# Nickel(II)–Bismuth(III) Bond Formation in Nickel(II) Complexes of Tris(*o*-dimethylarsinophenyl)bismuthine

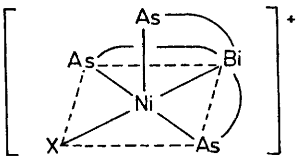
By William Levason, Charles A. McAuliffe,* and Stephen G. Murray

(*Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester* M60 1QD)

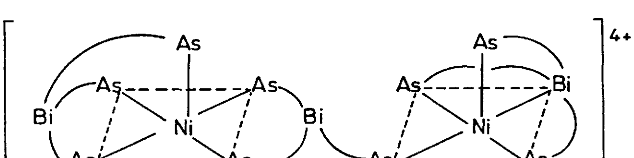
*Summary* Tris(*o*-dimethylarsinophenyl)bismuthine (bitas) forms the square pyramidal complexes $[Ni(bitas)X]BPh_4$ (X = halide), the first examples of trivalent bismuth co-ordinated to a 3*d* transition metal in a positive oxidation state, and $[Ni_2(bitas)_3]^{4+}$, which contains examples of bitas functioning as a tridentate and a tetradentate ligand.

Tripodal ligands $E(-LR_2)_3$ (L = P, As; R = Ph, Me) usually function as quadridentate chelates when the apical atom E is a group Vb element (N, P, As, Sb),[1] and as bi- or tri-dentate ligands when E is not a donor element, e.g. carbon.[2] We have now synthesised tris(*o*-dimethylarsinophenyl)bismuthine, $(o\text{-}C_6H_4AsMe_2)_3Bi$ (bitas). In complexes of bitas the possibility exists either of tetradentate co-ordination (and the formation of a novel bismuth–metal bond) or tridentate ($As_3$) behaviour with the bismuth remaining unco-ordinated.

The reaction of nickel(II) halides, bitas, and $NaBPh_4$ in a 1 : 1 : 1 molar ratio in ethanol produces $[Ni(bitas)X]BPh_4$ complexes. These are diamagnetic, 1 : 1 electrolytes in $10^{-3}$ M nitromethane solution, and their electronic spectra in dichloromethane and in the solid state exhibit one broad absorption in the 18—21 × $10^3$ $cm^{-1}$ range with a shoulder at lower energy characteristic of square-pyramidal geometry.[3] The $^1H$ n.m.r. spectra in $CDCl_3$ and $CH_2Cl_2$ show two methyl resonances at $\tau$ 8·2 and 8·3 (intensities 1 : 2) assigned to co-ordinated $-AsMe_2$ groups ($-AsMe_2$ groups in the free ligand absorb at $\tau$ 8·9). Thus, we assign the square-pyramidal structure (I) to these compounds with an apical As donor and a $BiAs_2X$ donor set in the basal plane. This contrasts with the essentially trigonal bipyramidal complexes of the corresponding $E(o\text{-}C_6H_4AsMe_2)_3$ (E = As, Sb) complexes[4] and is probably due to the inability of the large Bi atom to occupy an apical position of a trigonal bipyramid.[5]



(I)



(II)

Nickel(II) perchlorate hexahydrate and bitas react in ethanol to form brown $[Ni_2(bitas)_3](ClO_4)_4$, irrespective of the ratio of the reactants. This diamagnetic complex is a 1 : 4 electrolyte ($\Lambda_M$ = 312 $ohm^{-1}$ $cm^2$ $M^{-1}$ in $10^{-3}$ M nitromethane),[6] and its electronic spectrum is characteristic only of square pyramidal geometry ($E_{max}$ = 20·6 × $10^3$ $cm^{-1}$, $\epsilon$ = 1375). The $^1H$ n.m.r. spectrum shows two methyl signals ($\tau$ 7·9 and 8·0 intensities 1 : 3·4) due to co-ordinated arsines, but none corresponding to free arsine groups. The i.r. spectrum confirms the absence of water and of perchlorate co-ordination. All this information points strongly to structure (II) which contains bitas acting as both a tri- and tetra-dentate ligand.

The paramagnetic [Co(bitas)Br]$BPh_4$ and [Fe(bitas)$Cl_2$]-[$FeCl_4$] have also been obtained.

These complexes contain the first examples of bismuth co-ordinated to a 3d metal in a positive oxidation state.

We thank the S.R.C. for support.

(*Received, 30th December* 1974; *Com.* 1565.)

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