Contribution from Centro di Studio sulla Stabilità e Reattività dei Composti di Coordinazione,
C.N.R.—Istituto di Chimica Analitica, University of Padua, 35100 Padua, Italy

Cyanide Complexes of Nickel(II) with Hybrid Bidentate Ligands Containing Phosphorus and Nitrogen or Sulfur Donor Atoms

P. RIGO* and M. BRESSAN

Received September 19, 1974 AIC406580

Nickel cyanide complexes of the types $[Ni(CN)_2(ligand)_2]$ and $[Ni(CN)_2(ligand)_3]$ derived from the four hybrid bidentate ligands 1-(2'-pyridyl)-2-(diphenylphosphino)ethane, 1-(thiomethyl)-2-(diphenylphosphino)ethane, 1-(thioethyl)-2-(diphenylphosphino)ethane, and 1-(thiophenyl)-2-(diphenylphosphino)ethane are described. The complexes $[Ni(CN)_2(ligand)_2]$ can be four- or five-coordinate. In the first case the bidentate ligands act as monodentate groups by bonding only through phosphorus donor atoms, whereas in the five-coordinate complexes both mono- and bidentate types of coordination of the ligands are involved. The complexes $[Ni(CN)_2(ligand)_2]$ in solution can react with an excess of ligand to give five-coordinate species of the type $[Ni(CN)_2(ligand)_3]$, in which only the phosphorus end of the ligand is bonded to the metal atom. The coordination number and stereochemistry of the complexes have been established on the basis of spectroscopic, conductivity, and molecular weight measurements. With the ligands containing phosphorus and sulfur, five-coordinate cationic complexes of formula $[Ni(CN)(ligand)_2]^+$ are also obtained, for which, on the basis of the visible spectra, a square-pyramidal structure is proposed.

Introduction

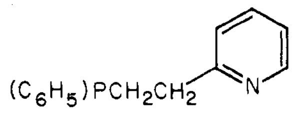
The cyanide group is particularly able in promoting five-coordination in nickel(II)–phosphino complexes. Thus, with secondary and tertiary phosphines, $[Ni(CN)_2(P)_3]$ complexes (P = phosphine) are easily formed, while the corresponding halogeno–tris(phosphine) adducts $[NiX_2(P)_3]$ (X = halogen) always prove to be much more unstable toward dissociation into $[NiX_2(P)_2]$ species.[1,2]

The tendency of the cyanide ion to stabilize $[Ni(CN)_2(P)_3]$ moieties is also apparent in the chemistry of di(tertiary phosphine) complexes. With the diphosphine 1,2-bis(diphenylphosphino)ethane (dpe) only the four-coordinate $[Ni(CN)_2(dpe)]$ has been isolated, but this complex in solution can add one dpe molecule to give the five-coordinate $[Ni(CN)_2(dpe)_2]$, which has a dangling phosphino group.[3] With $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$ (n = 3, 4) and $(CH_3)_2P(CH_2)_3P(CH_3)_2$ the complexes $[Ni(CN)_2(diphos)_{1.5}]_2$ have been obtained. A binuclear five-coordinate structure $[(diphos)(CN)_2Ni(diphos)Ni(CN)_2(diphos)]$ has been suggested, in which one diphosphine molecule bridges two different nickel atoms.[3,4]

In view of the unusual coordination mode of di(tertiary phosphines) observed in these nickel(II) cyanide complexes, it seemed interesting to determine the types of compounds formed by hybrid bidentate ligands containing one phosphorus and one nitrogen or sulfur donor atom.

In this paper we describe four- and five-coordinate complexes of the types $[Ni(CN)_2(ligand)_2]$ and $[Ni(CN)_2(ligand)_3]$, in which the bidentate ligands act as monodentate groups by utilizing only the phosphorus donor atom, five-coordinate $[Ni(CN)_2(ligand)_2]$, in which both mono- and bidentate coordinations of the ligands are involved, and five-coordinate cationic complexes of the type $[Ni(CN)(ligand)_2]^+$.

The ligands used are 1-(2'-pyridyl)-2-(diphenylphosphino)ethane (P-Py), 1-(thiomethyl)-2-(diphenylphosphino)ethane (P-SMe), 1-(thioethyl)-2-(diphenylphosphino)ethane (P-SEt), and 1-(thiophenyl)-2-(diphenylphosphino)ethane (P-SPh).



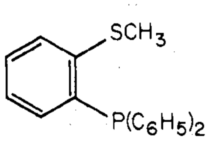
P-Py

$(C_6H_5)_2PCH_2CH_2SR$

R = CH_3, P-SMe
R = C_2H_5, P-SEt
R = C_6H_5, P-SPh

The reactions of the ligands P-Py with nickel salts have been previously studied by Uhlig and Maaser,[5] who reported the preparation of tetrahedral complexes $[NiX_2(P\text{-}Py)]$ (X = Cl, Br), square-planar $[Ni(NCS)_2(P\text{-}Py)]$ and $[Ni(P\text{-}Py)_2](ClO_4)_2$, and distorted octahedral $[NiI_2(P\text{-}Py)_2]$.

Complexes of nickel(II) with bidentate ligands containing phosphorus and sulfur donor atoms are also well-known. Meek and coworkers[6] prepared four-, five-, and six-coordinate complexes of the type $[NiX_2(SP)]$, $[NiX(SP)_2]ClO_4$, and $[NiX_2(SP)_2]$ (X = halogen, SP = diphenyl(*o*-methylthiophenyl)phosphine).



SP

$(C_2H_5)_2PCH_2CH_2S(C_2H_5)$

DPES

With the ligand 1-(thioethyl)-2-(diethylphosphino)ethane (DPES) Sieckhaus and Layloff[7] obtained square-planar $[Ni(DPES)_2](ClO_4)_2$ and five-coordinate $[NiX(DPES)_2]ClO_4$ (X = halogen). The thiocyanate complex $[Ni(NCS)_2(DPES)_2]$ is reported to exist in two isomeric forms, a diamagnetic four-coordinate species, in which DPES acts as a monodentate ligand bonding only through phosphorus, and a paramagnetic octahedral form, in which DPES is bidentate.

The nickel halide complexes with the ligands P-SR, examined in this work, are very similar to the halide adducts with SP and DPES and therefore they will be here only briefly mentioned.

Experimental Section

Starting Materials. All materials were of reagent grade quality. The solvents were purified by standard methods.

The ligand 1-(2'-pyridyl)-2-(diphenylphosphino)ethane was prepared following the method of Uhlig and Maaser.[5]

The ligands $(C_6H_5)_2P(CH_2)_2SR$ (R = CH_3, C_2H_5, C_6H_5) were prepared by addition of the appropriate chloro derivative $RS(CH_2)_2Cl$ to sodium diphenylphosphide in liquid ammonia. In a typical reaction 23 g of Na was dissolved in 1500 ml of liquid ammonia and 131 g of triphenylphosphine was added under vigorous stirring. After 1 hr 49 g of NH_4Br was added; the mixture was allowed to stir for 30 min and then $RS(CH_2)_2Cl$ was added dropwise until the red-orange color was discharged (ca. 0.5 mol). After stirring for 30 min the Dry Ice bath was removed and the liquid ammonia was allowed to evaporate. The remaining white solids were washed with water and recrystallized from CH_2Cl_2–methanol.

Anal. Calcd for $(C_6H_5)_2P(CH_2)_2SCH_3$ (mp 58°): C, 69.28; H, 6.60; S, 12.37. Found: C, 69.05; H, 6.88; S, 12.42. Calcd for $(C_6H_5)_2P(CH_2)_2SC_2H_5$ (mp 44°): C, 70.04; H, 6.98; S, 12.00. Found: C, 71.02; H, 7.08; S, 11.69. Calcd for $(C_6H_5)_2P(CH_2)_2SC_6H_5$ (mp 89°): C, 74.51; H, 5.94; S, 9.94. Found: C, 74.06; H, 5.93; S, 9.94.

Table I. Properties and Analytical Data of the Nickel(II) Complexes[a]

Compd	Color	Mp,[b] °C	Λ_M,[c] cm²/(ohm mol)	% C		% H		% N		% halogen	
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$[Ni(CN)_2(P\text{-}Py)_2]$	Yellow	197–198	1.0	69.23	69.08	5.14	5.26	8.07	8.00		
$[Ni(P\text{-}SPh)_2](ClO_4)_2$	Yellow	248–250	158	52.24	53.24	4.35	4.30			7.77	7.86
$[Ni(CN)(P\text{-}SPh)_2]ClO_4$	Red	199–200	23	59.42	59.12	4.59	4.63	1.69	1.71		
$[Ni(P\text{-}SEt)_2](ClO_4)_2$	Yellow	246–247	178	47.66	47.38	4.75	4.76				
$[Ni(Cl)_2(P\text{-}SEt)_2]$	Green	148–149	10.2	56.66	56.51	5.65	5.60			10.50	10.98
$[Ni(Br)_2(P\text{-}SEt)_2]$	Green	158–160	4.8	50.09	49.38	4.99	4.94			20.08	21.04
$[NiCl(P\text{-}SEt)_2]BPh_4$	Purple	85–86	27	69.91	68.88	6.07	6.01				
$[NiBr(P\text{-}SEt)_2]BPh_4$	Purple	139–140	27	66.82	65.41	5.80	5.75				
$[NiI(P\text{-}SEt)_2]BPh_4$	Purple	134–135	27	63.84	60.80	5.12	5.29			12.04	11.98
$[Ni(CN)(P\text{-}SEt)_2]ClO_4$	Red	192–193	22	54.08	54.76	5.10	5.07	1.91	1.98		
$[Ni(CN)_2(P\text{-}SEt)_2]$	Yellow	159–160	0.9	61.92	63.08	5.80	5.71	4.21	4.15		
$[Ni(P\text{-}SMe)_2](ClO_4)_2$	Yellow	265	176	46.38	46.61	4.40	4.44				
$[NiCl(P\text{-}SMe)_2]BPh_4$	Purple	66–68	26	69.36	70.07	5.82	5.97				
$[NiBr(P\text{-}SMe)_2]BPh_4$	Purple	86–88	28	66.35	66.19	5.56	5.77				
$[NiI(P\text{-}SMe)_2]BPh_4$	Purple	112–114	30	63.31	63.10	5.31	5.22				
$[Ni(CN)(P\text{-}SMe)_2]ClO_4$	Red	167–168	22	52.87	52.54	4.80	5.04	1.98	1.85		
$[Ni(CN)_2(P\text{-}SMe)_2]$	Orange	173–174	0.8	60.87	61.29	5.42	5.23	4.43	4.44		

[a] All of these complexes are diamagnetic except $Ni(Cl)_2(P\text{-}SEt)_2$ and $Ni(Br)_2(P\text{-}SEt)_2$ which leave $\mu_{eff} = 3.01$ and 2.97 BM, respectively. [b] All melting points are uncorrected. [c] Molar conductance of 10^{-3} *M* solutions in 1,2-dichloroethane, except for the diperchlorate complexes, which were determined in nitromethane.

Table II. Infrared and Visible Spectral Data of the Nickel(II) Complexes

Compd	ν_{CN},[a] cm⁻¹	λ_{max}, cm⁻¹ (ϵ_{max})[b]
$[Ni(CN)(P\text{-}SPh)_2]ClO_4$	2115	25,650 (2150), 20,000 (220)
$[Ni(CN)(P\text{-}SEt)_2]ClO_4$	2115	26,000 (1870), 20,000 (230)
$[Ni(CN)(P\text{-}SMe)_2]ClO_4$	2110	26,300 (1620), 20,000 (210)
$[Ni(CN)_2(P\text{-}SPh)_2]$	2105	27,800 (1570)
$[Ni(CN)_2(P\text{-}SEt)_2]$	2100	27,900 (1720), 22,000 (660) 28,500[c]
$[Ni(CN)_2(P\text{-}SMe)_2]$	2095	27,400 (1690), 22,500 (650)
$[Ni(CN)_2(P\text{-}Py)_2]$	2105	27,800 (1320)
$[Ni(CN)_2(PPh_2Et)_2]$	2105	27,800 (1365)

[a] In Nujol mulls. [b] In 1,2-dichloroethane solution, unless otherwise stated. Molar absorptivities in parentheses. [c] Solid-state spectra.

Preparation of Complexes. Some properties and analytical data are reported in Tables I and II.

$[Ni(P\text{-}SPh)_2](ClO_4)_2$. To 1 g of $Ni(ClO_4)_2 \cdot 6H_2O$ in 25 ml of tetrahydrofuran was added 2.5 g of ligand P-SPh in 25 ml of benzene. The yellow crystals obtained by evaporating the tetrahydrofuran were recrystallized from a benzene–tetrahydrofuran mixture.

$[Ni(P\text{-}SR)_2](ClO_4)_2$ (R = CH_3, C_2H_5). The ligand (2 mmol), dissolved in dichloromethane (10 ml), was added to a cold ethanolic solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (1 mmol in 25 ml). The yellow precipitate obtained was recrystallized from dichloromethane–ethanol.

$[NiX_2(P\text{-}SEt)_2]$ (X = Cl, Br). The ligand (6 mmol) dissolved in dichloromethane was added to a boiling solution of the appropriate nickel(II) salt (3 mmol) in 2-propanol. The resulting deep red solution was allowed to cool to room temperature to deposit green crystals, which were recrystallized from dichloromethane-2-propanol.

$[NiX(P\text{-}SR)_2]B(C_6H_5)_4$ (X = Cl, Br, I; R = CH_3, C_2H_5). Stoichiometric amounts (1 mmol) of nickel nitrate hexahydrate, sodium tetraphenylborate, and NaX were mixed in 25 ml of 2-propanol and sodium nitrate was filtered off. The ligand (2 mmol) in 10 ml of dichloromethane was added. The resulting deep red solution was warmed briefly and on cooling gave purple crystals, which were recrystallized from dichloromethane–2-propanol.

$[Ni(CN)_2(P\text{-}Py)_2]$. A suspension of $[Ni(P\text{-}Py)_2](ClO_4)_2$ (2 mmol) in 25 ml of ethanol was treated with KCN (4 mmol). The mixture was stirred and refluxed for 30 min and then cooled to room temperature. The $KClO_4$ was removed by filtration and a yellow crystalline precipitate was obtained by evaporating the solution to near dryness and adding ethyl ether. The complex was recrystallized from dichloromethane–ethanol.

$[Ni(CN)(P\text{-}SPh)_2]ClO_4$. A suspension of $[Ni(P\text{-}SPh)_2](ClO_4)_2$ (2 mmol) and NaCN (2 mmol) was stirred at room temperature for 24 hr. The red precipitate obtained was recrystallized from dichloromethane–ethanol.

$[Ni(CN)(P\text{-}SR)_2]ClO_4$ (R = CH_3, C_2H_5). $[Ni(P\text{-}SR)_2](ClO_4)_2$ (2 mmol) and KCN (2 mmol) were refluxed for 30 min in 25 ml of ethanol. The hot solution was filtered and, on cooling, red crystals were obtained, which were recrystallized from dichloromethane–benzene.

$[Ni(CN)_2(P\text{-}SPh)_2]$. $[Ni(P\text{-}SPh)_2](ClO_4)_2$ (2 mmol) dissolved in 25 ml of 1:1 ethanol–dichloromethane and NaCN (4 mmol) were refluxed for 30 min. By concentrating and cooling, yellow crystals precipitated from the solution, which were recrystallized from dichloromethane–methanol.

$[Ni(CN)_2(P\text{-}SR)_2]$ (R = CH_3, C_2H_5). $[Ni(P\text{-}SR)_2](ClO_4)_2$ (2 mmol) and NaCN (4 mmol) were refluxed in ethanol (25 ml) for 30 min. The solution was evaporated to dryness and the residue extracted with benzene. From the benzene solution yellow or orange crystals were obtained, by adding *n*-hexane. These products were purified from benzene–*n*-hexane.

Microanalyses and Physical Measurements. Microanalyses were performed by Mr. L. Turiaco, Istituto di Chimica Analitica, University of Padua. Infrared spectra were recorded on a Perkin-Elmer 450 instrument. Visible spectra were determined on an Optica CF4R spectrophotometer. Molecular weights were determined using a Mechrolab osmometer at 37°. Conductance data were obtained using a LKB Model 3216B conductance bridge. Magnetic susceptibilities were obtained by standard Gouy method.

Results and Discussion

Each of the four "hybrid" bidentate ligands reacts with nickel(II) perchlorate to produce yellow diamagnetic compounds of the composition $[Ni(ligand)_2](ClO_4)_2$. Nitromethane solutions of the complexes give conductivity values typical of 2:1 electrolytes and the ir spectra of the solids show no evidence for the coordination of the perchlorate groups. The complexes exhibit one band in the visible region of the spectrum, consistent with a four-coordinate planar structure.

Spectrophotometric titration of $[Ni(ligand)_2](ClO_4)_2$ complexes with $(C_6H_5)_4AsCl$, $(n\text{-}C_4H_{11})_4NBr$, and $(n\text{-}C_4H_{11})_4NI$ were performed in 1,2-dichloroethane solution to test the ability of the ligands to effect five-coordination in nickel(II) halide complexes.

When a solution of $[Ni(P\text{-}Py)_2]^{2+}$ is treated with chloride or bromide ions, displacement of a P-Py molecule occurs and the four-coordinate complexes $[NiX_2(P\text{-}Py)]$ (X = Cl, Br) are formed. The final products were identified by comparison of the spectra of the reacted solutions with those of the authentic samples prepared according to Uhlig et al.[5] Also with iodide ions a substitution reaction occurs, but the nature of the final products has not been established.

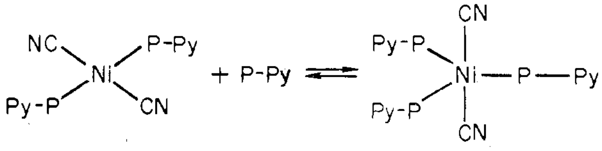
The spectrophotometric titrations of $[Ni(P\text{-}SR)_2](ClO_4)_2$ complexes give sharp end points at 1:1 mole ratios of halide ions to the complexes. The electronic absorption spectra of the solutions are characterized by an intense band in the 18,000–20,000-cm^{-1} region. Band maxima occur in the same energy range as those of square-pyramidal $[NiX(SP)_2]^{2}$ [6] and $[NiX(DPES)_2]^+$,[7] thus suggesting the formation of square-pyramidal cations of the type $[NiX(P\text{-}SR)_2]^+$. The absorption maxima produce the usual spectrochemical series Cl (20,000 cm^{-1}) > Br (19,700 cm^{-1}) > I (18,400 cm^{-1}). Five-coordinate diamagnetic complexes of composition $[NiX(P\text{-}SR)_2]B(C_6H_5)_4$, with spectral patterns identical with those discussed above, were isolated by reaction of the ligands P-SEt and P-SMe with "$NiXB(C_6H_5)_4$", while the ligand P-SPh shows no tendency to complex nickel salts in ethanolic solutions. Moreover the reactions of the ligand P-SEt with NiX_2 complexes (X = Cl, Br) yield six-coordinate paramagnetic $[NiX_2(P\text{-}SEt)_2]$ complexes. The properties of these compounds are very similar to those of the analogous complexes with the ligands SP[6] and DPES,[7] and therefore they will be not further discussed.

The complexes $[Ni(ligand)_2](ClO_4)_2$ react with CN^- ions to form a variety of cyanide derivatives, the structures and stoichiometry of which are dependent on the nature of the bidentate ligands and on the ratio of nickel complex to cyanide ions employed.

When $[Ni(P\text{-}Py)_2]^{2+}$ is allowed to react with KCN (molar ratio 1:2) in ethanol, red solutions are formed, from which a yellow crystalline diamagnetic product of composition $[Ni(CN)_2(P\text{-}Py)_2]$ can be isolated. When a molar ratio 1:1 is employed, a mixture of $[Ni(CN)_2(P\text{-}Py)_2]$ and of unreacted $[Ni(P\text{-}Py)_2](ClO_4)_2$ is recovered. The dicyano derivative is monomeric and nonelectrolytic in 1,2-dichloroethane. The ir spectra in Nujol mulls show in the CN stretching region a single peak at 2105 cm^{-1}, which is consistent with a trans arrangement of cyanide groups. Moreover the pyridine ring vibrations, in the 1570–1600-cm^{-1} region, occur in the same position of the uncomplexed ligand, thus indicating that pyridyl groups are uncoordinated.[8]

Therefore the ir data suggest for $[Ni(CN)_2(P\text{-}Py)_2]$ the structure I in which the ligand forms bonds with the metal only through the phosphorus atoms. Structure I is further supported by the visible spectra of the complex, which appear, both in solid and in 1,2-dichloroethane solutions, identical with those of *trans*-$[Ni(CN)_2(P(C_6H_5)_2C_2H_5)_2]$ (a band at 27,800 cm^{-1}).

When increasing amounts of the ligand P-Py are added to an ethanol solution of $[Ni(CN)_2(P\text{-}Py)_2]$, the band at 27,800 cm^{-1} decreases and a new band at 22,730 cm^{-1} gains in intensity. The occurrence of an isosbestic point at 26,500 cm^{-1} suggests that only two species are present in the solution, and the negligible conductivity indicates that nonionic species are formed. The data can be simply interpreted in terms of equilibrium 1, involving the formation of the five-coordinate compound $[Ni(CN)_2(P\text{-}Py)_3]$. The structure II is confirmed by the similarity of the visible spectra with those of the five-coordinate $[Ni(CN)_2(P(C_6H_5)_2C_2H_5)_3]$.



(1)

I II

The complexes $[Ni(P\text{-}SR)_2]^{2+}$ react with CN^- under mild conditions, to form $[Ni(CN)(P\text{-}SR)_2]^+$ species. These species will react further with CN^- to yield the dicyano derivatives $[Ni(CN)_2(P\text{-}SR)_2]$, in which one or both the sulfur ends of the bidentate ligand are displaced from the metal.

When a suspension of the cationic complexes $[Ni(P\text{-}SR)_2](ClO_4)_2$ was stirred in ethanol with NaCN (molar ratio 1:1), red crystals were slowly formed which analyzed as $[Ni(CN)(P\text{-}SR)_2]ClO_4$. All of these complexes are diamagnetic and their ir spectra show a 2110–2115-cm^{-1} a band of medium intensity assigned to the CN stretching frequency and the bands typical of a noncoordinated ClO_4^- ion.

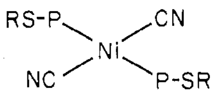
The compounds are uni-univalent electrolytes in 1,2-dichloroethane. Moreover when methyl iodide is added to dichloroethane solutions, no increases of the conductance are observed and this suggests the presence of five-coordinate cations in which both phosphorus and sulfur atoms are bound to the metal. Since the electronic spectra are similar in the solid state and in 1,2-dichloroethane solution, it is concluded that five-coordinate cations are present in the solid also.

The electronic spectra of the three $[Ni(CN)(P\text{-}SR)_2]^+$ (R = CH_3, C_2H_5, C_6H_5) complexes are given in Table II and are best interpreted in terms of a square-pyramidal structure. In fact, the relative positions and intensities of the bands are remarkably similar to those of the square-pyramidal $[Ni(CN)_2(dap)]$ (dap) = $(C_6H_5)P[(CH_2CH_2CH_2As(CH_3)_2]_2)$, whose structure has been determined by X-ray crystallography.[4]

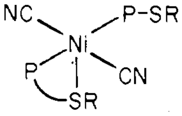
It is noteworthy that with diphosphine ligands all attempts to prepare the five-coordinate cation $[Ni(CN)(diphos)_2]^+$ were not successful and only four-coordinate $[Ni(CN)_2(diphos)]$ or five-coordinate $[Ni(CN)_2(P)_3]$ species were obtained (P = phosphorus atom of the diphosphine).[3,4]

The reactions of $[Ni(P\text{-}SR)_2]^{2+}$ complexes with CN^- (molar ratio 1:2) in boiling ethanol yield yellow to orange diamagnetic compounds, which analyze as $[Ni(CN)_2(P\text{-}SR)_2]$. All the complexes are nonelectrolytic and monomeric in 1,2-dichloroethane. However, the structures of the three complexes appear to be different and depend on the nature of the substituent to sulfur atom.

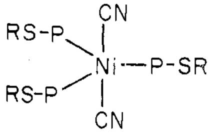
The ir spectrum in Nujol mull of the yellow $[Ni(CN)_2(P\text{-}SPh)_2]$ shows a single peak at 2105 cm^{-1}, indicating that the CN groups are in trans positions. The reflectance spectra and the solution spectra of the compound are identical with those of the trans-planar $[Ni(CN)_2(P(C_6H_5)_2C_2H_5)_2]$. Thus, visible and ir spectra are consistent with the trans-planar structure III in which the ligand P-SPh is bonded to nickel only through the phosphorus atom. The methyl iodide conductivity test is consistent with the conclusions drawn from spectral data.



III



IV



V

The visible and infrared spectra in the solid state of the complex $[Ni(CN)_2(P\text{-}SPEt)_2]$ are also consistent with the trans-planar structure III. However, when the yellow $[Ni(CN)_2(P\text{-}SEt)_2]$ was dissolved in 1,2-dichloroethane, orange-red solutions were formed and the visible spectra of these solutions are completely different from solid-state spectra. This suggests that the dissolution of the complex occurs with configurational rearrangement. While reflectance spectra exhibit only a band at 28,500 cm^{-1}, solution spectra show a band at 27,000 cm^{-1} with a well-defined shoulder on the low-energy side at about 22,000 cm^{-1} (Figure 1).

Since such features are usually found in the spectra of approximately square-pyramidal complexes of nickel(II), the five-coordinate structure IV is suggested for this complex in solution.[4,9] The two ligand field bands occur at intermediate frequencies in the complexes with donor atom sets $P_2S_2(CN)$ (around 26,000 and 20,000 cm^{-1}) and $P_3(CN)_2$ [4] (around 28,000 and 22,350 cm^{-1}) in reasonable agreement with a $P_2S(CN)_2$ donor set.

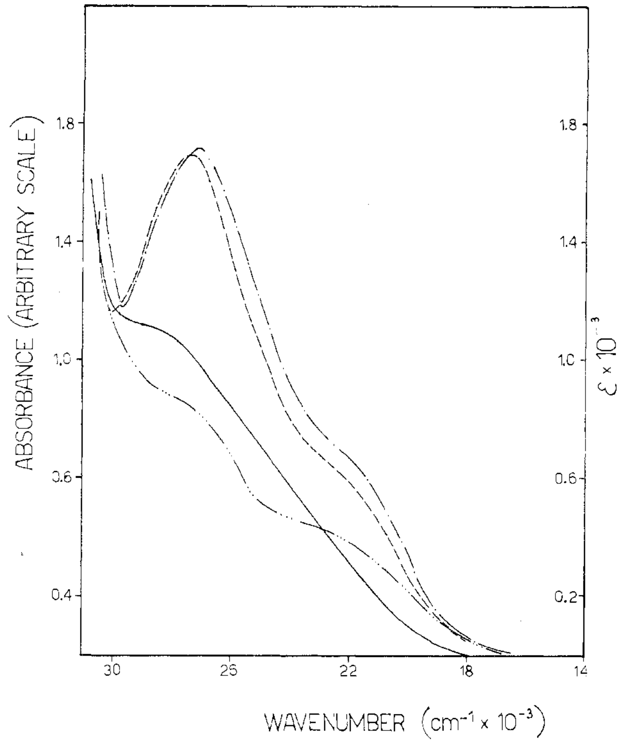


Figure 1. Electronic solid-state spectra: ——, $[Ni(CN)_2(P\text{-}SEt)_2]$; —· · ·—, $[Ni(CN)_2(P\text{-}SMe)_2]$. Electronic absorption spectra in 1,2-dichloroethane: · - · - ·, $[Ni(CN)_2(P\text{-}SEt)_2]$; - - -, $[Ni(CN)_2(P\text{-}SMe)_2]$.

The assumption that the cyanide groups are in trans position is based on the ir spectrum in 1,2-dichloroethane solution, which shows in the CN stretching region only one sharp absorption at 2118 cm^{-1}.

Thus, it is concluded that the complex $[Ni(CN)_2(P\text{-}SEt)_2]$ is four-coordinate in the solid state and becomes five-coordinate in solution by binding of the sulfur atom of one of the organic ligands to the metal.

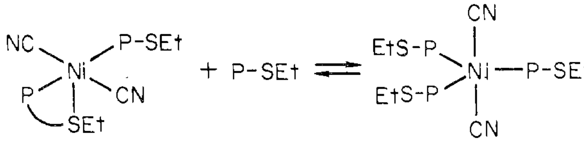
By contrast, the analogous complex with the ligand P-SMe appears to possess the five-coordinate structure IV both in the solid state and in solution. In fact, the visible spectra of $[Ni(CN)_2(P\text{-}SMe)_2]$, in the solid state and in 1,2-dichloroethane solution, exhibit the same absorption maxima (Figure 1), indicating that no substantial structural changes occur on going from the solid state to solution. Furthermore, the relative energies and intensities of the two bands are very close to those of the complex $[Ni(CN)_2(P\text{-}SEt)_2]$ in 1,2-dichloroethane solution (Figure 1) and it is thus reasonable to suggest an analogous stereochemistry for $[Ni(CN)(P\text{-}SMe)_2]$. Ir, conductivity, and molecular weight data in 1,2-dichloroethane solution are in agreement with the proposed formulation.

The results show that the stereochemistry of $[Ni(CN)_2(P\text{-}SR)_2]$ complexes depends on the nature of the organic substituent R, attached to the sulfur atom. When the substituent is a phenyl group, an unfavorable combination of inductive and steric effects probably prevents the attainment of five-coordination.

It is also interesting to note that with bidentate ligands of this type (PS donor set) the 2:1 adducts $[NiX_2(ligand)_2]$ (X = halogen) are high-spin six-coordinate in the solid state and dissociate in solution giving the low-spin five-coordinate $[NiX(ligand)_2]^+$. By contrast, the strong ligand field anion CN$^-$ imposes the formation of low-spin complexes with the rather unusual structures discussed above and no evidence of six-coordinate species has been obtained.

We have also examined the reaction of the complexes $[Ni(CN)_2(P\text{-}SR)_2]$ with the corresponding P-SR ligands. The yellow solutions in 1,2-dichloroethane of $[Ni(CN)_2(P\text{-}SPh)_2]$ turn red on addition of P-SPh and a continuous-variation spectrophotometric study shows that $[Ni(CN)_2(P\text{-}SPh)_2]$ reacts with P-SPh in the 1:1 molar ratio. The appearance at 23,200 cm^{-1} of the typical band of the $[Ni(CN)_2(P)_3]$ chromophores and the presence of an isosbestic point at 26,800 cm^{-1} in the solutions containing increasing amounts of P-SPh, indicate that the five-coordinate species $[Ni(CN)_2(P\text{-}SPh)_3]$ (V) are formed. The negligible value of the conductivity rules out the formation of ionic species.

When an excess of P-SEt (100:1) is added to the 1,2-dichloroethane solutions of $[Ni(CN)_2(P\text{-}SEt)_2]$, the visible spectrum is altered and a new absorption appears at 23,200 cm^{-1}. The observed spectral changes are consistent with equilibrium 2 which involves two five-coordinate species with



(2)

$[P_2S(CN)]$ and $[P_3(CN)_2]$ donor atom sets, respectively.

By contrast, the addition of excess of P-SMe (100:1) to 1,2-dichloroethane solutions of the five-coordinate $[Ni(CN)_2(P\text{-}SMe)_2]$ does not change appreciably the visible spectrum and no evidence of the formation in these conditions of $[Ni(CN)_2(P)_3]$ chromophores has been obtained.

These results confirm the ability of the CN group to stabilize the $[Ni(CN)_2(P)_3]$ moieties and suggest a favorable influence of the methyl group, as compared to the ethyl group, on the stability of the five-coordinate $[Ni(CN)_2(P\text{-}SR)_2]$ complexes.

Acknowledgment. The authors are grateful to Professor A. Turco for stimulating discussions and to Mr. G. Gomiero for technical assistance.

Registry No. $[Ni(CN)_2(P\text{-}Py)_2]$, 54751-28-9; $[Ni(P\text{-}SPh)_2](ClO_4)_2$, 54751-30-3; $[Ni(CN)(P\text{-}SPh)_2]ClO_4$, 54751-32-5; $[Ni(P\text{-}SEt)_2](ClO_4)_2$, 54751-34-7; $[Ni(Cl)_2(P\text{-}SEt)_2]$, 54751-35-8; $[Ni(Br)_2(P\text{-}SEt)_2]$, 54751-36-9; $[NiCl(P\text{-}SEt)_2]BPh_4$, 54751-38-1; $[NiBr(P\text{-}SEt)_2]BPh_4$, 54751-40-5; $[NiI(P\text{-}SEt)_2]BPh_4$, 54751-42-7; $[Ni(CN)(P\text{-}SEt)_2]ClO_4$, 54751-44-9; $[Ni(CN)_2(P\text{-}SEt)_2]$(solid), 54751-45-0; $[Ni(P\text{-}SMe)_2](ClO_4)_2$, 54751-47-2; $[NiCl(P\text{-}SMe)_2]BPh_4$, 54751-49-4; $[NiBr(P\text{-}SMe)_2]BPh_4$, 54751-51-8; $[NiI(P\text{-}SMe)_2]BPh_4$, 54751-53-0; $[Ni(CN)(P\text{-}SMe)_2]ClO_4$, 54751-55-2; $[Ni(CN)_2(P\text{-}SMe)_2]$, 54751-56-3; $[Ni(CN)_2(P\text{-}SPh)_2]$, 54751-57-4; $[Ni(CN)_2(PPh_2Et)_2]$, 16581-07-0; $[Ni(CN)_2(P\text{-}SEt)_2]$(soln), 54751-58-5; $[Ni(CN)_2(P\text{-}Py)_3]$, 54751-59-6; $[Ni(CN)_2(P\text{-}SPh)_3]$, 54751-60-9; $[Ni(CN)_2(P\text{-}SEt)_3]$, 54751-61-0; $[Ni(P\text{-}Py)_2](ClO_4)_2$, 15630-41-8; CN$^-$, 57-12-5.

References and Notes

(1) P. Rigo, C. Pecile, and A. Turco, *Inorg. Chem.*, **6**, 1636 (1967); P. Rigo, G. Guastalla, and A. Turco, *ibid.*, **8**, 375 (1969); P. Rigo and A. Turco, *Coord. Chem. Rev.*, **8**, 175 (1972).
(2) E. C. Alyea and D. W. Meek, *J. Am. Chem. Soc.*, **91**, 5761 (1969).
(3) P. Rigo, B. Corain, and A. Turco, *Inorg. Chem.*, **7**, 1623 (1968).
(4) J. C. Cloyd, Jr. and D. W. Meek, *Inorg. Chim. Acta*, **6**, 480 (1972), and references contained therein.
(5) E. Uhlig and M. Maaser, *Z. Anorg. Allg. Chem.*, **344**, 205 (1966).
(6) M. O. Workman, G. Dyer, and D. W. Meek, *Inorg. Chem.*, **6**, 1543 (1967).
(7) J. Sieckhaus and T. Layloff, *Inorg. Chem.*, **6**, 2185 (1967).
(8) M. M. da Mata, J. Rodgers, and S. M. Nelson, *J. Chem. Soc. A*, 2036 (1969).
(9) J. R. Preer and H. B. Gray, *J. Am. Chem. Soc.*, **92**, 7360 (1970), and references therein.