Co-ordination Complexes containing Multidentate Ligands. Part 12.[1] Nickel(II)–bismuth(III) Co-ordination in Nickel(II) Complexes of Tris(*o*-dimethylarsinophenyl)bismuthine and Tris(3-dimethylarsinopropyl)bismuthine

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Two potentially quadridentate chelating ligands containing bismuth atoms have been synthesised: tris(*o*-dimethylarsinophenyl)bismuthine (L^1) and tris(3-dimethylarsinopropyl)bismuthine (L^2). Reaction of L^1 with nickel(II) salts produces the essentially square-pyramidal $[NiL^1X]^+$ (X = Cl, Br, or I) and $[Ni_2L^1_3][ClO_4]_4$ species, whilst L^2 forms the trigonal-bipyramidal $[NiL^2(OH_2)][ClO_4]_2$. The resulting structures are discussed in terms of the structures of the ligands.

IN contrast to the extensive studies of phosphorus-, arsenic-, and antimony-donor ligands, tertiary bismuthines have received scant attention. This apparent neglect is due to the very poor σ-donor properties of the semi-metal bismuth and to the weakness of the carbon–bismuth bond which results in C–Bi bond fission on reaction with many substrates.[2] The reported tertiary bismuthine complexes, *viz.* $[M(BiPh_3)(CO)_5]$ (M = Cr, Mo, or W),[3] $[M(BiEt_3)(CO)_5]$,[4] $[Ni(BiEt_3)(CO)_3]$,[4] and $[Ir(BiPh_3)(CO)(PPh_3)_2][ClO_4]$,[5] contain the acceptor metal in a low formal oxidation state. Only two complexes of metals in higher formal oxidation states are known: $[Co(BiPh_3)(pdt)_2]$ (Hpdt = pentane-2,4-dithione) [6] and $[Ag(BiPh_3)][ClO_4]$; [7] the latter may contain silver–η-arene rather than Ag–Bi co-ordination. One possible method of obtaining transition-metal–bismuth bonds is by incorporation of the latter into a multidentate chelate, and here we report the synthesis of two tripod-type ligands tris(*o*-dimethylarsinophenyl)bismuthine, $Bi(C_6H_4AsMe_2\text{-}o)_3$ (L^1), and tris(3-dimethylarsinopropyl)bismuthine, $Bi(CH_2CH_2CH_2AsMe_2)_3$ (L^2) and some of their nickel(II) and cobalt(II) complexes. Additional interest is provided by a comparison of the stereochemical and spectrochemical properties of the resulting complexes with those of other tripod quadridentates,[8] since the apical donor markedly affects both properties. A preliminary communication of this work has been published.[9]

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RESULTS

Tris(*o*-dimethylarsinophenyl)bismuthine (L^1) was synthesised in a similar manner to the arsenic[10] and antimony[11] analogues and obtained as a pale yellow malodorous oil. The synthesis of tris(3-dimethylarsinopropyl)bismuthine (L^2) is much more difficult and is accompanied by extensive decomposition. The successful synthesis utilised the slow addition of a filtered tetrahydrofuran (thf) solution of 3-dimethylarsinopropylmagnesium chloride to bismuth trichloride in thf at —30 °C. Inverse addition or performing the reaction at room temperature failed to yield the ligand in more than trace amounts, suggesting both decomposition of the bismuthine by excess of Grignard reagent and that appreciable C–Bi bond formation occurs only at low temperatures. These observations are in keeping with the known instability of trialkylbismuthines.[2] Once isolated, the ligand appears to be stable for at least several weeks either as a neat oil or in dichloromethane solution.

TABLE 1

Analytical and spectroscopic data for the metal complexes

Complex	Colour	Analysis (%) [a] C	H	Halide	Λ [b] S cm² mol⁻¹	I.r. data (cm⁻¹)
$[NiL^1Cl][BPh_4]$	Dark brown	49.2 (49.4)	4.2 (4.3)	3.0 (3.0)	70	
$[NiL^1Br][BPh_4]$	Dark brown	47.6 (47.7)	4.4 (4.1)	6.4 (6.6)	68	
$[NiL^1I][BPh_4]$	Blue-black	45.8 (46.0)	3.8 (4.0)	10.2 (10.0)	65	
$[Ni_2L^1{}_3][ClO_4]_4$	Dark brown	31.4 (31.2)	3.3 (3.3)		312	1 085br, 625 (sh) ($[ClO_4]^-$)
$[NiL^2(OH_2)][ClO_4]_2$	Dark blue	18.9 (19.0)	4.0 (3.8)		145	3 300, 1 620 (H_2O); 1 090, 625 ($[ClO_4]^-$)
$[CoL^1Br][BPh_4]$	Green	48.0 (47.7)	4.1 (4.1)	6.3 (6.6)	95	

[a] Calculated values are given in parentheses. [b] 10^{-3} mol dm^{-3} solutions in nitromethane.

The reaction of the appropriate nickel(II) halide, L^1, and sodium tetraphenylborate in a 1 : 1 : 1 mol ratio in EtOH–CH_2Cl_2 yielded dark brown or blue-black $[NiL^1X][BPh_4]$ (X = Cl, Br, or I), Table 1. Attempts to prepare analogues with X = NO_3, CN, or NCS were unsuccessful. These complexes are diamagnetic and 1 : 1 electrolytes in freshly prepared 10^{-3} mol dm^{-3} nitromethane solution. The electronic spectra in dichloromethane solution exhibited one broad asymmetric peak (Cl or Br) with a shoulder at low energy (Table 2). In the case of $[NiL^1I][BPh_4]$, the spectrum exhibited two peaks. The solid reflectance spectra are generally similar. These spectra are characteristic of five-coordinate essentially square-pyramidal[12] rather than trigonal-bipyramidal Ni^{II}.[13] The spectra exhibited the normal spectrochemical series for change of anion, $Cl^- > Br^- > I^-$.

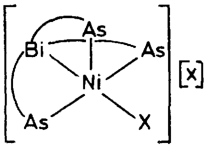
TABLE 2

Electronic and proton n.m.r. spectra of the metal complexes

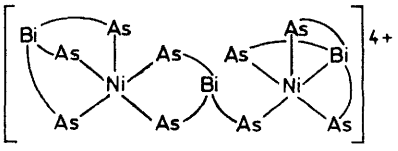
Complex	$E_{max.}$ [a]/10³ cm⁻¹ *b*	*c*	¹H N.m.r. (τ) [d]
$[NiL^1Cl][BPh_4]$	21.3 (1 480)	21.5, 18.3 (sh)	8.2, 8.3 (1 : 2)
$[NiL^1Br][BPh_4]$	20.8 (1 360)	21.0, 17.4 (sh)	8.15, 8.2 (1 : 2)
$[NiL^1I][BPh_4]$	20.8 (1 120), 18.6 (980)	20.0, 16.0 (sh)	8.2 8.3 (1 : 2)
$[Ni_2L^1{}_3][ClO_4]_4$	20.6 (1 375)	21.3br	7.9, 8.0 (1 : 3.4)
$[NiL^2(OH_2)][ClO_4]_2$ [e]	23.8 (sh), 17.1 (212)	22.8, 16.0br	8.45 (s)
$[CoL^1Br][BPh_4]$	23.4 (2 610), 16.2 (160), 6.0 (55)	22.2, 15.8, 5.9	8.19 (br)

[a] Absorption coefficients (ε/dm³ mol⁻¹ cm⁻¹) are given in parentheses. [b] In freshly prepared CH_2Cl_2 solution. [c] Diffuse, reflectance spectra. [d] Methyl absorption only; intensity ratios are given in parentheses. [e] In nitromethane.

The ¹H n.m.r. spectra of $[NiL^1X][BPh_4]$ showed two methyl resonances at τ 8.2 and 8.3 (intensity 1 : 2) compared with 8.9 for the methyl groups in the free ligand. This suggests two slightly different methyl environments in the complexes, again more consistent with square-pyramidal (1) rather than trigonal-bipyramidal structures.



(1)



(2)

Nickel(II) perchlorate hexahydrate and L^1 reacted, irrespective of the mol ratio of the reactants, to form $[Ni_2L^1{}_3][ClO_4]_4$, a diamagnetic 1 : 4 electrolyte[14] in 10^{-3} mol dm^{-3} nitromethane (Λ = 312 S cm² mol⁻¹). The i.r. spectrum confirms the absence of water and of co-ordinated perchlorate groups.[15] The electronic spectrum exhibited one broad absorption at 20 600 cm⁻¹, suggesting square-pyramidal geometry,[12] and the ¹H n.m.r. spectrum again showed two methyl signals (τ 7.9 and 8.0, intensity 1 : 3.4) assignable to co-ordinated methyl groups and no signal of τ *ca.* 8.9. This suggests that all the arsenic groups are co-ordinated and points strongly to structure (2).

Cobalt(II) bromide, L^1, and Na[BPh₄] reacted to yield

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the green paramagnetic ($\mu_{eff.}$ 2.09 B.M.) * $[CoL^1Br][BPh_4]$. The ^1H n.m.r. spectrum exhibited a broad signal at τ 8.19 attributable to co-ordinated $AsMe_2$ groups, and the electronic spectrum (Table 2) suggests five-co-ordinate Co^{II},[16] probably of similar structure to the nickel(II) analogue.

Tris(3-dimethylarsinopropyl)bismuthine (L^2) and nickel(II) perchlorate reacted in $EtOH-CH_2Cl_2$ to form a deep blue-green solution from which blue crystals of $[NiL^2(OH_2)][ClO_4]_2$ were obtained. The i.r. spectrum of this complex showed the presence of water and ionic perchlorate groups,[15] whilst the ^1H n.m.r. spectrum in CH_2Cl_2 showed only a single methyl signal at τ 8.45. The electronic spectrum both in the solid state and in solution showed two bands at 24 000 and 17 000 cm^{-1} characteristic of trigonal-bipyramidal geometry.[13] The complex is diamagnetic and a 1 : 2 electrolyte in nitromethane, and appears to be analogous to the corresponding phosphine [16] and arsine [17] complexes. The same cation is obtainable with the tetrafluoroborate anion.

The reaction of nickel(II) halides, '$NiX(ClO_4)$' or '$NiX(BPh_4)$' (X = halide), with L^2 in $EtOH-CH_2Cl_2$ or $BuOH-CH_2Cl_2$ produced blue-green solutions which rapidly decompose depositing a fine black powder. All attempts to isolate solid complexes were fruitless, although by mixing nickel(II) salts and L^2 in a spectrometer cell and rapidly scanning the visible region the presence of species exhibiting a broad band at 16 000—17 000 cm^{-1} was demonstrated, strongly suggesting the presence of trigonal-bipyramidal species $[NiL^2X]^+$ which then rapidly decompose. Qualitatively the decomposition is faster in the orders EtOH > BuOH and I > Br > Cl. Despite many attempts, we were unable to identify the decomposition products. Similar decomposition occurs with cobalt(II) and iron(III) salts.

DISCUSSION

The five-co-ordinate $[NiL^1X]^+$ moieties contain the first examples of nickel(II)$\leftarrow$bismuth(III) bond formation. Although the co-ordination of the bismuth atom is clearly aided by the steric constraints of the tripod ligand and by the chelate effect, there are undoubtedly some electronic factors which are favourable to Ni–Bi bond formation. With tripod ligands which contain a carbon atom at the apex, *e.g.* 1,1,1-tris(diethylphosphinomethyl)ethane, $CH_3C(CH_2PEt_2)_3$ (L^3),[18] and 1,1,1-tris(diphenylphosphinomethyl)ethane, $CH_3C(CH_2PPh_2)_3$ (L^4),[18] there is no possibility of apical-atom co-ordination and quadridentate behaviour, and only tridentate co-ordination of the three terminal donors occurs to give, for example, tetrahedral $[Ni(NO)L^3]^+$ or five-co-ordinate $[NiL^4X_2]$. Thus, L^1 could behave as a tridentate As_3 donor, with the bismuth remaining un-co-ordinated, and the fact that co-ordination of the bismuth occurs is clear evidence of the ability of bismuth to form donor bonds to 3*d* metal ions. The existence of $[NiL^2(OH_2)]^{2+}$ provides even stronger evidence of this electronic property of bismuth, since the aliphatic ligand L^2 is considerably less rigid than L^1, and the co-ordination possibilities are potentially more diverse.

The electronic and ^1H n.m.r. spectra of $[NiL^1X]^+$ (X = Cl, Br, or I) suggest a square-pyramidal environment about the nickel which contrasts with the trigonal-bipyramidal structures assigned [10,19,20] to the corresponding complexes of $E(C_6H_4AsMe_2\text{-}o)_3$ (E = As or Sb) or $E(C_6H_4PPh_2\text{-}o)_3$ (E = P, As, or Sb). The complexes exhibit an anomalous spectrochemical series for the apical donor, P > Sb > As. This has been rationalised as follows. The short C_2 (*o*-phenylene) backbone is too short to bridge the apical and equatorial positions of a regular trigonal bipyramid, and the complexes are distorted with the metal ion below the equatorial plane and with a short metal–apical-donor bond. This compression of the apical donor on to the metal results in the donor producing an unexpectedly large ligand-field splitting, which is related to the size of the apical donor. The even larger bismuth atom as the apical donor (in L^1) would be expected to produce an even greater compression effect, and a shift to higher energy of $E_{max.}$ of the *d–d* absorption band. However, the L^1 complexes exhibit electronic spectra consistent with a square-pyramidal structure, and this structural assignment is supported by the n.m.r. data. It is known that square-pyramidal nickel(II) complexes exhibit electronic spectral absorptions at higher energy than do the trigonal-bipyramidal complexes with the same donor set.[12] Thus, in the absence of *X*-ray data, it seems that the anomalous spectrochemical series previously attributed to compression effects [20,21] may be due to increasing distortion of the trigonal bipyramid towards a square pyramid as the apical donor becomes larger. Extrapolation of the results of the calculations of Dawson *et al.*[21] suggests that there is a large mismatch between Ni^{II} and L^1 for trigonal-bipyramid formation, but the paucity of *X*-ray data on bismuth compounds makes detailed calculations impossible.

Finally, the decomposition occurring on mixing nickel(II) halides with L^2 is probably due to Bi–C bond fission. (Aryl)C–Bi bonds are less readily cleaved,[2] and hence L^1 does not undergo similar reactions.

EXPERIMENTAL

Proton n.m.r. spectra were recorded on a Varian Associates HA 100 spectrometer, in $CDCl_3$ or CH_2Cl_2 solution, with $SiMe_4$ as internal reference. Other physical measurements were made as described previously.[11] All the preparations were conducted under a dry nitrogen atmosphere.

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* Throughout this paper: 1 B.M. $\approx 9.27 \times 10^{-24}$ A m^2; 1 mmHg $\approx 13.6 \times 9.8$ Pa.

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Tris(o-*dimethylarsinophenyl*)*bismuthine*, L^1.—(*o*-Bromophenyl)dimethylarsine [22] (21.0 g, 0.08 mol) and n-butyllithium (48 cm^3, 1.80 mol dm^{-3}, 0.085 mol) in light petroleum (200 cm^3) were stirred together under reflux for 2 h, during which time the yellow crystalline *o*-lithio-derivative separated. Bismuth trichloride (8.4 g, 0.026 mol) in dry thf (100 cm^3) was added dropwise to the cool stirred solution, and the mixture was heated gently under reflux for 1 h. Hydrolysis was effected with saturated aqueous ammonium chloride solution (200 cm^3), and the organic layer was separated and dried over anhydrous sodium sulphate. Filtration and removal of the solvent *in vacuo*, followed by warming to 50 °C (0.05 mmHg) to remove unchanged $AsMe_2(C_6H_4Br\text{-}o)$, produced a clear yellow oil, 7.5 g (yield 37%), which was dissolved in dichloromethane to give a solution of known concentration. Aliquot portions of this solution were used in the syntheses of the complexes [^{1}H n.m.r.: τ 2.7 (m) (Ph) and 8.9 (s) (Me); integral 2 : 3].

Tris(3-*dimethylarsinopropyl*)*bismuthine*, L^2.—The Grignard reagent prepared from (3-chloropropyl)dimethylarsine [23] (18.3 g, 0.1 mol) and magnesium (4 g, 0.16 mol) in thf (300 cm^3) was filtered and added dropwise to a stirred solution of $BiCl_3$ (9.5 g, 0.03 mol) in thf (100 cm^3), cooled to −30 °C (solid CO_2–ligroin). When addition was complete, the yellow-green solution was stirred at −30 °C for 2 h, allowed to warm to room temperature, and hydrolysed with aqueous $[NH_4]Cl$ (200 cm^3). The organic layer was separated, dried over anhydrous $Na[SO_4]$, and the solvent was removed *in vacuo* at room temperature. The product was a pale yellow liquid which was purified by warming to 50 °C (0.01 mmHg) for 4 h to remove all the volatile impurities. It was used as a solution of known concentration in CH_2Cl_2, average yield 15% [^{1}H n.m.r.: τ 9.07 (s) (Me) and 8.5 (m) (CH_2); integral 1 : 1].

$[NiL^1X][BPh_4]$ (X = Cl, Br, *or* I).—The appropriate hydrated nickel(II) halide (0.001 mol) was dissolved in dry ethanol (10 cm^3) and L^1 (0.001 mol) in dichloromethane was added. The dark red solution produced was stirred briefly, and then $Na[BPh_4]$ (0.35 g, 0.001 mol) in ethanol (10 cm^3) was added. The product was precipitated by addition of excess of diethyl ether and recrystallised from CH_2Cl_2–EtOH, yield 60%.

Tris[*tris*(o-*dimethylarsinophenyl*)*bismuthine*]*dinickel*(II) *Perchlorate*, $[Ni_2L^1_3][ClO_4]_4$.—Nickel(II) perchlorate hexahydrate (0.26 g, 0.001 mol) in ethanol was treated with L^1 (0.001 mol) in dichloromethane. The dark solution was precipitated by addition of diethyl ether, and the product was extracted into dichloromethane. Evaporation in a stream of nitrogen at room temperature yielded a brown crystalline solid (55%). The complex $[CoL^1Br][BPh_4]$ was prepared in a similar manner to the nickel analogues (40%).

Aqua[*tris*(3-*dimethylarsinopropyl*)*bismuthine*]*nickel*(II) *Perchlorate*, $[NiL^2(OH_2)][ClO_4]_2$.—Nickel(II) perchlorate hexahydrate (0.26 g, 0.001 mol) in n-butanol was treated with L^2 (0.001 mol) in dichloromethane. An intense blue-black colour developed. After stirring for 10 min, excess of diethyl ether was added. The resulting solid was filtered off and extracted into dichloromethane. Concentration of the solution *in vacuo* at room temperature yielded a dark blue powder (65%).

[6/1891 *Received*, 8*th October*, 1976]

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