Inorganica Chimica Acta 11 (1974) 33–40
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Bidentate Ligands Containing Very Soft Donor Atoms Nickel(II) Complexes of Arylarsines and Arylstibines

W LEVASON and C A McAULIFFE
Department of Chemistry University of Manchester Institute of Science and Technology Manchester M60 1QD U K

Received May 3 1974

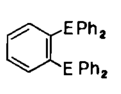
Twenty nine nickel(II) complexes of o phenylenebis(diphenylphosphine) o phenylenebis(diphenylarsine), o diphenylphosphinophenyldiphenylstibine (sbp), o diphenylarsinophenyldiphenylstibine, bisdiphenylarsinomethane (dam) 1 2 bisdiphenylarsinoethane and cis 1,2 bisdiphenylarsinoethylene have been isolated All ligands except dam form square pyramidal $[NiL_2X]^+$ cations, as well as four coordinate $NiLX_2$ The latter are planar complexes except when L = dam, sbp The structures and magnetic behaviour of the anomalous tetracoordinate complexes are discussed The factors influencing the formation of stable complexes of nickel(II) with very soft donors are considered, and it appears that the tendency for group VB donors to form diamagnetic square pyramidal nickel(II) complexes is Sb > As > P

Introduction

Whilst numerous nickel(II) complexes of diphosphine ligands[1] have been characterised corresponding complexes of arsenic and antimony donor ligands are rare To a large extent the paucity of complexes of the heavier donors is a reflection of the increasing softness of the group VB element and the resulting decreased tendency to bond to the moderately hard nickel(II) ion This decreased tendency of arsines and stibines to bond to 3d elements in their normal oxidation states has been overcome by (a) increasing the σ-donor power of the group VB element by alkyl substitution *e g* in *o* phenylenebisdimethylarsine[2] (b) by using multidentate chelates *e g* tris(*o* diphenylarsinophenyl) arsine[3] or (c) by combining these factors as in bis(3-dimethylarsinopropyl)methylarsine[4] Excepting such ligands as tris(3-dimethylarsinopropyl)stibine[5] and tris(*o* dimethylarsinophenyl)stibine[6] where coordination of the antimony atom is due at least in part, to the steric constraints of the ligand the only examples of Ni(II)–stibine coordination reported[7] are in Ni $(stars)_2X_2$ (stars = *o*-dimethylarsinophenyldimethyl stibine X = Cl Br, I NCS ClO_4)

The work reported here was undertaken with two objectives in mind to examine, (a) if it was possible under appropriate conditions to coordinate even softer donors such as largely aryl-substituted arsines and stibines to hard 3d elements in the divalent state and (b) what stereochemical and spectroscopic changes occurred in these complexes as a result of the different donor power of such species compared with the known diphosphine ligands

The complexes reported here include those of ligands of type



E = E = P	ligand	pp
E = E′ = As		aa
E = P E′ = Sb		sbp
E = As E = Sb		sba

The only study of this kind previously reported[8] is that where E = P E′ = As (ap) In addition our attempts to coordinate nickel(II) salts to the ligands $Ph_2As(CH_2)_nAsPh_2$ (n = 1 ligand = dam n = 2, ligand = dae) *cis*-$Ph_2AsCH{=}CHAsPh_2$ (vaa) and $Ph_2Sb(CH_2)_nSbPh_2$ (n = 1 ligand = dsbm n = 3, ligand = dsbp) are reported

Experimental

Physical measurements were made as previously described[9] Except for sbp and sba the preparations of which are described below the ligands were obtained by literature methods pp[10], aa[11], vaa[12], dae[13], dam[14], dsbm[15], dsbp[16]

o Diphenylphosphinophenyldiphenylstibine (sbp)

A solution of *o*-bromophenyldiphenylphosphine (30 g 0 088 mol) in dry diethyl ether (400 ml) was added dropwise to *n* butyllithium (100 ml 0 89*M*) at 0° C with vigorous stirring under nitrogen After 1 hr, a solution of diphenylchlorostibine[17] (27 g 0 088 mol) in dry ether (200 ml) was added dropwise and the mixture stirred for a further 2 hr The solution was then cautiously hydrolysed with deoxygenated aqueous ammonium chloride solution (400 ml), the ether layer separated and dried over anhydrous sodium sulphate. The ether was removed on a rotatory evaporator under nitrogen, the resulting brown oil dissolved in dichloromethane (100 ml) and added to cold methanol (500 ml). The white solid which separated on standing was recrystallised from *n*-butanol, yielding sbp as a white powder. Yield ~43% (22 g). Analyses: Found: C, 66.7; H, 5.0. $C_{30}H_{24}PSb$ requires C, 67.0; H, 4.5%. M.Pt. 160–162° C.

o-Diphenylarsinophenyldiphenylstibine (sba)

This was prepared in a similar manner from *o*-bromophenyldiphenylarsine, *n*-butyllithium and diphenylchlorostibine, as a white powder in 35% yield. Analyses: Found: C, 62.3%; H, 4.4%. $C_{30}H_{24}AsSb$ requires C, 62.0; H, 4.2%. M.Pt. 166° C.

Preparation of the Complexes

Ni(pp)Cl₂

A dichloromethane solution (10 ml) of pp (0.67 g, 1.5 mmol) was added to nickel(II) chloride hexahydrate (0.35 g, 1.5 mmol) in ethanol (10 ml), and the mixture heated under reflux for $^1/_2$ hr. The solution was evaporated to dryness and recrystallised from ethanol/dichloromethane, yielding a yellow powder (76%). $Ni(pp)X_2$ (X = Br, I, NCS) were made analogously.

[Ni(pp)₂](ClO₄)₂

The ligand (0.89 g, 20 mmol) and nickel(II) perchlorate hexahydrate (0.37 g, 1.0 mmol) were heated together at 50°C in a 1:1 ethanol/dichloromethane solution (50 ml) for $^1/_2$ hr. On concentration to ~5 ml yellow crystals separated. These were filtered, rinsed with ether, dissolved in the minimum quantity of boiling dimethylformamide, cooled, and reprecipitated by addition of diethyl ether. Yield ~85%.

[Ni(pp)₂X]ClO₄·CH₂Cl₂ (X = Cl, Br, I, NCS)

A dichloromethane solution (20 ml) of pp (0.89 g, 2.0 mmol) was added to a mixture of NiX_2 (0.5 mmol) and $Ni(ClO_4)_2 \cdot 6H_2O$ (0.5 mmol) in ethanol (25 ml). After refluxing for $^1/_2$ hr the solution was separated and the deep purple product formed was filtered and recrystallised from ethanol/dichloromethane. Yields 70–80%.

[Ni(sbp)₂X]ClO₄·xCH₂Cl₂ (X = Cl, Br, I, NCS)

These were prepared analogously in *n*-butanol/dichloromethane. Yields ~70%.

[Ni(sbp)₂H₂O](ClO₄)₂·CH₂Cl₂

This was obtained by refluxing $Ni(ClO_4)_2 \cdot 6H_2O$ (0.37 g, 1.0 mmol) and sbp (1.1 g, 2.0 mmol) in *n*-butanol/dichloromethane (25 ml), and evaporating to dryness. Purification was achieved by dissolution in dichloromethane and precipitating by dropwise addition of hexane. Yield 55%.

Ni(sbp)X₂ (X = Br, I)

Nickel(II) halide (1.0 mmol) was refluxed with sbp (0.57 g, 1.0 mmol) in *n*-butanol (30 ml) for $^1/_2$ hr. The resulting solid was filtered from the hot solution, washed with boiling *n*-butanol, acetone, and dried *in vacuo*. Yields ~50%.

Ni(aa)X₂ (X = Br, I)

The appropriate $NiX_2 \cdot xH_2O$ (1.0 mmol) was heated with aa (0.53 g, 1.0 mmol) in *n*-butanol/dichloromethane (25 ml), and the products filtered and recrystallised from dichloromethane. Yields ~80%. Ni(vaa)X_2 and Ni(dae)X_2 (X = Br, I) were similarly prepared.

Ni(dam)I₂

A solution of dam (0.47 g, 1.0 mmol) in dichloromethane (50 ml) was refluxed with finely powdered anhydrous nickel(II) iodide (0.31 g, 1.0 mmol) for 2 hr. The dark solution was filtered from a slight amount of unreacted metal salt, concentrated to ~8 ml, and allowed to stand. The solid which separated was dissolved in the minimum quantity of dichloromethane, dry hexane (2 ml) added, and allowed to stand; precipitation occurred after ~15 min. The solid was dried *in vacuo*. The yield was almost quantitative.

[Ni(vaa)₂X]BPh₄ (X = Br, I)

Anhydrous nickel(II) halide (1.0 mmol) in ethanol (5 ml) was added to vaa (0.96 g, 2.0 mmol) in dichloromethane (20 ml), and the solution stirred for $^1/_2$ hr, after which sodium tetraphenylborate (0.34 g, 1.0 mmol) in ethanol was added, and the deep green solution evaporated. Recrystallisation from dichloromethane produced black crystals. Yields ~90%.

[Ni(dae)₂I]I

Anhydrous nickel(II) iodide (0.31 g, 1.0 mmol) in ethanol (5 ml) was added to dae (0.97 g, 2.0 mmol) in dichloromethane (50 ml). After stirring for 2 hr and filtering, the solution was allowed to stand. The blue-black crystals which separated after 24 hr were recrystallised from dichloromethane. Yield 92%. $[Ni(aa)_2I]_2NiI_4$ was obtained similarly from *n*-butanol/dichloromethane solution.

[Ni(sba)₂I]₂NiI₄

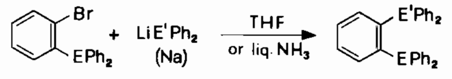
Anhydrous nickel(II) iodide (0.31 g, 1.0 mmol) in *n*-butanol (5 ml) was refluxed with sba (1.2 g, 2.0 mmol) in dichloromethane (30 ml) for 1 hr. The solution was filtered and dry hexane was added dropwise until a dark green solid precipitated. After standing for 1 hr the precipitate was filtered, washed with hexane, and dried *in vacuo*. Yield 55%.

Results

The Ligands

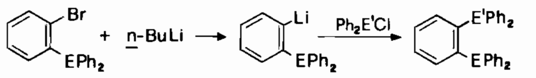
The *o*-phenylene-backbone ligands can be prepared by two routes:

(a)



E = P, As
E' = P, As, Sb

or (b)



Either route is satisfactory for pp, aa, or ap; yields being similar. In the case of sbp or sba the choice of route is critical. The reaction of sodium diphenylstibide in liquid ammonia with *o*-bromophenyldiphenylphosphine resulted in small yields of sbp (~10% of the solid product, plus a considerable quantity of uncrystallisable oil), while the corresponding reaction with *o*-bromophenyldiphenylarsine yielded only very impure sba in <10%. However, route (b) proceeds cleanly to yield both ligands in fairly high yield (40–50% sbp, 30–40% sba).

pp Complexes

o-Phenylenebisdiphenylphosphine (pp) forms planar diamagnetic $[Ni(pp)X_2]$ (X = Cl, Br, I, NCS) complexes (Table I) on reaction with the appropriate nickel(II) salt in ethanol/dichloromethane in a 1:1 ratio. The thiocyanato complex contains N-bonded –NCS groups on the evidence from the IR spectrum, ν(CN) at 2080 cm^{-1} in Nujol mull, and from the high energy of the lowest visible absorption (the spectrochemical series derived from these complexes is NCS > Cl > Br > I, Table II).[18] These complexes are only slightly soluble in, and are not solvolysed by, alcohols

TABLE I. Analytical Data and Some Physical Properties of the Complexes.

Compound	Colour	% C[a]	% H[a]	% X[a, b]	Λ_M[c]	M.Pt. (°C)
$[Ni(pp)Cl_2]$	yellow	61.8(62.5)	4.5(4.2)	12.5(12.3)	3	>350
$[Ni(pp)Br_2]$	orange	53.9(54.1)	3.2(3.6)	24.3(24.1)	5	>350
$[Ni(pp)I_2]$	purple	46.9(47.2)	3.5(3.5)	33.1(33.5)	8	320
$[Ni(pp)(NCS)_2]\cdot CH_2Cl_2$	yellow–brown	56.8(56.9)	3.5(3.7)	3.8(4.0)	4	280
$[Ni(pp)_2](ClO_4)_2$	yellow	61.8(62.1)	4.3(4.1)		173	288
$[Ni(pp)_2Cl]ClO_4\cdot CH_2Cl_2$	red–purple	62.5(62.4)	4.2(4.2)	3.1(3.0)	82	292
$[Ni(pp)_2Br]ClO_4\cdot CH_2Cl_2$	purple	60.4(60.3)	4.2(4.1)	6.8(6.8)	81	290
$[Ni(pp)_2I]ClO_4\cdot CH_2Cl_2$	purple	57.6(57.8)	4.2(3.9)	9.8(10.0)	80	277
$[Ni(pp)_2NCS]ClO_4\cdot CH_2Cl_2$	red–purple	61.7(62.2)	4.5(4.2)		84	237
$[Ni(pp)_2I]_2NiI_4$[d]	purple	52.0(52.6)	3.9(4.1)	27.7(27.9)	142	>350
$[Ni(aa)Br_2]$	purple	47.8(47.6)	3.2(3.1)	21.4(21.2)	<1[e]	>300
$[Ni(aa)I_2]$	dark blue	42.1(42.4)	3.0(2.8)	30.4(30.0)	<1[e]	256
$[Ni(aa)_2I]_2NiI_4$[f]	dark blue	47.4(47.0)	3.4(3.4)	24.7(24.8)	33[e]	261
$Ni(sbp)Br_2$[g]	brown	58.1(58.0)	3.8(3.2)	20.8(21.2)	insol.	232
$Ni(sbp)I_2$[h]	black	42.0(42.3)	3.2(2.8)	29.6(29.9)	insol.	237
$[Ni(sbp)_2H_2O](ClO_4)_2\cdot CH_2Cl_2$	purple	51.3(51.0)	4.2(3.9)		156	218
$[Ni(sbp)_2Cl]ClO_4$	purple	56.5(56.8)	3.9(3.8)	2.8(2.8)	81	222
$[Ni(sbp)_2Br]ClO_4\cdot {}^1/_2CH_2Cl_2$	purple	53.8(53.6)	3.6(3.6)	6.0(5.9)	77	238
$[Ni(sbp)_2I]ClO_4\cdot {}^1/_2CH_2Cl_2$	blue–black	51.8(51.7)	3.6(3.5)	9.0(9.1)	77	228
$[Ni(sbp)_2NCS]ClO_4$	purple	55.8(56.4)	3.9(3.6)		91	200
$[Ni(sba)_2I]_2NiI_4$[i]	green–black	44.5(44.2)	3.0(2.9)	23.5(23.3)	35[e]	~190
$[Ni(dam)I_2]$[j]	grey–black	37.9(38.2)	3.1(2.8)	32.9(32.6)	<1[e]	178
$[Ni(dae)Br_2]$	purple	44.1(44.3)	3.1(3.2)	22.4(22.7)	<1[e]	218
$[Ni(dae)I_2]$	dark blue	38.9(39.1)	2.9(3.0)	31.7(31.7)	<1[e]	203
$[Ni(vaa)Br_2]$	purple	44.5(44.3)	3.4(3.1)	22.5(22.7)	<1[e]	282
$[Ni(vaa)I_2]$	dark blue	39.2(39.2)	2.8(2.8)	32.0(31.7)	<1[e]	185
$[Ni(dae)_2I]I$	blue–black	48.8(48.6)	3.8(3.7)	20.2(19.8)	64	285
$[Ni(vaa)_2Br]BPh_4$	black	63.0(63.5)	4.9(4.7)	5.8(5.6)	19[e]	112
$[Ni(vaa)_2I]BPh_4$	black	62.0(61.9)	4.5(4.6)	8.7(8.5)	19[e]	142

[a] Found (calculated). [b] Halogen or nitrogen. [c] Ohm^{-1} M^{-1} cm^2; measured in ~10^{-3} M solution in nitromethane. [d] μ_{eff} = 3.2 B.M. (anion). [e] Measured in ~10^{-3} M solution in 1,2-dichloroethane. [f] μ_{eff} = 3.3 B.M. (anion). [g] μ_{eff} = 2.59 B.M. [h] μ_{eff} = 2.76 B.M. [i] μ_{eff} = 3.3 B.M. (anion). [j] μ_{eff} = 1.62 B.M., all other compounds are essentially diamagnetic with a small T.I.P. contribution.

or nitromethane; they are non-electrolytes in the latter. The yellow diperchlorate, $[Ni(pp)_2](ClO_4)_2$ is diamagnetic, exhibits IR absorptions indicative of ionic perchlorate groups,[19] and is a 1:2 electrolyte in nitromethane solution. Clearly it contains a NiP_4^{2+} chromophore and is analogous to the previously reported complexes of ap[8], $Ph_2PCH_2CH_2PPh_2$[20], *cis*-$Ph_2PCH{=}CHAsPh_2$[21], and $Ph_2PCH_2CH_2AsPh_2$.[22]

The haloperchlorate complexes, $[Ni(pp)_2X]ClO_4$ (X = Cl, Br, I, NCS), isolated as their dichloromethane solvates, are produced by the reaction of NiX_2, $Ni(ClO_4)\cdot 6H_2O$, and pp in a 1:1:4 ratio. They are intensely coloured, diamagnetic, and 1:1 electrolytes in nitromethane. Their electronic spectra are similar in the solid state and in dichloromethane solution, and are consistent with the presence of pentacoordinate square pyramidal nickel(II) complexes.[23] That the perchlorate groups are ionic is confirmed by the broad, unsplit $\nu_3(ClO_4)$ absorption at $\sim 1080\ cm^{-1}$.[19] Both the mull IR spectrum, which exhibits $\nu(CN)$ at $2070\ cm^{-1}$, and the electronic spectrum (Table II) of $[Ni(pp)_2(NCS)]ClO_4\cdot CH_2Cl_2$ indicate that in this complex, also, the thiocyanate group is N-bonded.

It may also be pointed out that a comparison of these pp complexes with those of the fluoroaryl analogue, *o*-$C_6F_4(PPh_2)_2$,[24] are completely in accord with the conclusions of Meek and co-workers[24,25] that the electronic spectra of the fluoroaryl and the unfluorinated ligand complexes are very similar in energy, but the tendency to stabilise pentacoordination is much smaller for the fluoroligand.

aa Complexes

The reaction of NiX_2 (X = Br, I) with aa in a 1:1 molar ratio in *n*-BuOH or, preferably *n*-BuOH/dichloromethane, produced planar, diamagnetic $[Ni(aa)X_2]$. The reaction with $Ni(NCS)_2$ produced a pale purple solution, and although it was not possible to isolate a solid complex, the electronic spectrum of this solution (Table II) on comparison with those of $Ni(aa)X_2$ (X = Br, I) strongly suggests that $Ni(aa)(NCS)_2$ is present. No reaction appeared to occur between $NiCl_2$ and aa. With nickel(II) perchlorate a deep blue solution formed, the nature of which will be discussed further below. The only pentacoordinate cation isolated with aa was $[Ni(aa)_2I]^+$, in $[Ni(aa)_2I]_2NiI_4$. This complex is decomposed by nitromethane but in 1,2-dichloroethane it has $\Lambda_M = 33\ ohm^{-1}\ cm^2\ M^{-1}$, suggesting that a 2:1 electrolyte is present.[26] The electronic spectrum consists of a very broad intense absorption at 17.3 kK due to the square pyramidal $[Ni(aa)_2I]^+$ ion; a very weak absorption at ~7.4 kK is assignable to the NiI_4^{2-} ion, but the other absorptions of this ion[27] are obscured by the intense cation absorption. Assuming that the cations are diamagnetic, the magnetic moment of the anion, 3.3 B.M., is attributable to tetrahedral tetraiodonickelate(II). Attempts to prepare $[Ni(aa)_2I]ClO_4$ or to convert $[Ni(aa)_2I]_2NiI_4$ to $[Ni(aa)_2I]BPh_4$ were unsuccessful. The isolation of $[NiL_2I]_2NiI_4$ (L = aa, pp, sbp, sba) rather than $[NiL_2I]I$ illustrates the importance of the counter ion in stabilising large ionic species.[28,29]

sbp Complexes

The reaction of sbp with $NiX_2/Ni(ClO_4)_2\cdot 6H_2O$ produced intensely coloured diamagnetic $[Ni(sbp)_2X]ClO_4$ (X = Cl, Br, I, NCS) complexes. The chloro and isothiocyanato complexes were not solvated, but the IR spectra of the bromo and iodo derivatives helped confirm the analytical indications of a $[Ni(sbp)_2X]ClO_4\cdot {}^1\!/_2CH_2Cl_2$ composition. In freshly prepared $10^{-3}M$ nitromethane solution these complexes approximate to 1:1 electrolytes, but the conductivities slowly increase with time, attributable to slow solvolysis. There are some differences in the energies of the d–d bands in the solid state and in solution (Table II), probably attributable to solid state distortions. The IR spectra indicate that the ClO_4^- ion is uncoordinated in both physical states.

The reaction of nickel(II) perchlorate with sbp in *n*-butanol/dichloromethane produced an intensely purple solution from which a red-purple solid was isolated. Analysis of the products from several preparations pointed to a constant composition $[Ni(sbp)_2(H_2O)](ClO_4)_2\cdot CH_2Cl_2$. The IR spectrum in Nujol shows the presence of both water and CH_2Cl_2, neither of which are lost below 150° C, and that the perchlorate groups are uncoordinated.[19] The electronic spectra in the solid state and in solution are similar and, moreover, the latter closely resembles those of nickel(II) perchlorate complexes of triarsines[4,30] which contain As_4O donor sets. In $10^{-3}M$ nitromethane solution the complex is a 1:2 conductor (Table I). All of this is consistent with the presence of a $NiSb_2P_2O^{2+}$ chromophore, *i.e.* square pyramidal $[Ni(sbp)_2(H_2O)](ClO_4)_2\cdot CH_2Cl_2$.

Considerable difficulty was experienced in attempts to prepare $Ni(sbp)X_2$ complexes. In *n*-butanol/dichloromethane a 1:1 mixture of NiX_2 (X = Cl, Br, I, NCS) and sbp produced substances of variable composition which could not be separated into pure components by repeated recrystallisations. The electronic spectra of the solutions suggest that $[Ni(sbp)_2X]^+$ are a major constituent. However, refluxing $NiBr_2$ or NiI_2 and sbp in neat *n*-butanol authentic $Ni(sbp)X_2$ complexes precipitated, but the electronic spectra of the purple filtrates again showed the presence of $[Ni(sbp)_2X]^+$ species. Once isolated the $Ni(sbp)X_2$ complexes were essentially insoluble in all solvents in which they did not decompose. The analogous reactions with $NiCl_2$ or $Ni(NCS)_2$ yielded only sticky oils and were not further studied. The properties of the $Ni(sbp)X_2$ (X = Br, I) species are anomalous. Both complexes are paramagnetic with μ_{eff} = 2.59 B.M.(Br) and

TABLE. II. Electronic and Infrared Spectral Data.

Compound	$E_{max}(\varepsilon_{max})$ kK[a]	E_{max}[b]	IR cm^{-1}	
$[Ni(pp)Cl_2]$	21.4(1,220), 30.2(sh)(2,200)	22.2	362, 324	Ni–Cl
$[Ni(pp)Br_2]$	20.8(1,420), 25.8(sh)(585)	21.8	290, 250	Ni–Br
$[Ni(pp)I_2]$	19.0(1,260), 29.9(sh)	20.0(br)		
$[Ni(pp)(NCS)_2]$	22.6(2,440)	23.2	[c]2080, 843 [a]2075, 2085(sh)	NCS^- ν(CN)
$[Ni(pp)_2](ClO_4)_2$	22.7(2,680), 28.1(26,400)	23.5, 27.0	1080, 622	ClO_4^-
$[Ni(pp)_2Cl]ClO_4 \cdot CH_2Cl_2$	20.0(2,480), 27.8(25,600)	19.9, 27.8	1080, 620	ClO_4^-
$[Ni(pp)_2Br]ClO_4 \cdot CH_2Cl_2$	19.7(3,450), 28.0(27,050), 29.0(28,700)	19.8, 27.6(sh)	1080, 620	ClO_4^-
$[Ni(pp)_2I]ClO_4 \cdot CH_2Cl_2$	18.6(2,310), 29.0(42,850)	16.0(sh), 19.1, 27.0	1080, 620	ClO_4^-
$[Ni(pp)_2NCS]ClO_4 \cdot CH_2Cl_2$	19.8(1,830), ~28.5(18,700)	19.8, 27.8(sh)	[c]2062(CN), 1090, 623 [a]2062(CN)	ClO_4^-
$[Ni(aa)Br_2]$	18.7(1,440), 24.8(1,335), 34.0(17,700)	18.8, 26.4	290	Ni–Br
$[Ni(aa)I_2]$	17.5(1,770), 32.3(20,050)	17.3, 29.8(sh)		
$[Ni(aa)_2I]_2NiI_4$	7.4, 17.3(4,850), 31.8(18,500)	13.0, 17.4, 28.0(sh)		
$Ni(sbp)Br_2$	insol.	14.7, 17.6, 20.6, 27.0	260, 215	Ni–Br
$Ni(sbp)I_2$	insol.	12.7, 17.8, 24.7, 27.3		
$[Ni(sbp)_2(H_2O)](ClO_4)_2 \cdot CH_2Cl_2$	18.4(2,560), 26.8(27,790)	19.0, 27.2	1090, 620 3350, 1630	ClO_4^- H_2O
$[Ni(sbp)_2Cl]ClO_4$	18.3(2,760), 26.8(18,700)	19.0, 27.0	1090, 625	ClO_4^-
$[Ni(sbp)_2Br]ClO_4 \cdot {}^1/_2CH_2Cl_2$	18.1(2,360), 27.5(20,760)	18.6	1085, 620	ClO_4^-
$[Ni(sbp)_2I]ClO_4 \cdot {}^1/_2CH_2Cl_2$	17.4(2,600), 27.8(18,700)	18.2, 26.3	1090, 620	ClO_4^-
$[Ni(sbp)_2NCS]ClO_4$	18.3(2,590), 27.4(15,500)	18.5, 28.1	[c]2070(CN), 1080, 620 [a]2060(CN)	ClO_4^-
$[Ni(sba)_2I]_2NiI_4$	7.7(50), 17.0(3,400), 28.2(10,050)	17.1, 26.8		
$[Ni(dam)I_2]$	12.4(1,025), 16.5(1,020), 21.0(1,580), ~29.0(sh)	11.5, 17.2, 19.6, 23.8(sh), 26.7		
$[Ni(dae)Br_2]$	19.1(730), 25.1(995), 33.5(12,040)	18.5, 25.2	270	Ni–Br
$[Ni(dae)I_2]$	17.6(2,110), 26.6(4,820), 33.2(23,060)	17.8, 26.2		
$[Ni(vaa)Br_2]$	18.7(1,510), 24.6(760), 34.0(17,800)	18.5, 25.7	278, 245	Ni–Br
$[Ni(vaa)I_2]$	17.3(1,780), 26.8(2,530), 33.1(23,100)	17.4, 26.3		
$[Ni(dae)_2I]I$	17.2(2,890), 26.4(6,520)	17.0, 26.0		
$[Ni(vaa)_2Br]BPh_4$	18.0(1,150), ~28.6(sh)	17.4, 26.7		
$[Ni(vaa)_2I]BPh_4$	16.9(790), 26.8(2,180)	17.2, 26.3		
$NiBr_2$–dam	18.8, ~25.3(sh)[d]			
$Ni(NCS)_2$–dac	20.2[d]			
$Ni(ClO_4)_2 \cdot 6H_2O$–dae	18.8[d]			
$NiCl_2$–vaa	19.3, ~25.6(sh)[d]			
$Ni(NCS)_2$–vaa	19.5, ~24.0(sh)[d]			
$Ni(ClO_4)_2 \cdot 6H_2O$–vaa	18.4[a]			
$Ni(NCS)_2$–aa	20.6[d]			
$Ni(ClO_4)_2 \cdot 6H_2O$–aa	18.3[d]			
$Ni(ClO_4)_2 \cdot 6H_2O$–sba	18.1[d]			
$NiBr_2$–sba	17.7[d]			
NiI_2–dsbm	12.3, 18.3[d]			
NiI_2–dsbp	12.6, 18.2, 20.2[d]			
NiI_2–$AsPh_3$	14.7, 18.5, 22.1, 24.3[d]			

[a] Dichloromethane solution. [b] Solid reflectance. [c] Nujol mull. [d] Obtained only in dichloromethane/*n*-butanol solutions.

2.76 B.M. (I), and their reflectance spectra exhibit bands at 14.7, 17.6(sh), 20.4, 27.0 kK (Br) and 12.7, 17.8, 24.7, 27.3 kK (I), both sets clearly inconsistent with planar nickel(II) complexes. The magnetic moments fall into the range observed for "anomalous" nickel(II) complexes,[31] being rather too low for either octahedral (2.8–3.3 B.M.) or tetrahedral (3.3–4.0 B.M.) species. Octahedral coordination, achieved *via* bridging halogens has been proposed[32] for Ni(*cis*-edas) Cl_2 (*cis*-edas = *cis*-$Me_2AsCH{=}CHAsMe_2$) with $\mu_{eff} = 2.8$ B.M. Two other possibilities involve tetrahedral nickel(II). An ionic formulation $[Ni(sbp)_2][NiX_4]$ (X = Br, I) is not ruled out by the magnetic data which, calculated on this formula, are 3,4 B.M. (Br) and 3.8 B.M. (I), assuming the planar $[Ni(sbp)_2]^{2+}$ cations are diamagnetic. However, the $[Ni(sbp)_2][NiX_4]$ formulation does not seem to be in accord with the reflectance spectra. A $[Ni(sbp)_2]^{2+}$ species might be expected to absorb at 22–18 kK, the E_{max} being relatively insensitive to changes in the $[NiX_4]^{2-}$ counter ion; and the $[NiX_4]^{2-}$ ions[27] absorb at low energy and low intensity. In fact the major bands in the $Ni(sbp)X_2$ species are at 17.8, 12.7 kK (I) and 20.4, 14.7 kK (Br); and the higher energy absorptions are also clearly sensitive to the nature of the halide present.

The second possible explanation is that the $Ni(sbp)X_2$ complexes are mixtures of planar (diamagnetic) and tetrahedral (paramagnetic) isomers. Such isomerism is well established for nickel(II) complexes of diphenylarylphosphines,[33] and occurs in solutions of $Ni(dpp)X_2$ (dpp = $Ph_2PCH_2CH_2CH_2PPh_2$).[34] The magnetic moments would agree with this formulation, the higher observed moment of the iodo complex being due to a greater proportion of the tetrahedral species present in the mixture (the tendency to produce tetrahedral complexes is Cl < Br < I[33]), whilst the electronic spectra are compatible with the superimposition of planar and tetrahedral $Ni(sbp)X_2$ spectra. Unfortunately, the low solubility of these complexes has prevented attempts to separate the isomeric forms.

sba Complexes

The only complex produced from NiI_2 and sba in molar ratios ranging from 2:1 to 1:4, and in a variety of solvents, was $[Ni(sba)_2I]_2NiI_4$, a dark green powder, very sensitive to hydroxylic solvents. This complex seems to be generally similar to $[Ni(aa)_2I]_2NiI_4$. No other complexes of this ligand with nickel(II) could be isolated, although complex formation with $NiBr_2$ and $Ni(ClO_4)_2 \cdot 6H_2O$ did occur in dichloromethane solution (Table II).

Other Ligands

Following the success of the attempts to coordinate triarylstibine (in sbp and sba) to nickel(II), and in view of the almost total lack of aryldiarsine complexes of 3d elements, the reaction of nickel(II) salts with 1,2-bisdiphenylarsinoethane (dae), *cis*-1,2-bisdiphenylarsinoethylene (vaa), and bisdiphenylarsinomethane (dam) was examined. The results for dae and vaa parallel those of aa. Thus, only planar $NiLX_2$ (L = dae, vaa; X = Br, I) and pentacoordinate square pyramidal $[Ni(dae)_2I]I$ and $[Ni(vaa)_2X]BPh_4$ (X = Br, I) could be isolated as solids, although some electronic spectral evidence for the formation in solution of thiocyanato, and in one case of a chloro analogue, was obtained (Table II). The nickel(II) perchlorate complexes, although not isolated, appear to belong to the same type as those of sbp and aa, on the basis of their solution electronic spectra.

With dam a $[Ni(dam)I_2]$ complex was isolated, which is a non-electrolyte in 1,2-dichloroethane and monomeric in chloroform (found 793, calc. m.wt for $[Ni(dam)I_2] = 785$), indicating that dam chelates to nickel(II). The diphosphine analogue $Ph_2PCH_2PPh_2$ was believed to function only as a monodentate ligand towards Ni(II), but recently stable diamagnetic planar $NiLX_2$ compounds, containing chelated ligands, have been prepared.[35] $[Ni(dam)I_2]$ is paramagnetic, however, ($\mu_{eff} = 1.62$ B.M.) and its electronic spectrum differs considerably from those of planar Ni(II) complexes. In the absence of X-ray data the structure of this complex cannot be established with certainty. However, a plausible explanation is that the nickel(II) is four coordinate, but that the ligand enforces a configuration markedly distorted from planarity. This distortion is probably due to strain inherent in a four-membered chelating ligand. X-ray studies[36] on $Mo(dam)_2(CO)_2Br_2$, which contains one chelating dam ligand shows evidence for considerable distortion in the four-membered ring, and a resultant distortion in the coordination sphere, whilst no distortion was found in $Mo(CO)_4(Ph_2PCH_2PPh_2)$.[37]

On refluxing nickel(II) iodide with triphenylarsine in dichloromethane under strictly anhydrous conditions a deep blue solution is formed, the electronic spectrum of which suggests the presence of a tetrahedral species (Table II). Similar interaction occurred between NiI_2 and $Ph_2SbCH_2SbPh_2$ and $Ph_2Sb(CH_2)_3SbPh_2$. All three solutions are instantly decomposed by traces of water or alcohols, and decomposition also takes place on standing in a few hours.

Discussion

The first aim of this study, to coordinate the soft arylarsine and arylstibine donors to Ni(II) has been achieved (Table I), and a brief discussion of some of the factors involved seems pertinent. In any attempt to coordinate a soft donor to a hard acceptor the choice of solvent is likely to be particularly crucial, since many common solvents (*e.g.*, the lower aliphatic alcohols, nitromethane, dimethylformamide), although not usually considered as ligands, do contain hard donor atoms (O or N) which successfully compete with the soft donor ligand for the metal ion. It is useful to recall that triphenylphosphine[38] does not complex with Ni(II) salts in ethanol. The most successful solvents for our purpose were found to be *n*-butanol/dichloromethane mixtures, or even neat dichloromethane.

The nickel(II) salt used has a considerable effect on the stability of the resulting complex, and although it must be emphasised that no measurements of thermodynamic stability were made on these complexes, it is clear from a comparison of the complexes isolated, or for which we have obtained spectral evidence of complex formation in solution, that the tendency for Ni(II) salts to complex with the ligands used in this study follows the order $I^- > Br^- > NCS^- > Cl^-$. This order is readily explicable in terms of the SHAB principle and Jørgensen's concept of symbiosis.[39] The softer the halide the greater amount of electron density it transfers to the nickel(II), "softening" the latter and increasing its ability to coordinate other soft donors.

The second objective was to examine what effect the coordination of arylarsines and arylstibines has on the structure and spectra of the resulting complexes, in view of the marked decrease in σ-donor power in the order P > As > Sb. The only complexes of bidentate ligands with predominantly arylarsine donors reported are Ni(dae)X_2 (X = Br, I) prepared by Sacconi *et al.*[40]

Five Coordinate Complexes

All the ligands with the *o*-phenylene linkage form one or more pentacoordinate cations $[NiL_2X]^+$ (Table I); and we also isolated $[Ni(dae)_2I]^+$ and $[Ni(vaa)_2X]^+$ (X = Br, I). A comparison of the electronic spectra of these species with those of square pyramidal and trigonal bipyramidal nickel(II) complexes[33] show that all may be assigned the former structure. The factors which determine whether a pentacoordinate complex will have a trigonal bipyramidal or a square pyramidal structure are much disputed,[41] but in the cases of the complexes studied here it is probable that the short C_2 ligand backbones are a major factor in producing square pyramidal complexes.

The trend previously observed in palladium(II) and platinum(II) complexes of group VB donors, that the ability to stabilise pentacoordination increases in the order P < As < Sb,[11] is also observed for nickel(II) complexes in the present study. This is particularly apparent in the ligand reactions with $Ni(ClO_4)_2 \cdot 6H_2O$; pp and ap[8] form four coordinate planar $[NiL_2](ClO_4)_2$ species, whilst sbp forms the five coordinate $[Ni(sbp)_2(H_2O)](ClO_4)_2$ complex. Although they could not be isolated as solids the diarsine ligands also produced pentacoordinate $[NiL_2(H_2O)]^{2+}$ ions in solution, as evidenced by their electronic spectra (Table II). The difficulty experienced in preparing Ni(sbp)I_2, and our inability to obtain Ni(sba)I_2, may also be due to this effect, although caution must be exercised in deducing trends from complexes of borderline stability such as these.

Four Coordinate Complexes

The ligands pp, ap,[8] aa, dae, and vaa produce planar $NiLX_2$ complexes. The anomalous behaviour of Ni (sbp)X_2 (X = Br, I) may be due to the relatively weak donor power of the ligand; certainly, the decreased ligand field strength along the series P(alkyl)$_3$ > P(alkyl)$_2$Ph > P(alkyl)Ph$_2$ > PPh$_3$ is believed to be an important factor in the move from planar to tetrahedral structures of the NiL_2X_2 complexes of this series of ligands.[33] However, judged from the spectra of the isostructural $[NiL_2X]^+$ complexes the ligand field strength of sbp is about the same as that of aa, dae, or vaa, all of which form normal planar complexes. The energy balance between normal and "anomalous" four coordinate structures must be very fine.

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