Four- and Five-co-ordinate Nickel(II) Complexes with *cis*-(2-Diphenylarsinovinyl)diphenylphosphine and 9,10-Bis(diphenylphosphino)phenanthrene

By **K. K. Chow, M. T. Halfpenny,** and **C. A. McAuliffe,*** Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD

The preparation and complexing properties of the new bidentate ligands *cis*-(2-diphenylarsinovinyl)diphenylphosphine, vasp, and 9,10-bis(diphenylphosphino)phenanthrene, dpph, are reported. Four-co-ordinate $[NiL_2X_2]$ (L = vasp or dpph; X = Cl, Br, I, or NCS) and $[NiL_2](ClO_4)_2$, and the square-pyramidal five-co-ordinate $[Ni(vasp)_2X]Y$ (X = Cl, Br, I, or NCS; Y = ClO_4 or BPh_4) and $[Ni(dpph)_2(NO_3)]BPh_4$ were characterised by magnetic, spectral, and conductivity measurements. The effect of chelate backbone on the complexing properties and the stereochemical and spectrochemical properties of the complexes is discussed.

BIDENTATE chelating ligands containing Group VB donor atoms have received a considerable amount of attention from inorganic chemists, but the chelate backbone or bridge has usually been either *o*-phenylene [1-5] or alkane.[6-9] In addition, the ligands 1,8-bisdimethylarsinonaphthalene [10] and 2,2′-biphenylylenebisdiethylphosphine [11] form nickel(II) complexes.

Although 1,2-bis(diphenylphosphino)ethane, dpe, does not form five-co-ordinate complexes with nickel(II) salts,[7,12] the unsaturated ligand *cis*-1,2-bis(diphenylphosphino)vinylene, vpp, was able to promote five-co-ordination.[13] Some reports of similar ligands and their complexes have appeared.[14] However, although such ligands as *cis*-1,2-bis(dimethylarsino)vinylene are obtained in small yield and are difficult to isolate,[15] the ligand reported here, *cis*-(2-diphenylarsinovinyl)diphenylphosphine, vasp, is obtainable in high yield.[16]

We have also included in this work a study of the complexing properties of the novel diphosphine 9,10-bis(diphenylphosphino)phenanthrene. It has been recently demonstrated that the intensity of visible absorptions of metal complexes of two similar tetratertiary arsines is dependent upon the amount of aryl substitution on the donor atoms, in as much as high intensities seem to be due, at least in part, to mixing of the *d*–*d* transitions with transitions of the type $\pi^* \longleftarrow \pi$ of the benzene rings.[17] It thus seemed important to us to investigate the electronic spectra of a diphosphine ligand with a highly aromatic backbone.

EXPERIMENTAL

Reagent grade tetrahydrofuran (THF) was dried by refluxing with sodium sand for several hours until the addition of benzophenone produced a deep blue colour; the tetrahydrofuran was then distilled under a dry nitrogen atmosphere. Reagent grade butanol was refluxed over barium oxide and then distilled from magnesium ribbon. Technical grade dichloromethane was refluxed over calcium chloride. Nitromethane was washed with 5% aqueous sulphuric acid and 5% aqueous sodium bicarbonate and fractionated.

cis-(2-*Diphenylarsinovinyl*)*diphenylphosphine*. A deep

---

[1] R. S. Nyholm, *J. Chem. Soc.*, 1950, 2061.

[2] R. S. Nyholm, *J. Chem. Soc.*, 1952, 2906.

[3] C. M. Harris, R. S. Nyholm, and D. J. Phillips, *J. Chem. Soc.*, 1960, 4379.

[4] J. Chatt, F. A. Hart, and H. R. Watson, *J. Chem. Soc.*, 1962, 2537.

[5] T. DuBois and D. W. Meek, *Inorg. Chem.*, 1967, **6**, 1395.

[6] W. W. Fogleman and H. B. Jonassen, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1536.

[7] G. Booth and J. Chatt, *J. Chem. Soc.*, 1965, 3238.

[8] G. R. Van Hecke and W. DeW. Horrocks, jun., *Inorg. Chem.*, 1966, **5**, 1968.

[9] L. Sacconi, I. Bertini, and F. Mani, *Inorg. Chem.*, 1968, **7**, 1417.

[10] L. Di Sipio, L. Sindellari, E. Tondello, G. de Michelis, and L. Oleari, *Co-ordination Chem. Rev.*, 1967, **2**, 129.

[11] D. W. Allen, I. T. Millar, F. G. Mann, R. M. Caradine, and J. Walker, *J. Chem. Soc.*, 1969, 1097.

[12] M. J. Hudson, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc.* (*A*), 1968, 40.

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

[14] H. N. Ramaswamy, H. B. Jonassen, and A. M. Aguiar, *Inorg. Chim. Acta*, 1967, **1**, 141.

[15] M. A. Bennet and J. D. Wild, *J. Chem. Soc.* (*A*), 1971, 536, and references therein.

[16] K. K. Chow and C. A. McAuliffe, unpublished results.

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

red solution of lithium diphenylarsenide was formed from triphenylarsine (30·6 g, 0·1 mol) and lithium rod (2·1 g, 0·3 mol) in THF (150 ml), and this was added dropwise over 2 h to *cis*-1,2-dichloroethylene (38·4 g, 0·4 mol) in THF (200 ml) at 0° under nitrogen. In order to avoid formation of the diarsine vigorous stirring was employed. As the arsenide was added immediate discolouration was observed, and finally a pale yellow solution resulted. After stirring for a further 1 h the mixture was hydrolysed with a saturated aqueous solution of ammonium chloride (70 ml). The THF layer was separated, dried over sodium sulphate for 5 h, filtered, and then the THF was removed by rotatory evaporation to yield a white solid. This white solid was recrystallised from ethanol to give white needles of *cis*-2-chlorovinyldiphenylarsine, m.p. 98°, yield 72% (Found: C, 57·7; H, 4·1. Calc. for $C_{14}H_{12}AsCl$: C, 57·9; H, 4·1%).

The *cis*-2-chlorovinyldiphenylarsine (29·4 g, 0·1 mol) was dissolved in dry THF (40 ml) in a 1 l 3-necked flask, and a THF solution (100 ml) of lithium diphenylphosphide was slowly added with stirring over 1 h. The deep red colour of the phosphide was immediately discharged. The reaction was exothermic and the solution was cooled and then hydrolysed with saturated aqueous ammonium chloride (70 ml). The THF layer was separated and dried over anhydrous sodium sulphate. After filtration the THF was removed by rotatory evaporation leaving a brown solid. Repeated crystallisations from CH_2Cl_2–EtOH afforded white needles of vasp, m.p. 105°, yield 68% (Found: C, 68·9; H, 4·8. Calc. for $C_{26}H_{22}AsP$: C, 69·9; H, 4·9%).

TABLE 1

Analytical data and physical properties of the complexes

Complex [a]	Colour	Dec. Pt. °C	Λ_M [b]	Carbon [c]		Hydrogen [c]	
[Ni(vasp)Cl_2]	Red-brown	248	12	55·9	(54·8)	4·0	(3·8)
[Ni(vasp)Br_2]	Red-brown	290	38	48·2	(47·4)	3·3	(3·3)
[Ni(vasp)I_2]	Purple	320	23	42·4	(41·4)	2·9	(2·9)
[Ni(vasp)$(NCS)_2$]	Orange-brown	230	29	54·4	(54·6)	3·6	(3·5)
[Ni$(vasp)_2$]$(ClO_4)_2$	Yellow	225	164	55·2	(54·8)	4·3	(3·8)
[Ni$(vasp)_2$Cl]ClO_4	Yellow-brown	220	85	56·9	(58·1)	4·4	(4·1)
[Ni$(vasp)_2$Br]BPh_4,CH_2Cl_2	Orange-brown	143	69	64·4	(64·9)	4·6	(4·6)
[Ni$(vasp)_2$I]BPh_4	Red-purple	110	60	67·0	(65·8)	4·9	(4·6)
[Ni$(vasp)_2$(NCS)]ClO_4,CH_2Cl_2	Orange	158	121	54·1	(54·0)	4·2	(3·9)
[Ni(dpph)Cl_2]	Orange	>310	0	67·9	(67·4)	4·5	(4·1)
[Ni(dpph)Br_2]	Dark orange	>330	24	60·5	(59·6)	4·0	(3·7)
[Ni(dpph)I_2]	Purple	305	19	52·5	(53·0)	3·6	(3·2)
[Ni(dpph)$(NCS)_2$]	Golden yellow	310	24	66·0	(66·6)	3·9	(3·8)
[Ni$(dpph)_2$]$(ClO_4)_2$	Yellow	242	129	68·0	(67·6)	4·3	(4·1)
[Ni$(dpph)_2$$(NO_3)$]$BPh_4$	Dark purple	220	94	75·0	(75·7)	5·9	(6·0)

[a] All the complexes were found to be effectively diamagnetic with small T.I.P. contributions. [b] All measurements in nitromethane (1×10^{-3} M). [c] Calculated values in parentheses.

9,10-*Bis(diphenylphosphino)phenanthrene*, dpph, was obtained in 65% yield as pale yellow crystals, m.p. 140°, from the reaction of lithium diphenylphosphide with 9,10-dichlorophenanthrene in boiling THF solution.

[Ni(vasp)X_2] (X = Cl, Br, I, *or* NCS).—The ligand (0·44 g, 1·0 mmol) 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 immediately developed. On cooling crystals were deposited. These were collected on a sintered glass funnel and recrystallised from CH_2Cl_2–EtOH (X = Br or I) or CH_2Cl_2–*n*-BuOH (X = Cl or NCS). Yields 80—85%.

[Ni$(vasp)_2$]$(ClO_4)_2$.—An ethanolic solution (20 ml) of nickel(II) perchlorate hexahydrate (0·18 g, 0·5 mmol) was added dropwise to a dichloromethane solution (20 ml) of vasp (0·44 g, 1·0 mmol). A deep red colouration was formed, but after stirring a yellow crystalline solid was deposited as the dichloromethane evaporated. Yield 68%.

[Ni$(vasp)_2$X]BPh_4 (X = Br *or* I).—To a dichloromethane solution (15 ml) of vasp (0·44 g, 1·0 mmol) was added an ethanolic solution of the appropriate nickel(II) salt (0·5 mmol), and the resulting intensely purple solution was stirred for 20 min, after which sodium tetraphenylborate (0·32 g, 1·0 mmol) in ethanol (10 ml) was added dropwise. A deep red-purple compound separated immediately. The compound was collected on a filter and redissolved in dichloromethane to remove any coprecipitated sodium salts. After addition of a small amount of ethanol the solution was set aside to crystallise. Yields 70—75%.

[Ni$(vasp)_2$X]ClO_4 (X = Cl *or* NCS).—A solution containing 1·0 mmol of ' $NiXClO_4$ ', conveniently prepared *in situ* by mixing equimolar amounts of NiX_2 and $Ni(ClO_4)_2,6H_2O$ in *n*-butanol, was treated with vasp (0·88 g, 2·0 mmol) in dichloromethane (10 ml). A solid separated from solution after standing. This was collected and recrystallised from CH_2Cl_2–EtOH. Yields *ca.* 70%.

[Ni(dpph)X_2] (X = Cl, Br, I, *or* NCS) *and* [Ni$(dpph)_2$]$(ClO_4)_2$.—Complexes were prepared by the same procedures used for the vasp complexes. Yields *ca.* 68%.

[Ni(dpph)(NO_3)]BPh_4.—An ethanolic solution (15 ml) of $Ni(NO_3)_2,6H_2O$ (0·145 g, 0·5 mmol) was added slowly to a solution of dpph (0·54 g, 1·0 mmol) in dichloromethane (10 ml). A deep purple colour developed immediately, and after addition of sodium tetraphenylborate (0·32 g, 1·0 mmol) in ethanol (15 ml) a dark purple solid separated instantly. The mixture was stirred for 20 min, filtered, and after collection, crystallised from CH_2Cl_2–EtOH. Yield 77%.

Physical Measurements.—Conductivities were measured on a Cambridge Instruments Ltd. conductivity bridge. I.r. spectra were measured in Nujol or hexachlorobutadiene mulls on a Perkin-Elmer 621 spectrophotometer, and electronic spectra on a Beckmann DK2 spectrophotometer (for reflectance spectra $BaSO_4$ was used as a dilutant).

RESULTS AND DISCUSSION

The [Ni(vasp)X_2] (X = Cl, Br, I, or NCS) complexes were all synthesised by mixing equimolar quantities of the appropriate nickel(II) salt with vasp in refluxing ethanol. The perchlorate, $[Ni(vasp)_2](ClO_4)_2$, was readily prepared, but all attempts to prepare a complex from nickel nitrate, *i.e.* $[Ni(vasp)(NO_3)_2]$ or $[Ni(vasp)_2](NO_3)_2$, were unsuccessful. This is quite an interesting phenomenon, especially in view of the fact that both the perchlorate and nitrate salts of $[Ni(vpp)_2]^{2+}$ have been isolated.[14] It is also interesting to note that no nickel(II) complexes could be isolated from reactions of the analogous diarsine, although Sacconi *et al.*, have isolated complexes of 1,2-bis(diphenylarsino)ethane.[9] Obviously, the chelate backbone does exert some significant effect on the complexing properties of these ligands.

The $[Ni(vasp)_2X]^+$ derivatives were also found to split into two groups as regards preparation; for X = Cl or NCS the method of Dubois and Meek [5] was used, but this did not yield pure complexes for X = Br or I, and for these derivatives the method of McAuliffe and Meek was found to be appropriate.[13]

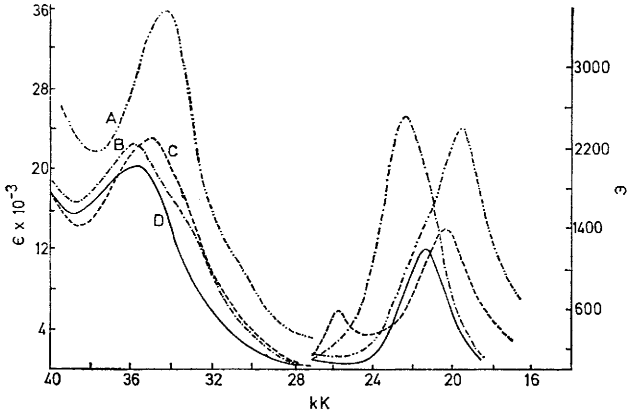

FIGURE 1 Electronic spectra of the vasp complexes $[Ni(vasp)X_2]$ in solution in dichloroethane; A, X = I; B, X = NCS; C, X = Br; D, X = Cl

The four-co-ordinate $[Ni(dpph)X_2]$ complexes were prepared by mixing the metal salt and the ligand in 1 : 1 ratio in ethanol. The only derivative of the type $[Ni(dpph)_2X]^+$ which could be isolated was $[Ni(dpph)(NO_3)]BPh_4$; no halogeno-complexes were obtainable, attempts always producing the $[Ni(dpph)X_2]$ compounds.

The $[Ni(vasp)X_2]$ complexes exhibit significant conductances in nitromethane solution (Table 1) but these values are still small compared with those expected for 1 : 1 electrolytes,[18] and so ionisation in this solvent is not complete. The visible spectra (Figure 1, Table 2) in the solid state and in dichloroethane solution are fairly similar, indicating similar structures in these two physical states. Except for the bromo-complex the spectra of these four-co-ordinate compounds exhibit one symmetrical absorption band in the visible region. The $[Ni(vasp)Br_2]$ complex has, in addition, a second peak at 25,600 cm⁻¹. This band would seem to have some special significance for complexes of the type $[Ni(bidentate)Br_2]$, because the visible spectra of both $[Ni(vpp)Br_2]$ and $[Ni(dpe)Br_2]$ [dpe = 1,2-bis(diphenylphosphino)ethane] also exhibit this second absorption.[13] The shift to higher energy of the maxima of the main visible band in the $[Ni(vasp)X_2]$ spectra follow the order NCS > Cl > Br > I, *i.e.* they follow the usual spectrochemical series. Moreover, when the spectra of the $[NiLX_2]$ (L = vpp or vasp) are compared it is found that the vpp complexes absorb at higher energy than do the vasp complexes, indicating a P > As spectrochemical series. It has recently been shown that for monodentate LR_3 (L = P, As, or Sb) ligands the order of ligand field strength is P > As > Sb,[19] whereas for a series of trigonal bipyramidal nickel(II) complexes containing quadridentate ligands this series did not obtain for the apical donor because of compression of the apical donor onto the nickel atom.[20] Our present results would seem to confirm that for ' uncompressed ' donors the P > As order is to be expected. Some significant i.r. spectral bands are listed in Table 3, and the absorptions due to the NCS^- groups indicate that

TABLE 2

Visible and u.v. spectra of the complexes

	Electronic spectra	
Complex	Solution [a]	Solid
$[Ni(vasp)Cl_2]$	35·7 (20,100)	
	32·5 (sh)	
	21·3 (1200)	20·6
$[Ni(vasp)Br_2]$	35·2 (22,600)	
	25·6 (590)	25·7
	20·3 (1400)	20·0
$[Ni(vasp)I_2]$	34·5 (35,000)	
	31·0 (sh)	
	27·5 (sh)	
	19·4 (2300)	19·3
$[Ni(vasp)(NCS)_2]$	36·0 (22,400)	
	22·3 (2500)	22·4
$[Ni(vasp)_2](ClO_4)_2$	33·0 (18,400)	
	27·0	26·4
	20·5 (sh)	
$[Ni(vasp)_2Cl]ClO_4$	37·9 (sh)	
	21·57 (1030)	21·7
$[Ni(vasp)_2Br]BPh_4,CH_2Cl_2$	38·8 (sh)	
	21·0 (1220)	21·3
$[Ni(vasp)_2I]BPh_4$	33·5 (16,466)	
	19·2 (1029)	19·5
$[Ni(vasp)_2(NCS)]ClO_4,CH_2Cl_2$	22·9 (3482)	23·1
$[Ni(dpph)Cl_2]$	35·8 (44,000)	
	27·6 (2100)	26·9
	21·8 (1750)	21·8
$[Ni(dpph)Br_2]$	35·3 (35,000)	
	27·5 (2400)	27·1
	21·0 (1550)	21·1
$[Ni(dpph)I_2]$	34·7 (29,500)	
	19·0 (1650)	18·9
$[Ni(dpph)(NCS)_2]$	35·8 (sh)	
	33·2 (sh)	
	27·2 (2900)	
	23·0 (2750)	22·7
$[Ni(dpph)_2](ClO_4)_2$		28·1
$[Ni(dpph)_2(NO_3)]BPh_4$	23·0 (sh)	
	32·0 (36,330)	

[a] In 1,2-dichloroethane; extinction coefficients in parentheses.

---

[18] W. J. Geary, *Co-ordination Chem. Rev.*, 1971, **7**, 81.

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

[20] B. R. Higginson, C. A. McAuliffe, and L. M. Venanzi, *Inorg. Chim. Acta*, 1971, **5**, 37; C. A. McAuliffe, D.Phil. Thesis, Oxford, 1967.

bonding is through the nitrogen atoms, a conclusion confirmed by the high energy of the visible absorption bands as compared to the halide complexes. From the i.r. spectra (Table 3) it can also be seen that the ν(C=C) is shifted very slightly to lower energy upon complexation of the ligand, but the frequencies of other ligand vibrations do not seem to follow any such regular pattern.

TABLE 3

Some characteristic i.r. absorptions of the vinylic ligand and its complexes [a]

Compound	(C=C)	Olefinic C–H in-plane def.	Olefinic C–H out-of-plane def.	Asym. C–H def.	Other bands
vasp	1585s	1060 1155w	1000vs	1430vs 1480vs	
$[Ni(vasp)Cl_2]$	1570w	1100vs	995vs	1433vs 1480vs	
$[Ni(vasp)Br_2]$	1570w	1098vs	998vs	1430vs 1478s	
$[Ni(vasp)I_2]$	1578w	1095m	995m	1430s 1480s	
$[Ni(vasp)(NCS)_2]$	1580w	1100vs	995s	1435vs 1481s	2085s ν(CN) 848 ν(CS) 500w δ(NCS)
$[Ni(vasp)_2](ClO_4)_2$	1580w		998s	1438s 1480s	1090vs ν(ClO_4) asym. 612w δ(ClO_4) asym.
$[Ni(vasp)_2Cl]ClO_4$	1565w		997s	1435vs 1480s	1090vs ν(ClO_4) asym. 615w δ(ClO_4) asym.
$[Ni(vasp)_2Br]BPh_4$	1578w	1100m	1000s	1435s 1480m	
$[Ni(vasp)_2I]BPh_4$	1578w	1098m	1000s	1440s 1483s	
$[Ni(vasp)_2(NCS)]ClO_4$	1577w	1097m	998s	1438s 1480s	2080s ν(CN) 830m ν(CS) 1095vs ν(ClO_4) asym. 620w δ(ClO_4) asym.

[a] In Nujol and hexachlorobutadiene mulls.

The $[Ni(vasp)_2](ClO_4)_2$ complex behaves as a typical 1 : 2 electrolyte in nitromethane, and the solid state i.r. spectrum of this complex shows no evidence of perchlorate co-ordination. In contrast to the $[Ni(vpp)_2](ClO_4)_2$ which is claimed to have a magnetic moment intermediate between values expected for a diamagnetic and paramagnetic species,[14] the vasp complex is effectively diamagnetic with a paramagnetic contribution from T.I.P.

All the $[Ni(vasp)_2X]^+$ complexes are diamagnetic and 1 : 1 complexes in nitromethane (except for the NCS complex, for which the Λ_M value is almost that of a 1 : 2 electrolyte, Table 1), and so it is reasonable to assign five-co-ordination to the nickel(II) ion in these species. Since the electronic spectra (Figure 3, Table 2) are so similar in both the solid state and in solution, then five-co-ordinate cations are present in the solid state also. The visible spectra exhibit absorptions *ca.* 20,000 cm^{-1} which are in the range for known square pyramidal complexes.[13,21] Thus, this band may be assigned to the transition of *d*-orbital character $d_{z^2} \longrightarrow d_{x^2-y^2}$. The i.r. spectrum of $[Ni(vasp)_2(NCS)]ClO_4,CH_2Cl_2$ in Nujol contains a broad absorption at 2080 cm^{-1}, ν(C≡N), as well as a ν(C–S) absorption at 830 cm^{-1}, indicating isothiocyanate co-ordination,[22] and the position of the isothiocyanato-complex in the ligand field strength of the X ligands in $[Ni(vasp)_2X]^+$ (NCS > Cl > Br > I) confirms this assignment.

The dpph ligand formed three types of diamagnetic complex which, by much the same reasoning as used above for the vasp derivatives, can be described as the four-co-ordinate square planar $[Ni(dpph)X_2]$ (X = Cl, Br, I, or CNS), the square planar $[Ni(dpph)_2](ClO_4)_2$, and the five-co-ordinate square pyramidal $[Ni(dpph)(NO_3)]BPh_4$. All attempts to prepare five-co-ordinate complexes containing co-ordinated halides were unsuccessful, in marked contrast to the situation we encountered in the vasp and vpp complexes.

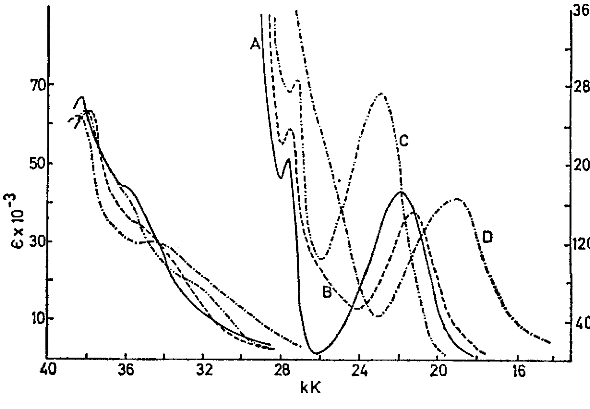

FIGURE 2 Electronic spectra of the $[Ni(dpph)X_2]$ complexes in dichloroethane; A, X = Cl; B, X = Br; C, X = NCS; D, X = I

The electronic spectra of the $[Ni(dpph)X_2]$ complexes (Table 2, Figure 2) are typical of diamagnetic, square planar species. The high position of the isothiocyanato-complex in the observed spectrochemical series once

---

[21] C. Furlani, *Co-ordination Chem. Rev.*, 1968, **3**, 141.

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

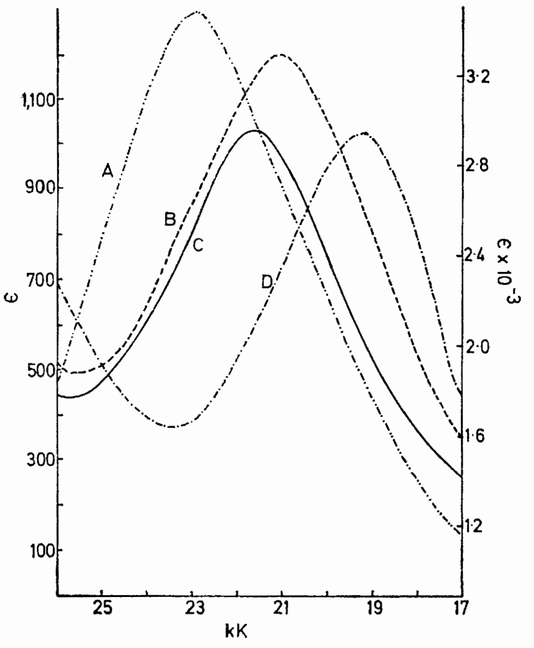

FIGURE 3 Electronic spectra of the $[Ni(vasp)_2X]^+$ complexes; A, X = NCS; B, X = Br; C, X = Cl; D, X = I; A is referred to the right-hand scale the others to the left

again is indicative of –NCS bonding. The ν(C≡N) vibrations consist of two bands of unequal intensity; a sharp band at 2100 and a broad band at 2080 cm^{-1}.

When the intensities of the bands in the visible spectra of the dpph complexes (Table 2, Figure 2) are compared with those of analogous vpp and dpe complexes [13] it is seen that there has been no marked increase in intensity as the amount of aromatic substitution of the phosphines is increased from (vinyl)PPh_2 and (alkyl)PPh_2 to (phenanthrene)PPh_2. This, however, does not disprove the suggestion that high extinction coefficients in complexes of this type are derived from $\pi^* \leftarrow \pi$ transitions on the benzene ring, but rather suggests that the amount of ' borrowing ' of intensity from electronic transitions on the aromatic substituents reaches a maximum before full aromatic substitution is reached, *i.e.* no increase in intensity results on changing (alkyl)PPh_2 to (aryl)PPh_2 donors.

K. K. C. is grateful to the British Council for a Fees Award; M. T. H. acknowledges the receipt of an S.R.C. Postdoctoral Fellowship; and we are grateful to Dr. D. J. Machin for the use of the Beckmann DK2 spectrophotometer.

[2/508 *Received, 6th March,* 1972]