Preparation and Properties of a Spectacular Thermochromic Solid

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Letters

Preparation and Properties of a Spectacular Thermochromic Solid

This *Journal* has published interesting articles on thermochromism or thermochromic solids that were strengthened by attractive demonstrations of the properties of these materials *(1–4)*. Using a solid-state synthesis similar to that employed earlier *(1)*, we synthesized a thermochromic complex, $[(CH_3)_2NH_2]_2NiCl_4$, that transitions among three colors. The successful synthesis resulted from one of the many attempts to synthesize a series of potentially thermochromic complexes of the general formula X_2MCl_4, where X = R_2NH_2 (R=CH_3, C_2H_5, etc.) and M = Cu, Co, Ni, Mn, … .

Because such types of complexes are deliquescent and air sensitive, we sealed the product in a glass ampoule immediately after the synthesis. This ensures that the compound can be used for demonstrations many times and enriches the series of publications entitled, "Prepare It Once, Use It Many Times" *(5–7)*. Details for the synthesis, including preparation of the ampoule and sealing of the product, are given in the online material.

At room temperature the solid has raspberry-red color (low-temperature polymorph). When the sample is heated to about 110 °C the color changes to deep blue (high-temperature polymorph), and when it cools down to room temperature, the color turns to light yellow (metastable form). After 2–3 weeks (the longer, the more complete the transition—see in the online material for details) the original raspberry-red color returns (Figure 1).

The synthesized compound seems ideal for demonstration of multiple thermochromic transitions in a single solid. Other phenomena (e.g., metastability) could be demonstrated as well. A minor disadvantage is that the phase transition occurs above 100 °C, so one could not use a beaker of boiling water.

A discussion about the possible structural characteristics of each phase is appropriate. On the basis of literature data *(8–10)*, one could safely conclude from the intense blue color that the high-temperature polymorph contains tetrahedral $NiCl_4^{2-}$ anions. By reasoning along the lines mentioned in ref *1*, it could be postulated that the metastable yellow form of the compound is due to a phase containing $NiCl_6$ octahedra, sharing bridging chlorine atoms (similar to the crystal structure of the yellow $NiCl_2$; ref *11*). Here too, hydrogen bonding may play an important role in maintaining the octahedral geometry and influencing the temperature at which the thermochromic transition occurs. Considering that the transition temperature is higher in this case than in the case of $[(C_2H_5)_2NH_2]_2NiCl_4$ *(1)*, one could deduce that the hydrogen bonds in $[(CH_3)_2NH_2]_2NiCl_4$ are stronger. Finally, the raspberry-red room temperature polymorph might contain square-planar $NiCl_4^{2-}$ anions (as in other nickel complexes with the same color and coordination; ref *8*). Unfortunately, there is no straightforward correspondence between the color, type of ligands, and coordination in nickel complexes *(8)*. Therefore, the question of the exact molecular or crystal structures of the three modifications is still open and will be subject to further studies.

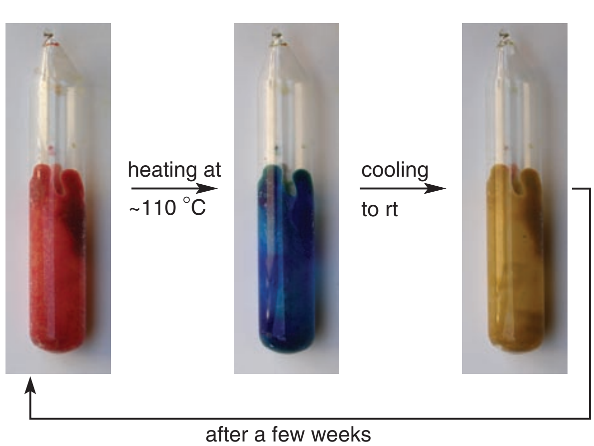

Figure 1. Photographs of the three polymorphs and a scheme of the transformations of $[(CH_3)_2NH_2]_2NiCl_4$.

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Supplement

Synthesis and properties of the complex

Preparation and sealing the ampoule

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