Co-ordination Complexes containing Multidentate Ligands. Part III.[1] The Visible Spectra of Some Five-co-ordinate Nickel(II) Complexes containing Tris(*o*-dimethylarsinophenyl)stibine. Trigonal Bipyramidal and Square Pyramidal Complexes

By **Livio Baracco, Michael T. Halfpenny,** and **Charles A. McAuliffe,*** Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD

The trisubstituted stibine, tris(*o*-dimethylarsinophenyl)stibine (sbta) reacts with nickel(II) salts to form complexes of type [Ni(sbta)X]Y (X = Cl, Br, I, NCS, and NO_3; Y = Cl, Br, I, CNS, NO_3, and BPh_4) and $[Ni(sbta)_2]Z_2$ (Z = ClO_4 and BPh_4). These diamagnetic complexes are five-co-ordinate, the $[Ni(sbta)X]^+$ species being trigonal bipyramidal while the $[Ni(sbta)_2]^{2+}$ species are square pyramidal. The visible spectra of these complexes are discussed and compared with those of other complexes containing ligands with the $SbAs_3$ and As_4 donor sets.

As part of a study of the stabilisation of metal–antimony bonds by chelation [2-5] we have paid particular attention to tris(*o*-dimethylarsinophenyl)stibine (sbta) because, as well as producing stable metal–stibine bonds, a number of other interesting facets of 'tripod' ligands and their complexes can be examined.

These tripod ligands have been extensively studied and generally they form trigonal bipyramidal complexes,[6] but some interesting structural differences have been observed for differing ligands. From *X*-ray studies it is thus apparent that when the apical and equatorial donor atoms are linked by *o*-phenylene chelate chains the equatorial atoms are above the metal atom,[7-9] but when a three-carbon chelate backbone such as the trimethylene chain is employed the equatorial donors are below the metal atom,[10] This, of course, is a consequence of the inability of the two-carbon and three-carbon chains to provide for an apical–metal–equatorial (L′–M–L) angle of 90°; for the two-carbon case the angle $L'\text{–}M\text{–}L < 90°$, and for the three-carbon case $\angle L'\text{–}M\text{–}L > 90°$.[11,12] This has been reflected in the visible spectral behaviour of the trigonal bipyramidal nickel(II) complexes formed by the $(o\text{-}Ph_2P{\cdot}C_6H_4)L'$ (L′ = P, As, and Sb) ligands, where it was found that as the apical donor atom, L′, was changed in any series of complexes an anomalous spectrochemical series for L′ was obtained, *viz.*, P > As < Sb [2] in contrast to the spectrochemical order $R_3P > R_3As > R_3Sb$ found for complexes of the unidentate ligands R_3L.[13] This effect was attributed to compression of the apical L′–Ni bond upon complexation. In this study we have further examined this phenomenon.

EXPERIMENTAL

Tris(*o*-dimethylarsinophenyl)stibine, sbta, was prepared as described.[5]

Preparation of the Complexes.—[Ni(sbta)X]X (X = Cl, Br, I, NCS, *and* NO_3) *and* $[Ni(sbta)_2](ClO_4)_2$.—When $NiX_2,6H_2O$ (0·0021 mol) in ethanol (15 ml) was added to a stirred solution of the ligand (1·33 g, 0·002 mol) in ethanol (20 ml) under nitrogen a deep blue-purple colour was immediately formed. The mixture was refluxed for 1 h and then allowed to cool in the refrigerator. Intensely coloured crystals were deposited during 3—7 h. These were filtered off and recrystallised from CH_2Cl_2–EtOH. Yields were *ca.* 70%. From [Ni(sbta)X]X the *complexes* [Ni(sbta)X]BPh_4 (X = Cl, Br, I, NCS, and NO_3) were obtained by metathesis (see Table 1).

Physical Measurements.—Magnetic susceptibilities were measured by the Gouy method. Conductivity measurements were carried out with a Cambridge Instruments Ltd. conductivity bridge. I.r. spectra were measured in Nujol or hexachlorobutadiene mulls on a Perkin-Elmer 621 spectrophotometer, and electronic spectra on a Beckman DK2 spectrophotometer (for reflectance spectra $BaSO_4$ was used as a diluent).

RESULTS AND DISCUSSION

We have applied the method of Feltham and Hayter [14] to determine the electrolyte-type of the $Ni(sbta)X_2$ and $Ni(sbta)(X)BPh_4$ complexes in nitromethane; we found that when $\Lambda_o - \Lambda_e$ was plotted against $\sqrt{c}$ slopes of 160—230 $\Omega^{-1}cm^2$ equiv.$^{-1}$ mol$^{-\frac{1}{2}}$ l$^{\frac{1}{2}}$ were obtained, a good indication that the complexes are 1 : 1 electrolytes and may be formulated [Ni(sbta)X]X and [Ni(sbta)X]BPh_4, respectively. Further evidence of co-ordinated and unco-ordinated anions can be obtained from the CNS^- and NO_3^- complexes. In the [Ni(sbta)(NCS)]CNS complex ν(C≡N) absorptions can be distinguished in the i.r. spectrum at 2098 and 2050 cm^{-1}, assignable to co-ordinated Ni–NCS and unco-ordinated CNS^- groups, respectively.[15] Further evidence

---

[1] Part II, W. E. Hill, J. Dalton, and C. A. McAuliffe, *J.C.S. Dalton*, 1973, 143.

[2] B. R. Higginson, C. A. McAuliffe, and L. M. Venanzi, *Inorg. Chim. Acta*, 1971, **5**, 37.

[3] B. R. Cook, C. A. McAuliffe, and D. W. Meek, *Inorg. Chem.*, 1971, **10**, 2676.

[4] C. A. McAuliffe and D. W. Meek, *Inorg. Chim. Acta*, 1971, **5**, 270.

[5] L. Baracco and C. A. McAuliffe, *J.C.S. Dalton*, 1972, 948.

[6] M. J. Norgett, J. H. M. Thornley, and L. M. Venanzi, *Co-ord. Chem. Rev.*, 1967, **2**, 99.

[7] T. L. Blundell, H. M. Powell, and L. M. Venanzi, *Chem. Comm.*, 1967, 763.

[8] L. P. Haugen and R. Eisenberg, *Inorg. Chem.*, 1969, **8**, 1072.

[9] G. A. Mair, H. M. Powell, and L. M. Venanzi, *Proc. Chem. Soc.*, 1961, 170.

[10] D. L. Stephenson and L. F. Dahl, *J. Amer. Chem. Soc.*, 1967, **89**, 3424.

[11] C. A. McAuliffe, D.Phil. Thesis, Oxford, 1967.

[12] J. W. Dawson, B. C. Lane, R. J. Mynst, and L. M. Venanzi, *Inorg. Chim. Acta*, 1971, **5**, 25.

[13] P. L. Goggin, R. J. Knight, L. Sindellari, and L. M. Venanzi, *Inorg. Chim. Acta*, 1971, **5**, 62.

[14] R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 1964, 4587.

[15] J. L. Burmeister, *Co-ord. Chem. Rev.*, 1966, **1**, 205, and references therein.

of Ni–NCS co-ordination is provided by the occurrence of bands attributable to ν(CS) and δ(NCS) at 832 cm^{-1} and 433 cm^{-1} respectively.[16] Similarly a strong i.r. absorption at 1370 cm^{-1} for [Ni(sbta)(NO$_3$)]BPh$_4$ is indicative of co-ordinated nitrate.[17] That the ligand co-ordinates *via* all three –AsMe$_2$ groups in the [Ni(sbta)X]$^+$ complexes is suggested by the appearance of only one resonance at *ca.* τ 8·3 in the ^{1}H n.m.r. spectra of the complexes, although fast exchange between co-ordinated and unco-ordinated –AsMe$_2$ groups cannot be excluded. The free ligand exhibits one resonance attributable to –AsMe$_2$ groups at τ 8·80.

TABLE 1

Some physical properties and analytical data of the nickel(II) complexes [a]

Analyses (%)

			Carbon		Hydrogen		Other		Electronic absorption spectra, $\bar{\nu}$/cm^{-1}	
Compound	Colour	M.p./°C	Calc.	Found	Calc.	Found	Calc.	Found	Solution [c]	Solid
[Ni(sbta)Cl]Cl	Deep blue	241—246	36·4	36·0	3·8	4·3	9·1	9·1 [b]		
[Ni(sbta)Cl]BPh$_4$	Deep blue	204—205	53·4	53·4	4·7	4·8			18,350(2620), 23,950(220), 30,700(2970)	18,050, 23,550
[Ni(sbta)Br]Br	Blue-purple	225—227	32·7	32·9	3·4	3·8				
[Ni(sbta)Br]BPh$_4$	Deep blue	207—209	51·4	51·4	4·5	4·6			18,000(2150), 23,500(65), 29,850(sh)	18,700, 24,400
[Ni(sbta)I]I	Black	207	29·6	28·8	3·1	3·2	25·9	26·1 [b]		
[Ni(sbta)I]BPh$_4$	Purple-black	208	49·1	48·1	4·3	4·2	10·9	10·8 [b]	17,450(3525), 23,250(735), 30,200(3500)	17,200, 23,250,
[Ni(sbta)(NCS)]CNS	Deep blue	204	37·2	37·4	3·6	3·6	3·3	3·3 [d]		
[Ni(sbta)(NCS)]BPh$_4$	Deep blue	203—205	53·6	52·6	4·6	4·8	1·3	1·3 [d]	19,400(3150), 24,250(605)	19,200, 24,050
[Ni(sbta)(NO$_3$)]NO$_3$	Deep blue	203—205	34·1	34·7	3·9	3·8	3·1	3·5 [d]		
[Ni(sbta)(NO$_3$)]BPh$_4$	Deep blue	205	52·3	52·0	4·6	4·6	1·2	1·2 [d]	18,850(1365), 31,000(sh)	18,700
[Ni(sbta)$_2$](ClO$_4$)$_2$	Blue-purple	215	36·2	35·9	3·8	4·2	3·7	3·8 [e]		
[Ni(sbta)$_2$](BPh$_4$)$_2$	Blue-purple	215	56·8	57·1	3·5	3·7	2·9	2·9 [e]		

[a] All the complexes are effectively diamagnetic with a small T.I.P. contribution. [b] Halogen. [c] In dichloroethane; extinction coefficients/l mol^{-1} cm^{-1} in parentheses. [d] Nitrogen. [e] Nickel.

The electronic spectra are in Table 2. The spectra are characterised by two absorptions at *ca.* 18 kK and 23 kK. These are indicative of trigonal bipyramidal geometry[18] and not square pyramidal geometry.[19] The two absorptions can be assigned to the one-electron transitions between the orbitals $e' \longrightarrow a'$ (*ca.* 18 kK) and $e'' \longrightarrow a'$ (*ca.* 23 kK) in a system of C_{3v} symmetry. There is also a band which occurs at *ca.* 30 kK, its frequency and intensity varying with the co-ordinated anion. This may be assigned to metal–arsenic or –antimony charge transfer.

As the co-ordinated anion on the *z*-axis is changed this would be expected to affect the a' level (*d*-orbital of character z^2) the most, and hence both the $e' \longrightarrow a'$ and $e'' \longrightarrow a'$ transitions will vary, though since the e'' level contains *d*-orbitals of character *xz* and *yz* this level, too will be affected and so the $e'' \longrightarrow a'$ transition energy shift is difficult to predict. However, it it can be seen that both transitions change in the order NCS$^-$ > NO$_3^-$ > Cl$^-$ > Br$^-$ > I, *i.e.*, a regular spectrochemical series. It may be noted that the high energy of the NCS$^-$ complex absorption is further evidence of Ni–NCS co-ordination.

Table 2 contains a comparison of the ligand-field bands in a series of trigonal bipyramidal [Ni(ligand)X]$^+$ complexes. The ligands are (o-Me$_2$As·C$_6$H$_4$)$_3$L′ L = As[20] and Sb) and (Me$_2$As·CH$_2$·CH$_2$·CH$_2$)$_3$L′ (L′ = As[21] and Sb[21]). For the complexes of ligand backbone o-C$_6$H$_4$ the Sb complexes absorb at higher energy than the As complexes, while for ligand backbone –CH$_2$·CH$_2$·CH$_2$– when X = Cl, As < Sb, but when X = I, As > Sb, with X = Br being a fairly intermediate case. This can be explained by the L′–M–L angle of less than 90°. The equatorial donors are lifted out of the plane and at the same time the apical donor is compressed on to the metal atom. As the size of the apical donor increases so does this compression, resulting in an increased ligand-field strength. Thus the (o-Me$_2$As·C$_6$H$_4$)$_3$Sb ligand exerts a stronger field than does (o-Me$_2$As·C$_6$H$_4$)$_3$As. On the other hand, the L′–M–L angle in the trimethylene ligand case is greater than 90° and no compression of the apical donor on to the nickel takes place. Thus for complexes [Ni(ligand)X]$^+$ with the (Me$_2$As·CH$_2$·CH$_2$·CH$_2$)$_3$L′, the L′ = As ligand should

TABLE 2

Factors affecting ligand-field strengths of triarsine-stibine ligands in [Ni(ligand)X]$^+$ complexes

X	Chelate backbone	As		Sb
Cl	o-C$_6$H$_4$	17,500		18,350
		23,300		23,950
Br	o-C$_6$H$_4$	17,300		18,000
		23,100		23,500
I	o-C$_6$H$_4$	16,800		17,550
		22,700		23,250
NCS	o-C$_6$H$_4$	18,800		19,400
		23,500		24,250
Cl	–CH$_2$·CH$_2$·CH$_2$–	16,560	>	16,400
Br	–CH$_2$·CH$_2$·CH$_2$–	16,050	~	16,130
I	–CH$_2$CH$_2$CH$_2$–	15,670	<	15,950

---

[16] A. Turco and C. Pecile, *Nature*, 1961, **191**, 66.

[17] N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, 1965, **4**, 804.

[18] G. Dyer, J. G. Hartley, and L. M. Venanzi, *J. Chem. Soc.*, 1965, 1293.

[19] C. A. McAuliffe and D. W. Meek, *Inorg. Chem.*, 1969, **8**, 904.

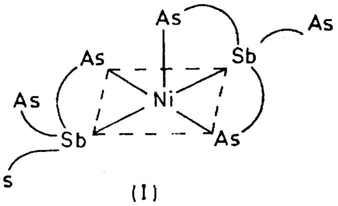
[20] O. St. C. Headley, R. S. Nyholm, C. A. McAuliffe, L. Sindellari, M. L. Tobe, and L. M. Venanzi, *Inorg. Chim. Acta*, 1970, **4**, 93.

[21] G. S. Benner and D. W. Meek, *Inorg. Chem.*, 1967, **6**, 1399.

have visible absorption bands at higher energy than for $L' = Sb$, since the normal ligand-field strength is $R_3As > R_3Sb$.[12] However, from point (2) above we find that the comparative energies of the visible bands are a function of the halogen donor as well as the apical As or Sb donor. Thus, As > Sb for X = Cl, As $\sim$ Sb for X = Br, but As < Sb, for X = I. This nephelauxetic behaviour can be explained in terms of the polarisability of the halide donors compared with that of the apical donors.[5,21]

Thus it can be seen that the effect which chelating ligands have on the structure and spectrochemistry of the resulting complexes can be a function of chelate chain length just as much as it can be a function of the nature of the donor atoms. Also, even when chelate chain length is constant in a set of similar ligands then nephelauxetic behaviour may well become important when the donors are polarisable.

We have briefly reported[22] on the reaction between nickel(II) perchlorate hexahydrate and sbta. After the reactants are mixed in ethanol deep blue crystals of $[Ni(sbta)_2](ClO_4)_2$ are soon deposited. Metal : ligand ratios of 1 : 1, 1 : 2, and 1 : 3 all lead to the formation of the same product. Addition of $NaBPh_4$ to a solution of $[Ni(sbta)_2](ClO_4)_2$ leads to quantitative precipitation of $[Ni(sbta)_2](BPh_4)_2$. The visible spectra in solution exhibit one band at 20·1 kK ($\varepsilon = 2300$) (ClO_4^- complex) and 19·9 kK ($\varepsilon = 2050$) (BPh_4^- complex); both of these bands exhibit a shoulder at lower frequencies. The position of these bands indicates that the $[Ni(sbta)_2]^{2+}$ cation is essentially square pyramidal[19,23] and not trigonal bipyramidal.[18,20] Hence in this five-co-ordinate complex the most likely type of ligand co-ordination must involve a structure *similar* to (I), *i.e.*, a square pyramidal complex containing a terdentate and a bidentate sbta ligand. It is inconceivable that the co-ordination could involve a quadridentate and a unidentate ligand, as it is not possible for sbta to chelate as a quadridentate ligand to a metal in a square pyramidal configuration.



(I)

The formation of $[Ni(sbta)_2](ClO_4)_2$ with a tripod ligand containing heavy donor atoms may be contrasted with the usual stoicheiometry obtained from these ligands and $Ni(H_2O)_6(ClO_4)_2$, *viz.*, $[Ni(L)(ClO_4)]ClO_4$ (L = qp or qas[18]) or $[Ni(L)(H_2O)](ClO_4)_2$ {L = ptas[24] or qa;[21] qa = tris(3-dimethylarsinopropyl)arsine}. The stability of the $[Ni(sbta)_2]^{2+}$ cation, which contains the novel $[Ni(Sb_2As_3)]^{2+}$ donor set, must be considerably greater than either $[Ni(sbta)(ClO_4)]^+$ or $[Ni(sbta)(H_2O)]^{2+}$, as the bis-ligand complex forms no matter what metal : ligand ratio is used in the reaction.

Also, it is interesting that one ligand, sbta, can form two types of five-co-ordinate complex with nickel(II), the trigonal bipyramidal $[Ni(sbta)X]^+$ and the square pyramidal $[Ni(sbta)_2]^{2+}$.

We thank the Leverhulme Trust and the S.R.C. for Postdoctoral Fellowships (to L. B. amd M. T. H. respectively).

[2/1603 *Received, 7th July*, 1972]

---

[22] L. Baracco, M. T. Halfpenny, and C. A. McAuliffe, *Chem. Comm.*, 1971, 1502.

[23] C. Furlani, *Co-ord. Chem. Rev.*, 1968, **3**, 141, and references therein.

[24] G. S. Benner, W. E. Hatfield, and D. W. Meek, *Inorg. Chem.*, 1964, **3**, 1544.