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Tin Dialkyldithiocarbamates: A Novel Group IV Metallothermochromic System

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Recent investigations in our laboratory show that previously reported tin(II)[1] and tin(IV) dialkyldithiocarbamates undergo a reversible thermochromic transition at low temperatures both when suspended in mineral oil mulls and in toluene solutions, the first known such system of Group IV compounds to exhibit this phenomenon. These complexes are bright orange in both solutions and mulls at room temperature and, depending on the compound, are light yellow or gold at –55 °C.

The room temperature absorption spectrum (using a Cary 17 instrument) of $Sn[(CH_3)_2NCS_2]_2$ in toluene in the 300–800 nm region consists of a broad, featureless band (Figure 1) with a weak shoulder at approximately 420 nm. Cooling this solution to –55 °C allows the formation of two new peaks at 324 and 342 nm, along with the concomitant orange to yellow color transition. Another noted change in the low temperature spectrum is an increase in "tailing" of the major, broad peak into the 800 nm region, whereas the room temperature absorption spectrum is restricted to the 300–500 nm region, a feature observed in the spectra of other thermochromic, metal–ammonium salt systems.[2] The exact cause of such broadening in this study is not presently understood, although solvent contraction of the toluene (thus effectively increasing the concentration of the complex) is one possible explanation. The room temperature absorption spectrum of $[(CH_3)_2NH_2]^+[(CH_3)_2NCS_2]^-$ in toluene (Figure 2) consists of a band which maximizes at 351 nm, but, when cooled to –55 °C, develops fine structure having bands at 325, 334 and 342 nm. Broad tailing in the spectrum of this compound is not observed upon cooling, and no visible thermochromism (which has been previously reported for non-metallic thiocarbonyl compounds[3]) is exhibited. Elevated temperature spectral measurements to +55 °C of both the ammonium salts and the tin complexes reveal no noticeable change from the room temperature absorption spectra.

One general trend derived from the room temperature absorption spectra is the red shift in the band

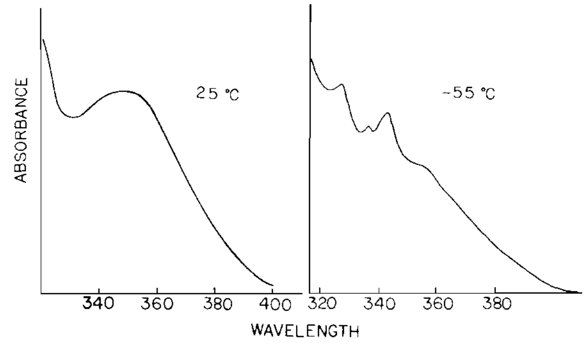

Figure 1. Variable temperature absorption spectrum of $Sn[(CH_3)_2NCS_2]_2$.

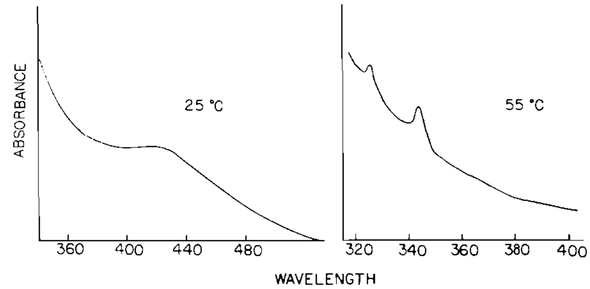

Figure 2. Variable temperature absorption spectrum of $[(CH_3)_2NH_2]^+[(CH_3)_2NCS_2]^-$.

TABLE. Room Temperature UV–Vis Absorption Spectra of Tin(II) and Tin(IV) Dithiocarbamates and Their Dialkylammonium Precursors.

Compound	λ_{max}, nm	ϵ, cm^{-1} M^{-1}	Concentration, *M*
I. $[(CH_3)_2NH_2]^+[(CH_3)_2NCS_2]^-$	351	47 ± 5	9.7 × 10^{-3}
II. $[(C_2H_3)_2NH_2]^+[(C_2H_3)_2NCS_2]^-$	352	45 ± 5	8.6 × 10^{-3}
III. $[(C_3H_7)_2NH_2]^+[(C_3H_7)_2NCS_2]^-$	352	41 ± 5	7.8 × 10^{-3}
IV. $Sn[(CH_3)_2NCS_2]_2$	~420	1100 ± 150	1.3 × 10^{-4}
V. $Sn[(C_2H_5)_2NCS_2]_2$	425	1100 ± 100	1.1 × 10^{-3}
VI. $Sn[(C_3H_7)_2NCS_2]_4$	415	260 ± 25	1.2 × 10^{-3}

maxima of approximately 70–75 nm upon complexation of the dithiocarbamate anion to the tin ions (see Table). These values are similar to those reported for other metal dithiocarbamates.[4] Also noteworthy is the absence of emission (< 1%) (using a Perkin–Elmer MPF-36 instrument) in the visible region (300–750 nm) for both the dimethylammonium dimethyldithiocarbamate and the tin(II) dimethyldithiocarbamate compounds at 25, –60, and –196 °C; also, no emission is observed in the same region for either the dipropylammonium salt (Compound III in the Table) or its tin(IV) analog (Compound VI) for the same temperatures.

Studies of both the tin(II) and tin(IV) complexes are being extended to include variable temperature infrared and Mössbauer investigations as well as the synthesis and study of new complexes.

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