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Complexes of Bidentate Group VB Ligands. Part XVIII. Nickel(II) Complexes of *Cis*-1-dimethylarsino-2-diphenylarsinoethylene

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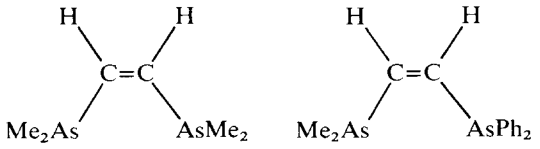
The ligand cis-1-dimethylarsino-2-diphenylarsinoethylene (vda) forms square pyramidal $[Ni(vda)_2X]^+$ *(X = Cl, Br, I, NCS) species. The tendency for vda to promote pentacoordination is shown by the conversion of the planar* $[Ni(vda)_2](ClO_4)_2$ *to* $[Ni(vda)_2(MeNO_2)](ClO_4)_2$ *in nitromethane and to* $[Ni(vda)_2(ClO_4)]ClO_4$ *in 1,2-dichloroethane. The* ^1H *n.m.r. and infrared spectra are discussed in terms of the changes that occur in the spectra on coordination.*

Introduction

The coordination chemistry of diarsine ligands is dominated by the extremely versatile *o*-phenylenebis (dimethylarsine) (das) and, to a much lesser extent, by the recently prepared *cis*-1,2-bis(dimethylarsino) ethylene, *cis*-edas.[2] Direct reaction of both ligands with nickel(II) salts in ethanol leads to bisligand complexes $[Ni(das)_2X]X$[3] and $[Ni(cis\text{-}edas)_2X]Y$[4] (X = Cl, Br, I, *etc.*; Y = ClO_4, BPh_4, PF_6), and $[Ni(das)_2](ClO_4)_2$ and $[Ni(cis\text{-}edas)_2](PF_6)_2$. Aryl substituted diarsine ligands such as 1,2-bis(diphenylarsino)ethane (dae) or *cis*-1,2-bis(diphenylarsino)ethylene (vaa) exhibit much less tendency to coordinate to nickel(II), but $[NiLX_2]$ (L = dae, vaa), $[Ni(dae)_2I]I$ and $[Ni(vaa)_2X]BPh_4$ (X = Br, I) can be isolated if due care is paid to the reaction conditions.[5] During the course of a study of the stereochemistry of vinylic substitution reactions[6] we have prepared the new diarsine ligand *cis*-1-dimethylarsino-2-diphenylarsinoethylene, *cis*-$Ph_2AsCHCHAsMe_2$ (vda). Unlike *cis*-edas, which is obtained only in low yield accompanied by an excess of the *trans* isomer from the reaction of *cis*-$C_2H_2Cl_2$ and $2NaAsMe_2$, vda is obtained in high yield from the stereospecific reaction of $NaAsMe_2$ with *cis*-$Ph_2AsCHCHCl$.[6]



cis-edas   vda

Experimental

Physical measurements were made as described previously.[7] The ligand, vda, was obtained as a heavy colourless oil,[6] and was made up to a solution of known concentration in acetone and manipulated via a syringe.

Complexes were prepared under a dry nitrogen atmosphere and solvents were deoxygenated before use to avoid oxidation of the ligand.

[Ni(vda)$_2$Cl]Cl

Nickel(II) chloride hexahydrate (0.262 g, 1.1 mmol) in ethanol (20 cm^3) was added rapidly to a solution of vda (1.58 g, 2.2 mmol). The deep purple solution was stirred and the acetone removed by warming in a stream of nitrogen. After the acetone had evaporated the purple solid which remained was filtered off, dissolved in dichloromethane (40 cm^3) and ethanol (10 cm^3) and concentrated under reduced pressure until purple microcrystals separated. Yield 40%.

[Ni(vda)$_2$Br]BPh$_4$

Anhydrous nickel(II) bromide (0.218 g, 1.0 mmol) in ethanol (20 cm^3) was added rapidly to the vda (1.44 g, 2.0 mmol) solution. The resulting purple solution was stirred for 20 min. and then sodium tetraphenylborate (0.34 g, 1.0 mmol) in ethanol (15 cm^3) was added. The purple precipitate which formed immediately was recrystallised from dichloromethane/ethanol. Yield 85%.

[Ni(vda)$_2$I]I

Hydrated nickel(II) iodide (0.42 g, 1.0 mmol) in ethanol (20 cm^3) and the vda (1.44 g, 2.0 mmol) solution were stirred together for 30 min, and the solution was then concentrated to *ca.* 20 cm^3. Dark purple crystal separated on cooling. Yield 55%.

TABLE I. Analytical, Electronic and Proton N.M.R. Data of the Nickel(II) Complexes.

Compound	Dec.Pt. °C	Colour	% C[a]	% H[a]	% Hal[a]	Λ_M[b] ohm^{-1} cm^2 M^{-1}	E_{max} (ε_{mol})[c] cm^{-1}	E_{max}[d] cm^{-1}	^{1}H N.M.R.[e] τ Me	Ph	Vinyl
$[Ni(vda)_2](ClO_4)_2$	160	Red-brown	40.2(39.2)	4.0(3.6)		158	20,000 (980)	21,200	8.8	2.1	
$[Ni(vda)_2Cl]Cl$	104	Dark purple	45.1(45.0)	4.2(4.4)	8.3(8.35)	79	18,400 (580)	18,700	8.6	2.1	3.2
$[Ni(vda)_2Br]BPh_4$	100	Purple	56.5(57.6)	4.8(4.9)	7.0(6.8)	69	18,000 (650)	18,000	8.4	2.0	2.8
$[Ni(vda)_2I]I$	103–6	Purple-black	38.7(38.1)	3.4(3.4)	24.3(24.6)	77	17,510 (570)	17,200	8.6	2.2	3.4
$[Ni(vda)_2NCS]BPh_4$	118	Purple	58.9(59.3)	5.2(4.8)	1.0(1.2)[f]	64	19,800 (1220)	21,000	8.5	2.1	3.0
vda									9.0	2.8	3.4,3.8

[a] Found (Calc.). [b] 10^{-3} M in $MeNO_2$. [c] In CH_2Cl_2. [d] Solid reflectance spectra. [e] Satd. $CDCl_3$ soln., rel. to TMS, except ligand (neat liquid). [f] Nitrogen analysis.

TABLE II. Infrared Spectral Data of the Nickel(II) Complexes (cm^{-1})[a].

Compound	ν(C=C)	Olefin C–H in-plane deformn.	Olefin C–H out-of-plane deformn.	Assymm. C–H def. ($AsPh_2$)	Sym. C–H def. ($AsMe_2$)	C–H rock ($AsMe_2$)	Other	
$[Ni(vda)_2](ClO_4)_2$	1574m		735vs	1438, 1480s	1305w	870vs, 915s	1098, 620	ClO_4^-
$[Ni(vda)_2Cl]Cl$	1578w	1075m	735vs	1432, 1480s	1260w	860m, 910m		
$[Ni(vda)_2Br]BPh_4$	1575m	1070s	730vs	1435, 1480s	1260w	865s, 910s		
$[Ni(vda)_2I]I$	1575m	1070s	730vs	1435, 1480s	1265m	845s, 905s		
$[Ni(vda)_2NCS]BPh_4$	1575m	1070s	730vs	1430, 1478s	1265m	875s, 910s	2060s	ν(CN)
vda[b]	1580s	1075vs, 1180vs	740s	1430, 1473s	1300s	880m, 900m		

[a] Nujol mull. [b] Liquid film.

[Ni(vda)$_2$NCS]BPh$_4$

An ethanolic solution of nickel(II) thiocyanate (0.174 g, 1.0 mmol) was added to vda (1.44 g, 2.0 mmol) in acetone. The mixture was stirred for 30 min and then sodium tetraphenylborate (0.34 g, 1.0 mmol) in ethanol (20 cm^3) was added dropwise. A red-purple solid precipitated immediately. The crude product was recrystallised from dichloromethane/ethanol.

[Ni(vda)$_2$](ClO$_4$)$_2$

An ethanolic solution (30 cm^3) of nickel(II) perchlorate hexahydrate (0.36 g, 1.0 mmol) was added dropwise to a gently refluxing solution of vda (1.44 g, 2.0 mmol) in acetone. On cooling, the red solution afforded a red-brown crystalline solid. Yield 60%.

Results and Discussion

No 1:1 complexes of vda and nickel(II) salts could be isolated; reaction of vda with nickel(II) halides in ethanol in an equimolar ratio produced only the 2:1 complexes. In this respect vda resembles das and *cis*-edas which do not readily afford 1:1 complexes by direct reaction.[3,4]* In contrast 1,2-bis(methylphenylarsino)ethane[8] and dae[5] readily afford 1:1 nickel(II) complexes, whilst vaa can only be induced to form 1:2 complexes, [Ni(vaa)$_2$X]BPh$_4$, in the presence of a large anion–in the absence of tetraphenylborate ions even a large excess of vaa fails to produce anything but the 1:1 complexes.[5] These results thus indicate that a number of factors are important in determining the stoichiometry of the isolated complex, and these include the substituents on the terminal arsenics (alkylarylarsino- groups seem to be borderline) and the tendency to promote pentacoordination,[9] lattice energy and the nature of the counter ion,[10] and the solubility of the various possible products which may result in preferential precipitation of a form which is only a minor component in solution.[4]

The 1:2 complexes [Ni(vda)$_2$X]Y (X = Y = Cl, I; X = Br, NCS, Y = BPh$_4$) (Table I) are diamagnetic and are 1:1 electrolytes in $10^{-3}M$ nitromethane, the lower conductivities of the bromo and isothiocyanato complexes are due to the large BPh_4^- ion which has reduced ionic mobility. The infrared spectrum (Nujol mull) of [Ni(vda)$_2$NCS]BPh$_4$ exhibits ν(CN) at 2060 cm^{-1}, consistent with isothiocyanato coordination, and this is confirmed by the shift of the "*d–d*" band in the visible spectra of the complexes in the order NCS > Cl > Br > I.[11] The electronic spectra of the complexes in both the solid state and in dichloromethane are in the general range expected for square pyramidal rather than trigonal bipyramidal nickel(II) complexes,[12,13] which seems to be the preferred geometry for bidentate ligands with a C_2 backbone.[8] There is some difference in the energy maximum of the main "*d–d*" band between the solid reflectance and solution spectra of the isothiocyanato complex, but the cause is not clear. Comparison with the electronic spectra of other vinyldiarsine complexes[4,5] produces the expected spectrochemical series of ligands *cis*-edas > vda > vaa.

The diperchlorate complex, [Ni(vda)$_2$](ClO$_4$)$_2$, is a 1:2 electrolyte in nitromethane (Table I) and in the solid state its IR spectrum confirms that the perchlorate groups are uncoordinated.[14] However, the electronic spectra reveal a more complicated situation. The reflectance spectrum exhibits E_{max} at 21,200 cm^{-1}, but on dissolution of the red-brown complex in nitromethane a purple solution is formed with $E_{max} \sim 19{,}500$ cm^{-1}, consistent with the presence of a pentacoordinate moeity.[12] Since the complex in nitromethane is a 1:2 electrolyte the five-coordination must be achieved by coordination of a nitromethane molecule, [Ni(vda)$_2$(MeNO$_2$)](ClO$_4$)$_2$. However, in dichloromethane or 1,2-dichloroethane E_{max} is 20,000 cm^{-1}, also suggesting five-coordination, but here the fifth donor is a perchlorato group, as confirmed by the conductance value of 17.5 ohm^{-1} $cm^2 M^{-1}$ in 1,2-dichloroethane, a value within the range expected for 1:1 electrolytes in this solvent.[15] We thus observe with the vda ligand not only a very strong tendency to form bisligand complexes with nickel(II), but also an equally strong tendency to form pentacoordinate species by coordination of halide and pseudohalide or even perchlorate or solvent molecules.

The ^1H n.m.r. spectra of the complexes (Table I) all exhibit a shift to low field of the methyl resonances consistent with coordination to the metal ion.[4,16] Characteristic infrared spectral frequencies are listed in Table II. The complexes all show ν(C=C) at ~1575 cm^{-1} confirming the presence of a *cis*-substituted olefinic ligand.[4] The in-plane and out-of-plane deformation vibrations of the olefin are not particularly sensitive to coordination, but the symmetrical C–H deformation and the C–H rock in the methyl group are shifted to lower frequencies on coordination (Table II).

Although no specific attempts were made to oxidise these complexes to nickel(III), we did not observe any tendency of the preformed complexes to air oxidise, and in this respect vda seems to be rather less ready to promote the Ni(II)→Ni(III) oxidation than either das or *cis*-edas.

* An octahedral polymeric [Ni(*cis*-edas)Cl$_2$]$_n$ has been obtained[4] from ethanolic solutions of the constituents, probably due to its low solubility which results in preferential precipitation of the complex.

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