I19

SYNTHESIS AND MAGNETICS OF LAYERED TRANSITION METAL FLUORO COMPOUNDS

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A convenient route to layered materials of the type $M(SbF_6)_2$, with M=Ni, Pd, Cu and Ag is found in the solvolysis reaction:

$$M(SO_3F)_2 + 6SbF_5 \xrightarrow{25\text{-}60°C} M(SbF_6)_2 + 2Sb_2F_9SO_3F$$

The syntheses are performed in glass vessels, and at ambient or slightly elevated temperatures, leading to analytically pure products. Physical methods including vibrational spectroscopy and low temp. magnetic measurements are used for product characterization. Vibrational assignments of all the species are given and the principal ligand-field parameters Dq and B of $Pd(SbF_6)_2$ ($^3A_{2g}$ ground state) are obtained and compared with those of the precursor $Pd(SO_3F)_2$.

In contrast to the recently[1] reported paramagnetic, blue $Ag(SbF_6)_2$, made via a fluoride abstraction:

$$AgF_2 + 2SbF_5 \xrightarrow{HF} Ag(SbF_6)_2$$

solvolysis yields unexpectedly a white, diamagnetic material of identical composition, best formulated as $Ag(I)Ag(III)(SbF_6)_4$, a valence isomer of the blue compound. Some conversion reactions are described leading to the diamagnetic species, including the thermal conversion, all of which indicate the higher thermodynamic stability of the diamagnetic white compound. A similar, but less pronounced case for valence isomerism is postulated for $Cu(SbF_6)_2$, based on its magnetic behaviour, X-ray powder diffraction data, vibrational spectra and differential scanning calorimetry.

1 D. Gantar et al., J. Chem. Soc., Dalton Trans. 2379 (1987).