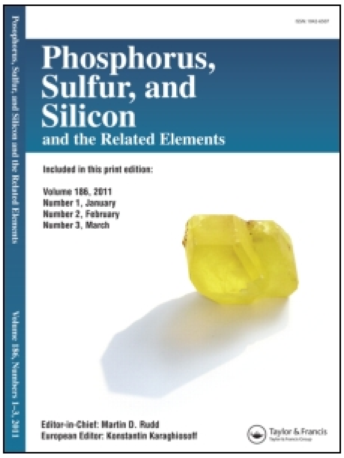

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THERMOCHROMIC MOLECULES WITH BONDS OF Se OR Te AND Sb OR Bi

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THERMOCHROMIC MOLECULES WITH BONDS OF Se OR Te AND Sb OR Bi

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Abstract The syntheses and properties of stibino or bismuthino selenides or tellurides of the types $R_2EE'R$, $(R_2E)_2E'R$, $RE(E'R)_2$; E = Sb, Bi; E' = Se, Te; R = CH_3, C_2H_5, C_6H_5 are described. Reversible change of color with variation of temperature (thermochromism) is observed in the case of $(CH_3)_2SbTeCH_3$, $(C_2H_5)_2SbTeCH_3$, $[(CH_3)_2Sb]_2Se$ and $[(CH_3)_2Sb]_2Te$.

INTRODUCTION

Molecules with an Sb-Se, Sb-Te or Bi-Te bond were unknown in the literature[1] until very recently. Our interest in molecular compounds that change color on cooling or heating as certain homodinuclear Sb-, Bi-, Se-, and Te-compounds do, stimulated attempts to synthesize selenides and tellurides of Sb and Bi. If thermochromism occurs in compounds with Sb_2-, Bi_2-, Se_2- or Te_2- units, color changes should also be possible in heteronuclear species containing Sb-Se-, Sb-Te-, Bi-Se- or Bi-Te- units.

COMPOUNDS OF THE TYPE R_2E-E'R' (E = Sb, Bi; E' = Se, Te; R, R' = ALKYL, ARYL)

The title compounds are obtained by complete dismutation of distibines[2,3] or dibismuthines[4] with diselenides or ditellurides at or below room temp. (eqn. 1). Interpretation of these results in terms of Pauling's concept of ionic covalent resonance energy is not straightforward because of the small differences in the electronegativities between Te and Sb or Bi. The antimony

$$R_2E\text{-}ER_2 + R'E'\text{-}E'R' \longrightarrow 2\ R_2E\text{-}E'R' \qquad (1)$$

E = Sb, E' = Se: $R = CH_3, C_2H_5$; $R' = CH_3, C_6H_5$
E = Sb, E' = Te: $R = CH_3, C_2H_5$; $R' = CH_3, pCH_3C_6H_4$
E = Bi, E' = Te: $R = C_3H_7$; $R = p\text{-}CH_3C_6H_4$

selenides and tellurides are fairly stable and may be distilled at reduced pressure[2,3]. The expected thermochromism is found in the case of $(CH_3)_2SbTeCH_3$ (orange solid, red liquid) and $(C_2H_5)_2SbTeCH_3$ (orange solid, yellow liquid). The measurement of UV-VIS diffuse reflection spectra is in progress. The bismuth telluride decomposes rapidly at 25°C.

COMPOUNDS OF THE TYPE $RE(E'R')_2$ (E = Sb, E' = Se, Te)

Selenides of the type $R_2Sb\text{-}E'R'$ give scrambling of substituents at elevated temperatures with formation of trialkylstibines and the title compounds in equilibrium (eqn. 2).

$$2\ R_2Sb\text{-}ER' \rightleftharpoons R_3Sb + RSb(ER')_2 \qquad (2)$$

E = Se; $R = CH_3, C_2H_5$; $R' = CH_3, C_6H_5$

The novel antimony selenides are obtained, when the trialkylstibines are removed from the equilibrium by distillation. Experimental data are given in table 1.

TABLE I Experimental data of compounds of the type $RSb(SeR')_2$

Compound	Yield (%)	m.p. (°C)
$CH_3Sb(SeCH_3)_2$	74	54
$CH_3Sb(SeC_6H_5)_2$	78	73
$C_2H_5Sb(SeC_6H_5)_2$	48	50

Prolonged heating of $(CH_3)_2SbSeCH_3$ gives not only $CH_3Sb(SeCH_3)_2$ but also $Sb(SeCH_3)_3$. The scrambling of substituents is less selective in the case of the antimony tellurides. Mass spectrometry revelas the presence of species of the types R_3Sb, R'_2Te, RR'Te, R'TeTeR' and $RSb(TeR')_2$ in the product mixture. Separation is not worthwhile.

COMPOUNDS OF THE TYPE $R_2E\text{-}E'\text{-}ER_2$ (E = Sb, Bi; E' = Se, Te; R = ALKYL, PHENYL)

Action of Se or Te on distibines or dibismuthines results[5,6] in the insertion of a chalcogen atom (eqn. 3).

$$R_2E\text{-}ER_2 + E' \longrightarrow R_2E\text{-}E'\text{-}ER_2 \qquad (3)$$

$E = Sb$, $E' = Se, Te$; $R = CH_3, C_2H_5, C_6H_5$

$E = Bi$, $E' = Se, Te$; $R = C_3H_7$

Thermochromism is found in the case of the methyl derivatives $(CH_3)_2Sb\text{-}Se\text{-}Sb(CH_3)_2$ (red solid, orange liquid) and $(CH_3)_2Sb\text{-}Te\text{-}Sb(CH_3)_2$ (blue violet solid, brown liquid). Investigations of the diffuse reflectance spectra of the different phases are in progress. The Sb compounds are thermally much more stable than the Bi analogues, which decompose rapidly with formation of $(C_3H_7)_3Bi$ and black solids.

DISCUSSION

The compounds are characterized by elemental analyses, ^1H-nmr-, mass-, ir-, and Raman spectra. Selected spectroscopic data are given in the tables II and III. The number and the relative intensities of the ^1H-nmr signals are as expected. The singlet signals of the methyl derivatives (table II) show an increase of deshielding in the sequence CH_3Sb, CH_3Te, CH_3Se. The ^1H-nmr spectra of the compounds with ethyl or phenyl groups are more complex. At 360 MHz we observe two multiplet signals for the C_6H_5

TABLE II ^1H nmr data of methyl derivatives

Compound	δ CH_3Sb	δ CH_3Se	δ CH_3Te
$(CH_3)_2SbSeCH$	1,20	2,08	
$(CH_3)_2SbTeCH_3$	1,35		1,90
$CH_3Sb(SeCH_3)_2$	1,52	2,24	
$[(CH_3)_2Sb]_2Se$	1,30		
$[(CH_3)_2Sb]_2Te$	1,46		

protons in compounds of the type $R_2SbEC_6H_5$ or $RSb(EC_6H_5)_2$ with $R = CH_3$, C_2H_5; E = Se, Te. In the case of the derivatives with an ethyl group on Sb there are typical changes in the number of signals depending on the degree of substitution. For compounds of the type $C_2H_5Sb(SeR)_2$ we observe a quartet and a triplet for the C_2H_5 protons. The spectra of compounds of the type $(C_2H_5)_2SbE'R'$ show in contrast 16 lines of an ABX_3 spin system for the C_2H_5 protons. This indicates that there is no inversion on Sb and therefore there is a diastereotopic situation. Selected ir and Raman data are given in table III.

TABLE III Ir and Raman data of methyl derivatives compound

Compound	ν SbSe (cm^{-1})		ν SbTe (cm^{-1})
	Ir	R	R
$(CH_3)_2SbSeCH_3$	230	230	
$[(CH_3)_2Sb]_2Se$	230	225	
$CH_3Sb(SeCH_3)_2$	230	200	
$(CH_3)_2SbTeCH_3$			180
$[(CH_3)_2Sb]_2Te$			180

The methyl derivatives are very useful systems for the study of the vibrations of the heavy atom skeleton in antimony selenides and tellurides. The Sb-Se or Sb-Te valence vibrations give rise to intensive Raman signals and are easily observed. The values for ν SbSe or ν SbTe are in accordance with estimations based on Siebert's formula[7]. The low position of ν $SbSe_2$ in the Raman spectrum of $CH_3Sb(SeCH_3)_2$ is, however, unexpected. The EI mass spectra are very useful for the characterization of the title compounds, too. All the chalcogenides are volatile and molecular ions are of high intensity. Fragmentation generally proceeds with complete splitting off of the organic substituents leaving fragments of the type EE', E_2E' or EE'_2 (E = Sb, Bi; E' = Se, Te).

Important contributions to the field of antimony and bismuth selenides and tellurides have come from the laboratories of A. J. Ashe III[8] and M. Wieber[9]. Their results are in accordance with our findings. Almost all types of structures derived from trivalent Sb or Bi and divalent Se or Te have been synthesized as organometallic compounds with unexpected properties including thermochromism in some examples. Because structural data for the compounds are not available, the reason for the color changes that often occur at the melting point is not known. We assume that there are similarities with thermochromic distibines, in which close intermolecular contacts have been observed and are regarded as responsible for the bathochromic shift of the solid state spectra compared with the liquid. Our present activities are concentrated on the measurement of UV-VIS spectra of the title compounds.

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