The Bis[tris-(*o*-dimethylarsinophenyl)stibine]nickel(II) Cation. A Pentaco-ordinate Complex Containing the Novel $[Ni(Sb_2As_3)]^{2+}$ Donor Set

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Summary The structure of the unusual complex $[Ni(Sbtas)_2](ClO_4)_2$ [Sbtas = tris-(*o*-dimethylarsinophenyl)-stibine] is essentially square-pyramidal involving the $[Ni(Sb_2As_3)]^{2+}$ donor set.

SOME "tripod" quadridentate ligands containing Group VB donors, tris-(*o*-diphenylphosphinophenyl)phosphine (QP) and tris-(*o*-diphenylarsinophenyl)arsine (QAS) have been found to react with $Ni(ClO_4)_2,6H_2O$ to yield low-spin trigonal bipyramidal complexes, $[Ni(QL)(ClO_4)]ClO_4$ (L = P, As), which contain co-ordinated perchlorate.[1] We now report the complex formed by the reaction of a similar quadridentate Group VB ligand, tris-(*o*-dimethylarsinophenyl)-stilbine, Sbtas. This ligand forms the unusual $[Ni(Sbtas)_2](ClO_4)_2$ complex.

When ethanolic solutions of $Ni(ClO_4)_2,6H_2O$ and Sbtas are mixed in a 1:1 molar ratio, immediate precipitation of the blue-purple diamagnetic complex, $[Ni(Sbtas)_2](ClO_4)_2$, occurs. Dissolving this complex in a CH_2Cl_2–EtOH mixture and adding $NaBPh_4$ leads to quantitative precipitation of $[Ni(Sbtas)_2](BPh_4)_2$. Elemental analyses are in excellent agreement with these formulations.

The results of conductivity dilution studies in $MeNO_2$, when plotted as a graph of $(\Lambda_0 - \Lambda_e)$ against $\sqrt{C}$ yield slopes of 412 (ClO_4^- complex) and 430 (BPh_4^- complex), which is strong evidence for the existence of 1:2 electrolytes in solution.[2] The electronic spectra in dichloroethane solution and in the solid state are essentially similar, indicating similar structures in both physical states. The visible solution spectra exhibit one band at 20·1 kK (ϵ 2300) (ClO_4^- complex) and 19·9 kK (ϵ 2050) (BPh_4^- complex); in both cases this band is asymmetric with an unresolved shoulder at lower energy. The position of these bands indicates that the cation $[Ni(Sbtas)_2]^{2+}$ is essentially square pyramidal[3] and not trigonal bipyramidal.[1,4] Although several possible structures exist, we feel that the most likely one involves three dimethylarsino-groups co-ordinated and three unco-ordinated. N.m.r. spectra provide evidence for this formulation. The ^1H n.m.r. spectrum of Sbtas shows the presence of one type of Me_2As group by a resonance at τ 8·80. In the pentaco-ordinate $[Ni(Sbtas)Cl]^+$ ion, which contains three co-ordinated Me_2As groups the spectrum exhibits a band at τ 8·25.[5] In the spectrum of $[Ni(Sbtas)_2](BPh_4)_2$ two absorptions, integrating 1:1·1, appear at τ 8·25 and 8·90. If there is any exchange between co-ordinated and unco-ordinated Me_2As groups, this must be slow on the n.m.r. time scale. Any structure involving the bidentate Sbtas ligand donating *via* two terminal arsine groups, as was found to exist in $[Hg(QAS)Br_2]$,[6] can thus be ruled out.

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