Nickel(II) Complexes of 1,3-Bis(dimethylstibino)propane. Stable Nickel(II)–Stibine Complexes

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Summary 1,3-Bis(dimethylstibino)propane (dmsp) has been synthesised and forms stable square-pyramidal nickel(II) complexes.

THE co-ordination chemistry of nickel with Group VB donor ligands has been extensively studied,[1] not least because of the potential of these compounds as catalysts, *e.g.* nickel(0)-stibine complexes are effective in promoting the cyclo-oligomerisation of butadiene.[2] However, except for two unstable $[Ni(SbMe_3)_3X_2]$ (X = Br, I) complexes,[3] the only reported examples of nickel(II)–SbR_3 co-ordination are in bi- or multi-dentate ligands which also contain phosphorus or arsenic donors; the latter are expected to contribute markedly to the stability of the complexes.[4,5] Here we report the preparation of stable nickel(II) complexes of a chelating diantimony donor, 1,3-bis(dimethylstibino)propane (dmsp).

The ligand dmsp is obtained as a colourless, extremely air-sensitive liquid in 45% yield from the reaction of sodium dimethylstibide and 1,3-dibromopropane in liquid ammonia. The reaction of NiX_2, $Ni(ClO_4)_2,6H_2O$, and dmsp in a 1 : 1 : 4 molar ratio in $Bu^nOH–CH_2Cl_2$ yields air-stable, purple, diamagnetic crystalline $[Ni(dmsp)_2X]ClO_4$ (X = Cl, Br, I).† These complexes are insoluble in halogenated organic solvents or acetone, but dissolve readily in nitromethane in which they function as 1 : 1 electrolytes. The electronic spectra both in nitromethane solution and the solid state exhibit one broad absorption at 18—20 × 10^3 cm^{-1}, with a shoulder at low energy, consistent with an essentially square-pyramidal geometry.[6] Interestingly, the corresponding complexes of 1,3-bis(dimethylarsino)propane are trigonal bipyramidal.[7] With $Ni(ClO_4)_2,6H_2O$ alone, dmsp forms purple $[Ni(dmsp)_2(H_2O)](ClO_4)_2$, a 1 : 2 electrolyte, which exhibits an electronic spectrum consistent with a square-pyramidal $NiSb_4O^{2+}$ chromophore, ϵ_{max} 19·3 × 10^3 cm^{-1}. The i.r. spectrum confirms the presence of water and that the perchlorate groups are ionic. The tendency of antimony donors to promote five-co-ordination in bisperchlorate complexes, rather than the four-co-ordinate structures formed by phosphorus and arsenic analogues, has been noted previously.[4] Attempts to prepare 1 : 1 adducts, $[Ni(dmsp)X_2]$, were unsuccessful.

Palladium(II) and platinum(II) form only planar $[M(dmsp)X_2]$ (M = Pd, Pt; X = Cl, Br, I, SCN), even in the presence of a five-fold excess of dmsp; neither $[M(dmsp)_2]X_2$ nor $[M(dmsp)_2X]^+$ could be isolated.

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† Satisfactory analyses have been obtained for the complexes.

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