Discontinuous Thermochromic Phase Transitions in Transition Metal Salts

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A thermochromic material is a substance which changes color as a function of temperature. A particularly interesting class of thermochromic materials involves transition metal salts that exhibit an abrupt color change which is the result of a structural phase transition [1]. These types of discontinuous thermochromism are associated with changes in coordination geometry and/or ligand field strength.

For copper halide salts, discontinuous thermochromism has been known for some time. For certain quaternary salts of $CuCl_4^{2-}$, the green to yellow thermochromic transition results from a change in the anion geometry from square planar to a less crowded distorted tetrahedral configuration [2]. Willett et al. have proposed that the phase transition in these salts results from the weakening of hydrogen bonding and crystal packing forces in the high temperature phase [3].

Discontinuous thermochromism of copper(II) and nickel(II) complexes of N,N-diethylethylenediamine have also been known for some time. The BF_4^-, ClO_4^-, and NO_3^- salts of the copper(II) derivative all exhibit an abrupt change from brick red to deep violet at the phase transition. A number of workers postulated that the thermochromic transition resulted from increasing axial interaction of the anion which resulted in the formation of a tetragonally distorted octahedral arrangement [4]. Recently, however, it has been shown via X-ray analysis and NMR studies that the color change results from a decrease in the ethylenediamine ligand field strength due to rapid flipping of the ethylenediamine chelate ring [5].

Mori and coworkers have investigated the sudden purple-to-green transition of $Cu(NO)_2)_2(NH_3)_2$ [6]. By comparing the infrared spectra of the two phases it was concluded that the color change results from linkage isomerization of the NO_2^- ligand. Below the transition temperature NO_2^- is coordinated through the nitrogen atom while in the green phase it is oxygen bound. Mori has also found it possible to "fine-tune" the transition temperature from approximately -50 to 30 C by partially replacing the NO_2^- ligand with chloride or bromide ions.

One of the oldest examples of discontinuous thermochromism is found in the transition metal salts of the HgI_4^{2-} anion. The mechanism of the phase transition has been shown to be an order-disorder transition with the cations being ordered below the transition temperature and disordered above the phase transition temperature [7]. These compounds have received renewed interest as they show high electrical conductivity above the phase transition (due to the increased mobility of the cations). Because they also contain a very reproducible hysteresis loop they may be suitable for use as a high density, erasable IR recording medium.

The phenomenon of thermochromism in inorganic compounds gives one an opportunity to gain much insight into the processes which occur during a solid state phase transition. In only a relatively few complexes have investigations of the static and dynamic nature of the thermochromic transition been undertaken.

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