Characterization and Electronic Structures of Trigonal-Bipyramidal Nickel(II) Complexes

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Abstract: The preparation and characterization of several complexes of the types $Ni(PR_3)_2(CN)_2$ and $Ni(PR_3)_3(CN)_2$ are reported. The four-coordinate complexes have the *trans*-planar structure, whereas the five-coordinate complexes have the *trans*-trigonal-bipyramidal structure. A self-consistent charge and configuration (SCCC) molecular orbital calculation is reported for a model trigonal-bipyramidal system of the type *trans*-$Ni(PR_3)_3(CN)_2$. Based on this model, electronic spectral assignments are made for *trans*-$Ni[PhP(OCH_3)_2]_3(CN)_2$, and electronic factors affecting the structure of low-spin d^8 systems are discussed in some detail.

The number of stable five-coordinate metal complexes has grown enormously in recent years.[2] Alongside the highly productive synthetic efforts, there have been a few initial attempts directed toward elucidation of the electronic structures and energy levels in five-coordinate systems. Recent work of interest includes the crystal-field models proposed by Ciampolini[3] and Dyer and Venanzi,[4] and the molecular orbital model for $CuCl_5^{3-}$ proposed by Hatfield and coworkers.[5] The initial efforts have been very helpful in interpreting a limited portion of the electronic spectra of the complexes in question, and thus the way has been paved for more extensive electronic structural investigation.

A particularly attractive system for the fruitful study of electronic structures includes the trigonal-bipyramidal complexes *trans*-$Ni[PPh(OR)_2]_3(CN)_2$, in which $R = CH_3, C_2H_5$. One intriguing and highly pertinent fact is that the related complexes formed between $Ni(CN)_2$ and the phosphines PPh_3 and $PPh_2(OR)$ exhibit low-spin, four-coordinate structures. Thus, there is an opportunity in this series of phosphine-substituted dicyanonickel(II) complexes to sort out some of the steric and electronic effects that contribute to determining whether a low-spin Ni(II) complex adopts a four-coordinate or a five-coordinate structure. In this paper, major effort is concentrated on a molecular orbital model of bonding and energy levels for the *trans*-$Ni[PPh(OR)_2]_3(CN)_2$ complexes. Based on this model, proposals are put forward concerning the relative importance of various electronic factors in determining whether a low-spin d^8 system will favor a square-planar or a trigonal-bipyramidal structure.

Experimental Section

Chemicals. Nickel(II) cyanide was obtained from E. H. Sargent and made anhydrous by heating at 200° under nitrogen. Triphenylphosphine and triethyl phosphite were obtained from Eastman Organic Chemicals and used as received. Diphenylphosphinous chloride and benzenephosphorus dichloride were obtained from Stauffer Chemical Co. and used as received. All other chemicals used were reagent grade.

Preparations. Ligands. The ethyl ester of diphenylphosphinous acid was prepared from diphenylphosphinous chloride according to the method of Rabinowitz and Pellon.[6] The methyl and ethyl diesters of phenylphosphonous acid were prepared by a similar process using benzenephosphorus dichloride.

$Ni(Ph_3P)_2(CN)_2$. Anhydrous nickel cyanide (1.1 g, 0.01 mole) and triphenylphosphine (7.0 g, 0.027 mole) were added to 100 ml of absolute ethanol under nitrogen and the mixture was refluxed for 5 days. The unreacted nickel cyanide was dispersed in the ethanol and could be decanted away from the yellow crystalline product which settled out. The crystals were washed with ethanol and acetone. The yield of $Ni(Ph_3P)_2(CN)_2$ was 31%, and many modifications of the technique were tried without substantial improvement, though Schrauzer and Glockner[7] reported almost quantitative yields. *Anal.* Calcd: C, 71.85; H, 4.76; N, 4.41. Found: C, 70.83; H, 4.56; N, 4.49.

$Ni(Ph_2POC_2H_5)_2(CN)_2$. Anhydrous nickel cyanide (0.01 mole) and $Ph_2POC_2H_5$ (0.02 mole) were added to 100 ml of absolute ethanol under nitrogen and the mixture was refluxed for 4 hr. It was then filtered while still hot, and, upon cooling the filtrate, yellow crystals (about 0.007 mole) were obtained. The product was washed with cold ethanol. *Anal.* Calcd: C, 63.08; H, 5.29; N, 4.90; P, 10.85; Ni, 10.28. Found: C, 62.85; H, 5.33; N, 4.85; P, 10.68; Ni, 10.42.

$Ni(Ph_2POC_3H_7)_2(CN)_2$. Anhydrous nickel cyanide (0.12 mole), $Ph_2POC_3H_7$ (0.24 mole), and 1-propanol (1200 ml) were placed in a flask under a nitrogen atmosphere, and the mixture was refluxed for 25 hr. The reaction mixture was filtered while hot. Subsequent cooling of the filtrate failed to precipitate any of the complex. The filtrate was evaporated to dryness. The residue (66 g) was dissolved in benzene (240 ml), and the complex was precipitated from solution by addition of hexane (3000 ml). There was thus obtained a 68% yield of the yellow $Ni(Ph_2POC_3H_7)_2(CN)_2$. An analytical sample was prepared by recrystallization from methyl ethyl ketone, mp 136–137°. *Anal.* Calcd: C, 64.13; H, 5.72; N, 4.67; P, 10.34; Ni, 9.80; mol wt, 599. Found: C, 63.70; H, 5.87; N, 5.10; P, 10.40; Ni, 9.80; mol wt, 592.

$Ni[PhP(OCH_3)_2]_3(CN)_2$. Anhydrous nickel cyanide (0.01 mole) and $PhP(OCH_3)_2$ (0.03 mole) were added to 100 ml of methanol under nitrogen; the mixture was refluxed for 4 hr and then filtered while hot. Cooling the filtrate did not produce crystallization, so it was evaporated to dryness. The red-orange powder thus obtained (about 0.005 mole) was recrystallized from hexane, mp 137–138°. *Anal.* Calcd: C, 50.27; H, 5.34; N, 4.51; P, 14.96; Ni, 9.45. Found C, 49.43; H, 5.46; N, 4.49; P, 14.67; Ni, 9.38.

$Ni[PhP(OC_2H_5)_2]_3(CN)_2$. This complex was made by the same procedure as the one above, using $PhP(OC_2H_5)_2$ with absolute ethanol as the solvent, mp 105°. *Anal.* Calcd: C, 54.54; H,

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6.43; N, 3.97; P, 13.09; Ni, 8.33; mol wt, 705. Found: C, 54.87; H, 7.00; N, 4.12; P, 13.28; Ni, 8.62; mol wt, 690.

$Ni[P(OC_2H_5)_3]_3(CN)_2$. Several attempts were made to prepare $Ni[P(OC_2H_5)_3]_3(CN)_2$ by the above method, but no crystals were obtained. The oil which was produced was the same color as the five-coordinate compounds, however, and its spectrum was taken in ethanol.

Physical Measurements. Electronic spectra were measured using a Cary Model 14 recording spectrophotometer. Spectral grade solvents were used. Infrared spectra were measured with a Perkin-Elmer Model 137 spectrophotometer using Nujol mulls. Magnetic susceptibility measurements were made at room temperature by the Gouy method using $Hg[Co(NCS)_4]^8$ as calibrant. Molecular weights were determined by thermometry with acetone as solvent.

Results

Determination of the molecular weights of two representative complexes establishes their monomeric nature in solution. The molecular weights found for $Ni(Ph_2POC_3H_7)_2(CN)_2$ and $Ni[PhP(OC_2H_5)_2]_3(CN)_2$ are 592 and 690, in good agreement with the values calculated from their formulas (599 and 705). All of the complexes were found to be diamagnetic. Infrared spectra of all samples show only *one* sharp C≡N stretching band, at 2100–2125 cm^{-1}. This is most easily interpreted by assuming a *trans*-square-planar structure for the four-coordinate complexes and a *trans*-trigonal-bipyramidal structure for the five-coordinate complexes.

Positions of major electronic spectral bands are given in Table I. Spectra taken in hexane, carbon tetrachloride, DMF, and ethanol show essentially the same positions as those listed for acetonitrile solutions. We have checked the extent of the dissociation reaction

$$trans\text{-}Ni[PhP(OC_2H_5)_2]_3(CN)_2 \rightleftharpoons Ni[PhP(OC_2H_5)_2]_2(CN)_2 + PhP(OC_2H_5)_2$$

by examining electronic spectra of solutions containing excess ligand. The bands at 24,400, 29,000, and 33,600 cm^{-1} were studied for complex concentrations between 0.00005 and 0.001 *M* and free ligand concentrations up to 0.01 *M*. In hexane, no appreciable dissociation occurs, as indicated by the very slight change in the positions and intensities (after correction for free ligand absorption) of the three bands attributable to the five-coordinate species. In this solvent, all three bands appear as well-defined maxima. In acetonitrile, slight dissociation is indicated; this is probably the reason that the 33,600-cm^{-1} band appears as a shoulder in that medium. The spectrum of *trans*-$Ni(Ph_2POC_2H_5)_3(CN)_2$ was obtained by adding approximately 1000-fold excess $Ph_2POC_2H_5$ to a solution of $Ni(Ph_2POC_2H_5)_2(CN)_2$. It should be noted that the five-coordinate complexes are rather air-sensitive, decomposing to give nickel cyanide in a few days. In the experimental studies reported in this paper, the compounds were handled under nitrogen.

Table I. Positions of Electronic Spectral Bands in *trans*-$Ni(PR_3)_n(CN)_2$ Complexes

Complex	Band maxima[a]
trans-$Ni(Ph_3P)_2(CN)_2$	27,000 (800)
	sh 33,500 (9000)
	38,800 (30,000)
trans-$Ni[Ph_2P(OC_2H_5)]_2(CN)_2$	29,400 (2000)
	sh 33,900 (10,000)
	36,800 (30,000)
trans-$Ni[Ph_2P(OC_2H_5)]_3(CN)_2$	sh 22,500 (2000)
	sh 27,500 (4000)
trans-$Ni[PhP(OC_2H_5]_3(CN)_2$	sh 24,400 (800)
	sh 29,000 (1700)
	sh 33,600 (5000)
	38,800 (30,000)
trans-$Ni[PhP(OCH_3)_2]_3(CN)_2$	sh 24,400 (800)
	sh 29,000 (1500)
	sh 33,300 (5000)
	39,000 (20,000)
$Ni[P(OC_2H_5)_3]_3(CN)_2$[b]	sh 24,000
	29,000
$PhP(OC_2H_5)_2$	40,300 (5000)

[a] Units of cm^{-1} for acetonitrile solutions. Molar extinction coefficients are in parentheses. [b] Ethanol solution.

Molecular Orbitals for ***trans*-$Ni(PR_3)_3(CN)_2$ Complexes. Choice of Model.** The electronic and infrared spectra of the dicyanotrisphosphine complexes are consistent with a trigonal-bipyramidal structure having the cyanide groups in the axial positions,[9] and thus the assumed coordination microsymmetry is D_{3h}. Reasonable approximations for bond distances were made by considering known structures. For example, some nickel–phosphorus distances which have been reported are: 2.26 Å in $Ni(PEt_3)_2Br_2$,[10] 2.28 Å in $Ni(PPh_3)_2Cl_2$,[11] and 2.23 Å in $[Ni(TAP)CN]ClO_4$[12] (TAP = $P[CH_2CH_2CH_2As(CH_3)_2]_3$). The structure of $[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$[13] shows both an approximately tetragonal-pyramidal and an approximately trigonal-bipyramidal anion. In the former, the Ni–C distance in the base is 1.87 Å. In the trigonal bipyramid, the equatorial Ni–C distance is 1.93 Å, but the axial Ni–C distance is only 1.84 Å, with the corresponding C–N distance 1.16 Å. A survey of structural work on nickel–cyanide bonds shows that Ni–C distances are in the range 1.84–1.95 Å, whereas C–N distances are 1.15–1.18 Å.[12–15]

The bond distances used in the calculation are as follows: Ni–P, 2.25 Å; Ni–C, 1.90 Å; C–N, 1.15 Å.

Coordinate System. The coordinate system and the ligand numbering used in the calculation are given in Figure 1. The *z* axis of the Ni coordinate system coincides with the threefold axis of the molecule. The *x* axis was chosen so that one of the equatorial ligands lies on it, and the *y* axis was made normal to the *xz* plane forming a right-handed system. The ligand coordinate systems were set up with the z_l axes pointing directly at the metal. The x_l axes of the axial ligands are parallel to the metal *x* axis, while the x_l axes of the equatorial ligands are parallel to the metal *z* axis. The y_l axes were set normal to the x_l and z_l so as to make each ligand system left-handed.

Valence Orbitals. The nickel orbitals used were the 3d, 4s, and 4p. The phosphine σ, π, and π^* orbitals were chosen in this manner. A separate MO calcula-

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Table II. Orbital Transformation Scheme in D_{3h} Symmetry and Ligand–Ligand Overlap Corrections for H_{ii}

Irred. repr	Metal orbitals	Ligand orbitals	H_{ii} cor factor
A_1'	$3d_{z^2}$	$\frac{1}{\sqrt{3}}(\sigma_1 + \sigma_2 + \sigma_3)$	1.0841
	4s	$\frac{1}{\sqrt{2}}(\sigma_4 + \sigma_5)$	1.0241
		$\frac{1}{\sqrt{2}}(\sigma_4' + \sigma_5')$	1.0298
A_2'	. . .	$\frac{1}{\sqrt{3}}(y_1 + y_2 + y_3)$	0.9671
		$\frac{1}{\sqrt{3}}(y_1^* + y_2^* + y_3^*)$	0.9565
E′	$3d_{xy}$, $3d_{x^2-y^2}$	$\frac{1}{\sqrt{2}}(\sigma_2 - \sigma_3)$, $\frac{1}{\sqrt{6}}(2\sigma_1 - \sigma_2 - \sigma_3)$	0.9517
	$4p_x$, $4p_y$	$\frac{1}{\sqrt{2}}(x_4 + x_5)$, $\frac{1}{\sqrt{2}}(y_4 - y_5)$	1.0023
		$\frac{1}{\sqrt{2}}(x_4^* + x_5^*)$, $\frac{1}{\sqrt{2}}(y_4^* - y_5^*)$	1.0059
		$\frac{1}{\sqrt{2}}(y_2 - y_3)$, $\frac{1}{\sqrt{6}}(2y_1 - y_2 - y_3)$	1.0155
		$\frac{1}{\sqrt{2}}(y_2^* - y_3^*)$, $\frac{1}{\sqrt{6}}(2y_1^* - y_2^* - y_3^*)$	1.0203
A_2''	$4p_z$	$\frac{1}{\sqrt{2}}(\sigma_4 - \sigma_5)$	0.9746
		$\frac{1}{\sqrt{2}}(\sigma_4' - \sigma_5')$	0.9682
		$\frac{1}{\sqrt{3}}(x_1 + x_2 + x_3)$	1.0158
		$\frac{1}{\sqrt{3}}(x_1^* + x_2^* + x_3^*)$	1.0207
E″	$3d_{xz}$, $3d_{yz}$	$\frac{1}{\sqrt{2}}(x_4 - x_5)$, $\frac{1}{\sqrt{2}}(y_4 + y_5)$	0.9977
		$\frac{1}{\sqrt{2}}(x_4^* - x_5^*)$, $\frac{1}{\sqrt{2}}(y_4^* + y_5^*)$	0.9940
		$\frac{1}{\sqrt{2}}(x_2 - x_3)$, $\frac{1}{\sqrt{6}}(2x_1 - x_2 - x_3)$	0.9918
		$\frac{1}{\sqrt{2}}(x_2^* - x_3^*)$, $\frac{1}{\sqrt{6}}(2x_1^* - x_2^* - x_3^*)$	0.9892

tion was performed on $P(OCH_3)_3$.[16] The resulting orbitals, combinations of phosphorus 3s and 3p and oxygen sp hybrids, were used to calculate metal–ligand overlaps. For reasons of computational expediency, combinations of phosphorus s and p alone were chosen so as to give the same (±5%) overlaps. These sp hybrids were used in the calculation. The cyanide σ, σ', π, and π^* orbitals were obtained from a separate calculation.[17] The radial functions for Ni were taken from calculations by Richardson, *et al.*[18] Clementi's functions were used for the carbon, nitrogen, phosphorus, and oxygen orbitals.[19]

Description of the Calculation. The transformation scheme for the metal and ligand orbitals in D_{3h} symmetry is given in Table II. The group overlap integrals, G_{ij}, including consideration of ligand–ligand overlap, and the ligand–ligand overlap correction factors for the diagonal elements H_{ii} were calculated using an IBM 7094 FORTRAN program written by J. Finholt.[16] The Coulomb integrals H_{ii} for the Ni orbitals were taken to be the valence orbital ionization potentials (VOIP's) as described previously.[20] The H_{ii}'s for the ligand orbitals were obtained from the separate calculations mentioned above. The value for the phosphine σ orbital was lowered by 10,000 cm^{-1}, as an interatomic Coulomb correction.[21] The off-diagonal elements were approximated as $H_{ij} = FG_{ij}(H_{ii} + H_{jj})/2$. The factor F was varied to give reasonable agreement with the spectral data. The secular equations were of order 5(a_1'), 7(e′), 5(a_2''), and 5(e″). The a_2' basis orbitals are ligand π and π^* combinations which are nonbonding with respect to the metal orbitals. The secular equations were solved for eigenvalues and eigenvectors, and a Mulliken population analysis was performed for

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(16) Ligand wave functions, overlap integrals, eigenvectors, and eigenvalues have been deposited as Document No. 9907 with the American Documentation Institute, Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. Copies may be secured by citing the document number and remitting in advance $1.25 for photoprints or $1.25 for 35-mm microfilm, payable to Chief, Photoduplication Service, Library of Congress.

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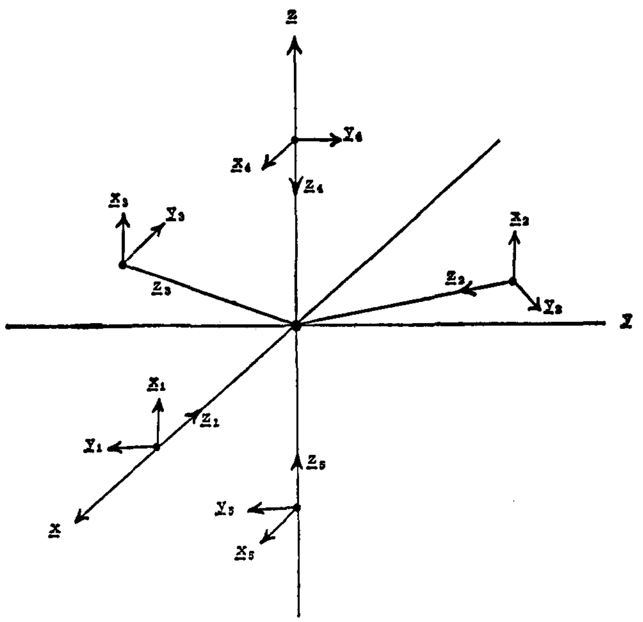

Figure 1. Coordinate system for designation of molecular orbitals for trigonal-bipyramidal complexes.

each occupied level, using an IBM 7094 FORTRAN program written by P. T. Manoharan, A. Viste, and H. Basch. The calculation was of the SCCC type,[22] described in detail elsewhere.[23] Successive cycles are carried out until the computed charge and configuration on the central metal (output) agree with the assumed charge and configuration (input) to within a preset limit.

Evaluations. Reasonable agreement with the lowest bands in the electronic spectrum of *trans*-Ni[PhP$(OCH_3)_2]_3(CN)_2$ was obtained using these values for the factor *F*: for metal–σ interaction, 2.2; for metal–π 1.7; for ligand–ligand, 2.0. Final H_{ii} input parameters are given in Table III. A diagram of the levels used in spectral assignments is given in Figure 2.[16] It is worth noting that fairly wide variations in *F* values did not change the order of the important levels. Furthermore, neither lowering the energy of the phosphine π^* level nor raising the cyanide π^* affected the occupied levels appreciably. A sample result showing this is given in Table IV.

Table III. Final H_{ii} Input Parameters[a]

Orbital	H_{ii}, 1000 cm^{-1}	Orbital	H_{ii}, 1000 cm^{-1}
Ni 3d	−89.4	CN$^-$ π	−113.0
Ni 4s	−69.3	CN$^-$ π^*	−40.0
Ni 4p	−34.4	PR$_3$ σ	−102.8
CN$^-$ σ	−129.0	PR$_3$ π	−146.5
CN$^-$ σ'	−104.0	PR$_3$ π^*	−10.0

[a] For Ni(+0.084) 3d (9.090) 4s (0.477) 4p (0.350).

Discussion

Assignment of Spectral Bands. We shall deal with the stable five-coordinate complex *trans*-Ni[PhP$(OCH_3)_2]_3(CN)_2$. The calculated ground-state electronic structure is $\ldots(3e'')^4(4e')^4 = {}^1A_1$, consistent with the observed diamagnetism. The $4a_1'$, $4e'$, and $3e''$ levels correspond to the usual ligand-field d levels, though the population analysis shows that the first two of these have a substantial degree of phosphine σ character (30 and 20%, respectively) along with the metal d.

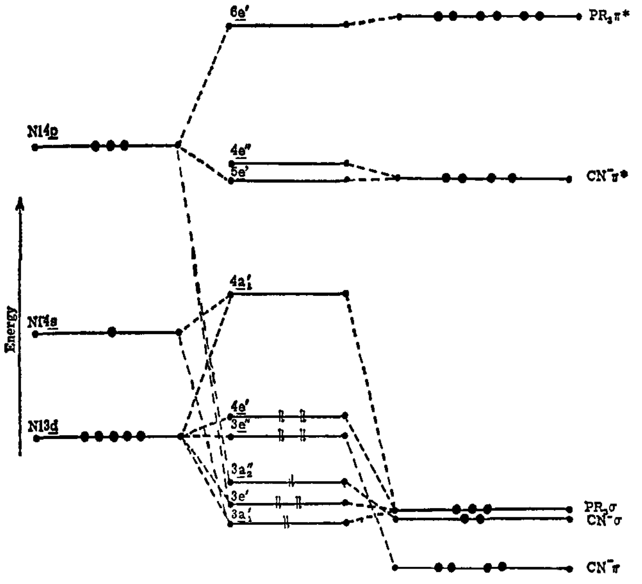

Figure 2. Relative energies of some molecular orbitals for *trans*-Ni$(PR_3)(CN)_2$ complexes.

Table IV. Effect of Variation of π^*-H_{ii} Input on Calculated MO Levels

MO	Energy, 1000 cm^{-1} [a]	Energy, 1000 cm^{-1} [b]
$4e''$	−37.0	−28.0
$5e'$	−40.5	−31.4
$4a_1'$	−61.8	−61.7
$4e'$	−84.8	−84.6
$3e''$	−88.1	−87.8
$3a_2''$	−96.3	−96.4
$3e'$	−101.0	−100.8

[a] For PR$_3$ π^* = −10,000 cm^{-1}, CN$^-$ π^* = −40,000 cm^{-1}; Ni (+0.0838) 3d (9.0896) 4s (0.4769) 4p (0.3497). [b] For PR$_3$ π^* = −20,000 cm^{-1}, CN$^-$ π^* = −30,000 cm^{-1}; Ni (+0.0837) 3d (9.0948) 4s (0.4758) 4p (0.3457).

The assignment and comparison of calculated and observed band positions for *trans*-Ni[PhP$(OCH_3)_2]_3(CN)_2$ are given in Table V. The bands at 24,400 and 29,000 cm^{-1} are at energies consistent with their assignment as the two expected "d–d" bands. In fact, the

Table V. Assignment of Spectral Bands for *trans*-Ni[PhP$(OCH_3)_2]_3(CN)_2$

Assignment	Obsd, cm^{-1}	Calcd, cm^{-1} [a]	Calcd, cm^{-1} [b]
$4e' \rightarrow 4a_1'$	24,400	23,000	15,900 (0.38)
$3e'' \rightarrow 4a_1'$	(29,000)	26,300	17,500 (0.56)
$4e' \rightarrow 5e'$	29,000	44,300	34,300 (0.78)
$3e'' \rightarrow 5e'$	33,300	47,600	33,800 (0.96)
$4e' \rightarrow 4e''$	...	47,800	48,400 (0.87)
$3a_2'' \rightarrow 4a_1'$	...	34,500	62,000 (−0.38)

[a] No interelectronic repulsion correction. [b] Interelectronic repulsion correction by redistribution of charge in excited configurations, as prescribed by Valenti and Dahl.[26] The calculated charge on Ni in the ground state is +0.0838. After charge redistribution, the calculated charges on Ni in the excited configurations are given in parentheses.

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Table VI. Lowest Ligand-Field Maxima (δ) for Analogous Square-Planar and Trigonal-Bipyramidal Complexes

Complex	δ_{SP}, cm^{-1}	Complex	δ_{TBP}, cm^{-1}	δ_{TBP}/δ_{SP}
trans-Ni($Ph_2POC_2H_5$)$_2$(CN)$_2$	29,400	*trans*-Ni[$Ph_2POC_2H_5$]$_3$(CN)$_2$	22,500	0.765
Ni[P(CH_3)$_3$]$_2$$Br_2$ [a]	18,500	Ni[P(CH_3)$_3$]$_3$$Br_2$ [b]	14,100	0.762
$Ni(CN)_4^{2-}$ [c]	30,800	$Ni(CN)_5^{3-}$ [c]	23,800	0.772

[a] M. A. A. Beg and H. C. Clark, *Can. J. Chem.*, **39**, 595 (1961). [b] From ref 34. [c] From ref 36.

first predicted transition (4e′ → 4a$_1$′, calculated 23,000 cm^{-1}) has some M → L character, and the second predicted transition (3e″ → 4a$_1$′, calculated 26,300 cm^{-1}) is from a level which is almost pure metal (97% d) to one of considerable ligand character (40% d, 39% phosphine σ). The fact that the intensities of the two bands are similar, even though only the first transition is symmetry allowed, leads us to reassess the assignment scheme. It can be argued that Ni → π^*CN transitions should appear in this region. For example, $Ni(CN)_4^{2-}$ exhibits three Ni → π^*CN bands below 40,000 cm^{-1}, the lowest being at 32,00 cm^{-1}.[24] It is tempting to speculate that the 3e″ → 4a$_1$′ band is weak and is buried under the stronger 29,000-cm^{-1} absorption, which is assigned as the first Ni → π^*CN band 4e′ → 5e′. It is also possible that the strong absorption at 29,000 cm^{-1} arises from a splitting of the 4e′ → 4a$_1$″ transition due to a distortion in the complex which lowers the symmetry from D_{3h}.

The band at 33,300 cm^{-1} also presents a problem; the simple calculation suggests assignment of this band to the L → M transition 3a$_2$″ → 4a$_1$′. However, such an assignment can be discredited on examining several selected experimental facts. One is the constancy of this band position through the series of different phosphines in both four- and five-coordinate structures (Table I). A L → M band always shifts with the changing stability of the acceptor level, in this case 4a$_1$′. Even more inconsistent is the fact that the complex Ni(Et$_4$dien)Cl$^+$, with its first "d-d" band at 18,800 cm^{-1}, exhibits Cl → Ni(II) charge transfer no lower than 32,000 cm^{-1}.[25] With the first d-d band at 29,000 cm^{-1} (in the planar case), the lowest L → M charge transfer in a complex such as Ni(phosphine)$_2$(CN)$_2$ should not appear below 40,000 cm^{-1}.

The problem is the need for an interelectronic repulsion correction in SCCC-type calculations of L → M bands. Valenti and Dahl have encountered this same problem and have suggested a simple method by which the large redistribution of charge in L → M excited configurations may be taken into account.[26] The calculated transition energy of 3a$_2$″ → 4a$_1$′ by charge redistribution moves out to 62,000 cm^{-1}, as shown in Table V. The M → L transitions, on the other hand, move down after correction for interelectronic repulsion. Thus, on considering both the available experimental evidence and the charge-corrected calculations, the 33,300-cm^{-1} band is assigned as 3e″ → 5e′.

The spectrum shows an intense band at 39,000 cm^{-1}; the ligands absorb strongly in this region (40,000 cm^{-1} for PhP(OC_2H_5)$_2$), and it is probable that the 39,000-cm^{-1} band is primarily due to an internal ligand transition.

Ligand-Field Splitting. Figure 3 shows the splitting of the d levels of octahedral, square-planar, and trigonal-bipyramidal ligand fields. In the octahedral case the $x^2 - y^2$, which points at the four equatorial ligands, and the z^2, interacting with the four equatorial *and* the two axial ligands, are equivalent. In the square-planar situation, the $x^2 - y^2$ still interacts with four equatorial ligands, but in the trigonal bipyramid the z^2 has two axial and only *three* equatorial ligands. Assuming the dominance of σ bonding, this leads to a smaller ligand-field splitting for a trigonal bipyramid than for a closely related square-planar complex. A simple calculation, assuming $H_{dd} = H_{L_\sigma L_\sigma}$ and considering only the d_{z^2} (TBP) and $d_{x^2-y^2}$ (SP) σ bonding, predicts that $\delta_{TBP}/\delta_{SP} = 0.9$. Furthermore, in the trigonal bipyramid the $x^2 - y^2$, xy level has some σ^* character as well as π^*, which should make δ_{TBP}/δ_{SP} slightly less than 0.9. A slight distortion of the D_{3h} structure would also lower the ratio further. Three known systems in which both four- and five-coordinate complexes are stable are listed in Table VI. It will be noted that the values of δ_{TBP}/δ_{SP} fall in the very small range 0.76–0.77. The observed relationship of electronic energy levels in square-planar and trigonal-bipyramidal complexes should prove of considerable value in establishing solution structures of five-coordinate species.

The σ bonds to the axial ligands strongly involve 3d$_z{}^2$ and 4p$_z$ metal orbitals, whereas the equatorial σ bonds contain large components of 4p$_x$ and 4p$_y$ orbitals. The calculation indicates that the equatorial bonding orbitals contain more 4p character and therefore are more expanded than the axial ones. Since the σ orbitals on substituted phosphines are largely 3p, they are more expanded than those on cyanide, which are 2s and 2p in character. Thus it is consistent from overlap considerations that phosphines occupy the equatorial positions.

Table VII. Bond Distances in Some TBP Complexes

Complex	(Type of bond)	Axial distance, Å	Equatorial distance, Å
PCl_5 [a]	(P–Cl)	2.19	2.04
PPh_5 [b]	(P–C)	1.99	1.85
$Fe(CO)_5$ [c]	(Fe–C)	1.797	1.842
$Co(CNCH_3)_5^+$ [d]	(Co–C)	1.84	1.88
$Ni(CN)_5^{3-}$ [e]	(Ni–C)	1.80	1.93
$CuCl_5^{3-}$ [f]	(Cu–Cl)	2.29	2.39

[a] M. Rouault, *Ann. Phys.*, **14**, 78 (1940). [b] P. J. Wheatley, *J. Chem. Soc.*, 2206 (1964). [c] M. I. Davis and H. P. Hanson, *J. Phys. Chem.*, **69**, 3405 (1965). [d] F. A. Cotton, T. G. Dunne, and J. S. Wood, *Inorg. Chem.*, **4**, 318 (1965). [e] From ref 13. [f] D. W. Meek and J. A. Ibers, to be published.

Table VII gives central atom–ligand bond distances for several TBP complexes. It should be pointed out that the older data are in some cases open to question,[2] but there does appear to be a trend suggesting that axial bonds in phosphorus complexes are longer than the equatorial ones, whereas complexes of transi-

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(25) Z. Dori, Ph.D. Thesis, Columbia University, 1967.

(26) V. Valenti and J. P. Dahl, *Acta Chem. Scand.*, 20, 2387 (1966).

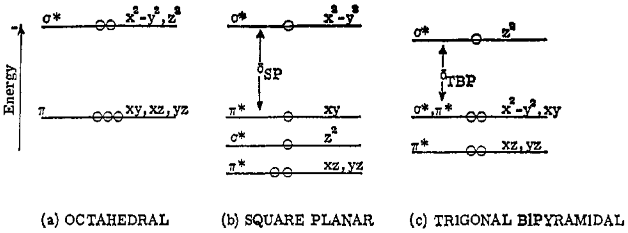
tion metals have approximately equal bond lengths, with the axial slightly shorter (and in one case much shorter). These few data are consistent with a simple σ-bonding model, because in the phosphorus complexes the d orbital involved in the axial bonding is the "outer" one, 3d, which is *more expanded* than the orbitals 3s and 3p used in the equatorial bonds; in the transition metal cases the axial bonds involve the "inner" 3d orbital, *more contracted* than any of the primary orbitals (4s and 4p) in the equatorial bonds.

Four- *vs.* **Five-Coordination**. Of greatest interest to us are the various important factors controlling whether a low-spin d^8 metal complex will choose to adopt a four- or a five-coordinate structure in its ground state. At the present time, the known examples of d^8 four-coordinate structures greatly outnumber the established cases of d^8 five-coordinate structures. This uneven distribution is particularly extreme in the case of complexes containing only monodentate ligands, as can be seen from the scarcity of Ni(II) complexes containing five monodentate ligands. Chatt and Shaw prepared $(PhPEt_2)_3Ni(C{\equiv}CPh)_2$, but reported that it "dissociates reversibly in solution."[27] Hayter has prepared complexes of the form $(Ph_2PH)_3NiX_2$, but says that, when X = Br or I, the complexes are "extensively dissociated in solution" and, when X = Cl, the complex decomposes rapidly."[28] A similar situation exists with $[(Ph_2MeAsO)_4Ni(ClO_4)]^+$,[29] and although Raymond and Basolo have obtained $Ni(CN)_5^{3-}$ in a crystalline compound,[30] it is in solution "one of the weakest complexes whose existence is unequivocally established."[31] This work and that of Verkade and coworkers[32] provide the first known examples of five-coordinate Ni(II) complexes which contain only monodentate ligands and are stable in solution in the absence of excess ligand. The availability of analogous four- and five-coordinate complexes offers an opportunity for considering those factors which favor stability for five-coordination. From consideration of the molecular orbital model, the following electronic factors appear to be of possibly major importance.

1. **d Orbital σ Bonding**. It is expected on theoretical grounds, and confirmed by spectroscopic analysis in the examples cited in Table VI, that the d orbital σ bonding is of relatively greater importance in the square-planar case. Thus ligands which bind to d orbitals in preference to the more expanded valence s and p orbitals will favor a four-coordinate, square-planar arrangement.

2. **s and p Orbital σ Bonding**. The trigonal-bipyramidal structure makes greater use of the relatively expanded s and p metal valence orbitals. Thus heavier donor atoms with relatively expanded valence orbitals, such as P and As, will tend to favor the five-coordinate structure on σ bonding grounds.

3. **d Orbital π Back-Bonding**. The trigonal-bipyramidal structure leads to molecular orbitals in which all four of the filled d orbitals can be used in π bonding, if suitable π-acceptor ligands are available. In the square-planar structure, for symmetry reasons, only three d orbitals can be used. Thus complexes containing good π-acceptor ligands and d^8 metals in low oxidation states will favor the TBP structure.



(a) OCTAHEDRAL (b) SQUARE PLANAR (c) TRIGONAL BIPYRAMIDAL

Figure 3. d-Level splittings in three principal structures.

In the series of complexes under investigation, we can infer the d orbital σ-bonding preference from the electronic spectra set out in Table I. The order of ligand-field splitting of the phosphines appears to be $Ph_3P < Ph_2P(OR) < PhP(OR)_2 \sim P(OR)_3$. This is reasonable since we would expect the more electronegative –OR groups to withdraw electron density from the phosphorus, producing a relatively contracted and stable σ donor orbital. Extension of this argument would lead to the expectation that the contracted σ donor orbitals of $PhP(OR)_2$ and $P(OR)_3$ would not be as well suited for σ bonding to Ni 4s and 4p orbitals as those of Ph_3P and $Ph_2P(OR)$. Therefore, on σ-bonding grounds alone, there should be *increasing tendency toward square-planar structure as –OR groups are added;* this, of course, is absolutely contrary to the observed trend.

Ordinarily, we would expect some type of π-bonding argument to rescue us from this sad state of affairs.[33] Unfortunately, it is difficult to find unequivocal evidence that π back-bonding is an important influence in deciding the relative stabilities of the structures containing Ph_3P, $Ph_2P(OR)$, and $PhP(OR)_2$ ligands; for example, the *experimental* spectra show essentially constant positions for the Ni → π^*CN charge-transfer bands in the complexes under consideration. A possible explanation is that the phosphines Ph_3P and Ph_2POR would prefer to be in five-coordinate complexes of the type *trans*-$Ni(PR_3)_3(CN)_2$, but their *bulkiness* prevents it. This steric argument is also compatible with the fact that $NiBr_2$ forms a five-coordinate $Ni[P(CH_3)_3]_3Br_2$ complex,[34] but can only manage a distorted tetrahedral $Ni(PPh_3)_2Br_2$ complex.[11,35]

The ligands which form complexes in which steric crowding is likely not to be so important are $PhP(OR)_2$ and $P(OR)_3$. In complexes containing these ligands, it should be possible to evaluate the relative importance of σ bonding to Ni 4s and 4p orbitals and π back-bonding. Although our evidence is not unequivocal, it does appear that in ethanol solution the equilibrium *trans*-$Ni[P(OC_2H_5)_3]_3(CN)_2 + 3PhP(OC_2H_5)_2 \rightleftharpoons$ *trans*-$Ni[PhP(OC_2H_5)_2]_3(CN)_2 + 3P(OC_2H_5)_3$ is rapidly established and lies substantially to the right-hand side.[36] In addition, we have recently prepared the Ni(O)

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[33] "Ashes to ashes and dust to dust, if σ bonding won't do it, π bonding must!": R. W. Parry, private communication.

[34] B. B. Chastain, D. W. Meek, E. Billig, and H. B. Gray, to be published.

[35] L. M. Venanzi, *J. Chem. Soc.*, 719 (1958).

[36] B. B. Chastain and H. B. Gray, to be published.

complexes $Ni[PhP(OC_2H_5)_2]_4$ and $Ni[P(OC_2H_5)_3]_4$.[36] It is of some interest that the former complex has considerably more thermal and solution stability. Our tentative conclusion is that both these results suggest that $PhP(OC_2H_5)_2$ is a better π acceptor than $P(OC_2H_5)_3$ and that the structural patterns in the relatively nonhindered systems containing $PhP(OR)_2$ and $P(OR)_3$ ligands are substantially determined by a balance of σ and π electronic effects. We suggest that $PhP(OR)_2$ is a better π acceptor than $P(OR)_3$ (R = alkyl) because the phenyl group provides a low-energy, empty π molecular orbital level which can act in concert with an appropriately situated phosphorus 3d orbital. The -OR groups withdraw electron density from the phosphorus part of the (PhP) π acceptor, which gives stability to the 3d level; thus, according to this model, both Ph and OR groups play a role in the π-acceptor strength, and for his reason $PhP(OR)_2$ is expected to be a better π acceptor than either PPh_3 or $P(OR)_3$. We shall deal with this matter fully in a subsequent paper.[36]

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Volume Changes in Ion Association Reactions. Inner- and Outer-Sphere Complexes

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Abstract: Molar volume changes have been measured dilatometrically for substitution of water in $Co(NH_3)_5H_2O^{3+}$ by various anions. They were found to decrease in the order $OH^- > CH_3CH_2COO^- > SO_4^{2-} > Cl^- > Br^- > NO_3^-$. This order corresponds to the degree of structuring of water by the anions. Volume changes were determined as well for complexing of Ce^{3+} by SO_4^{2-}, $CH_3CH_2COO^-$, Cl^-, and NO_3^-, and of Eu^{3+} by NO_3^-. Comparison of both volume and entropy changes for the lanthanon complexes with the corresponding Co(III) systems support the view that sulfate and propionate complexes of Ce^{3+} are inner sphere while the chloride complex is outer sphere. However, the nitrate complexes of the lanthanons show intermediate behavior. The volume changes for outer-sphere complexing of $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5H_2O^{3+}$ by sulfate were measured in dilute solution ($I = 0.1$) and found, unexpectedly, to be of the same magnitude as for inner-sphere substitution of sulfate in $Co(NH_3)_5H_2O^{3+}$. Again this behavior is paralleled by the entropy changes. Raising the ionic concentration to 1 *M* $NaClO_4$ markedly lowers both the volume and entropy change on outer-sphere binding of SO_4^{2-} to $Co(NH_3)_5H_2O^{3+}$. The wide variability of both inner-sphere and outer-sphere values militates against the establishment of a general criterion for distinguishing between the two structural types based either on volume or entropy changes. Nevertheless, comparisons for related systems under closely similar conditions may be useful.

Ions in solution compress solvent molecules in their vicinity. Molar volumes of ions have been interpreted in terms of this effect, known as electrostriction,[1] by a number of approaches.[2] When oppositely charged ions combine, the solution volume is expected to increase as electrostriction is relieved. Many measurements on Brønsted acid-base systems have documented the expansion accompanying proton transfer from cations to anions.[3,4] The effect is quite large. For example, the reaction $H_{aq}^+ + OH_{aq}^- = H_2O$ has an associated volume increase of 21.9 ml/mole[5] (at infinite dilution and 25°) which is some 4 ml greater than the molar volume of water itself. The expansions associated with other proton-transfer reactions are also substantial. Their magnitudes are of interest with respect to the question of solvent ordering by solutes of various structures and have been used as probes into protein structures.[3,6]

Volume changes accompanying nonprotonic charge neutralization reactions have so far received little attention. Recently Strauss and Leung[7] measured volume changes accompanying the mixing of anionic polyelectrolytes with alkali metal and alkaline earth cations. Some of the molar expansions were of the order of those observed for analogous protonation reactions and were interpreted by the authors as evidence for site binding of the cations to the polyanions, as opposed to ionic atmosphere binding. Volume changes accompanying simple nonprotonic ion association reactions have not previously been determined. Their magnitudes should be of relevance to an understanding of solvent structure and ion hydration, and comparisons with protonic systems should be instructive.

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