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Bidentate Group VB Chelates. Part X. An Examination of the Electronic Spectra of Some Nickel(II) Complexes of 2-Diphenylarsinodiphenylphosphinoethane[1–4]

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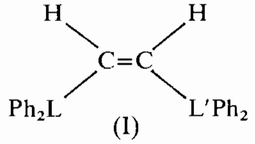
A relatively facile synthesis of the phosphine-arsine ligand, 2-diphenylarsinodiphenylphosphinoethane (pae) is described. This ligand forms low-spin square planar complexes $[Ni(pae)_2](ClO_4)_2$ *and* $[Ni(pae)X_2]$ *(X = Cl, Br, I, NCS), and the square pyramidal* $[Ni(pae)_2Cl]BPh_4$*. These complexes have been characterised by magnetic measurements and by electronic and infrared spectral measurements. A comparison of the electronic spectra of the planar* $[Ni(Ph_2P\frown Y\frown AsPh_2)Cl_2]$ *(*$\frown Y\frown$ *= cis-vinyl, dimethylene, o-phenylene) indicates that a spectrochemical series, cis-CH=CH– >–CH*$_2$*CH*$_2$*>o-C*$_6$*H*$_4$*, exists. The occurrence of pentacoordinate nickel(II) with pae in the solid state, but not with the corresponding diphosphine ligand, 1,2-bisdiphenylphosphinoethane, is discussed.*

Introduction

A considerable number of nickel(II) complexes of bidentate group VB chelates have been prepared and studied,[1–18] and the linkage between the two donor atoms has been *o*-phenylene,[2–6] methylene,[6] dimethylene,[7,9,12] trimethylene,[8] tetramethylene,[9] 1,8-naphthalene,[10] 2,2′-biphenylene,[11] 9,10-phenanthrene,[1] and *cis*-1,2-ethylene.[1,13–15] We have recently become interested in the changes in properties which result upon changing the type of linkage between donor atoms in chelating ligands.

In studies on the complexing properties of the ditertiary phosphine *cis*-1,2-bisdiphenylphosphinoethylene, vpp[16] (I; L = L′ = P), it was found, somewhat surprisingly that, as well as the planar four-coordinate $[Ni(vpp)X_2]$ derivatives, pentacoordinate square-pyramidal $[Ni(vpp)_2X]^+$ (X = hal, NCS) complexes were also isolable. This contrasted with the inability of several groups of workers to isolate solid pentacoordinate nickel(II) complexes of the saturated analogue of vpp, 1,2-bisdiphenylphosphinoethane (dpe) (II; L = L′ = P),[10,15,16] although a recent report has provided some evidence for pentacoordination in solution.[19] We have since synthesised an arsine–phosphine ligand with an ethylene backbone, *cis*-2-diphenylarsinovinyldiphenylphosphine, vasp (I; L = P, L′ = As), and found that this ligand forms both square-planar and square-pyramidal nickel(II) complexes.[20] We now wish to report a study of complexes derived from an arsine–phosphine containing a saturated chelate linkage, 2-diphenylarsinodiphenylphosphinoethane, pae (II; L = P, L′ = As). Our interest centred around the stereochemistry of the resulting complexes, and a spectrochemical comparison of pae with the ligands vasp, vpp, and dpe.


(I)

$Ph_2LCH_2CH_2L'Ph_2$

(II)

Experimental

Reagents

Nitromethane was washed with 5% aqueous sulphuric acid and 5% aqueous sodium bicarbonate, and fractionated, the fraction boiling at 101° C being collected. Reagent grade tetrahydrofuran was dried over sodium wire for 2 days, refluxed over calcium hydride for 24 hr and then fractionated (b.pt. 65° C).

The Ligand

Synthesis of 1-chloro-2-diphenylarsinoethane, $ClCH_2CH_2AsPh_2$

In dry apparatus, under a stream of nitrogen triphenylarsine (30.6 g, 0.1 mol) was dissolved in THF (200 ml). Lithium metal (2.1 g, 0.3 mol) was cut into small pieces and slowly added with stirring. The mixture became slowly red and the temperature gradually rose. It was then refluxed for 3 hr, and transferred under nitrogen to another 3-necked 1 l flask *via* a tube containing a plug of glass wool (to remove unreacted

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lithium). To this solution was added t-butyl chloride (5.5 g, 0.06 mol) in THF (15 ml) with stirring; heat was generated during this addition causing the solution to reflux. The arsenide solution was then added dropwise, under nitrogen, to a solution of 1,2-dichloroethane (29.1 g, 0.3 mol) in THF (200 ml) at 0° C; vigorous stirring was employed. The reaction was exothermic, and immediate decolouration of the arsenide solution occurred upon contact with the dihalide. Complete addition required 3 hr and resulted in a cloudy white suspension. The excess 1,2-dichloroethane was evaporated at 25° C *in vacuo*, and the white residue was treated successively with equivalent amounts of chloroform and water. The two layers were separated and the water layer washed with 100 ml chloroform; the combined organic layers were then dried over anhydrous sodium sulphate. The chloroform was removed on a rotatory evaporator to leave a pale yellow liquid. Distillation yielded the chloroarsine as a colourless oil, b.pt. 144–148° C/2 mmHg. Yield 82% (based on diphenylarsenide). *Analyses.* Calc. for $C_{14}H_{14}AsCl$: C, 57.56; H, 4.7%. Found: C, 57.4; H 4.6%.

The chloroarsine is readily oxidised on standing in open air, to form the white arsine oxide (a strong infrared absorption appears at 850 cm^{-1}). Calculated for $C_{14}H_{14}AsClO$: C, 54.54; H, 4.5%. Found: C, 54.60; H, 4.7%. M.pt. 160° C.

Synthesis of 2-diphenylarsinodiphenylphosphinoethane (pae)

A solution of lithium diphenylphosphide formed by treating triphenylphosphine (39.3 g, 0.15 mol) and lithium (2.82 g, 0.4 mol) in THF (200 ml) was treated with the chloroarsine (29.3 g, 0.10 mol) in THF (40 ml) at 0° C. Stirring was continued for $^1/_2$ hr after addition was complete, after which time all of the red colour due to the phosphide had disappeared. The mixture was refluxed for 1 hr, cooled, hydrolysed by the addition of saturated ammonium chloride solution (100 ml), separated, and dried over anhydrous sodium sulphate. The THF was then removed by rotatory evaporation, leaving a white solid. The crude solid was dissolved in a minimum amount of dichloromethane, filtered, ethanol was added, and set aside to crystallise. White crystals were obtained which were filtered, washed with ethanol and petroleum ether (40–60° C), and dried *in vacuo*. Yield 80% (based on chloroarsine). M.pt. 120° C. *Analyses.* Calc. for $C_{26}H_{24}PAs$: C, 70.58; H, 5.4%. Found: C, 70.60; H, 5.5%.

Preparation of the Complexes

[Ni(pae)X_2] (X = Cl, Br, I, NCS)

The ligand (0.442 g, 1.0 mmol) in acetone (20 ml) was added to a refluxing solution of the appropriate nickel(II) salt (1.0 mmol) in ethanol (30 ml), and a deep red-purple colour developed immediately. On cooling, crystals were deposited, which were collected on a sinter-glass funnel, and recrystallised from CH_2Cl_2/EtOH. Yields 75–80%.

[Ni(pae)$_2$](ClO_4)$_2$

An ethanolic solution (20 ml) of $Ni(H_2O)_6(ClO_4)_2$ (0.365 g, 1.0 mmol) was added slowly to an acetone solution (20 ml) of pae (0.884 g, 2.0 mmol). A red solution formed initially, but after stirring a yellow crystalline solid was deposited as the acetone slowly evaporated. The complex was recrystallised from hot acetone. Yield 72%.

[Ni(pae)$_2$Cl]BPh_4

A solution of $Ni(H_2O)_6Cl_2$ (0.237 g, 1.0 mmol) in ethanol (20 ml) was added dropwise to a solution of pae (0.884 g, 2.0 mmol) in acetone (20 ml). A deep red-purple colour developed immediately, but no solid was observed. A solution of $NaBPh_4$ (0.34 g, 1.0 mmol) in ethanol (20 ml) was added slowly to the mixture, resulting in an immediate purple precipitate. the mixture was stirred for $^1/_2$ hr and reduced to almost half-volume by gentle warming. It was then cooled, filtered, and the crude product recrystallised from CH_2Cl_2/EtOH. Yield 68%.

Physical Measurements

Conductivities were measured by the use of a Cambridge Instruments Ltd. conductivity bridge. Infrared spectra were measured as mulls in Nujol or hexachlorobutadiene on a Perkin Elmer 621 spectrophotometer. Electronic spectra were obtained in dichloroethane on a Unicam SP700 spectrophotometer, and reflectance spectra were obtained on a Beckman DK2A spectrophotometer using MgO as dilutant. Magnetic susceptibilities were measured by the Gouy method.

Results and Discussion

An alternative preparation of the potentially bidentate chelate, 2-diphenylarsinodiphenylphosphinoethane, pae, has already been reported by King and Kapoor.[21] Their method involved the reaction of diphenylvinylphosphine with diphenylarsine:

$$Ph_2PCH{=}CH_2 + HAsPh_2 \xrightarrow[C_6H_6]{KOBu^t} Ph_2PCH_2CH_2AsPh_2 \quad (77\%)$$

Although the yield of this particular reaction is quite high the reactants are difficult to prepare and not easy to handle. The method reported here also proceeds in high yield and involves only materials which are easy to handle:[22]

$$Ph_2AsLi + ClCH_2CH_2Cl \xrightarrow{THF} ClCH_2CH_2AsPh_2$$

$$Ph_2PLi + ClCH_2CH_2AsPh_2 \xrightarrow{THF} Ph_2PCH_2CH_2AsPh_2$$

It was found that the isolation of the chloroarsine was preferable to the chlorophosphine, as reaction of lithium diphenylphosphide with 1,2-dichloroethane always produced some diphosphine (dpe) irrespective of the excess of dichloroethane used.

By mixing nickel(II) salts with pae in a 1:1 ratio it was found that the $[Ni(pae)X_2]$ (X = Cl, Br, I, NCS) (Table I) complexes formed immediately. These diamagnetic complexes are non-electrolytes in nitromethane and may thus be assigned a monomeric square planar structure. Additional evidence for this assignment is derived from the infrared spectrum of the thiocyanate complex. A split $\nu(C{\equiv}N)$ absorption is observed with peaks at 2082 and 2075 cm^{-1}, and this is indicative of N-bonded isothiocyanate[8,23] in a *cis* configuration. Additional vibrations of the isothiocyanato group, $\nu(CS)$ at 840 cm^{-1} and $\delta(NCS)$ at 470 cm^{-1}, were distinguished by comparing the spectra of $[Ni(pae)(NCS)_2]$ with that of the free ligand and of the bromo complex. The electronic absorption spectra (Table I, Figure 1) in the solid state and in dichloroethane solution exhibit very similar absorption maxima suggesting that the complexes have the same structure in both physical states. The spectra are characterised by an intense absorption in the visible, and this absorption corresponds to the transition which has *d*-orbital character $d_{xy} \rightarrow d_{x^2-y^2}$. This band moves to higher energy in the series $I^- < Br^- < Cl^- < NCS^-$, and it is noticeable that the extinction coefficients of these bands increase in a parallel order. In Figure 2 we have compared the absorption maxima of a series of $[Ni(Ph_2P{\frown}Y{\frown}AsPh_2)Cl_2]$ (where ${\frown}Y{\frown}$ represents the chelate linkages *cis*-vinyl, dimethylene, or *o*-phenylene) complexes, in which the coordination around the nickel atom is $NiPAsCl_2$ in each case. It can be seen that merely changing the type of the two-carbon chelate link from vinyl to dimethylene to *o*-phenylene can cause the $d_{xy} \rightarrow d_{x^2-y^2}$ transition on the metal to shift *ca.* 1,000 cm^{-1}. This comparison allows us to make a rather novel "spectrochemical series of chelate links", *viz.*: *cis*-$CH{=}CH{-} > {-}CH_2CH_2{-} > o{-}C_6H_4$.

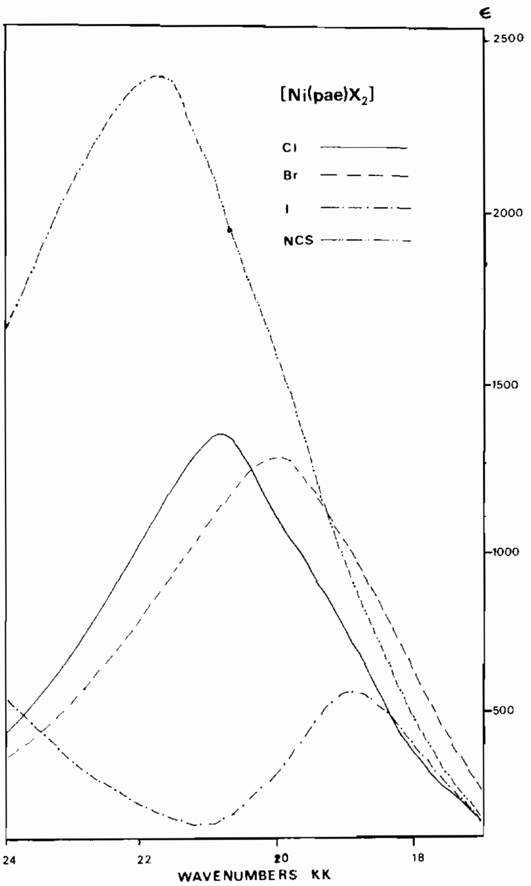


Figure 1. Electronic spectra of $[Ni(pae)X_2]$.

The $[Ni(pae)_2](ClO_4)_2$ complex is also diamagnetic and behaves as a 1:2 electrolyte in nitromethane (Table I). The infrared spectrum of this complex

TABLE I. Some Physical and Spectral Properties, and Analytical Data of the Nickel(II) Complexes.

Compound	Colour	M.Pt. (°C)	Λ_M[a]	% Carbon	% Hydrogen	$E_{max}(\varepsilon_{max})$[b] (kK)	E_{max}[c] (kK)
$[Ni(pae)Cl_2]$[d]	Red	218–221	0	53.8(54.5)[e]	4.6(4.2)[e]	20.8 (1,335)	20.7
$[Ni(pae)Br_2]$	Purple	217–220	8	46.9(47.1)	3.7(3.6)	20.1 (1,260), 25.5 (750)	20.0, 26.3
$[Ni(pae)I_2]$	Purple-black	210–212	8	41.8(41.3)	3.5(3.2)	19.0 (580), 27.2 (1,375)	18.9, 27.4
$[Ni(pae)(NCS)_2]$[f]	Red-brown	227–230	0	54.0(54.5)	3.9(3.8)	21.7 (2,425), 36.1 (7,580)	21.5
$[Ni(pae)_2](ClO_4)_2$	Yellow	221–224	192	54.3(55.4)	4.8(4.3)	20.1[g]	20.1sh
$[Ni(pae)_2Cl]BPh_4$	Deep purple	134–136	77	69.8(70.7)	5.2(5.2)	20.0 (825)	19.6

[a] In Λ^{-1} cm^2 l mol^{-1} for *ca.* 10^{-3} *M* nitromethane solutions at 20° C. [b] In dichloroethane. [c] Solid reflectance. [d] All the complexes were found to be effectively diamagnetic with small T.I.P. contribution. [e] Calculated percentage in parentheses. [f] Nitrogen: calc. 4.5%; found 4.4%. [g] Decomposition occurs gradually, thus extinction coefficients not calculated.

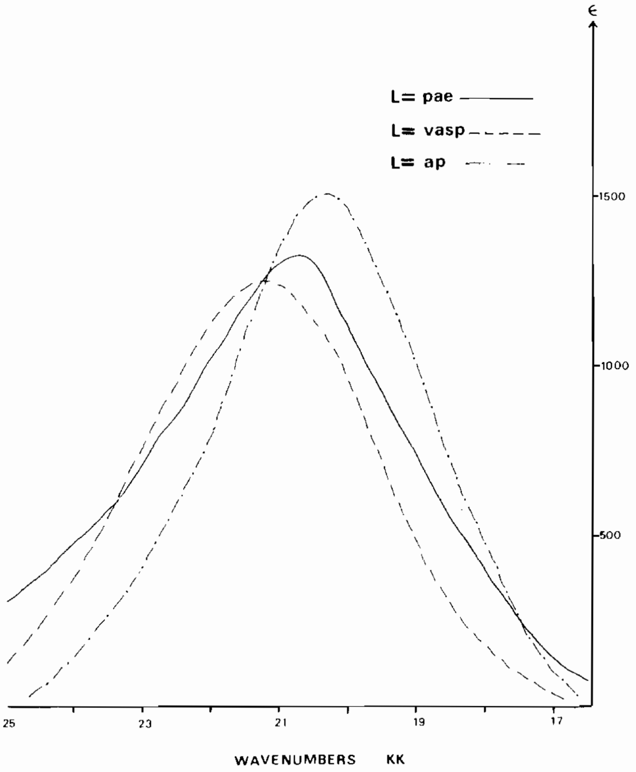
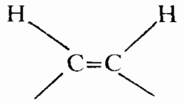


Figure 2. Electronic spectra of $[NiLCl_2]$ complexes.

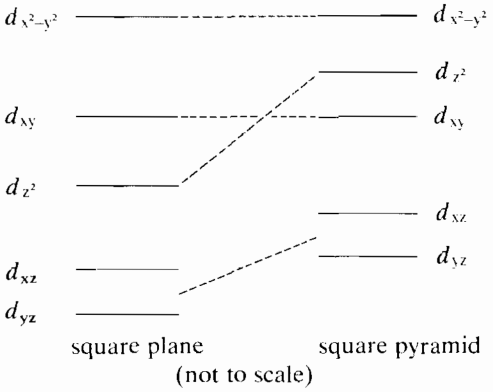
exhibits bands at 1100 cm^{-1} and 620 cm^{-1} associated with the perchlorate anions. These bands are not split, which is further evidence that the perchlorate groups are ionic and not coordinated.[24]

The tendency for multidentate ligands containing heavy donor atoms to promote pentacoordination in nickel(II) complexes is now well catalogued.[25,26] It has been noticed that the bidentate ligands with vinyl backbones, vpp[16] and vasp,[20] and the *o*-phenylene backbone, diphenyl(*o*-diphenylarsinophenyl)phosphine (ap),[8] all form square pyramidal $[NiL_2X]^+$ derivatives. However, no pentacoordinate complexes have been isolated as solids with the diphosphine containing the saturated dimethylene linkage, dpe, despite several deliberate attempts.[16,27] It was postulated that the $-CH_2CH_2-$ linkage can allow the *o*-phenyl hydrogen atoms and/or the methylene hydrogens in the gauche conformation of the $-CH_2CH_2-$ chelate ring to block the coordination sights above and below the nickel atom; however the planar



linkage of the vpp ligand leaves these sites open for coordination of an anion.[16] It was therefore somewhat surprising to find that the pentacoordinate $[Ni(pae)_2Cl]BPh_4$ formed with ease. This diamagnetic complex has a conductivity in nitromethane typical of a 1 : 1 conductor (Table I), but the energy of the visible absorption band in the solid state and in dichloromethane solution, while being similar, are rather lower than expected for a square pyramidal complex.[16,28] Figure 3 compares the spectra of $[NiL_2Cl]^+$ (L = vasp, pae) complexes, and it can be seen that the energy difference between the two bands is *ca.* 1,600 cm^{-1}.

Both the occurrence of pentacoordination with pae and the observed low-energy absorption can be justified in the following way: Molecular models of the $[Ni(pae)_2]^{2+}$ species indicate that the increased size of the arsenic atom (compared with the phosphorus in dpe) results in the hydrogen atoms on the $-CH_2CH_2-$ chain being less able to hinder the approach of an anion along the z-axis of the $[Ni(pae)_2]^{2+}$ complex. This thus explains the occurrence of pentacoordination for Ni–pae complexes and the non-occurrence in Ni–dpe complexes. However, approach of a fifth ligand to $[Ni(pae)_2]^{2+}$ is still more hindered than in the completely steric hindrance-free $[Ni(vasp)_2]^{2+}$ species. When a fifth ligand coordinates to a planar complex the energies of the orbitals may be expected to vary in the following manner:



and it can be reasoned that the orbitals most affected will be d_{z^2}, d_{xz}, d_{yz}, whereas the orbitals in the x–y plane will be least affected. Thus, in the complexes derived from bidentate ligands of the type described here the visible absorption in the planar complexes is ascribed to the transition $d_{xy} \rightarrow d_{x^2-y^2}$ and in the square pyramidal complexes to the transition of *d*-orbital character $d_{z^2} \rightarrow d_{x^2-y^2}$. It would seem, however, that in the $[Ni(pae)_2Cl]^+$ complex, because approach of the Cl^- ligand is somewhat hindered, the destabilisation of the d_{z^2} orbital does not result in the expected $d_{z^2} > d_{xy}$ energy-level order. In the $[Ni(pae)_2Cl]^+$ complex the order of energy of the *d*-orbitals is thus $d_{x^2-y^2} > d_{xy} > d_{z^2} > d_{xz}, d_{yz}$, *i.e.* the same order of levels, though in relatively different energies, as in the original planar

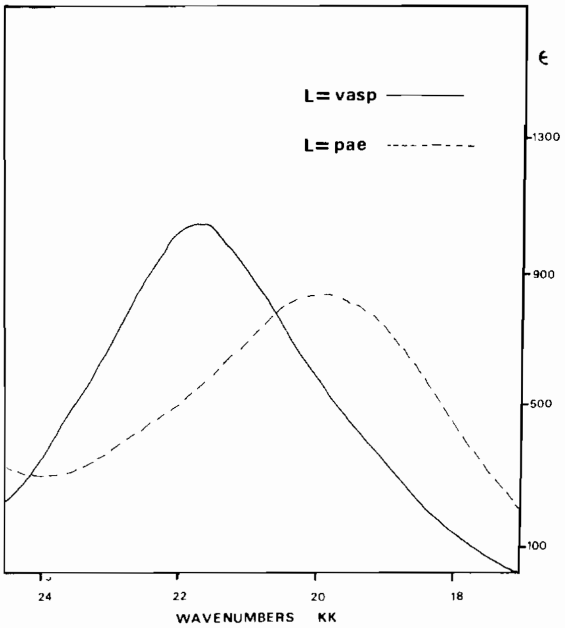


Figure 3. Electronic spectra of $[NiL_2Cl]^+$ complexes.

$[Ni(pae)_2]^{2+}$ species. Thus the transition observed in the visible absorption spectrum of $[Ni(pae)_2]^{2+}$ and of $[Ni(pae)_2Cl]^+$ corresponds to that which has the d-orbital character $d_{xy} \rightarrow d_{x^2-y^2}$, and this is why they are so similar in energy, and why the absorption for $[Ni(pae)_2Cl]^+$ is of lower energy than expected. Quite recently, Gray and Preer have confirmed[30] that the expected $d_{z^2} > d_{xy}$ order exists in the square pyramidal $[Ni(das)_2X]^+$ (das = *o*-phenylenebisdimethylarsine) complexes.

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