

SECTION A

Inorganic, Physical, and Theoretical Chemistry

Complexes of Mixed Phosphorus–Nitrogen Ligands. Part II.¹ Some Complexes of Cobalt(II) and Nickel(II) with Three *o*-Dimethylamino-phenylphosphines

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The ligands *o*-Me₂N·C₆H₄PPh₂, (*o*-Me₂N·C₆H₄)₂PPh, and (*o*-Me₂N·C₆H₄)₃P (abbreviated, respectively, to PN, PDN, and PTN) form high-spin cobalt(II) complexes of the type [CoX₂(ligand)] (X = Cl, Br, and I) which have pseudo-tetrahedral structures, in which one phosphorus and only one of the nitrogen atoms are bonded to the cobalt atom. The following structural assignments have been made for the high-spin nickel complexes of these ligands: (1) [NiX₂(PN)] (X = Cl and Br) are pseudo-tetrahedral in dichloromethane solution and are pentaco-ordinate dimeric, with bridging halogen atoms, in the solid state; (2) [Ni₂(PN)] is pseudo-tetrahedral both in the solid state and in dichloromethane solution; (3) [NiX₂(ligand)] (X = Cl and Br; ligand = PDN and PTN) are pentaco-ordinate dimeric, with bridging halogen atoms, in the solid state and, in dichloromethane solution, they are likely to occur as mixtures of tetrahedral and pentaco-ordinate species with one phosphorus and two nitrogen atoms bonded to the nickel atom; (4) [Ni₂(ligand)] (ligand = PDN and PTN) is pseudo-tetrahedral in dichloromethane solution with one phosphorus and one nitrogen atom co-ordinated to the nickel atom and, in the solid state, there appears to be a mixture of tetrahedral and pentaco-ordinate species.

In Part I,¹ we reported that ligands *o*-dimethylamino-phenyldiphenylphosphine, PN, *o*-Me₂N·C₆H₄PPh₂; bis-(*o*-dimethylaminophenyl)phenylphosphine, PDN, (*o*-Me₂N·C₆H₄)₂PPh, and tris-(*o*-dimethylaminophenyl)-phosphine, PTN, (*o*-Me₂N·C₆H₄)₃P give complexes with palladium(II) and platinum(II) of the type [MX₂(ligand)] and that, in all cases, only the phosphorus and *one* nitrogen atom are co-ordinated to the metal atom. We report here the preparation of complexes of the above ligands with cobalt(II) and nickel(II).

All the complexes, of the type [MX₂(ligand)], were prepared by adding one equivalent of the inorganic salt to the ligand in a suitable solvent. Most of the nickel complexes were microcrystalline and sparingly soluble. The complexes and some of their physical properties are listed in Table 1.

The co-ordination number and stereochemistry of the complexes can be established only indirectly from the physical measurements carried out. The main structures which will be considered are the tetrahedral and the pentaco-ordinate trigonal bipyramidal or square pyramidal. All these structures would show marked departure from regularity because of the stereochemical requirements of the ligands.

Cobalt Complexes.—Complexes [CoX₂(ligand)] (X = Cl, Br, and I; ligand = PN, PDN, and PTN) are assigned tetrahedral structure *both in solution and in the solid state* mainly on the basis of their visible and ultraviolet spectra (Table 2) which are very similar to those of tetrahedral [CoX₂(Ph₃P)₂] (see Figure 1),² both sets of compounds showing the same distribution of bands which, in the case of the triphenylphosphine complexes, are shifted towards lower energy. Following the assignment

of Cotton *et al.*^{2b} for [CoX₂(Ph₃P)₂] we assign bands in the region 14,000–18,000 cm.⁻¹ to transitions corresponding to ⁴A₂ → ⁴T₁(P) in T_d symmetry and bands

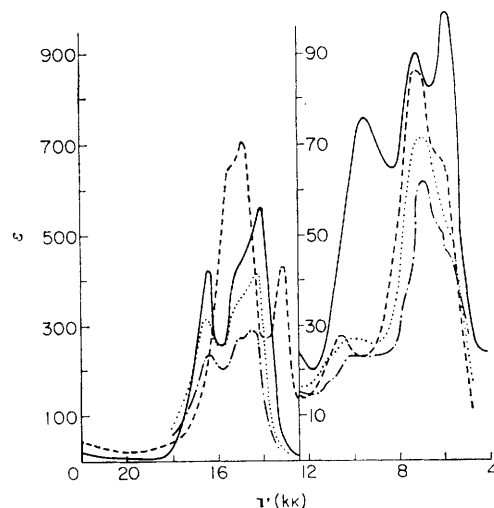


FIGURE 1 Visible and ultraviolet spectra of some cobalt(II) complexes in dichloromethane

— [CoBr₂(Ph₃P)₂]
 - - - [CoBr₂(PN)]
 . . . [CoBr₂(PDN)]
 - . - [CoBr₂(PTN)]

in the region 5000–11,000 cm.⁻¹ to transitions ⁴A₂ → ⁴T₁(F) in T_d symmetry.

In complexes of ligands PDN and PTN we postulate that the co-ordination polyhedron is made up of the two halide ions, one phosphorus atom, and *one* nitrogen atom.

¹ Part I, H. P. Fritz, I. R. Gordon, K. E. Schwarzahns, and L. M. Venanzi, *J. Chem. Soc.*, 1965, 5210.

² (a) M. C. Browning, R. F. B. Davies, D. J. Morgan, L. E. Sutton, and L. M. Venanzi, *J. Chem. Soc.*, 1961, 4816; (b) F. A. Cotton, O. D. Faut, D. M. L. Goodgame, and R. H. Holm, *J. Amer. Chem. Soc.*, 1961, **83**, 1780.

Evidence for this assignment is: (a) the conductivities in acetone indicate that they are non-electrolytes (the values observed in nitromethane solution are probably due to solvolysis of the type previously observed);³ (b) the molecular weights in chloroform indicate the presence of monomers (see Experimental section); (c) the far-infrared spectra of the complexes show two bands attributable to Co-X stretching vibrations, analogous to those found in $[\text{CoX}_2(\text{Ph}_3\text{P})_2]$ ⁴ (see Tables 3

PTN) are sufficiently similar to exclude a different co-ordination environment (Figure 1 and Table 2).

The magnetic moments of the cobalt complexes, which range from $\mu_{\text{eff.}} = 4.46\text{--}4.93$ B.M., are comparable with those of complexes $[\text{CoX}_2(\text{Ph}_3\text{P})_2]$ ^{2b} ($\mu_{\text{eff.}} = 4.51\text{--}4.73$ B.M.) and are indicative of intermediate quenching.

Nickel Complexes.—The magnetic moments of all the nickel complexes range from $\mu_{\text{eff.}} = 3.17\text{--}3.28$ B.M.

TABLE 1
Cobalt(II) and nickel(II) complexes with mixed phosphorus-nitrogen ligands

No.	Compound	Colour	Decomp. pt.	Λ_M^a		$\mu_{\text{eff.}}^b$	Yield (%)
				(c)	(d)		
1	$[\text{CoCl}_2(\text{PN})]$	Royal blue	254—255°	19	4	4.46	50
2	$[\text{CoBr}_2(\text{PN})]$	Royal blue	219—220	24	3	4.46	78
3	$[\text{CoI}_2(\text{PN})]$	Green	226—227	27	7	4.64	60
4	$[\text{CoCl}_2(\text{PDN})]$	Royal blue	210—211	32	5*	4.67	58
5	$[\text{CoBr}_2(\text{PDN})]$	Blue-green	192—193	26		4.60	42
6	$[\text{CoI}_2(\text{PDN})]$	Green	233—234	54	54	4.93	65
7	$[\text{CoCl}_2(\text{PTN})]$	Royal blue	196—197	8	16*	4.71	88
8	$[\text{CoBr}_2(\text{PTN})]$	Blue	182—183	40	19*	4.74	68
9	$[\text{CoI}_2(\text{PTN})]$	Dark brown	179—180	57	21	4.87	65
10	$[\text{NiCl}_2(\text{PN})]$	Brown	245—246	13	ins.	3.28	89
11	$[\text{NiBr}_2(\text{PN})]$	Dark brown	238—239	19	5	3.24	77
12	$[\text{NiI}_2(\text{PN})]$	Black	208—209	78	33	3.22	48
13	$[\text{NiCl}_2(\text{PDN})]$	Olive green	238—239	28*	ins.	3.20	51
14	$[\text{NiBr}_2(\text{PDN})]$	Brown	255—256	29*	3	3.25	73
15	$[\text{NiI}_2(\text{PDN})]$	Black	209—210	56	14	3.25	32
16	$[\text{NiCl}_2(\text{PTN})]$	Pale green	253—254	ins.	ins.	3.17	quant.
17	$[\text{NiBr}_2(\text{PTN})]$	Ochre	238—239	ins.	ins.	3.23	quant.
18	$[\text{NiI}_2(\text{PTN})]$	Maroon	211—212	11	55	3.25	53

No.	C (%)		H (%)		N (%)		P (%)		Metal (%)		M	
	Found	Reqd.	Found	Reqd.	Found	Reqd.	Found	Reqd.	Found	Reqd.	Found	Reqd.
1	55.0	55.2	4.5	4.6	3.3	3.2	7.0	7.1	13.5	13.5	—	—
2	45.6	45.8	3.9	3.9	2.8	2.7	6.0	5.9	11.1	11.2	525	524
3	39.5	38.9	3.4	3.3	2.9	2.3	4.9	5.0	9.4	9.5	—	—
4	55.1	55.2	5.2	5.3	6.0	5.9	6.5	6.5	12.3	12.3	—	—
5	46.4	46.6	4.5	4.4	4.9	4.9	5.5	5.5	10.5	10.4	553	567
6	40.0	40.0	3.6	3.8	5.6	4.2	4.5	4.7	9.1	8.9	—	—
7	54.5	55.3	5.8	5.8	8.1	8.1	6.0	5.9	11.4	11.3	—	—
8	47.5	47.2	5.4	5.0	6.6	6.9	5.0	5.1	9.7	9.7	614	610
9	40.7	40.9	4.3	4.3	6.4	6.0	4.4	4.4	8.3	8.4	—	—
10	54.4	55.2	4.6	4.6	3.1	3.2	7.1	7.1	13.3	13.5	—	—
11	46.0	45.9	4.2	3.9	2.8	2.7	5.8	5.9	11.2	11.2	—	—
12	38.9	38.9	3.5	3.3	2.1	2.3	5.0	5.0	9.6	9.5	591	618
13	55.0	55.3	5.5	5.3	5.7	5.9	6.7	6.5	12.2	12.3	—	—
14	46.8	46.6	4.6	4.4	4.8	4.9	5.5	5.5	10.3	10.4	551	567
15	40.1	40.0	4.0	3.8	4.6	4.2	4.7	4.7	8.9	8.9	669	661
16	56.1	55.3	6.3	5.8	8.5	8.1	5.8	5.9	11.2	11.3	—	—
17	48.2	47.3	5.1	5.0	6.8	6.9	5.1	5.1	9.4	9.6	—	—
18	40.8	40.9	4.3	4.3	6.3	6.0	4.4	4.4	8.5	8.3	708	704

^a In mhos, for 10^{-3}M solutions at 20°. ^b In B.M. ^c In nitromethane solution. ^d In acetone solution. ^e Heating was required to obtain solutions of these complexes and this is likely to have caused some solvolysis.

and 4); (d) complexes $[\text{CoX}_2(\text{ligand})]$ (ligand = PDN and PTN) show bands in the region 2750—2800 cm^{-1} (Table 5) which are diagnostic of unco-ordinated dimethyl-amino-groups,⁵ which are absent from complexes $[\text{CoX}_2(\text{PN})]$; and (e) the spectra of any one set of complexes, e.g., $[\text{CoCl}_2(\text{ligand})]$ (ligand = PN, PDN, and

and are similar to those of complexes $[\text{NiX}_2(\text{Ph}_3\text{P})_2]$ ($\mu_{\text{eff.}} = 3.27\text{--}3.41$ B.M.),⁶ which are pseudo-tetrahedral,⁷ and to those of $[\text{NiX}_2\{\text{MeN}(\text{CH}_2\text{CH}_2\text{NMe}_2)\}]$ ($\mu_{\text{eff.}} = 3.38$ B.M.), which are pentaco-ordinate.⁸

The conductivities of the complexes in acetone are close to those expected for non-electrolytes. Those in nitromethane solution are intermediate between those of non-electrolytes and 1:1-electrolytes. These

³ D. M. L. Goodgame and L. M. Venanzi, *J. Chem. Soc.*, 1963, 616.

⁴ R. E. Christopher and L. M. Venanzi, unpublished observations.

⁵ (a) G. C. Meakins and R. D. Hill, *J. Chem. Soc.*, 1958, 760; (b) J. T. Braunholtz, E. A. V. Ebsworth, F. G. Mann, and N. Sheppard *J. Chem. Soc.*, 1958, 2780.

⁶ F. A. Cotton, O. D. Faut, and D. M. L. Goodgame, *J. Amer. Chem. Soc.*, 1961, **83**, 344.

⁷ G. Garton, D. E. Henn, H. M. Powell, and L. M. Venanzi, *J. Chem. Soc.*, 1963, 3625.

⁸ M. Ciampolini and G. P. Speroni, *Inorg. Chem.*, 1966, **5**, 45.

TABLE 2

Visible and ultraviolet spectra of cobalt and nickel complexes with mixed phosphorus-nitrogen ligands

Dichloromethane soln.				Solid		Dichloromethane soln.				Solid															
Complex	$E_{\max.}$ (cm^{-1})	$\epsilon_{\max.}$	$E_{\max.}$ (cm^{-1})	'A' α	Complex	$E_{\max.}$ (cm^{-1})	$\epsilon_{\max.}$	$E_{\max.}$ (cm^{-1})	'A' α																
[CoCl ₂ (PN)]	6300	64	6000	0.30	[CoCl ₂ (PTN)]	32,000 ^b	(3500) ^c	5500	0.28																
	7600	70	7800	0.28		36,000 ^b	(5000) ^c																		
	10,600	20	11,400	0.23		5800 ^b	(44) ^c																		
	14,400	462	14,500	0.53		7000	53																		
	15,400	300	17,000	0.72 ^d		10,000	24			9000	0.25														
	17,400	357										26,000 ^b	(0.90) ^e												
	[CoBr ₂ (PN)]	36,500 ^b	(7000) ^c	35,000		1.3	14,600			250	12,200	0.15													
		37,400 ^b	(8000) ^c	38,000 ^b		(1.5) ^e	15,400			221	14,700	0.28													
		6000 ^b	(64) ^c	6700		0.52	[CoBr ₂ (PTN)]			17,100	206	16,600	0.52												
		7300	86	7600		0.60						17,400	0.53												
10,600		28	10,600	0.35	21,000 ^b	(0.03) ^c																			
14,200		561	14,200	1.14	26,000 ^b	(0.50) ^c																			
14,800 ^b		(462) ^c	15,300	1.03	28,000 ^b	(0.75) ^c																			
16,600		426	16,600	1.07	[CoI ₂ (PN)]	30,000 ^b		(1000) ^c	38,000			1.1 ^d													
22,000 ^b		(800) ^c	20,000 ^b	(0.20) ^e									34,000 ^b	(6500) ^c											
			25,000 ^b	(1.0) ^e									5800 ^b	(45) ^c	5400	0.28									
34,000 ^b	(5000) ^c	35,000 ^b	1.3 ^d	7000									61	8500	0.28										
38,100 ^b	(8000) ^c	38,000 ^b	(1.5) ^e	10,000 ^b									(23) ^c	12,000	0.18										
6000 ^b	(68) ^c	6000 ^b	(0.38) ^e	14,500			284			14,100	0.30														
7000	103	7200	0.41	15,100			270			[CoI ₂ (PTN)]	16,200 ^b		(0.08) ^c												
10,200	39	10,400	0.26	16,400			230							17,100	0.65										
13,700	553	13,600	0.95	[CoI ₂ (PDN)]			26,600 ^b							(900) ^c	21,000 ^b	(0.09) ^c									
14,200	554	14,100	1.02												26,000 ^b	(0.65) ^c									
15,400	528	15,200	0.92		29,000 ^b	(1.1) ^c																			
22,800	1560	18,000 ^b	(0.36) ^e		32,400 ^b	(2000) ^c		[NiCl ₂ (PN)]	5000 ^b			(0.23) ^c													
		22,600	1.15		34,000 ^b	(5500) ^c									8800	0.42									
29,400 ^b	(2600) ^c	27,500 ^b	(1.07) ^e		5000 ^b	(40) ^c									5000 ^b	(0.50) ^c									
34,600 ^b	(6300) ^c	36,000	1.2 ^d		6500	75									6800	0.63									
36,400 ^b	(7800) ^c				8800	41									9600	0.42									
[CoCl ₂ (PDN)]	6000 ^b	(42) ^c	5400		0.20	13,000 ^b				(390) ^c	13,500 ^b		(1.0) ^c												
	7200	61	8200		0.17	13,700				441	14,400		1.14												
	10,700 ^b	(19) ^c		14,500		370	15,500			1.07															
	14,600	327	11,400	0.17	22,000 ^b	(1000) ^c	23,000 ^b			(1.0) ^c															
	15,400	328	15,800	0.48	[NiCl ₂ (PDN)]	28,000 ^b	(3000) ^c			26,000 ^b	(1.1) ^c														
	17,400	230	17,300	0.44				37,000 ^b	(1.2) ^c																
	[CoBr ₂ (PDN)]	30,000 ^b	(1000) ^c	18,400 ^b				(0.40) ^e	[NiBr ₂ (PN)]	8200 ^b	(52) ^c	5000 ^b	(0.23) ^c												
				26,000 ^b				(0.60) ^e						9800	(63) ^c	8800	0.42								
		35,600 ^b	(7000) ^c	38,000				1.2 ^d						11,000	80	12,500	0.43								
		37,500 ^b	(8500) ^c											19,700	184	19,000 ^b	(0.37) ^c								
5800 ^b		(50) ^c	5300	0.24				[NiBr ₂ (PDN)]						37,600	8600 ^c	21,300	0.60								
7100		71	7900	0.22												26,500	1.40								
10,200		27	11,100	0.24												28,000 ^b	(2000) ^c	[CoI ₂ (PDN)]	12,200	0.46					
14,300		417														30,400	2400								
15,000 ^b		(360) ^c	15,400	0.61	36,600 ^b	(8000) ^c	[CoI ₂ (PDN)]									17,000 ^b	(0.33) ^c								
16,500		313	16,500	0.61	37,600	8600 ^c															20,500	0.61			
27,000 ^b	(1000) ^c	27,000 ^b	(0.93) ^c	[NiBr ₂ (PDN)]	8200 ^b	(50) ^c			25,000 ^b	(1.4) ^c															
29,000 ^b	(2000) ^c	29,000 ^b	(1.1) ^c						8700	0.42															
33,700 ^b	(5500) ^c	36,000	1.3 ^d						10,800	126	[CoI ₂ (PDN)]	12,200	0.46												
37,600 ^b	(8000) ^c								9600 ^b	(83) ^c											15,000 ^b	(25) ^c			
[CoI ₂ (PDN)]	6000	56	4600					0.25	[NiBr ₂ (PDN)]	10,800				126	12,200						0.46				
			7200					48														6500	0.39	15,000 ^b	(25) ^c
	13,300	300	8000 ^b					(0.33) ^c										[NiBr ₂ (PDN)]	19,000	205		17,000 ^b	(0.33) ^c		
			13,800 ^b					(0.41) ^c																27,200	2700
	14,700	484	16,000				0.70	31,800 ^b								(6000) ^c	[CoI ₂ (PDN)]							25,000 ^b	(1.4) ^c
	15,400 ^b	(318) ^c	22,500 ^b				(0.67) ^c	35,400 ^b								(6100) ^c									
	23,000 ^b	(800) ^c	27,000	1.0 ^d	36,900 ^b	(6300) ^c	[CoI ₂ (PDN)]	37,500								1.6 ^d									
	26,800	2100	27,000	1.0 ^d	37,600	6600 ^c																			

TABLE 2 (Continued)

Dichloromethane soln.				Solid		Dichloromethane soln.				Solid	
Complex	$E_{\max.}$ (cm. ⁻¹)	$\epsilon_{\max.}$	$E_{\max.}$ (cm. ⁻¹)	'A' ^a	Complex	$E_{\max.}$ (cm. ⁻¹)	$\epsilon_{\max.}$	$E_{\max.}$ (cm. ⁻¹)	'A' ^a		
[NiI ₂ (PN)]			5200	0.31				11,300	0.48		
			7600 ^b	(0.35) ^c				13,600	0.42		
	8000 ^b	(54) ^c				21,000 ^b	(1000) ^c	21,600	1.4		
	10,400	224	10,400	0.69				23,000 ^b	(1.5)		
			13,600	0.40		24,500 ^b	(3000) ^c	29,000 ^b	(1.6) ^c		
	14,000 ^b	(110) ^c				29,800	3800	36,000	(1.7) ^d		
			16,000 ^b	(0.60) ^e		34,400 ^b	(4000) ^c				
			17,000 ^b	(0.80) ^e							
			18,000 ^b	(1.0) ^e							
			20,000 ^b	(1.4) ^e	[NiCl ₂ (PTN)]	Insoluble		9100	0.49		
[NiCl ₂ (PDN)]	20,500	2130	23,000	1.6				13,600	0.47		
	23,900	2900						18,600 ^b	(0.24) ^e		
	29,400	3700						22,000	0.48		
	33,700 ^b	(7000) ^c						28,400	1.3		
	36,800 ^b	(8000) ^c						36,400	3.6		
	8400	57			[NiBr ₂ (PTN)]	8200	63	8800	0.39		
			9000	0.52		11,300	84				
	11,400	52 ^c				13,000 ^b	(57) ^c	13,400	0.40		
	13,000 ^b	(50) ^c	13,400	0.46				18,400 ^b	(0.24) ^e		
	19,300	140	19,000 ^b	(0.32) ^e		20,300 ^b	(135) ^c	21,500	0.47		
[NiBr ₂ (PDN)]			22,000	0.50		25,000 ^b	(800) ^c	27,400	1.1		
			29,000 ^b	(1.0) ^e							
	30,000 ^b	(4000) ^c				29,000 ^b	(7000) ^c				
	34,200 ^b	(8000) ^c				34,000 ^b	(8000) ^c				
	36,000	9350	36,400 ^b	(1.7) ^e				36,000	1.4		
	8500 ^b	(64) ^c	8700	0.42		37,600	8500				
	11,000	83									
	13,000 ^b	(56) ^c	13,000	0.41							
	19,600 ^b	(200) ^c	19,000 ^b	(0.36) ^e	[NiI ₂ (PTN)]	8000 ^b	(72) ^c	8400	0.49		
			21,400	0.50		11,000	152	11,600	0.53		
[NiI ₂ (PDN)]	28,000 ^b	(3000) ^c	28,000 ^b	(1.08) ^e				13,500 ^b	(0.47) ^e		
			29,200 ^b	(1.09) ^e				20,000 ^b	(1.2) ^e		
	32,000 ^b	(7000) ^c				21,000 ^b	(2000) ^c	23,400	1.3		
	35,000 ^b	(8000) ^c				24,300	3050				
	36,700 ^b	(9000) ^c	36,000	1.4 ^d		29,900	4100	29,000 ^b	(1.7) ^e		
	8000 ^b	(70) ^c	8000	0.42		34,000 ^b	(8000) ^c	38,000	1.8 ^d		
	10,600	165									

^a Arbitrary absorbance scale. ^b Shoulder; frequency at the inflection-point. ^c Shoulder; band height at the inflection-point. ^d Broad absorption band. ^e Shoulder, absorbance at the inflection-point.

TABLE 3

Far-infrared spectra of mixed phosphorus-nitrogen ligands and their cobalt(II) and nickel(II) complexes in Nujol mulls ^a

PN	139w, 180sh, 206sh, 211m, 220w, 249m, 260w, 287vw, 302vw, 334m, 367m, 394s, 402sh
[CoCl ₂ (PN)]	104m, 121m, 134w, 190m, 202sh, 216m, 222m, 237s, 250sh, 261sh, 275m, 309vs, 323sh, 350vs, 390m, 400sh
[CoBr ₂ (PN)] ...	148w, 188m, 200m, 212w, 234m, 256s, 265sh, 280s, 321w, 340vw, 392m
[CoI ₂ (PN)]	120w, 140sh, 166m, 178m, 198m, 223s, 240s, 260sh, 323w, 366m, 386m
[NiCl ₂ (PN)]	110w, 135sh, 150m, 195m, 215m, 227w, 239sh, 253m, 264sh, 299s, 311sh, 350w, 391m, 401m
[NiBr ₂ (PN)]	120w, 153m, 160m, 179m, 193m, 210m, 227s, 249m, 260sh, 268sh, 280sh
[NiI ₂ (PN)]	126m, 140w, 169m, 185m, 201m, 223s, 239s, 254m, 262sh, 280vw, 325w
PDN	108w, 121w, 214m, 222sh, 254m, 268m, 291w, 347m, 360m, 396m, 405sh, 411s, 432m, 444w
[CoCl ₂ (PDN)] ...	115m, 129m, 172m, 190sh, 213m, 250sh, 265s, 305s, 325sh, 346sh, 354sh, 369m, 390m, 418s, 432m, 440s
[CoBr ₂ (PDN)] ...	106w, 122sh, 151m, 190m, 222sh, 242s, 270w, 281sh, 318sh, 348w, 370m, 390m, 417s, 429m, 442s
[CoI ₂ (PDN)] ...	174w, 210sh, 225sh, 235s, 250sh, 263w, 275m, 285w, 320w, 347vw, 375m, 401w, 416m, 435s, 442s
[NiCl ₂ (PDN)] ...	96m, 128m, 149sh, 164s, 177sh, 201m, 217m, 233m, 245sh, 278s, 315s, 326sh, 392m
[NiBr ₂ (PDN)] ...	105m, 123sh, 130sh, 140s, 157s, 177m, 201s, 219s, 236sh, 254vs, 265vs, 327m, 393m
[NiI ₂ (PDN)] ^b ...	95m, 114m, 152m, 178sh, 175—192m, 202s, 217s, 244s, 257sh, 284m, 330w, 395m
PTN	130m, 143w, 150w, 175sh, 200sh, 215sh, 234m, 265w, 285sh, 301w, 333sh, 344m, 356s, 379s
[CoCl ₂ (PTN)] ...	98s, 110m, 123s, 136m, 159w, 165w, 180w, 205sh, 213m, 234m, 288vs, 330sh, ^c 337vs, ^c 369m, 386m, 391sh
[CoBr ₂ (PTN)] ...	100s, 105sh, 123w, 130w, 160sh, 169m, 188m, 212s, 230sh, 241s, 270s, 285sh, 334w, 355sh, 368m, 387m, 394sh
[CoI ₂ (PTN)] ...	110sh, 140s, 175sh, 205s, 235vs, 290w, 328w, 345w, 371m, 392m
[NiCl ₂ (PTN)] ...	105m, 123m, 143m, 158s, 169s, 200vw, 216m, 233sh, 241m, 279sh, 284s, 321vs, 332sh, 370m, 389m, 392m
[NiBr ₂ (PTN)] ...	95w, 110m, 125m, 143m, 164sh, 170s, 196m, 211m, 233sh, 249s, 273s, 285sh, 334m, 368m, 389m, 394m
[NiI ₂ (PTN)] ^b ...	115w, 144w, 166sh, 180m, 209m, 216w, 235s, 247sh, 259m, 270sh, 288sh, 335m, 366m, 371m, 390m, 400m

vw = Very weak, w = weak, m = medium, s = strong, vs = very strong; sh = shoulder.

^a Bands in italics below 150 cm.⁻¹ are assigned to Cl—Co—Cl bending modes; those in italics above 150 cm.⁻¹ are assigned to metal-halogen stretching modes. ^b No nickel-iodine mode can be assigned in these complexes; the spectra are very much more complicated in the 200—280 cm.⁻¹ region than for the cobalt analogues. See text. ^c Probably a Fermi doublet arising from the interaction between the higher-frequency cobalt-chlorine stretching mode and the weak ligand band at ca. 330 cm.⁻¹.

high values are probably due to solvolysis as indicated by the time-dependence of the conductivity which is accompanied by changes of colour of the solutions.

Molecular-weight determinations, in chloroform, could be carried out for $[\text{NiI}_2(\text{ligand})]$ (ligand = PN, PDN, and PTN) and for $[\text{NiBr}_2(\text{PDN})]$ and gave values close to those calculated on the basis for a monomeric structure (see Experimental section).

Bidentate ligand, PN. Complexes $[\text{NiX}_2(\text{PN})]$ ($\text{X} = \text{Cl}, \text{Br}, \text{and I}$) are assigned tetrahedral structure in dichloromethane solution on the basis of the similarity of their spectra (see Table 2 and Figure 2) with those of the pseudo-tetrahedral complexes $[\text{NiX}_2(\text{Ph}_3\text{P})_2]$,⁶ the latter being shifted towards lower energy. Assignment of absorption bands in our complexes can be made by analogy with those of triphenylphosphine:⁶ thus bands at *ca.* 10,000–11,000 and at *ca.* 19,000–20,000 cm^{-1} are assigned to transitions ${}^3T_1(F) \rightarrow {}^3A_2(F)$ (ν_2) and to ${}^3T_1 \rightarrow {}^3T_1(P)$ (ν_3), respectively. The shoulders on the low-energy side of the ν_2 band, by analogy with those found by Goodgame and Goodgame⁹ in a variety of pseudo-tetrahedral nickel(II) complexes, may be due to components of the ν_1 transition. The infrared

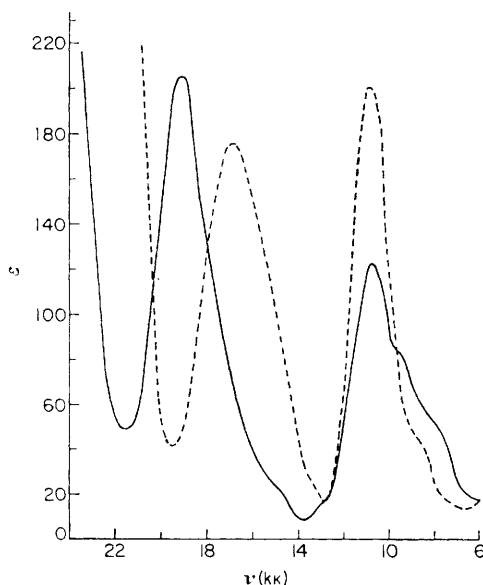


FIGURE 2 Visible and ultraviolet spectra of some nickel(II) complexes in dichloromethane

----- $[\text{NiBr}_2(\text{Ph}_3\text{P})_2]$
 ————— $[\text{NiBr}_2(\text{PN})]$

spectra of solutions of our complexes, obtained in several solvents, show the expected symmetric and anti-symmetric nickel-halogen stretches and are similar to those observed in the corresponding cobalt complexes (see Table 3).

Tetrahedral structure is also assigned to $[\text{NiI}_2(\text{PN})]$ in the solid state as its reflectance spectrum is very similar to that of the compound in dichloromethane solution and to that of pseudo-tetrahedral $[\text{NiI}_2(\text{Ph}_3\text{P})_2]$ (see Table 2 and Figure 3).⁷ In agreement with this the

infrared spectrum in the region 150–400 cm^{-1} is very similar to that of the corresponding cobalt complex (Tables 4 and 5).

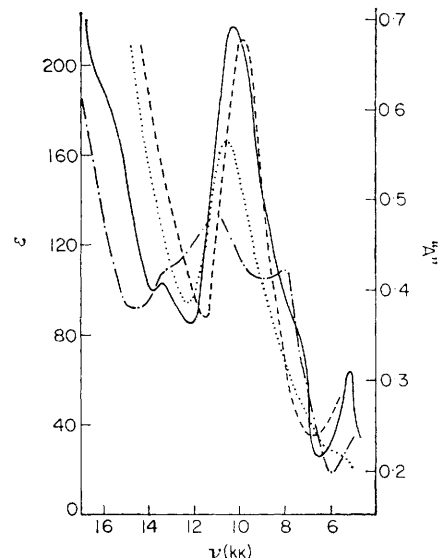


FIGURE 3 Visible and ultraviolet spectra of some nickel(II) iodo-complexes

----- $[\text{NiI}_2(\text{Ph}_3\text{P})_2]$ (in diffuse reflectance)
 ————— $[\text{NiI}_2(\text{PN})]$ (in diffuse reflectance)
 - · - · - $[\text{NiI}_2(\text{PDN})]$ (in diffuse reflectance)
 $[\text{NiI}_2(\text{PDN})]$ (in dichloromethane solution)

On the other hand, complexes $[\text{NiX}_2(\text{PN})]$ ($\text{X} = \text{Cl}$ and Br) in the solid state appear to be pentaco-ordinate as their reflectance spectra are dissimilar from those of

TABLE 4

Metal-halogen stretching vibrations in cobalt(II) and nickel(II) complexes with mixed phosphorus-nitrogen ligands in solution

Compound	Frequencies (cm^{-1})		
	<i>cis</i> -1,2-Dichloro-ethylene	Dichloro-methane	Dibromo-methane
$[\text{CoCl}_2(\text{PN})]$	361, 324	361, 322	^a
$[\text{CoBr}_2(\text{PN})]$	286, 253	^b	285, 254
$[\text{CoCl}_2(\text{PDN})]$	355, ^c 320	354, 315sh ^d	^a
$[\text{CoBr}_2(\text{PDN})]$	282, ^c	^b	^a
$[\text{NiCl}_2(\text{PN})]$	354, ^c 306	351, ^b	352, ^b
$[\text{NiBr}_2(\text{PN})]$	280, ^c 253 ^c	^b 256	275, ^b

^a Not recorded. ^b The M-X stretch or stretches are masked by strong solvent absorption in this region. ^c Coincident with a solvent band of medium intensity but seen as a band of increased intensity. ^d Visible as a shoulder on the side of a very strong solvent band.

their dichloromethane solutions and similar to those of pentaco-ordinate $[\text{NiX}_2\{\text{MeN}(\text{CH}_2\text{CH}_2\text{NMe}_2)_2\}]$ ⁸ and $[\text{NiX}\{\text{N}(\text{CH}_2\text{CH}_2\text{NMe}_2)_3\}]^+$ ¹⁰ (Figure 4). The infrared spectra of Nujol mulls of our complexes differ from those of their cobalt analogues in that there is only one halogen-sensitive band in the region of terminal metal-halogen stretches and one, or more, new bands appear at lower

⁹ D. M. L. Goodgame and M. Goodgame, *Inorg. Chem.*, 1965, **4**, 139.

¹⁰ M. Ciampolini and N. Nardi, *Inorg. Chem.*, 1966, **5**, 41.

TABLE 5
Characteristic infrared bands of 'free' dimethylamino-groups

Compound	Frequencies (cm. ⁻¹)	
	Mull ^a	Solution ^b
'Free' ligands ^c	2800	2800
[CoX ₃ (PN)] ^e	<i>f</i>	<i>f</i>
[CoCl ₃ (PDN)]	2815, 2800	2805
[CoBr ₃ (PDN)]	<i>d</i>	<i>d</i>
[CoI ₃ (PDN)]	<i>d</i>	<i>d</i>
[CoCl ₃ (PTN)]	2820, 2810	2805
[CoBr ₃ (PTN)]	2820, 2810	2810
[CoI ₃ (PTN)]	2820, 2815sh	2810
[NiX ₃ (PN)] ^e	<i>f</i>	<i>f</i>
[NiCl ₃ (PDN)]	2800, 2790	<i>g</i>
[NiBr ₃ (PDN)]	2820, 2810	2795
[NiI ₃ (PDN)]	2800, 2790	2795
[NiCl ₃ (PTN)]	2820, 2805	<i>g</i>
[NiBr ₃ (PTN)]	2815, 2800	<i>g</i>
[NiI ₃ (PTN)]	2815, 2800	2795

^a In hexachlorobutadiene. ^b In chloroform. The complexes in which 'free' dimethylamino-groups are present show a single band in solution although a split band is present in the solid state. This splitting is likely to be due to lattice interactions. ^c PN, PDN, and PTN. ^d Not recorded. ^e X = Cl, Br, and I. ^f Absent. ^g Insoluble in chloroform.

frequencies which could be due to bridging metal-halogen vibrations (Table 3).

Terdentate ligand, PDN and quadridentate ligand, PTN. Complexes [NiX₂(ligand)] (X = Cl and Br and ligand = PDN and PTN), *in the solid state*, are assigned pentaco-ordinate structures on the basis of similarity of their solid reflectance spectra (Table 2 and Figures 4 and 5) with those of the corresponding complexes with the bidentate ligand PN and with MeN(CH₂·CH₂·NMe₂)₂.

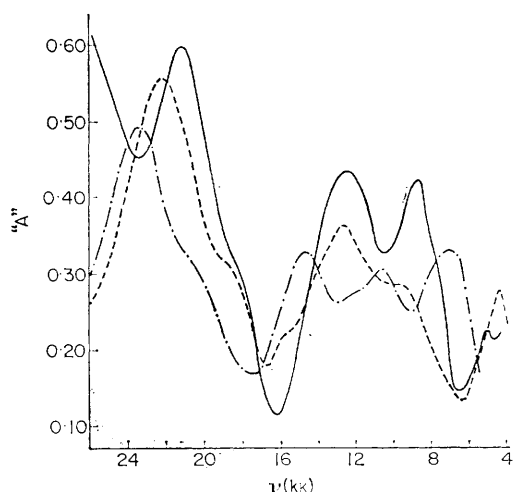


FIGURE 4 Diffuse reflectance spectra of some pentaco-ordinate nickel(II) complexes

— [NiCl₂(PN)]
 - - - [NiCl₂(MeN(CH₂·CH₂·NMe₂)₂)]
 - · - [NiCl₂(N(CH₂·CH₂·NMe₂)₃)Cl]

Pentaco-ordination in the PDN and PTN complexes could be achieved either by ligation of one phosphorus and two nitrogen atoms of the organic ligand as well as the two halogen atoms, or by dimerisation as found in complexes of the bidentate ligand PN, *i.e.*, through one

nitrogen and one phosphorus atom and one terminal and two bridging halogen atoms. Infrared evidence (Table 5) indicates the presence of an unco-ordinated -NMe₂ group in the complexes of the terdentate ligand PDN,

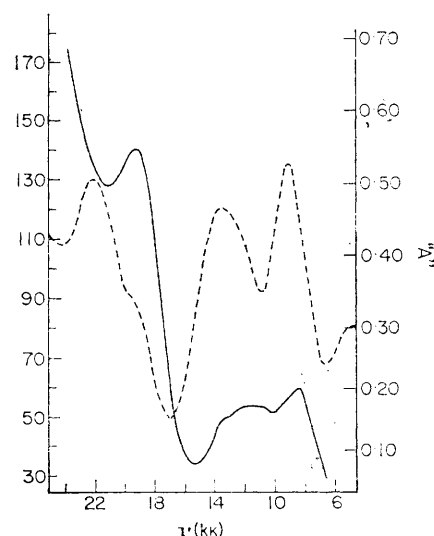


FIGURE 5 Visible and ultraviolet spectra of some nickel(II) complexes [NiCl₂(PDN)]

— Solution spectrum
 - - - Diffuse reflectance spectrum

and, therefore it is concluded that in the PDN and, presumably also in the PTN complexes, pentaco-ordination is achieved by dimerisation. This conclusion is supported by the infrared spectra of the complexes in the region 150–400 cm.⁻¹. Like the PN analogues, comparison of cobalt and nickel complexes shows that in the latter there is only one halogen-sensitive band in the region of terminal metal-halogen stretches and one or more new bands appear in the metal-halogen bridging range of frequencies (Tables 3 and 4).

The structures of PDN and PTN complexes *in dichloromethane solution* are more difficult to establish. The complexes which were sufficiently soluble in chloroform proved to be monomeric and, as the visible and ultraviolet spectra of the complexes in the two solvents are identical, we assume that the complexes are monomeric also in dichloromethane. These spectra (Table 2 and Figure 5) differ from those of the corresponding solids, which are pentaco-ordinate and dimeric, and from the solution spectra of the corresponding PN complexes which are tetrahedral in this medium. We tentatively suggest that complexes [NiX₂(ligand)] (X = Cl and Br; ligand = PDN and PTN) in dichloromethane are present as a mixture of tetrahedral and pentaco-ordinate forms. In the latter the donor atoms would be one phosphorus atom, two nitrogen, and two halogen atoms.

Finally, complexes [NiI₂(ligand)] (ligand = PDN and PTN) *in dichloromethane* appear to be tetrahedral as indicated by their visible and ultraviolet spectra (Figure 3) while in *the solid state* the complexity of the electronic

spectra suggest that they are mixtures of tetrahedral and pentaco-ordinate species (Figure 3). This is supported by their far-infrared spectra which are more complex than those of the corresponding cobalt compounds (Table 3).

In conclusion, ligands containing more than one aryl-dimethylamino-group tend to co-ordinate with only one such donor group to cobalt(II) and nickel(II) as found for complexes of palladium(II) and platinum(II),¹ and it is likely that this behaviour is due to deactivation of the dimethylamino-nitrogen atoms, which are known to be weak donors, by electron withdrawal, induced by co-ordination of the two bound donor atoms, and transmitted through the aromatic system. It is noteworthy that the tendency towards pentaco-ordination shown by the nickel(II) complexes is fulfilled preferentially by use of bridging halogen atoms, and it appears that the combined steric and electronic effects give the following relative sequence of donor power towards nickel: bridging chloro-ligand > bridging bromo-ligand > aryl-dimethylamino-ligand > bridging iodo-ligand.

EXPERIMENTAL

The organic ligands were prepared as described elsewhere.¹ Solutions of nickel iodide were prepared by mixing solutions

¹¹ G. Dyer, J. G. Hartley, and L. M. Venanzi, *J. Chem. Soc.*, 1965, 1293.

of nickel nitrate hexahydrate (1 mol.) and sodium iodide (2.2 mol.) in n-butanol, and filtering off the precipitated sodium nitrate.

The nickel complexes were prepared by mixing stoichiometric amounts of the hydrated salt in hot n-butanol (or the appropriate solution, prepared as described above) and the ligand in hot n-butanol and filtering off the *product* which separated out and proved to be analytically pure.

The cobalt chloro- and bromo-complexes were prepared like their nickel analogues using ethanol as a solvent and were recrystallised from ethanol. The iodo-complexes were prepared in n-butanol and proved to be analytically pure.

Analyses.—Nickel,¹¹ cobalt,¹² and phosphorus¹¹ were determined spectrophotometrically.

Physical Measurements.—Conductivity and magnetic measurements were as described elsewhere.¹³ Visible and ultraviolet spectra of dichloromethane solutions were taken on a Unicam SP 700 spectrophotometer and the diffuse reflectance spectra on a Unicam SP 735 attachment with the SP 700 spectrophotometer. Infrared spectra in the region 650—4000 cm.⁻¹ were recorded on a Perkin-Elmer 337 spectrophotometer and in the region 90—650 using a Beckman I.R.11 spectrophotometer. Molecular weights were determined in chloroform solution on a Mechrolab osmometer model 301 A.

We thank the S.R.C. for a studentship (to I. R. G.).

[7/785 Received, June 27th, 1967]

¹² M. McNaught, *Analyst*, 1941, **67**, 97.

¹³ J. P. Day and L. M. Venanzi, *J. Chem. Soc. (A)*, 1966, 1363.