6H_{12}N_4 \cdot 10H_2O$	Pink to blue	75, 35	*b, c*
$CoBr_2 \cdot 2C_6H_{12}N_4 \cdot 10H_2O$	Pink to blue	40	*c*
$CoI_2 \cdot 2C_6H_{12}N_4 \cdot 10H_2O$	Pink to green	50	*c*
$Co(NO_3)_2 \cdot 2C_6H_{12}N_4 \cdot 10H_2O$	Pink to blue	155, 90, 75	*b, c*
$CoSO_4 \cdot 2C_6H_{12}N_4 \cdot 9H_2O$	Pink to violet	60	*c*
$Co(CNS)_2 \cdot 2C_6H_{12}N_4 \cdot 10H_2O$	Pink to blue	130, 60	*b, c*
$[Co(NH_3)_5Cl]Cl_2$	Purple to blue-black	190	*c*
$[Co(NH_3)_5Cl]SiF_6$	Purple to gray	200	*c*
$[Co(NH_3)_6]PO_4$	Yellow to violet	210–220	*c*
	Violet to brown	250–270	*c*
	Brown to black	320–350	
$[Co(NH_3)_6]HP_2O_7$	Yellow to gray-blue	280	*c*
	Gray blue to violet	400	*c*
$CoNH_4PO_4 \cdot H_2O$	Dark blue to gray	500	*c*
$CoCO_3$	Violet to black	330	*b*
CoC_2O_4	Pink to black	400	*b*
$NiCl_2 \cdot 6H_2O$	Light green to yellow	200	*b*
$NiSO_4 \cdot 7H_2O$	Light green to yellow	155	*b*
$NiCl_2 \cdot 2C_6H_{12}N_4 \cdot 10H_2O$	Light green to violet	160, 60	*b, c*
$NiBr_2 \cdot 2C_6H_{12}N_4 \cdot 10H_2O$	Light green to pale blue	175, 60	*b, c*
$NiCO_3$	Green to brownish green	260	*b*
NiC_2O_4	Light blue to black	410	*b*
$Ni(NH_4)PO_4 \cdot 6H_2O$	Light green to grayish	120	*c*
$Ni(CNS)_2 \cdot 4$pyridine	Blue to green	135	*c*
	Green to yellow	210	
	Yellow to brown	340	
$Ni(MoO_4)_6 \cdot 8H_2O$	Gray to blue	180–210	*c*
$Cu(OH)_2$	Blue to black	185	*b*
$Cu(NO_3)_2 \cdot 3H_2O$	Blue to brown-black	250	*b*
$CuSO_4 \cdot Cu(OH)_2$	Green to brownish	265	*b*
$CuCO_3 \cdot Cu(OH)_2$	Green to black	320	*b*
$CuC_2O_4 \cdot 5H_2O$	Light blue to black	355	*b*
$CuC_4H_4O_6 \cdot 3H_2O$	Blue to black-red	295	*b*
$2Cu(CNS)_2 \cdot 2$pyridine	Green to yellow	135	*c*
	Yellow to black	220	
$[Cr(NH_3)_6]_4(P_2O_7)_3$	Yellow to violet	140–150	*c*
	Violet to yellow-blue	220–230	
	Yellow-blue to brown	280	
$(NH_4)_2Cr_2O_7$	Orange to green	225	*b*
$[Cr(NH_3)_5Cl]C_2O_4$	Light blue to brown	260	*c*
$Cd(OH)_2$	White to brown	230	*b*
$CdCO_3$	White to brown	375	*b*
$CdC_2O_4 \cdot 3H_2O$	White to brown	450	*b*
$MnCO_3$	Light brown to black	345	*b*
$MnC_2O_4 \cdot 5H_2O$	White to black	400	*b*
$MnC_4H_4O_6$	Light pink to black	410	*b*
$Mn(NH_4)_2P_2O_7$	Violet to white	400	*c*
$(NH_4)_3PO_4 \cdot 12MoO_3$	Yellow to black	140–160	*c*
$H_4(NH_4)_3[Fe(MoO_4)_6] \cdot 7H_2O$	Black to yellow	220	*c*
	Yellow to white	80	*c*
NH_4VO_3	White to brown	150, 200	*b, c*
	Brown to black	170	*c*
$FeC_2O_4 \cdot 2H_2O$	Yellow to brown	375	*b*
$(NH_4)_2U_2O_7$	Gray to yellow	200	*c*
ZnO	White to pale green	>250	1, *d*
HgI	Yellow to orange-red	54–82	1, *d*
CuI	Gray-tan to orange	60–62	1, *d*

[a] Compounds of footnote *c* were cast as crayons of paraffin wax. [b] F. G. Brickwedde, *Physica*, **24**, 128 (1958). [c] Z. Cimpl, F. Kosek, M. Stanek, and J. Klazar, *Strojienstvi*, **15**, 543 (1965); *Chem. Abstr.*, **64**, 1673*g* (1966). [d] C. H. Bachman and J. B. Maginnis, *Am. J. Phys.*, **19**, 424 (1951).



The 8′-hydroxymethyl compound in ethanol or acetone is not photochromic but yields a purple solution. When cobalt ion is added an orange complex forms; then the color fades. The color can be regenerated with heat but not with light. In the case of zinc ion, a wine complex forms which fades with application of heat but regenerates on exposure to ultraviolet light. The piperidinomethyl-substituted compound also forms complexes with zinc, cobalt, and cupric ion, whose colors are a function of both light and heat. Thus, some photochromic and thermochromic complexes can be formed from chelating agents which themselves do not possess these properties.

Photochromic spiropyrans which have a chelating function have been reported.[50] It seems likely that some of these are also to a degree thermochromic.

Dilute alcoholic solutions of uranyl salts with diphenylcarbazone or 1,5-diphenylcarbohydrazide are practically colorless but develop a red color at low temperature. The color is attributed to the formation of coordination compounds. Dilute mixtures of mercuric iodide and diphenylcarbazine behave similarly.[51]

Monocyclopentadienyltitanium dichloride is a violet solid which forms a light blue solution in acrylonitrile; this changes to green at −44° and to yellow at −78°. The color is believed due to a monomer–dimer equi-

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librium, with lower temperature favoring the colored dimer.[52]

V. "IRREVERSIBLE" TRANSITIONS

Phosphomolybdic acid, silicotungstic acid, and phosphovanadomolybdic acid, cast into a polymer film, suddenly turn black above a threshold intensity of incident heat or light of 7.5 g cal/(cm^2 min). The film remains black and does not revert to the transparent state.[53,54]

The use of inorganic compounds to indicate temperature is well known. The compounds are usually made into a crayon with paraffin wax or a similar binder and the temperature of the visible color transition may in some cases be regulated by the composition of the crayon. When such crayons are used, the transitions are for practical purposes not reversible, though in fact many would be reversible under conditions of high humidity and given sufficient time. As noted earlier, dispersion of a thermochromic material in a binder greatly reduces the rate at which the material reverts to its initial color on cooling. Representative of truly irreversible transition is the decomposition of cobalt oxalate. A number of these temperature-indicating compounds are listed in Table IV.

ACKNOWLEDGMENT.—Grateful acknowledgment for helpful discussions is due to Jerome Goodman of Nuclear Research Associates.

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