Inorganica Chimica Acta, 41 (1980) 133–141
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Nickel(II) Complexes of Hybrid Nitrogen–Phosphorus, Nitrogen–Arsenic, and Nitrogen–Antimony Ligands. A Comparison

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Receved December 27, 1979

The reactions of the isostructural bidentates o-$C_6H_4(NMe_2)(PMe_2)$,*(*NP^{Me}*),* o-$C_6H_4(NMe_2)(AsMe_2)$*, (*NAs^{Me}*) and* o-$C_6H_4(NMe_2)(SbMe_2)$*, (*NSb^{Me}*), with nickel(II) salts are described and compared with those of the corresponding diamine and* o-$C_6H_4(PMe_2)(AsMe_2)$*, (*PAs^{Me}*). The amine–phosphine forms planar* $Ni(NP^{Me})X_2$ *(X = Cl, Br), octahedral* $[Ni(NP^{Me})(NCS)_2]_n$*, planar* $[Ni(NP^{Me})_2](BF_4)_2$ *and low spin square pyramidal* $[Ni(NP^{Me})_2X]ClO_4$*. The amine–arsine forms tetragonal* $Ni(NAs^{Me})_2X_2$ *(*$N_2As_2X_2$*) which become tetrahedral (*N_2X_2*) in non-polar solvents, planar* $[Ni(NAs^{Me})_2]I_2$ *(*N_2As_2*) and octahedral* $Ni(NAs^{Me})_2(NCS)_2$ *and* $[Ni(NAs^{Me})(NCS)_2]_n$*. The* $[Ni(NAs^{Me})_2X]ClO_4$ *(X = Cl, Br, I) are diamagnetic and planar (*N_2AsX*) in the solid state and decomposed by polar solvents. The amine–stibine did not complex with nickel(II). The diamine* o-$C_6H_4(NMe_2)_2$*(*NN^{Me}*) in contrast forms tetrahedral* $Ni(NN^{Me})X_2$ *(X = Cl, Br) which absorb water to become octahedral* $Ni(NN^{Me})(H_2O)_2X_2$*, and* $[Ni(NN^{Me})(NCS)_2]_n$*. The (*PAs^{Me}*) forms planar* $Ni(PAs^{Me})Cl_2$*, square pyramidal* $[Ni(PAs^{Me})_2X]^+$ *(X = Cl, Br, I, NCS,* NO_3*) and planar* $[Ni(PAs^{Me})_2](ClO_4)_2$*. The various behaviour of these ligands is compared and discussed in terms of the differing effects of hard-*NMe_2 *and soft-*PMe_2*, -*$AsMe_2$*, -*$SbMe_2$ *donors upon the spin state and stereochemistry of the nickel(II).*

Introduction

The nickel(II) complexes of hybrid ligands usually reflect the different structural preferences of the hard and soft donor atoms. Nitrogen favours octahedral and tetrahedral structures whilst the heavier group VB donors promote the formation of planar and five coordinate metal complexes. Similarly hard donors produce the high spin-state whilst softer donors form low-spin complexes. The chemistry of hybrid ligands is complicated due to the subtle balance between these different preferences, and their behaviour is often difficult to predict. The most detailed studies are by Sacconi's group on tri- and tetra-dentate ligands and their influence on the spin-state and stereochemistry of five-coordinate nickel(II), [1, 2]. A variety of bidentate hybrids have been complexed with nickel(II) [3–9], but detailed comparison of the influence of different donors is complicated by the range of ligand structures and the often less than complete data on the complexes. As part of a study [10] on the ability of various donor sets to promote the formation of Ni(III), we have synthesised as nickel(II) starting materials, complexes of the isostructural ligands (Table I). These provided the basis for a detailed comparison of the effects due to different group VB donors without the complicating factor of different ligand geometries, and the results of this study are communicated below.

Results

It is convenient to discuss the complexes of each ligand separately. Comparisons will be reserved for the final section.

TABLE I.

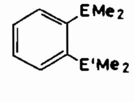	E = E′ = N	o-phenylenebis(dimethylamine), NN^{Me}
	E = N, E′ = P	o-dimethylaminophenyldimethylphosphine, NP^{Me}
	E = N, E′ = As	o-dimethylaminophenyldimethylarsine, NAs^{Me}
	E = N, E′ = Sb	o-dimethylaminophenyldimethylstibine, NSb^{Me}
	E = E′ = P	o-phenylenebis(dimethylphosphine), PP^{Me}
	E = P, E′ = As	o-dimethylphosphinophenyldimethylarsine, PAs^{Me}

TABLE II. Analytical and Physical Data.

Compound	Colour	C%[a]	H%	N%	ΛM ohm^{-1}[b] cm^2 M^{-1}	μ_{eff} BM[c]
$Ni(NN^{Me})(H_2O)_2Cl_2$	green	35.85(36.41)	6.14(6.11)	8.21(8.49)	<1[d]	3.09
$Ni(NN^{Me})(H_2O)_2Br_2$	green	28.88(28.68)	5.04(4.81)	6.64(6.68)	<1[d]	3.18
$Ni(NN^{Me})(NO_3)_2$	turquoise	34.83(34.63)	4.79(4.65)	15.93(16.14)	<1[d]	3.38
$Ni(NN^{Me})(NCS)_2$	blue-green	42.26(42.50)	4.86(4.76)	16.50(16.51)	–	3.31
$Ni(NP^{Me})Cl_2$	red-purple	38.90(38.58)	4.72(5.15)	4.90(4.50)	<1[d]	D
$Ni(NP^{Me})Br_2$	red-purple	30.05(30.06)	4.32(4.03)	3.34(3.50)	<1[d]	D
$Ni(NP^{Me})(NCS)_2$	green	39.91(40.48)	4.39(4.33)	11.83(11.80)	–	3.22
$[Ni(NP^{Me})_2](BF_4)_2$	yellow	40.30(40.47)	5.54(5.94)	4.92(4.72)	161[e]	D
$[Ni(NP^{Me})_2Cl]ClO_4$	yellow	43.12(43.13)	5.50(5.75)	5.32(5.03)	97[e]	D
$[Ni(NP^{Me})_2Br]ClO_4$	orange-yellow	40.10(39.93)	5.00(5.33)	4.30(4.65)	94[e]	D
$[Ni(NP^{Me})_2I]ClO_4$	brown	37.51(37.03)	4.80(4.94)	4.56(4.32)	102[e]	D
$Ni(NAs^{Me})_2Cl_2$	green	40.70(41.49)	5.53(5.56)	4.71(4.83)	<1[d]	3.25
$Ni(NAs^{Me})_2Br_2$	green	35.67(35.92)	4.86(4.82)	4.27(4.19)	<1[d]	3.31
$Ni(NAs^{Me})_2I_2$	brown	31.56(31.49)	4.24(4.23)	3.63(3.67)	<1[d]	D
$Ni(NAs^{Me})_2(NCS)_2$	blue	42.37(42.27)	5.16(5.16)	8.98(8.98)	–	3.30
$Ni(NAs^{Me})(NCS)_2$	green	35.30(36.00)	3.71(4.00)	10.62(10.50)	–	3.35
$[Ni(NAs^{Me})_2Cl]ClO_4$	red	37.54(37.30)	5.23(5.01)	4.19(4.35)	–	D
$[Ni(NAs^{Me})_2Br]ClO_4$	red	34.64(34.90)	4.90(4.68)	3.91(4.07)	–	D
$[Ni(NAs^{Me})_2I]ClO_4$	purple	32.73(32.67)	4.50(4.39)	3.78(3.81)	~4.5[d]	D
$[Ni(PP^{Me})_2](ClO_4)_2$	yellow	36.13(36.73)	4.45(4.93)	–	168[e]	D
$[Ni(PP^{Me})_2Cl]ClO_4$	red-orange	41.10(40.64)	5.30(5.42)	–	84[e]	D
$[Ni(PP^{Me})_2Cl_2$	orange	45.00(45.32)	6.35(6.30)	–		D
$Ni(PAs^{Me})Cl_2$	orange	31.93(32.31)	4.34(4.34)	–	14[e]	D
$Ni(PAs^{Me})_2I_2$	brown	30.15(30.11)	3.96(4.02)	–	84.5[e]	D
$Ni(PAs^{Me})_2(NCS)_2 \cdot CH_2Cl_2$	red-brown	37.49(37.13)	4.66(4.61)	3.95(3.76)	91[e]	D
$Ni(PAs^{Me})_2(NO_3)_2 \cdot CH_2Cl_2$	orange	33.83(33.55)	4.64(4.56)	3.82(3.72)	112[e]	D
$[Ni(PAs^{Me})_2](ClO_4)_2$	yellow	31.37(32.38)	4.35(4.35)	–	165[e]	D
$[Ni(PAs^{Me})_2Cl]ClO_4 \cdot CH_2Cl_2$	maroon	33.25(33.07)	4.53(4.49)	–	85[e]	D
$[Ni(PAs^{Me})_2Br]ClO_4 \cdot CH_2Cl_2$	red-brown	31.11(31.24)	4.21(4.24)	–	74[e]	D
$[Ni(PAs^{Me})_2I]ClO_4 \cdot CH_2Cl_2$	dark brown	29.47(29.53)	3.96(4.01)	–	85[e]	D

[a] Found (calc.). [b] *ca.* 10^{-3} *M* solutions in: [c] ±0.05 BM; D = diamagnetic – none had $\mu_{eff} > 0.7$ BM. [d] 1,2-dichloroethane, [e] nitromethane. 1:1 Electrolytes in 1,2-dichloroethane have ΛM *ca.* 10–24 ohm^{-1} cm^2 M^{-1}, and in nitromethane 1:1 electrolytes have ΛM *ca.* 70–100, and 2:1 *ca.* 150–180 ohm^{-1} cm^2 M^{-1} [W. J. Geary, *Coord. Chem. Rev., 7,* 81 (1971)].

o-*Phenylenebis(dimethylamine) (NN^{Me})*

The reaction of nickel(II) chloride or bromide with the diamine in n-butanol produced pink solutions which deposited red crystals on concentration. On exposure to air these red crystals rapidly turn fawn and then pale green. The green crystals were identified by analysis (Table II) as $[Ni(NN^{Me})(H_2O)_2X_2]$ (X = Cl, Br) and show intense IR absorptions at ~3300 and ~1630 cm^{-1} characteristic of the water present. The far IR spectra were complex and ν(Ni–X) were not identified. The magnetic moments and solid state electronic spectra (Tables II, III) are consistent with pseudo-octahedral nickel(II). The green crystals dissolve in dichloromethane and alcohols to reform pink solutions which are non-conductors and have electronic spectra similar to that reported by Sacconi [11] for $[Ni(Me_4en)Br_2]$ {Me_4en = N,N,N′,N′ ≡ tetramethylethylenediamine}, which is pseudotetrahedral. The red crystals isolated from such solutions also have solid state electronic spectra consistent with a tetrahedral structure. Nickel(II) thiocyanate and NN^{Me} formed a blue-green complex which was insoluble in all solvents tried. The solid state electronic spectrum shows that the nickel(II) is six-coordinate, and the high frequency of the ν(CN) vibrations are consistent with bridging thiocyanate groups [12]. A $[Ni(NN^{Me})(NO_3)_2]$ was also obtained which is pseudo-octahedral, in this case with an N_2O_4 donor set provided by the diamine and two bidentate nitrate groups [11].

Attempts to prepare complexes of NN^{Me} with a Ni:ligand ratio of 1:2 or 1:3 were unsuccessful.

o-Dimethylaminophenyldimethylphosphine (NP^{Me})

The reaction of NP^{Me} with NiX_2 (X = Cl, Br, NCS) in either a 1:1 or 2:1 molar ratio produced only $Ni(NP^{Me})X_2$ complexes. The halides are diamagnetic, non-electrolytes in 1,2-dichloroethane solution, and have similar 'd–d' electronic spectra in the solid state and in solution in dichloromethane, (Table III), consisting of a single band at 18–20 × 10^3 cm^{-1}. On this evidence they are assigned planar structures [13], which is also supported by the identification of two ν(Ni–X) vibrations in the far IR spectra. The $Ni(NP^{Me})(NCS)_2$ is a green paramagnetic solid which on the basis of its IR and electronic spectra is clearly analogous to $Ni(NN^{Me})(NCS)_2$, a pseudo-octahedral polymer with thiocyanate bridges. Unlike the latter it dissolves in dichloromethane to form a yellow solution with an electronic spectrum consistent with a planar species. A pure iodocomplex was not isolated. Reaction of nickel(II) iodide and NP^{Me} in n-butanol produced a dark red solution, with an electronic spectrum consistent with $Ni(NP^{Me})I_2$, and a dark red solid was produced on evaporation. This became sticky on exposure to air and had very poor and unreproducible C/H analyses. The solution in alcohol decomposed slowly in a stoppered vessel, and immediately became almost colourless when oxygen was admitted. It seems probable that the ligand oxidation is catalysed by NiI_2, but we have not studied this reaction further.

Planar $[Ni(NP^{Me})_2]^{2+}$ cations are readily formed in the presence of weakly coordinating anions ClO_4^-, BF_4^- or BPh_4^-. Although an excess of NP^{Me} produced only 1:1 complexes with nickel(II) halides, the use of '$NiXClO_4$' [14, 15] readily yielded $[Ni(NP^{Me})_2X]ClO_4$ complexes. These were diamagnetic, 1:1 electrolytes in nitromethane solution, and a comparison of the solid and solution electronic spectra indicates the same metal environment is present in both states. The strong bands in the region 2750–2800 cm^{-1} in the IR spectrum of NP^{Me} are absent in the spectra of the complexes, showing that uncoordinated $-NMe_2$ groups are absent [3, 16]. IR criteria for the coordination of the $-PMe_2$ groups are not well developed, but in the present case the ν(P–C) and $-PMe_2$ rocking modes were very similar in $[Ni(NP^{Me})_2X]ClO_4$, to those in $Ni(NP^{Me})X_2$ and $[Ni(NP^{Me})_2](BF_4)_2$, strongly suggesting the $-PMe_2$ groups are also coordinated in the halide perchlorates. This evidence shows that a N_2P_2X donor set is present, and the electronic spectrum confirms that the geometry is the expected square pyramid [17]. The use of ^1H nmr to establish coordination of the donors was prevented by poor solubility in suitable solvents and by the presence of residual paramagnetism (presumably TIP).

o-Dimethylaminophenyldimethylarsine (NAs^{Me})

With one exception (*vide infra*) all the complexes of NAs^{Me} have a 1:2 Ni:NAs^{Me} ratio; repeated attempts to prepare 1:1 or 1:3 complexes directly were unsuccessful. The green $Ni(NAs^{Me})_2X_2$ (X = Cl, Br) are paramagnetic solids with electronic spectra characteristic of a tetragonal octahedral structure [13], and the single ν(Ni–X) vibration in the far IR suggests *trans* X groups. They dissolve in dichloromethane to give pink non-conducting solutions with electronic spectra similar to those of the pseudotetrahedral $Ni(diamine)X_2$ [11] and hence we conclude that the Me_2As- groups are uncoordinated in solution (N_2X_2 donor set). The solutions do not seem to be air sensitive, presumably the inductive effects of the coordination of the $-NMe_2$ group results in the Me_2As- group becoming air stable (*cf.* quaternisation of one donor in *o*-phenylene-backbonded bidentates). Only the green octahedral form was recovered on evaporation. The complexes dissolve in donor solvents (MeCN, DMSO, $MeNO_2$ *etc*) with partial displacement of NAs^{Me}. The brown $Ni(NAs^{Me})_2I_2$ was diamagnetic in the solid state. The IR spectrum showed that the bands in the region 2750–2800 cm^{-1} in the free ligand had disappeared upon coordination, hence the $-NMe_2$ groups are coordinated [3, 16]. The $-AsMe_2$ rocking modes in NAs^{Me} at 842, 883 cm^{-1} shift to higher frequency in $Ni(NAs^{Me})_2I_2$ by *ca.* 15 cm^{-1}, which by analogy with *o*-phenylenebis(dimethylarsine) [18] may be taken as evidence that the $-AsMe_2$ groups are also coordinated. The electronic spectrum has broad absorptions at 29.0, 24.2 and 20.6 × 10^3 cm^{-1}, which together with the diamagnetism and IR data, indicates a planar structure (N_2As_2 donors) for $Ni(NAs^{Me})_2I_2$. The possibility of a square pyramidal $[Ni(NAs^{Me})_2I]I$ was rejected after comparison of the electronic spectrum with that of $[Ni(NP^{Me})_2I]ClO_4$, (Table III), which would require NAs^{Me} to produce a greater ligand field than NP^{Me} if the complexes were isostructural. In CH_2Cl_2 solution the complex is a non-electrolyte and has a similar electronic spectrum to the other halides, hence rearrangement to the pseudotetrahedral (N_2I_2) form has occurred. A few samples of $Ni(NAs^{Me})_2I_2$ prepared contained (in addition to the brown form) small amounts of dark green material (*ca.* <10%). These samples had

TABLE III. Spectroscopic Data on the Complexes.

Compound	E_{max} (ϵ_{mol}) × 10^{-3} cm^{-1} [a]	E_{max} × 10^{-3} cm^{-1} [b]	IR Data cm^{-1}
$Ni(NN^{Me})(H_2O)_2Cl_2$	26.80 (40); 20.00 (154); 18.1 sh; 15.30 (46) sh; 11.90 (93); 9.90 (142)	33.0 sh; 24.2; 14.0; 13.1 sh, 8.5	3380, 1630 H_2O
$Ni(NN^{Me})(H_2O)_2Br_2$	29.05(963); 19.25(170); 17.6 sh, 11.50 sh; 9.80(89)	32.2 sh; 24.3; 13.85; 8.0 br	3380, 1630 H_2O
$Ni(NN^{Me})(NO_3)_2$	26.25 (56); 15.30 (62); 10.25 (30)	26.2; 15.0 br; 13.4 sh; 8.3	1540, 1515, 1284, 1273, 810, NO_3
$Ni(NN^{Me})(NCS)_2$	INSOLUBLE	28.3; 21.0 w; 15.3; 13.8 sh; 9.0	2125, 2115 ν(CN)
$Ni(NP^{Me})Cl_2$	30.55 (1917); 19.35 (439)	19.4	356, 348 ν(Ni–Cl)
$Ni(NP^{Me})Br_2$	33.30 (2696); 26.50 sh (936); 18.87 (298)	25.4; 19.2	286, 254 ν(Ni–Br)
$Ni(NP^{Me})(NCS)_2$	35.00 sh; 28.13 (1019); 21.26 (569)	27.1; 16.4; 13.6 w; 10.1 sh; 8.6	2110, 2096 ν(CN) 765 ν(CS); 468 δ(NCS)
$[Ni(NP^{Me})_2](BF_4)_2$	34.30 (2346); 23.40 (253)	31.5 sh; 23.6	990 BF_4^-
$[Ni(NP^{Me})_2Cl]ClO_4$	34.30 (8296); 22.70 (622)	32.0 sh; 22.4; 19.0 sh	1080, 620 ClO_4^-
$[Ni(NP^{Me})_2Br]ClO_4$	34.20 (8335); 21.90 (946); 18.70 (384)	30.55; 22.4; 18.0 sh	1080, 620 ClO_4^-
$[Ni(NP^{Me})_2I]ClO_4$	34.10 (4824); 28.70 (2156); 19.50 (555)	33.0 sh; 27.8; 20.4	1080, 620 ClO_4^-
$Ni(NAs^{Me})_2Cl_2$	29.30 (2923); 22.51 (10); 19.22 (119); 18.0 sh 15.60(8); 10.6(81); 9.30(78)	28.5; 24.0 sh; 14.8 9.4; 8.5	254 ν(Ni–Cl)
$Ni(NAs^{Me})_2Br_2$	28.40 (10860); 18.81 (251); 15.90 (86) 10.21(155); 9.31 (125)	27.2; 23.5 sh; 14.4 8.8; 7.7	183 ν(Ni–Br)
$Ni(NAs^{Me})_2I_2$	29.30(2940); 23.00(2590); 21.22(2516) 17.31 sh; 9.53(208); 8.6 (114)	29.00; 24.2; 20.6	—
$Ni(NAs^{Me})_2(NCS)_2$	INSOLUBLE	27.7; 16.6; 13.0; 11.7 10.6; 8.0	2060 ν(CN) 782 ν(CS); 460 δ(NCS)
$Ni(NAs^{Me})(NCS)_2$	INSOLUBLE	22.6; 15.9; 10.0 sh; 7.8	2122 sh, 2110 ν(CN) 786 ν(CS); 466 δ(NCS)
$[Ni(NAs^{Me})_2Cl]ClO_4$ [c]	19.8	29.1 sh; 19.8	1080, 620, ClO_4
$[Ni(NAs^{Me})_2Br]ClO_4$ [c]	19.6	28.7 sh; 19.3	1080, 620, ClO_4
$[Ni(NAs^{Me})_2I]ClO_4$	29.40 (1627); 23.40 (1109); 21.0 (1139); 17.0 (283)	26.4; 18.0	1080, 620, ClO_4
$[Ni(PP^{Me})_2](ClO_4)_2$ [d]	31.80 (3430); 24.25 (778)	30.9 sh; 24.5 sh	1080, 620 ClO_4
$[Ni(PP^{Me})_2Cl]ClO_4$	30.40 (3052); 24.80 (925); 22.00 sh	25.0; 22.0 sh	1080, 620 ClO_4
$Ni(PAs^{Me})Cl_2$	31.90 (4994); 25.05 sh (269); 21.30 (842)	32.0; 21.4	300, 340 ν(Ni–Cl)
$[Ni(PAs^{Me})_2Cl]ClO_4 \cdot CH_2Cl_2$	31.20 sh (6494); 23.50 (1259); 22.67 (1052)	32.0; 28.0; 23.0	1080, 620 ClO_4
$[Ni(PAs^{Me})_2Br]ClO_4 \cdot CH_2Cl_2$	30.95 (5679); 23.00 (750); 21.60 sh	28.9; 23.0; 21.0 sh	1080, 620 ClO_4
$[Ni(PAs^{Me})_2I]ClO_4 \cdot CH_2Cl_2$	30.50 (6219); 20.66 (982)	30.0; 24.1; 21.0 sh	1080, 620 ClO_4

$Ni(PAs^{Me})_2I_2$	30.35 (7889); 20.68 (868)	28.0; 21.0	–
$Ni(PAs^{Me})_2(NCS)_2 \cdot CH_2Cl_2$	26.15 (2170); 23.10 sh (1333)	30.1; 26.0; 22.8 sh	2065, 2045 ν(CN)
$Ni(PAs^{Me})_2(NO_3)_2$	30.85 (1310); 25.80 (1352)	28.0; 24.0 sh	1432, 1385, 1322, 840, 725 NO_3
$[Ni(PAs^{Me})_2](ClO_4)_2$[d]	31.00 sh (2583); 23.90 (871)	30.7 sh; 24.3	1080, 620 ClO_4

[a]CH_2Cl_2 solution except (e) (d). [b]Nujol mulls. [c]Nitromethane. [d]MeCN.

identical IR spectra (4000–700 cm^{-1}) with the pure brown form. We were unable to separate the green material and its nature remains uncertain, but it is possible that it is the pseudo-octahedral isomer ($N_2As_2I_2$).*

The blue $Ni(NAs^{Me})_2(NCS)_2$ is a pseudo-octahedral complex (Table III) with *trans* isothiocyanate groups [12]. The complex was insoluble in non-polar solvents and upon attempted recrystallisation from ethanol it was converted into green $Ni(NAs^{Me})(NCS)_2$, which is assigned an analogous structure to $Ni(NN^{Me})(NCS)_2$. This is the only example of a 1:1 complex of NAs^{Me} isolated, presumably a reflection of its insolubility, and the ability of NCS ligands to bridge two metal centres and retain the favoured six-coordination.

Particular attention was paid to the isolation of halide–perchlorates and related complexes, not only because we hoped to obtain 5-coordinate species, but also because the Σ_{n^o} and Σ_{χ^o} criteria of Sacconi [19] predict that N_2As_2Cl and N_2As_2Br donor sets may produce spin cross-over systems for Ni(II). Evaporation of n-butanol solutions containing a 1:1:4 ratio of NiX_2:$Ni(ClO_4)_2$:NAs^{Me} produced red (X = Cl, Br) or purple (X = I) $[Ni(NAs^{Me})_2I]ClO_4$ complexes. Similar complexes were obtained with BF_4^- or PF_6^- replacing ClO_4^-. Attempts to produce $[Ni(NAs^{Me})_2NCS]ClO_4$ yielded only $Ni(NAs^{Me})_2(NCS)_2$. The $[Ni(NAs^{Me})_2I]ClO_4$ is slightly soluble in CH_2Cl_2 but decomposes fairly rapidly in solution, the chloro and bromo complexes were insoluble in non-polar solvents, and were decomposed by DMF, DMSO or MeCN. Only in concentrated nitromethane solutions were red species present and even these solutions decomposed rapidly on standing or dilution. This instability in solution restricted measurements to the solid state. It is important to point out that recrystallisation was not possible, and no crystals suitable for X-ray study were obtained. The importance of this is that some samples had anomalous magnetic moments $2.0 > \mu_{eff} > 0.5$ BM, and in addition to the main band at 19–20 × 10^3 cm^{-1} in the electronic spectra had weak bands at lower energy. The possibility of a spin-equilibrium was ruled out when the magnetic moments were found to be temperature independent. Moreover the 'paramagnetism' and extra electronic spectral bonds disappeared if the complexes were prepared in n-BuOH in the presence of excess $Ni(ClO_4)_2$. Samples prepared in the presence of excess of the large anion (ClO_4^-, BF_4^- *etc.*) were essentially diamagnetic $\mu_{eff} \leqslant$ 0.6 BM and had no electronic spectral absorptions below 17 × 10^3 cm^{-1}. The 'paramagnetism' of some

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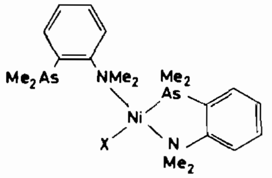
*Green and brown 'forms' of $Ni(diars)_2I_2$, diars = *o*-phenylenebis(dimethylarsine), have been noted [23], but again the green form is of unknown structure.

samples is thus attributable to contamination with octahedral $Ni(NAs^{Me})_2X_2$ whose formation was suppressed by excess ClO_4^-.

The diamagnetism of $[Ni(NAs^{Me})_2X]^+$ (X = Cl, Br) was slightly surprising *assuming* the cations are five-coordinate. In fact application of the IR spectral criteria for diagnosis of coordination of the $-NMe_2$ and $-AsMe_2$ groups, discussed above revealed that while the $-NMe_2$ groups were coordinated, the $-AsMe_2$ case was more complicated. Both the $-AsMe_2$ rocking mode and the aryl CH deformation regions of the IR spectra were very complicated. Comparison with the IR spectra of $Ni(NAs^{Me})_2X_2$ and free NAs^{Me} revealed the presence of both coordinated (evidenced by a shift to higher frequency ~12 cm^{-1}) and uncoordinated (essentially unchanged from NAs^{Me}) $-AsMe_2$ groups were present. The complexity of the CH deformation region is not unreasonable if both monodentate (–N) and bidentate (NAs) coordinated ligands are present. The possibility that the complexity of the spectra reflects two different environments of coordinated $-AsMe_2$ groups, *e.g.* apical and basal in a square pyramid, was rejected since in *cis*-$[Co(diars)_2X_2]^+$ all the $-AsMe_2$ rocking modes are shifted to higher frequency [20].

Thus structure I is assigned to these $[Ni(NAs^{Me})_2X]ClO_4$ complexes. The electronic spectra show a shift to lower energy in E_{max} Cl > Br > I, confirming the halide is coordinated, and are similar to those of nickel(II) complexes of multidentate nitrogen–arsenic donor ligands with N_2AsX donor sets [21, 22]. Several attempts to isolate planar $[Ni(NAs^{Me})_2]Y_2$ (Y = ClO_4, BF_4) were unsuccessful, producing only green oils, and similarly no nickel(II) nitrate complex was isolated.



I

o-*Dimethylaminophenyldimethylstibine* (NSb^{Me})

No nickel(II) complexes of this ligand were isolated. The reactions of NiX_2 (X = Cl, Br, I, NCS) and '$NiXClO_4$' with NSb^{Me} in i-propanol/CH_2Cl_2, n-butanol, or tetrahydrofuran did not produce solid complexes, and electronic spectra of the solutions did not provide evidence of significant interaction.

o-*Phenylenebis(dimethylphosphine)*(PP^{Me}) *and* o-*Dimethylphosphinophenyldimethylarsine* (PAs^{Me})

The behaviour of these ligands was straightforward, and the isolated complexes were of types $[Ni(L–L)_2](ClO_4)_2$, and $[Ni(L–L)_2X]Y$ (L–L = PP^{Me}, PAs^{Me}; X = Cl, Br, I, NCS, NO_3; Y = X, ClO_4); representative examples are given in Tables II, III. The PP^{Me} complexes have been reported elsewhere [23] and except for small differences in the solution spectra, probably due to solvent effects, the agreement in physical data is good. The assignment of planar structures to $[Ni(L–L)_2](ClO_4)_2$ and five-coordinate square pyramidal structures to the $[Ni(L–L)_2X]^+$ (at least in solution) follows from comparison of the data in Tables II, III with that of similar complexes [15, 23, 24].

The solid state structures of the $[Ni(L–L)_2X]X$ are not certain. It has usually been assumed [23, 24] that they are tetragonal with weak Ni···X interaction. The structure [25] of $Ni(diars)_2I_2$ (diars = *o*-$C_6H_4(AsMe_2)_2$) reveals a planar $NiAs_4$ geometry with very long (3.21 Å) axial Ni···I bonds. However the structure of $[Ni(Et_2PCH_2CH_2PEt_2)_2I]^+$ contains discrete square pyramidal ions [26]. The differences between the solution and solid state electronic spectra of these $[Ni(L–L)_2X]X$ complexes are small and may be due to solvent effects rather than major changes in the metal environment. For the $[Ni(L–L)_2X]ClO_4$ the electronic spectra could also have been interpreted in terms of discrete five-coordinate ions in the solid state, perhaps with a very weak interaction with the ClO_4^- in the sixth position as found [23] in the isoelectronic $[Cu(PP^{Me})_2Cl](ClO_4)_2$.

The IR spectrum of $Ni(PAs^{Me})_2(NCS)_2$ contains two ν(CN) vibrations at 2065, 2045 cm^{-1} assignable to N-bonded and ionic thiocyanate groups respectively clearly showing five-coordination is present in the solid state here. In $Ni(PAs^{Me})_2(NO_3)_2$ there is IR evidence for both ionic and coordinated nitrate [27].

Generally only 2:1 complexes were isolated with these two ligands, but a $Ni(PAs^{Me})Cl_2$ compound was also formed. This was diamagnetic, a non-electrolyte in nitromethane, and had no electronic spectral absorption below 20 × 10^3 cm^{-1}, which rule out a $[Ni(PAs^{Me})_2][NiCl_4]$ formulation. Hence we conclude this is a rare example of a 1:1 complex with this type of ligand [23, 24].

Discussion

The complexes formed by NP^{Me} and especially NAs^{Me} are considerably different to those of PP^{Me} and PAs^{Me} which are typical of heavy group VB donor ligands including *o*-$C_6H_4(AsMe_2)_2$ [17, 24], *o*-$C_6H_4(AsMe_2)(SbMe_2)$ [28] and *o*-$C_6H_4(PPh_2)_2$ [15]. The formation of low-spin planar $Ni(NP^{Me})X_2$ and low-spin five-coordinate $[Ni(NP^{Me})_2X]ClO_4$ can be compared directly with the occurrence [3] of high-spin $Ni(NP^{Ph})X_2$, [NP^{Ph} = *o*-$C_6H_4(NMe_2)(PPh_2)$] which are tetrahedral monomers in solution, and five-coordinate dimers with X-bridges in the solid state. The difference is most readily explained by the greater σ donor power of the $-PMe_2$ group which accounts for the change in structure and spin-state. Indeed in NP^{Me} the phosphorus donor appears to dominate the $-NMe_2$ since the type of complexes formed are characteristic of the former rather than of weak field amine donors.

The unusual behaviour of NAs^{Me} is less readily rationalised. It appears to form a wider range of complexes than the primary amine analogue $o\text{-}C_6H_4(AsMe_2)(NH_2)$ [5]. One would expect the latter to produce a slightly greater ligand field, although since Chiswell *et al.* [5] did not report the electronic spectra of the complexes below 12000 cm^{-1} Dq^{xy} for the ligand cannot be calculated.

In fact NAs^{Me} behaves as a rare example of a weak field ligand with an $-AsMe_2$ donor. A ligand containing tertiary amine and soft tertiary arsine donor groups does not bond very strongly to 'hard' high-spin Ni(II) and does not produce a strong enough ligand field to cause spin-pairing [contrast $Ni(NP^{Me})X_2$]. The high spin Ni(II) clearly prefers the amine to the arsine donor as is shown by the formation of NiN_2X_2 species in solution. The subtle effects which lead to a planar $[Ni(NAs^{Me})_2]I_2$ in the solid state rather than octahedral $[Ni(NAs^{Me})_2I_2]$ are difficult to determine, although if the green form is the octahedral isomer the energy difference may be very small.

The formation of planar $[Ni(NAs^{Me})_2X]^+$ (N_2AsX) rather than five-coordinate N_2As_2X is unexpected. Since these ions appear to be stable only in the solid, packing and lattice energy considerations may be important. Sacconi [21, 22] has reported several examples of planar NiN_2AsX chromophores with multidentate ligands containing tertiary amine and diphenylarsino (Ph_2As-) donors and suggests that steric hindrance may contribute to the reluctance of these species to take up other $-AsPh_2$ donors present and become five-coordinate. Steric factors are unlikely to be dominant with NAs^{Me}; possibly an electronic explanation in terms of cooperativity and symbiotic [29] effects is more realistic.

The failure to prepare complexes of NSb^{Me} is also surprising, since ditertiary stibine complexes are known [30, 31]. One might have thought that incorporation of an amine donor would increase the tendency of the ligand to bond to Ni(II). Application of this argument to the arsine series would predict that NAs^{Me} complexes would be more stable than those of $o\text{-}C_6H_4(AsMe_2)_2$, clearly not true from the results discussed above. In fact extrapolation from NAs^{Me} to NSb^{Me} suggests that the latter would produce a weaker ligand field and hence the nickel(II) will be high spin. Although Me_2Sb- donors coordinate to low-spin nickel(II) they will have very little tendency to bond to the harder high-spin ion. Thus NSb^{Me} may be viewed as a 'sterically hindered' (by $o\text{-}Me_2Sb-$) dialkylarylamine, and at least under the experimental conditions described it showed no ability to bond to Ni(II). Probably the solvent effectively competes for the metal ion.

In conclusion these hybrid ligands reflect the conflict between the properties of hard N and soft P, As, Sb donors toward Ni(II), the characteristic behaviour of each type being typified by $o\text{-}C_6H_4(NMe_2)_2$ and $o\text{-}C_6H_4(PMe_2)(AsMe_2)$. In NP^{Me} the Me_2P is dominant, whilst in NAs^{Me} the differing demands are more balanced but with $-NMe_2$ usually winning.

Experimental

Elemental analyses (C, H, N) were performed at University College London or on a F & M Analyser at Southampton. IR spectra were measured in nujol and HCB mulls on Perkin Elmer 225 and Beckmann IR 11 spectrometers, and electronic spectra on a Unicam SP 700. Magnetic measurements were made by the Gouy method, and conductivities in *ca.* 10^{-3} *M* solutions on a Cambridge Instruments Conductivity Bridge.

The preparation of the ligands has been described elsewhere [32]. Nickel(II) salts were the best commercial grade available, except for nickel(II) thiocyanate which was made *in situ* by metathesis of KCNS and $Ni(NO_3)_2\cdot 6H_2O$ in ethanol [15], and $[Ni(H_2O)_6](BF_4)_2$ prepared from $NiCO_3$ and aqueous HBF_4.

Complexes were generally prepared under dinitrogen although except for those of NP^{Me}, preparation in the absence of a dinitrogen atmosphere appeared to have no adverse effects.

$Ni(NN^{Me})(H_2O)_2X_2$ ($X = Cl, Br$)

Hydrated nickel(II) halide (2.0 mmol) was dissolved in hot ethanol (25 cm^3), the solution filtered and treated with the ligand (2.0 mmol). The red solutions were refluxed with stirring to give green crystalline precipitates. Yields ~70%.

The complex $Ni(NN^{Me})(H_2O)_2Br_2$ dissolved in hot n-butanol to give a red solution, which on concentration under reduced pressure gave deep red crystals.

$Ni(NN^{Me})(NO_3)_2$

Hydrated nickel(II) nitrate (2.75 mmol) was dissolved in ethanol (30 cm^3) and treated with the ligand (2.75 mmol). The solution was refluxed for 0.5 h and the solvent removed under reduced pressure. The residue was recrystallised from a dichloromethane/n-butanol mixture to give turquoise crystals (55%).

$Ni(NN^{Me})(NCS)_2$

A solution of the ligand (2.75 mmol) in ethanol (5 cm^3) was added to a refluxing solution of nickel(II) thiocyanate, (2.75 mmol), in ethanol (30 cm^3). Blue-green crystals separated immediately (60%).

$Ni(NP^{Me})X_2$ $(X = Cl, Br)$

Nickel(II) halide hexahydrate (2.0 mmol) was dissolved in hot ethanol (25 cm^3) the solution filtered and treated with the ligand (2.0 mmol). The initial dark brown solutions became dark red on prolonged reflux and dark red crystals separated. Yields ~65%.

$Ni(NP^{Me})(NCS)_2$

A solution of the ligand (2.75 mmol) in ethanol (10 cm^3) was added to a refluxing solution of nickel(II) thiocyanate (2.75 mmol) in ethanol (30 cm^3). A green precipitate formed immediately. Yield 60%.

$[Ni(NP^{Me})_2]Y_2$ $(Y = ClO_4, BF_4)$

The ligand (2.2 mmol) was syringed directly into a solution of $[Ni(H_2O)_6]Y_2$ (Y = ClO_4 or BF_4) in hot ethanol (30 cm^3). A yellow solid precipitated immediately. Yields ~50%.

$[Ni(NP^{Me})_2X]ClO_4$ $(X = Cl, Br, I)$

A solution of the ligand (4.0 mmol) in dichloromethane (15 cm^3) was added to a solution of hydrated nickel(II) halide (1 mmol) and nickel(II) perchlorate hexahydrate (1 mmol) in hot ethanol (30 cm^3). The precipitates that formed were recrystallised from dichloromethane/n-butanol. Yields ~45%.

$Ni(NAs^{Me})_2X_2$ $(X = Cl, Br)$

A solution of the ligand (4.0 mmol) in ethanol (5 cm^3) was added to a filtered solution of the hydrated nickel(II) halide (2.0 mmol) in hot ethanol (20 cm^3). The brown solutions slowly deposited green crystals on cooling. Yields ~60%.

$Ni(NAs^{Me})_2I_2$

A solution of hydrated nickel(II) iodide (2.0 mmol) in ethanol (25 cm^3) was treated with the ligand (4.0 mmol). The mixture was refluxed for 0.5 h and the solvent removed under reduced pressure. The residue was recrystallised from dichloromethane to give dark brown crystals (65%).

$Ni(NAs^{Me})_2(NCS)_2$

Hydrated nickel(II) thiocyanate (2.75 mmol) in hot ethanol (30 cm^3) was treated with the ligand (5.50 mmol) in ethanol (5 mmol). Blue-grey crystals separated immediately (65%).

$Ni(NAs^{Me})(NCS)_2$

This complex was obtained as a green solid when an attempt was made to recrystallise $Ni(NAs^{Me})_2(NCS)_2$ from ethanol at room temperature.

$[Ni(NAs^{Me})_2X]ClO_4$ $(X = Cl, Br, I)$

A solution of the ligand (4.0 mmol) in dichloromethane (10 cm^3) was added to a solution of hydrated nickel(II) halide (1 mmol) and nickel(II) perchlorate hexahydrate (1 mmol) in hot ethanol (30 cm^3). The solvent was removed under reduced pressure and the green residues dissolved in dichloromethane (40 cm^3) and n-butanol (15 cm^3) and concentrated under reduced pressure until a red microcrystalline solid separated. Yields ~65%.

$Ni(PAs^{Me})Cl_2$

A solution of the ligand (4.0 mmol) in dichloromethane (10 cm^3) was added to a solution of nickel(II) chloride hexahydrate (2.0 mmol) in hot ethanol (25 cm^3) to give a red solution. The solvent was removed under reduced pressure and the residue recrystallised from a dichloromethane/n-butanol solvent mixture to give orange crystals (70%).

$Ni(PAs^{Me})_2X_2(CH_2Cl_2)$ $(X = Br, NCS, NO_3)$

A solution of the ligand (4.0 mmol) in dichloromethane (10 cm^3) was added to a solution of $[Ni(H_2O)_6]X_2$ (X = Br, NCS, NO_3) in hot ethanol (30 cm^3). The precipitates which formed were recrystallised from dichloromethane/n-butanol. Yields ~55%.

$[Ni(PAs^{Me})_2X]ClO_4(CH_2Cl_2)$

A solution of the ligand (4.0 mmol) in dichloromethane (10 cm^3) was added to a solution of hydrated nickel(II) halide (1 mmol) and nickel(II) perchlorate hexahydrate (1 mmol) in hot ethanol (30 cm^3). The crystals which separated where recrystallised from dichloromethane/n-butanol. Yields ~55%.

The complexes $[Ni(PP^{Me})_2](ClO_4)_2$ and $[Ni(PP^{Me})_2Cl]ClO_4$ were prepared by the methods described by Bennett [23].

Acknowledgement

We are grateful to the SRC for the award of a postdoctoral fellowship (K.G.S.) and to Dr. S. M. Nelson for the variable temperture magnetic studies and helpful discussion.

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