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Five-Coordination. XI. Nickel(II) Complexes of *cis*-1,2-Bis(diphenylphosphino)ethylene

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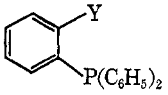
cis-1,2-Bis(diphenylphosphino)ethylene forms five-coordinate, diamagnetic $[Ni(ligand)_2X]B(C_6H_5)_4$ (X = Cl, Br, I) complexes, as well as the diamagnetic, four-coordinate $[Ni(ligand)X_2]$ (X = Cl, Br, I, NCS) complexes. The compounds were characterized by conductivity and magnetic measurements, electronic and infrared spectra, and elemental analyses. The electronic spectra of the five-coordinate complexes differ considerably from known trigonal-bipyramidal complexes and are assigned a square-pyramidal structure. The donor properties of the ethylene–diphosphine ligand are compared with those of its saturated analog, bis(diphenylphosphino)ethane, and the differences in the types of complexes formed are discussed in terms of π bonding and steric requirements of the ligand.

Introduction

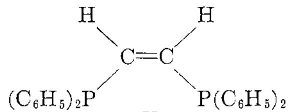
A number of bidentate ligands have been used in recent years to form five-coordinate complexes with nickel(II). Nyholm, *et al.*, prepared $Ni(DAS)_2X^+$ complexes (DAS = *o*-phenylenebis(dimethylarsine)),[1,2] while Meek and coworkers prepared three series of five-coordinate $Ni(YP)_2X^+$ complexes with the chelating phosphines I–III.[3,4] Booth and Chatt obtained a series of planar $Ni(dpe)X_2$ (X = Cl, Br) and six-coordinate $Ni(dpe)_2X_2$ (X = Br, I) complexes with bis(diphenylphosphino)ethane (dpe), IV.[5] Nyholm and coworkers also obtained the $Ni(dpe)X_2$ series (X = Cl, Br, I, NCS) and commented that they were unable to obtain five-coordinate complexes with dpe.[6] However, recently Turco, *et al.*, reported two types of five-coordinate complexes of dpe with nickel(II) cyanide.[7]



I,[3] Y = $As(C_6H_5)_2$, L = AsP
II,[4] Y = SCH_3, L = SP
III,[4] Y = $SeCH_3$, L = SeP

$(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$

IV



V

All of the above ligands (I–IV) contain good π-acceptor ligand atoms (P, As, S, Se); in addition, all except IV contain the π-conjugated *o*-phenylene linkage. As part of our investigation into the factors that promote five-coordination, we chose the unsaturated diphosphine *cis*-1,2-bis(diphenylphosphino)ethylene (VPP), V, because this ligand contains the simplest possible unsaturated connecting linkage. Thus, it should have similar coordination properties to, but be somewhat more flexible than, the usual *o*-phenylene bidentate ligands. Ramaswamy, *et al.*,[8] also recently prepared a few nickel(II) and cobalt(II) complexes with VPP.

Experimental Section

Reagents.—Absolute ethanol and reagent grade dichloromethane were used without further purification. Nitromethane was washed with 5% aqueous sodium bicarbonate and then with 5% aqueous sulfuric acid, dried over calcium chloride, and fractionated (bp 101°). Hydrated nickel(II) iodide and other anhydrous nickel(II) salts were obtained from the City Chemical Corp., New York, N. Y.

The Ligand.—*cis*-1,2-Bis(diphenylphosphino)ethylene, $C_{26}H_{22}P_2$, was prepared by B. R. Cook in this laboratory according to the method of Aguair and Daigle.[9]

General Preparations of the Complexes. $Ni(C_{26}H_{22}P_2)X_2$ (X = Cl, Br, I, NCS).—The diphosphine (0.4 g, 1 mmol) was added to a refluxing solution of the appropriate nickel(II) salt (0.5 mmol) in absolute ethanol (40 ml). The resulting deep red solution soon changed to yellow-brown, and after *ca.* 5 min the complex began to precipitate. The mixture was stirred and refluxed 1 hr and then it was filtered while hot. Each complex was collected on a sintered-glass funnel and recrystallized from dichloromethane–ethanol; yields, 90–95%.

$[Ni(C_{26}H_{22}P_2)_2X]B(C_6H_5)_4$ (X = Cl, Br, I, NCS).—The diphosphine (0.4 g, 1 mmol) dissolved in dichloromethane (10 ml) was added to a cold ethanolic solution of the appropriate nickel(II) salt (0.5 mmol). The resulting intensely purple solutions were stirred for 15 min, and then sodium tetraphenylborate (0.38 g, 1.1 mmol) in absolute ethanol (5 ml) was added. In all cases except for the light brown thiocyanate, a red-purple compound separated immediately. Each compound was collected on a filter, dissolved in dichloromethane, and reprecipitated by addition of anhydrous ethyl ether (50 ml); yields, *ca.* 90%.

$Ni(C_{26}H_{24}P_2)X_2$ (X = Br, I).—These complexes of the analogous

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Table I

Analytical Data and Physical Properties of the Complexes

Compound	Color	$10^6\chi_M$[a]	Λ_M[b]	Anal., %					
				C		H		N	
				Calcd	Found	Calcd	Found	Calcd	Found
$[NiL_2Cl]B(C_6H_5)_4$[c]	Purple	429	66.4	75.65	75.38	5.35	5.45		
$[NiL_2Br]B(C_6H_5)_4$	Purple	421	66.1	72.96	72.84	5.16	5.13		
$[NiL_2I]B(C_6H_5)_4$	Black	450	63.8	70.31	70.18	4.97	4.86		
$[NiL_2(NCS)]B(C_6H_5)_4$	Light brown	1454	52.9	75.23	75.47	5.25	5.20	1.14	1.21
$NiLCl_2$	Light brown	154	7.3	59.33	59.18	4.22	4.40		
$NiLBr_2$	Red-brown	48	6.8	56.10	56.13	3.57	3.71		
$NiLI_2$	Black	111	7.8	44.10	44.08	3.13	3.02		
$NiL(NCS)_2$	Light brown	49	7.1	58.90	58.46	3.97	4.04	4.91	4.78
$Ni(dpe)Br_2$	Red			50.81	50.73	4.33	4.32		
$Ni(dpe)I_2$	Purple			43.94	44.50	3.40	3.11		

[a] χ_M is the corrected molar susceptibility in cgs units. All of the compounds, except $[NiL_2(NCS)]B(C_6H_5)_4$, are effectively diamagnetic with a paramagnetic contribution from the temperature-independent paramagnetism. μ_{eff} calculated for $[NiL_2(NCS)]B(C_6H_5)_4$ is 1.86 ± 0.03 BM at 25°. [b] These are molar conductance values obtained on *freshly prepared* $\sim 10^{-3}$ *M* solutions in nitromethane. The values of the ionic compounds fall to ~40 cm²/ohm mol after about 2 hr. [c] L is *cis*-1,2-bis(diphenylphosphino)ethylene, $C_{26}H_{22}P_2$.

saturated ligand bis(diphenylphosphino)ethane (dpe), IV, were prepared by the same procedure as the above $Ni(C_{26}H_{22}P_2)X_2$ complexes.

Spectral, Conductance, and Magnetic Measurements.—These were obtained as previously described.[3]

Table II

Electronic Absorption Spectra

Compound	ν, cm^{-1}	
	Solution,[a,b]	Solid
$[NiL_2Cl]B(C_6H_5)_4$[c]	28,900 (12,220)	28,590
	20,750 (1490)	20,600
$[NiL_2Br]B(C_6H_5)_4$	28,900 (13,230)	28,100
	20,160 (1563)	19,800
$[NiL_2I]B(C_6H_5)_4$	32,050 (26,310)	
	29,570 (25,930)	28,000
	18,280 (2493)	18,340
$[NiL_2(NCS)]B(C_6H_5)_4$	29,100 (8605)	
	22,710 (1928)	23,040
	23,120[d] (1770)	
$NiLCl_2$	21,830 (1955)	22,400
$NiLBr_2$	36,140 (27,540)	30,930
	26,400 (649)	26,510
	21,230 (1908)	21,230
$NiLI_2$	34,100 (36,450)	31,600
	19,230 (2547)	19,600
$NiL(NCS)_2$	36,230 (34,770)	31,720
	22,780 (2121)	22,810
$Ni(dpe)Br_2$	26,600 (2190)	26,600
	21,050 (2185)	21,120
$Ni(dpe)I_2$	19,080 (2241)	19,130

[a] In dichloromethane. [b] Molar extinction coefficient in parentheses. [c] L is *cis*-1,2-bis(diphenylphosphino)ethylene, $C_{26}H_{22}P_2$. [d] In nitromethane.

Results and Discussion

cis-1,2-Bis(diphenylphosphino)ethylene (VPP), V, forms diamagnetic, four-coordinate $Ni(C_{26}H_{22}P_2)X_2$ complexes when mixed with nickel(II) salts in a 1:1 stoichiometric ratio (Table I). Except for the bromide case, these four-coordinate $Ni(VPP)X_2$ complexes exhibit one symmetric electronic absorption band in the visible region of the spectrum. Both the $Ni(VPP)Br_2$ and $Ni(dpe)Br_2$ complexes have a second peak at *ca.* 26,500 cm^{-1}. The band maxima in Figure 1 produce the typical spectrochemical series, *i.e.*, NCS > Cl > Br > I. When the spectral data for the VPP complexes are compared with those of the corresponding dpe complexes, the complexes of the unsaturated ligand, VPP, are seen to absorb at higher energy.

When VPP is mixed with nickel(II) halides in a 2:1 mole ratio in a concentrated mixture of dichloromethane and ethanol, the solution becomes deep purple. Evaporation of the dichloromethane resulted in the precipitation of the planar $Ni(VPP)X_2$ complexes. However, if a solution of sodium tetraphenylborate was added to the dichloromethane–ethanol mixture, purple-black precipitates separated. The solids were purified by dissolving them in dichloromethane and adding just enough anhydrous ether to precipitate the complexes. In the case of nickel thiocyanate, addition of sodium tetraphenylborate gave a light brown compound instead of a purple one. However, the brown thiocyanate dissolves in dichloromethane, and its electronic spectrum in this solvent is similar to the other $Ni(VPP)_2X^+$ species, Figure 2.

All of the $[Ni(VPP)_2X]B(C_6H_5)_4$ complexes are diamagnetic and 1:1 electrolytes in nitromethane. Thus, it is concluded that five-coordinate cations are present in solution. Since the electronic spectra (Table II, Figure 2) are similar in the solid state (Nujol mulls) and in dichloromethane solution, five-coordinate cations must be present in the solid state also. The visible absorption band of the $Ni(VPP)_2Cl^+$ complex (20,750 cm^{-1}, ϵ 1490) occurs at considerably higher energy than the complex $Ni(QP)Cl^+$ (QP = tris(*o*-diphenylphosphinophenyl)phosphine) (17,500 cm^{-1}, ϵ 4950).[10] The latter complex is an $Ni(P_4)Cl^+$ chromophore that has been assigned a trigonal-bipyramidal structure. The band maximum in the $Ni(VPP)_2Cl^+$ complex occurs in the same energy range as that of $Ni(SP)_2Cl^+$;[4,11] the

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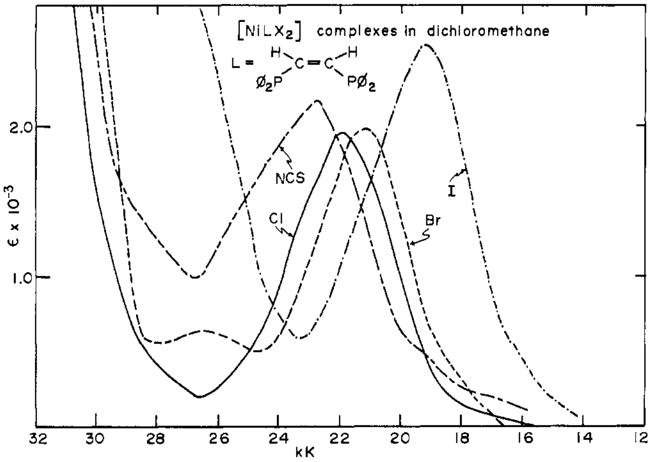


Figure 1.—Visible region of the electronic absorption spectra of the square-planar $NiLX_2$ complexes dissolved in dichloromethane; L = *cis*-1,2-bis(diphenylphosphino)ethylene.

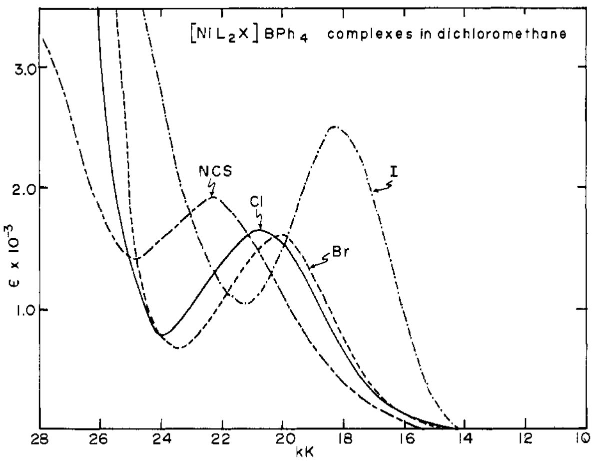


Figure 2.—Electronic spectra of the five-coordinate $[NiL_2X]B(C_6H_5)_4$ complexes dissolved in dichloromethane.

latter complex has been assigned a square-pyramidal geometry on the basis of a spectral comparison with a known square-pyramidal complex.[11] Thus, the band which occurs at *ca.* 21,000 cm^{-1} in the electronic absorption spectra of these $Ni(VPP)_2X^+$ complexes is assigned to the transition of d-orbital character $d_{z^2} \rightarrow d_{x^2-y^2}$.

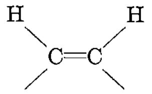
The light brown complex $[Ni(VPP)_2(NCS)]B(C_6H_5)_4$ exhibits a C≡N infrared absorption at 2070 cm^{-1}, characteristic of N-bonded thiocyanate. There is no absorption in region (2150 cm^{-1}) that is diagnostic of bridging thiocyanates. The complex has μ_{eff} = 1.86 BM at room temperature, and it is a 1:1 electrolyte in nitromethane. The complex dissolves in dichloromethane to form a deep purple solution, and the similarity between the electronic spectrum of this solution and those of the other $[Ni(VPP)_2X]B(C_6H_5)_4$ complexes, Figure 2, suggests that this complex also has a square-pyramidal structure in dichloromethane. The electronic spectrum in the solid state is different from that in dichloromethane, Table II, and in the absence of further evidence the solid-state structure of this complex is unknown.

The band at *ca.* 21,000 cm^{-1} in the pentacoordinate complexes shifts to lower energy in the order NCS > Cl > Br > I, consistent with the established spectrochemical series. The strong absorption at *ca.* 29,000 cm^{-1} (Table II) is assigned to a metal–phosphorus charge-transfer band; its relatively constant value rules out its assignment as a metal–halogen charge-transfer band. However, the fifth ligand apparently exerts some effect on the metal–phosphorus charge-transfer transition since the intensity of the 29,000-cm^{-1} band decreases in the order I > Br > Cl > NCS; this order parallels the polarizability of these anions.

When the yellow $[Ni(VPP)_2](ClO_4)_2$ complex is dissolved in dichloromethane and sodium bromide or sodium iodide is added, the solution becomes deep purple. The visible absorption band due to the $Ni(VPP)_2X^+$ moiety reaches a maximum with NaI almost immediately and with NaBr after 5–10 min; however, no color change was observed with NaCl. Similarly, when excess ligand is added to a dichloromethane solution of the planar $Ni(VPP)X_2$ complexes, similar results are obtained, indicating that the tendency for the square-planar complexes to become pentacoordinate depends upon the halide ion involved, in the order I > Br >> Cl.

All attempts to prepare hexacoordinate complexes of the type $Ni(VPP)_2X_2$, similar to the $Ni(dpe)_2X_2$ complexes reported by Booth and Chatt,[5] were not successful. However, it must be pointed out that the latter yellow complexes produce deep maroon solutions when dissolved in nonaqueous solvents. Also the conductance values reported in nitrobenzene solutions showed that extensive ionization occurred in this solvent. Since no magnetic measurements which would have distinguished between the four-coordinate $[Ni(dpe)_2]X_2$ and the six-coordinate $Ni(dpe)_2X_2$ types were reported, Booth and Chatt's assignment[5] of six-coordination must remain questionable. Nyholm and coworkers[6] attempted unsuccessfully to prepare five-coordinate dpe complexes of nickel(II). We have also been unsuccessful in attempts to prepare complexes of the type $Ni(dpe)_2X^+$ with a variety of solvents. The only well-characterized materials that were isolated were the previously discussed square-planar $Ni(dpe)X_2$ complexes. The position and intensity of the band maxima in the visible spectra of the $Ni(L)X_2$ series (L = VPP, dpe; X = Br, I) indicate some electronic differences in the donor properties of these ligands. Based on the electronic spectra the unsaturated diphosphine ligand VPP exerts a slightly stronger ligand field. Thus, the unsaturated, planar connecting linkage of the VPP ligand appears to aid formation of five-coordinate nickel(II) complexes. To rationalize the differentiating properties of the two diphosphines in forming five-coordinate complexes, one may focus on the nature of the connecting linkages between the phosphorus atoms. For example, recently King and Eggers[12] have shown that the ν(CO) infrared stretching frequencies in the $(VPP)M(CO)_4$ (M = Cr, Mo, W) complexes are slightly higher than in the corresponding dpe derivatives. These data indicate that VPP has a slightly higher π-acceptor character than does dpe. This effect may arise from the presence of empty antibonding orbitals in the C=C bond, but it may also be due to the more electronegative sp^2 carbon atoms. Furlani[13] pointed out that in a "regular" square pyramid the efficiency for π bonding is almost as good as in a square-planar complex. The d_{z^2} orbital becomes more fully σ^*, but d_{xy}, d_{xz}, and d_{yz} remain fully π in character for both in-plane and out-of-plane bonds. Similarly, if the metal is located in the basal plane of the square pyramid any interligand π conjugation would be most effective when the ligands are coplanar.

Another possible difference between the two diphosphines may be steric in origin. Molecular models indicate 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 sites above and below the nickel atom. However, the planar



linkage of the VPP ligand leaves these sites open for coordination of an anion. The recent preparation of $[Ni(dpe)_{1.5}(CN)_2]_2$[7] would seem to fit this argument. The latter complex contains one chelating dpe ligand and one which bridges between the nickel atoms, thus facilitating attachment of the two cyano groups. However, it must also be remembered that cyano groups are particularly good at promoting five-coordination with nickel(II) and that the resulting complex is usually a trigonal bipyramid.[14]

Acknowledgments.—We are indebted to the National Science Foundation (Grant No. GP-8365) for financial support, to The Ohio State University for a postdoctoral fellowship to C. A. M., and to B. R. Cook for a supply of the ligand.

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Equilibrium Studies of Copper(II) Complexes of Iminodiacetates with Amino Acid Esters and the Kinetics of Ester Hydrolysis

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Formation constants for the interaction of various amino acids, HA, and amino acid esters, E, with a series of substituted iminodiacetate $(RN(CHR'CO_2)(CH_2CO_2)^{2-})$ complexes of Cu(II), Cu(RIMDA), indicate there are steric repulsions between bulky R groups of the substituted iminodiacetates and large groups on the esters. The amino acid esters in the complexes, Cu(IMDA)(E), hydrolyze with rates of hydrolysis decreasing in the order: MeGly > MeAla > EtSar > EtGly > BuGly > EtLeu. No hydrolysis is observed near pH 7 for esters such as ethylbetaine and N-benzoylglycine methyl ester which do not complex appreciably with Cu(IMDA). The equilibrium and kinetic data are consistent with the reactions

$$\mathrm{Cu(RIMDA)} + \mathrm{HE}^+ \rightleftarrows \mathrm{H}^+ + \mathrm{Cu(RIMDA)(E)} \xrightarrow[k]{\mathrm{OH^-\,attack}} \mathrm{Cu(RIMDA)(A)}^-$$

In the case of catalysis by Cu(IMDA), there is evidence that the last step also proceeds partially by H_2O attack. In both the OH^- and H_2O attack mechanisms it is assumed that the ester group is directly coordinated to the metal ion when the nucleophilic attack occurs. The rates of hydrolysis in Cu(RIMDA)(E) depend relatively little upon the nature of R except when R contains a coordinating group.

Introduction

Equilibrium and kinetic investigations of metal complexes of amino acid ester -N,N- diacetates, $MN(CH_2CO_2)_2(CHRCO_2C_2H_5)$ where the ester group is incorporated into the iminodiacetate ligand,[1-3] form the basis for extending our studies to the basic hydrolysis of amino acid esters (E) in the presence of metal ion complexes. The equilibria and kinetics of ester hydrolysis associated with the interaction of amino acid esters with the nitrilotriacetate (NTA) complex of copper(II)[4,5] have been published. The present

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