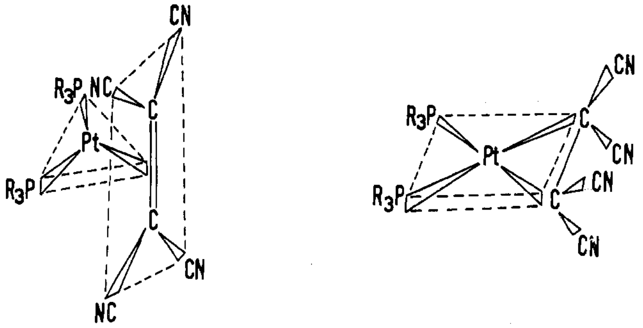

Figure 1.—Possible structure for $Pt(PR_3)_2(C_6N_4)$.

region, tetracyanoethylene exhibits two strong bands at 2214 and 2262 cm.$^{-1}$ with shoulders at 2202 and 2229 cm.$^{-1}$.[20] Both $Pt[P(C_6H_5)_3]_2(C_6N_4)$ and $Pt[P(C_2H_5)_3]_2(C_6N_4)$ show a single, strong absorption at 2220 cm.$^{-1}$. Since coordination of alkylnitriles through the nitrogen atoms usually results in an increase in the infrared-active $C\equiv N$ stretching frequency,[21] it is assumed that such coordination is not in effect in these complexes of tetracyanoethylene. For comparison, the $C\equiv N$ stretch in CH_3CN occurs at 2250 cm.$^{-1}$,[22] but shifts to 2320 cm.$^{-1}$ when coordinated to platinum in the complex $Pt(CH_3CN)_2Cl_2$.[23]

A detailed discussion of the electronic structures of the tetracyanoethylene complexes will be deferred until an X-ray study of $Pt[P(C_2H_5)_3]_2(C_6N_4)$, which is now in progress, is completed. The chemical evidence at hand, however, seems to indicate that the complexes should be regarded as derivatives of Pt(II) rather than Pt(0) because tetracyanoethylene oxidized the *bona-fide* Pt(0) complex $Pt(P(C_6H_5)_3)_4$ under very mild conditions to the divalent state.

The two methods of preparation of $Pt[P(C_6H_5)_3]_2(C_6N_4)$ illustrate the unorthodox reactivity of tetracyanoethylene toward platinum complexes. Chatt and co-workers[13] prepared a series of complexes of the type $Pt[P(C_6H_5)_3]_2(ac)$ where ac represents various acetylenes. It was observed that one acetylene would displace another in solution at room temperature,

$$Pt[P(C_6H_5)_3]_2ac + ac' \rightleftarrows Pt[P(C_6H_5)_3]_2ac' + ac \qquad (1)$$

and that the stability of complexes decreased as the acetylene was changed in the order $C_6H_5C\equiv CC_6H_5 > C_6H_5C\equiv CH > \text{alk—}C\equiv C\text{—alk} > HC\equiv CH$. An analogous series of complexes of the type $Pt[(C_6H_5)_3P]_2$(olefin) were prepared,[24] but these were much less stable than the acetylene complexes. Even gaseous acetylene itself displaced the olefin from the most stable olefin complex. In contrast to this, we now find that an olefin, tetracyanoethylene, displaces phenylacetylene from $Pt[P(C_6H_5)_3]_2(C_6H_5C\equiv CH)$ quite easily. Thus, tetracyanoethylene is the first olefin known that will displace an acetylene from complexes of the type $Pt[P(C_6H_5)_3]_2ac$.

The behavior of tetracyanoethylene toward *trans*-$Pt[P(C_6H_5)_3]_2HCl$ and *trans*-$Pt[P(C_2H_5)_3]_2HCl$ is quite different from that of other olefins toward metal hydrides. For example, ethylene was found to react with *trans*-$Pt[P(C_2H_5)_3]_2HCl$ at 95° and 40 atm. over a period of 18 hr. to give a 25% yield of the alkyl complex, $Pt[P(C_2H_5)_3]_2(CH_2CH_3)Cl$.[14] This is to be contrasted with the reaction of tetracyanoethylene with the same hydride, in which equimolar amounts of the reactants yield $Pt[P(C_2H_5)_3]_2(C_6N_4)$ almost quantitatively at room temperature in a matter of minutes.

The kinetic and mechanistic aspects of this rather unusual reaction are presently under investigation.[25]

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CONTRIBUTION FROM THE ISTITUTO DI CHIMICA GENERALE DELL'UNIVERSITA,
FLORENCE, ITALY

A Crystal Field Model for High-Spin Five-Coordinated Nickel(II) Complexes

BY MARIO CIAMPOLINI

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The splitting of the terms of the free nickel(II) ion in fields of five point dipoles arranged in trigonal-bipyramidal and square-pyramidal configurations is calculated. The weak-field scheme with interaction of configurations has been used. Only for large field strengths or extensive nephelauxetic effects, the five-coordinated nickel(II) complexes are expected to be diamagnetic. The spectra of two high-spin nickel(II) complexes of approximate trigonal-bipyramidal and square-pyramidal stereochemistries are compared with the predicted transitions. The agreement is found to be satisfactory. The crystal field stabilization energies of both configurations are discussed.

Introduction

During the past years five-coordinated nickel(II) complexes have been shown to be more common than previously believed. The first examples reported have been low-spin complexes[1,2]. Recently, however, the first cases of high-spin nickel(II) complexes have been

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(1) G. A. Barclay and R. S. Nyholm, *Chem. Ind.* (London), 378 (1953); C. M. Harris, R. S. Nyholm, and D. J. Phillips, *J. Chem. Soc.*, 4379 (1960); G. A. Mair, H. M. Powell, and L. M. Venanzi, *Proc. Chem. Soc.*, 170 (1961); R. G. Hayter, *Inorg. Chem.*, **2**, 932 (1963); G. S. Benner, W. E. Hartfield, and D. W. Meek, *ibid.*, **4**, 1544 (1965).

(2) G. Dyer, J. G. Hartley, and L. M. Venanzi, *J. Chem. Soc.*, 1293 (1965).

described. These complexes have distorted square-pyramidal[3,4] and trigonal-bipyramidal[5] configurations.

Although many theoretical treatments have been performed for the energy levels of six- and four-coordinated nickel(II),[6–8] no detailed treatment has been reported on five-coordinated nickel(II) complexes. Recently, a correlation diagram of the energy levels for a d^8 configuration in strong and weak crystalline fields of C_{3v} symmetry has been published.[9]

The present work deals with the splitting of the free nickel(II) ion terms in fields of five ligands arranged in square-pyramidal and trigonal-bipyramidal configurations. Distortions of the coordination polyhedra which do not alter the crystal field symmetry are also taken into consideration. Spectra, magnetic, and energy behavior of five-coordinated nickel(II) complexes is discussed on the basis of the results.

Method of Calculation

The well-known weak field scheme with configuration interaction has been used in order to calculate the splitting of the singlet and triplet terms of the nickel(II) ion in crystalline fields of the trigonal-bipyramidal (D_{3h}) and square-pyramidal (C_{4v}) symmetry. Spin–orbit coupling and intermixing of configurations with contribution from 4s and 4p orbitals have been neglected. The electrostatic energy due to the ligands has been calculated for five point dipoles with strength μ—pointing toward the nickel atom—at the corners of the coordination polyhedron. The nickel–dipole distances have been taken as 2.00 Å. This is the mean nickel–ligand distance found in these five-coordinated high-spin complexes.[4,5,10]

The highest symmetry axis of the coordination polyhedron is taken as the z axis of the coordinate system. The angle L_{ax}–Ni–L_{base}, where L_{ax} = axial ligand(s) and L_{base} = any of the basal ligands, is hereafter called β. This angle is 90° in the trigonal bipyramid but may be different from 90° in the square pyramid. The coordinate system is defined by placing one of the equivalent basal ligands on the axis $\theta = \beta$, $\varphi = 0°$.

The matrix elements of the potential energy between the one-electron 3d orbitals $\chi(\mathrm{m})$

$$\int \chi(\mathrm{m})^*(\Sigma_L V_L)\chi(\mathrm{m}')d\tau = (\mathrm{m}|V|\mathrm{m}')$$

(where V_L is the electrostatic potential set up by each ligand L) are as follows: Trigonal bipyramid

$$(2|V|2) = \mu_{base}(3B_0 + 3B_2/7 + 3B_4/56) + \mu_{ax}(2B_0 - 4B_2/7 + 2B_4/21)$$

$$(1|V|1) = \mu_{base}(3B_0 - 3B_2/14 - 3B_4/14) + \mu_{ax}(2B_0 + 2B_2/7 - 8B_4/21)$$

$$(0|V|0) = \mu_{base}(3B_0 - 3B_2/7 + 9B_4/28) + \mu_{ax}(2B_0 + 4B_2/7 + 4B_4/7)$$

Square pyramid, $\beta = 90°$

$$(2|V|2) = \mu_{base}(4B_0 + 4B_2/7 + B_4/14) + \mu_{ax}(B_0 - 2B_2/7 + B_4/21)$$

$$(1|V|1) = \mu_{base}(4B_0 - 2B_2/7 - 2B_4/7) + \mu_{ax}(B_0 + B_2/7 - 4B_4/21)$$

$$(0|V|0) = \mu_{base}(4B_0 - 4B_2/7 + 3B_4/7) + \mu_{ax}(B_0 + 2B_2/7 + 2B_4/7)$$

$$(2|V|-2) = \mu_{base}(5B_4/6)$$

Square pyramid, $\beta = 100°$, five equivalent dipoles

$$(2|V|2) = \mu(5B_0 + 0.2340B_2 + 0.0983B_4)$$

$$(1|V|1) = \mu(5B_0 - 0.1170B_2 - 0.3932B_4)$$

$$(0|V|0) = \mu(5B_0 - 0.2340B_2 + 0.5898B_4)$$

$$(2|V|-2) = \mu(0.7838B_4)$$

Square pyramid, $\beta = 110°$, five equivalent dipoles

$$(2|V|2) = \mu(5B_0 + 0.0852B_2 + 0.0483B_4)$$

$$(1|V|1) = \mu(5B_0 - 0.0426B_2 - 0.1932B_4)$$

$$(0|V|0) = \mu(5B_0 - 0.0852B_2 + 0.2898B_4)$$

$$(2|V|-2) = \mu(0.6497B_4).$$

The radial integrals B_0, B_2, B_4, as defined in ref. 11, have been taken from the tables of Ballhausen and Ancmon,[12] where they are calculated for hydrogen-like wave functions. The actual figures, $B_0 = 1.6006$ cm.$^{-1}$, $B_2 = 0.8713$ cm.$^{-1}$, $B_4 = 0.4113$ cm.$^{-1}$, are valid for the effective charge $Z_{3d} = 7.08$. This is the value also used by Furlani for nickel(II) complexes.[7] The ratio B_2/B_4 varies only slightly for moderate variations of the nickel–dipole distance. This, and the fact that μ is to be regarded as a semiempirical parameter allows formally the treatment of minor variations of nickel–ligand distance by varying the μ value.

It is well known that in complexes the Condon–Shortley correlation parameters F_n are reduced in magnitude with respect to the free-ion values. In these calculations it is assumed that $F_2/14 = F_4 = 100$ cm.$^{-1}$, which corresponds to a reduction of the free-ion term distances of *ca.* 15%. This is about the mean of the reductions found in hexaaquo and hexaammine nickel ions, *i.e.*, 11 and 16%, respectively.[13]

Results

The energies of the nickel(II) states in the weak field limit are reported in Tables I and II for the trigonal-bipyramidal and square-pyramidal configurations, re-

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TABLE I

ENERGY LEVELS OF Ni^{2+} IN TRIGONAL-BIPYRAMIDAL CRYSTALLINE FIELDS

Term	Sym.	Linear combination[a]	The coefficients of (m/V/m) of the perturbation matrix elements		
			$(2\|V\|2)$	$(1\|V\|1)$	$(0\|V\|0)$
^3F	$^3A'_2$	(3.0)	2/5	8/5	0
	$^3A_1''$	$\sqrt{1/2}[(3.3) - (3.\bar{3})]$	1	1	0
	$^3A_2''$	$\sqrt{1/2}[(3.3) + (3.\bar{3})]$	1	1	0
	$^3E'$	(3,2); (3,$\bar{2}$)	1	0	1
	$^3E''$	(3,1); (3,$\bar{1}$)	3/5	1	2/5
^3P	$^3A_2'$	(1,0)	8/5	2/5	0
	$^3E''$	(1,1); (1,$\bar{1}$)	2/5	1	3/5
^1D	$^1A_1'$	(2,0)	8/7	2/7	4/7
	$^1E'$	(2,2); (2,$\bar{2}$)	4/7	6/7	4/7
	$^1E''$	(2,1); (2,$\bar{1}$)	6/7	1	1/7
^1G	$^1A_1'$	(4,0)	2/35	32/35	36/35
	$^1A_1''$	$\sqrt{1/2}(4,3) + (4,\bar{3})]$	1	1	0
	$^1A_2''$	$\sqrt{1/2}[(4,3) - (4,\bar{3})]$	1	1	0
	$^1E'(1)$	(3,2); (4,$\bar{2}$)	3/7	8/7	3/7
	$^1E''(2)$	(4,4); (4,$\bar{4}$)	2	0	0
^1S	$^1A_1'$	(0,0)	0	0	0
^3F, ^3P	$^3A_2'$		4/5	−4/5	0
	$^3E''$		$\sqrt{6}/5$	0	$-\sqrt{6}/5$
^1D, ^1G	$^1A_1'$		$4/\sqrt{245}$	$8/\sqrt{245}$	$-12/\sqrt{245}$
	$^1E(1)$		$\sqrt{12/7}$	$-\sqrt{48/7}$	$\sqrt{12/7}$
	$^1E'(2)$		0	0	0
	$^1E''$		$\sqrt{6}/7$	0	$-\sqrt{6}/7$
^1D, ^1S	$^1A_1'$		$8/\sqrt{70}$	$-4/\sqrt{70}$	$-4/\sqrt{70}$
^1G, ^1S	$^1A_1'$		$4/\sqrt{350}$	$-16/\sqrt{350}$	$12/\sqrt{350}$

[a] (L,M_L) is for $\psi(L,S,M_L,M_S)$; the values of S and M_S are omitted for brevity.

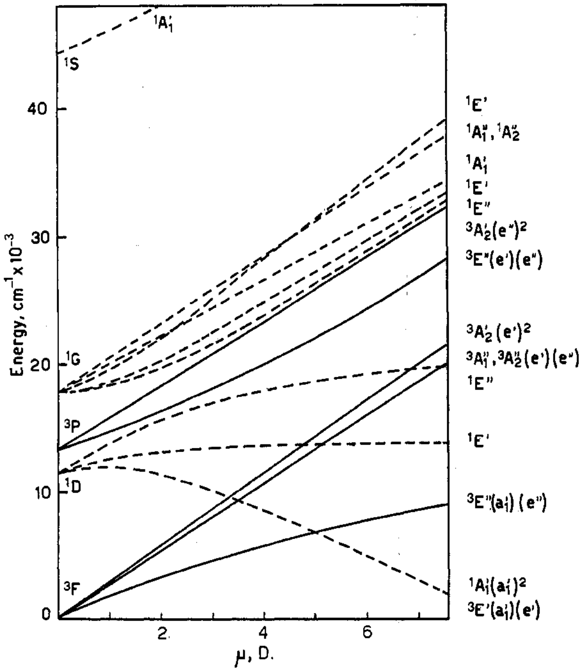

Figure 1.—Energy level diagram for the nickel(II) ion in fields of five equivalent dipoles of strength μ arranged in a trigonal-bipyramidal configuration. The $^3E'$ state is taken as the zero of the energy.

spectively. The tables also report the perturbation matrix elements for the interacting levels. The energy levels systems for environments of five equivalent ligands are plotted in Figures 1–4 as a function of the dipole strength, μ. Throughout, the ground states have been taken as zero energy states. Figure 1 shows the results for the trigonal-bipyramidal arrangement; Figures 2–4 refer to square-pyramidal and configurations for β angles of 90, 100, and 110°, respectively.

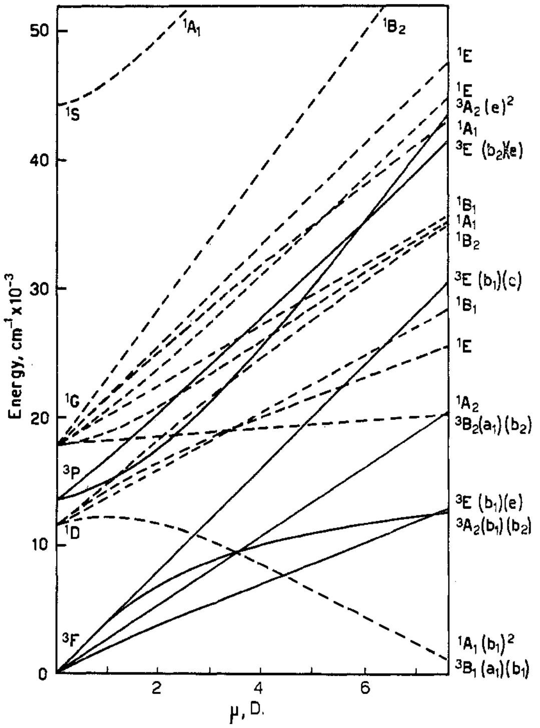

Figure 2.—Energy level diagram for the nickel(II) ion in fields of five equivalent dipoles of strength μ arranged in a square-pyramidal configuration. The angle L_{ax}–Ni–L_{base} is 90°. The $^3B_1$ state is taken as the zero of the energy.

The labeling of all states is that of Mulliken. All of the triplets and the lowest-lying singlet are also labeled according to the strong field limit configurations, the hole formalism being used. In this connection the symmetry designation of d orbitals is: $a_1' = d_{z^2}$; $e' = d_{x^2-y^2}, d_{xy}$; $e'' = d_{xz}, d_{yz}$ in D_{3h} symmetry; and $a_1 = d_{z^2}$; $b_1 = d_{x^2-y^2}$; $b_2 = d_{xy}$; $e = d_{xz}, d_{yz}$ in C_{4v} symmetry.

TABLE II

ENERGY LEVELS OF Ni^{2+} IN SQUARE-PYRAMIDAL CRYSTALLINE FIELDS

Term	Sym.	Linear combination[a,b]	The coefficients of $(m\|V\|m')$ of the perturbation matrix elements[b]			
			$(2\|V\|2)$	$(1\|V\|1)$	$(0\|V\|0)$	$(2\|V\|-2)$
^3F	$^3A_2$	$(3,0)$	2/5	8/5	0	0
	$^3B_1$	$\sqrt{1/2}[(3,2) - (3,\bar{2})]$	1	0	1	1
	$^3B_2$	$\sqrt{1/2}[(3,2) + (3,\bar{2})]$	1	0	1	−1
	$^3E(1)$	$\sin \delta_a(3,1) - \cos \delta_a(3,\bar{3})$ $\sin \delta_a(3,\bar{1}) - \cos \delta_a(3,3)$	3/5	1	2/5	$\sqrt{3/5} \cot \delta_a$
	$^3E(2)$	$\cos \delta_a(3,1) + \sin \delta_a(3,\bar{3})$ $\cos \delta_a(3,\bar{1}) + \sin \delta_a(3,3)$	1	1	0	$-\sqrt{3/5} \cot \delta_a$
^3P	$^3A_2$	$(1,0)$	8/5	2/5	0	0
	^3E	$(1,1); (1,\bar{1})$	2/5	1	3/5	0
^1D	$^1A_1$	$(2,0)$	8/7	2/7	4/7	0
	$^1B_1$	$\sqrt{1/2}[(2,2) + (2,\bar{2})]$	4/7	6/7	4/7	4/7
	$^1B_2$	$\sqrt{1/2}[(2,2) - (2,\bar{2})]$	4/7	6/7	4/7	−4/7
	^1E	$(2,1); (2,\bar{1})$	6/7	1	1/7	0
^1G	$^1A_1(1)$	$\sin \delta_b(4,0) - \sqrt{1/2} \cos \delta_b[(4,4) + (4,\bar{4})]$	2/35	32/35	36/35	$-\sqrt{1/35} \cot \delta_b$
	$^1A_1(2)$	$\cos \delta_b(4,0) + \sqrt{1/2} \sin \delta_b[(4,4) + (4,\bar{4})]$	2	0	0	$\sqrt{1/35} \cot \delta_b$
	$^1A_2$	$\sqrt{1/2}[(4,4) - (4,\bar{4})]$	2	0	0	0
	$^1B_1$	$\sqrt{1/2}[(4,2) + (4,\bar{2})]$	3/7	8/7	3/7	6/7
	$^1B_2$	$\sqrt{1/2}[(4,2) - (4,\bar{2})]$	3/7	8/7	3/7	−6/7
	$^1E(1)$	$\sin \delta_c(4,1) - \cos \delta_c(4,\bar{3})$ $\sin \delta_c(4,\bar{1}) - \cos \delta_c(4,3)$	1/7	1	6/7	$-\sqrt{1/7} \cot \delta_c$
	$^1E(2)$	$\cos \delta_c(4,1) + \sin \delta_c(4,\bar{3})$ $\cos \delta_c(4,\bar{1}) + \sin \delta_c(4,3)$	1	1	0	$\sqrt{1/7} \cot \delta_c$
^1S	$^1A_1$	$(0,0)$	0	0	0	0
^3F, ^3P	$^3A_2$		4/5	−4/5	0	0
	$^3E(1)$		$\sqrt{6/25} \sin \delta_a$	0	$-\sqrt{6/25} \sin \delta_a$	$\sqrt{2/5} \cos \delta_a$
	$^3E(2)$		$\sqrt{6/25} \cos \delta_a$	0	$-\sqrt{6/25} \cos \delta_a$	$-\sqrt{2/5} \sin \delta_a$
^1D, ^1G	$^1A_1(1)$		$\sqrt{16/245} \sin \delta_b$	$\sqrt{64/245} \sin \delta_b$	$-\sqrt{144/245} \sin \delta_b$	$-\sqrt{16/7} \cos \delta_b$
	$^1A_1(2)$		$\sqrt{16/245} \cos \delta_b$	$\sqrt{64/245} \cos \delta_b$	$-\sqrt{144/245} \cos \delta_b$	$\sqrt{16/7} \sin \delta_b$
	$^1B_1$		$\sqrt{12/49}$	$-\sqrt{48/49}$	$\sqrt{12/49}$	$\sqrt{12/7}$
	$^1B_2$		$\sqrt{12/49}$	$-\sqrt{48/49}$	$\sqrt{12/49}$	$-\sqrt{12/7}$
	$^1E(1)$		$\sqrt{6/49} \sin \delta_c$	0	$-\sqrt{6/49} \sin \delta_c$	$-\sqrt{6/49} \cos \delta_c$
	$^1E(2)$		$\sqrt{6/49} \cos \delta_c$	0	$-\sqrt{6/49} \cos \delta_c$	$\sqrt{6/49} \sin \delta_c$
^1D, ^1S	$^1A_1$		$\sqrt{32/35}$	$-\sqrt{8/35}$	$-\sqrt{8/35}$	0
^1G, ^1S	$^1A_1(1)$		$\sqrt{8/175} \sin \delta_b$	$-\sqrt{128/175} \sin \delta_b$	$\sqrt{72/175} \sin \delta_b$	$-\sqrt{8/5} \cos \delta_b$
	$^1A_1(2)$		$\sqrt{8/175} \cos \delta_b$	$-\sqrt{128/175} \cos \delta_b$	$\sqrt{72/175} \cos \delta_b$	$\sqrt{8/5} \sin \delta_b$

[a] (L,M_L) is for $\psi\ (L,S,M_L,M_S)$; the values of S and M_S are omitted for brevity. [b] The δ's are defined as follows: $\delta_a = {}^1/_2 \text{ arc tan } \{\sqrt{15}(2|V|-2)\ [(2|V|2) - (0|V|0)]^{-1}\}$; $\delta_b = {}^1/_2 \text{ arc tan } \{-\sqrt{35/4}(2|V|-2)[17(2|V|2) - 8(1|V|1) - 9(0|V|0)]^{-1}\}$; $\delta_c = {}^1/_2 \text{ arc tan } \{-\sqrt{7/9}(2|V|-2)[(2|V|2) - (0|V|0)]^{-1}\}$.

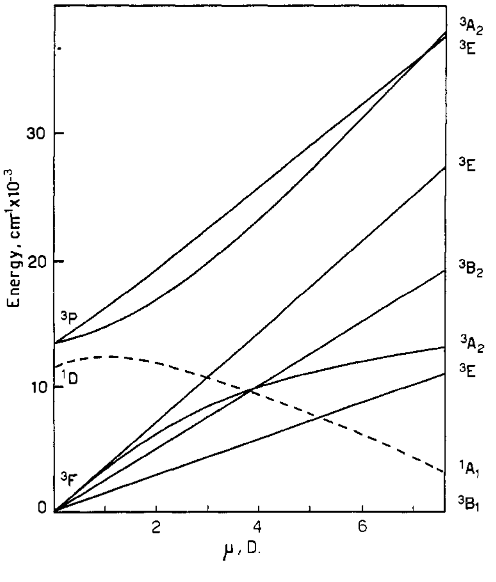

Figure 3.—Energy level diagram for the nickel(II) ion in crystalline fields of square-pyramidal symmetry. The angle L_{ax}–Ni–L_{base} is 100°.

In Figure 5 the behavior of the triplets and of the lowest-lying singlet for variations of the ratio μ_{ax}/μ_{base} in the range 0.8–1.2 is reported. Such distortions do not change the point group of the environment. The plot is valid for $\mu_{base} = 4.0$ D.

Discussion

Spectra of Five-Coordinated Nickel(II) Complexes of High-Spin Type.—The only five-coordinated high-spin complexes for which X-ray structural information is so far available are bis(N-methylsalicylaldimino)-nickel(II) (I) and bis(N-β-diethylaminoethylsalicylaldimino)nickel(II) (II). Compound I presumably exhibits trigonal-bipyramidal configuration[5] when it is a guest in the lattice of the zinc analog whose structure has been demonstrated by X-ray analysis.[10] A distorted square-pyramidal coordination has been found, for compound II by direct X-ray measurements.[4] The nickel atom is above the mean plane of the four basal donor atoms. The mean bond angle β is about 101°.

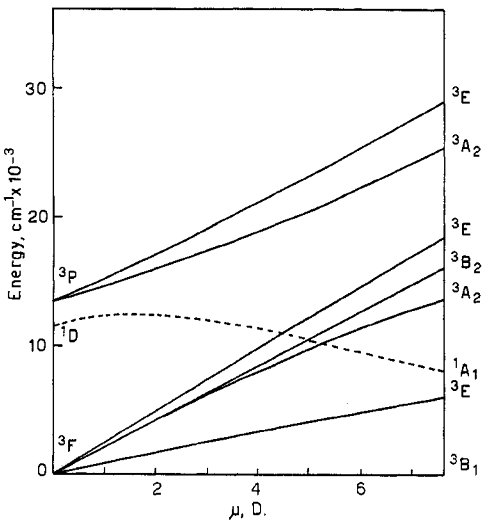

Figure 4.—Energy level diagram for the nickel(II) ion in crystalline fields of square-pyramidal symmetry. The angle L_{ax}–Ni–L_{base} is 110°.

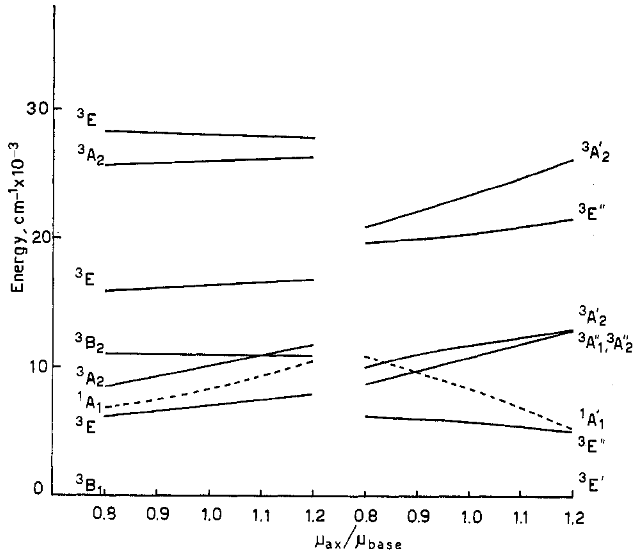

Figure 5.—The effects of axial perturbations on the energy levels of nickel(II) in square-pyramidal fields (left side) and in trigonal-bipyramidal fields (right side). The diagram is valid for μ_{base} = 4.0 D.

Both complexes I and II show some deviations from D_{3h} and C_{4v} symmetry. In fact: (a) the donor atoms are not equivalent; actually the donor sets are N_2O_3 for compound I and N_3O_2 for compound II; (b) bond lengths and angles do not strictly conform to the D_{3h} or C_{4v} symmetries. Hence, the spectra of compounds I and II could not be compared rigorously with the energy level diagrams of Figures 1–4. It must be recalled, however, that large deviations from octahedral and tetrahedral symmetry have frequently been found not to affect significantly the nickel spectra.[14] In such cases spectra have been fairly well interpreted by assuming a higher field symmetry than is actually present (rule of average environment). Since in solution both compounds I and II give rise to conformational equilibria, solid spectra have been recorded by the diffuse reflectance technique.[3,5] This limits band resolution and allows only approximate evaluation of band intensities.

The agreement between the observed frequencies of the band maxima and the frequencies of the electronic transitions is satisfactory (Table III). The best overall fit is achieved for μ values of 5.20 D. with compound I and of 4.85 D. with compound II (actually, the mean of bond distances is greater for compound II than for compound I).[4,10] These figures seem plausible when compared with μ = 3.3–4.1 D. used by Furlani[7] and Maki[8] in connection with shorter nickel–dipole distances. The energy levels are very sensitive to values for the dipole moment. For instance, the change of 1 D. in the chosen μ values affects the calculated energies of the transitions (Table III) of about 500–300 cm.$^{-1}$. For high-spin trigonal bipyramidal nickel complexes, five spin-allowed transitions are expected (Figure 1 and Table III). With the exception of the $^3E'(F) \rightarrow {}^3A_2''(F)$, $^3A_2''(2)$, all transitions can gain intensity if nickel d and p orbitals are mixed. One of these transitions, namely the $^3E'(F) \rightarrow {}^3A_2'(P)$, should be weak, as it corresponds to a two-electron jump in the strong field limit. The spectrum of compound I shows two bands and two poorly defined shoulders in the range 6000–20,000 cm.$^{-1}$ Tentatively, the first band can be assigned to the $^3E'(F) \rightarrow {}^3E''(F)$ transition, the second band to the unresolved transitions from the ground state $^3E'(F)$ to the accidentally degenerate states $^3A_1''(F)$ and $^3A_2''(F)$ and to the state $^3A_2'(F)$. The transitions to levels $^3A_2'(P)$ and $^3E'(P)$ are probably hidden by the strong bands of the ligands.

In the case of square-pyramidal nickel(II) complexes, six spin-allowed transitions are predicted (Figures 2–4 and Table III). One of these—$^3B_1(F) \rightarrow {}^3A_2(P)$—is a two-electron transition in the strong field limit. The transitions to the states $^3E(F)$ and $^3E(P)$ can acquire intensity by the mixing of metal d and p orbitals. The spectrum of compound II exhibits four bands in the range 6000–20,000 cm.$^{-1}$. The first and fourth bands are more intense than the others. From solution spectra,[3] with a rough allowance for the absorbing species of different stereochemistry, one obtains $\epsilon_1 \sim 50$, $\epsilon_2 \sim 15$, $\epsilon_3 \sim 15$, $\epsilon_4 \sim 50$. Tentatively, these bands can be assigned to the four transitions within the levels arising from the ^3F term of the free ion. The best overall fit is found by using the energy level diagram of Figure 3. In the diagram a β angle of 100° is assumed. This is very close to the actual mean angle, namely 101°, found for compound II.[4] Fitting of the spectrum with the diagram in Figure 2, which assumed β = 90°, is worse and requires μ = 4.0 D. Such dipole strength appears to be inconsistently low when compared with the analogous value for compound I. The trend of the energy levels *vs.* β (Figures 2–4) shows that a better numerical fit is achieved for β angles slightly larger than 100°. When β = 110°, however, no reasonable agreement is found. The assignment of the first and fourth

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[14] C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 1362 (1955); **10**, 887 (1956); O. Bostrup and C. K. Jørgensen, *ibid.*, **11**, 1223 (1957); J. T. Donoghue and R. Drago, *Inorg. Chem.*, **1**, 866 (1962); L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Am. Chem. Soc.*, **85**, 411 (1963).

TABLE III

COMPARISON BETWEEN PREDICTED AND OBSERVED SPECTRA OF FIVE-COORDINATED HIGH-SPIN NICKEL(II) COMPLEXES

Stereochemistry	Spin-allowed transitions	Frequencies, cm.$^{-1}$	
		Calcd.	Obsd.
Trigonal bipyramid		(μ = 5.20 D.)	(compound I)[c]
	$^3E' \rightarrow {}^3E''$[a]	7,000	7,500
	$^3A_1''$, $^3A_2''$	13,900	14,400
	$^3A_2'$[a]	14,900	
	$^3E''$[a]	22,500	
	$^3A_2'$[a,b]	26,200	
Square pyramid		(μ = 4.85 D.)	(compound II)[d]
	$^3B_1 \rightarrow {}^3E$[a]	7,200	7,700
	$^3A_2$	10,800	9,900
	$^3B_2$	12,300	12,600
	^3E[a]	17,300	16,500
	$^3A_2$[b]	26,400	
	^3E[a]	28,400	

[a] This transition can acquire intensity if the nickel d and p orbitals are mixed. [b] Two-electron jump in the strong field limit. [c] *Cf.* ref. 5. [d] *Cf.* ref. 3.

bands to transitions to ^3E states is also in agreement with their higher intensities. In fact, this indicates that some mixing of nickel d and p orbitals occurs. For this compound, too, transitions to the states coming from the ^3P term are presumably hidden by the strong ligand transitions.

Magnetic Properties.—The diagrams given in Figures 1–4 show that triplets prevail over singlets as ground states of both trigonal-bipyrimidal and square-pyramidal complexes for dipole strengths from zero to slightly above 8 D. The cross-over point, therefore, should occur only for much higher field strengths than those found in compounds I and II. The energy separation between the lowest-lying triplet and singlet states depends also on axial perturbations and, in the case of square-pyramidal complexes, on the β angle. Specifically, spin pairing is favored in trigonal-bipyramidal complexes by an increase in the axial field strength. Square-pyramidal compounds behave in the opposite manner (Figure 5). Furthermore, for the latter compounds spin pairing is disfavored by an increase in the β angle (see Figures 2–4). In any case, the crossing of the lowest singlet and triplet states occurs at lower μ values if a larger decrease of the Condon–Shortley parameters is allowed.

Many diamagnetic five-coordinated complexes of nickel(II) possessing both trigonal-bipyramidal and square-pyramidal structures are known.[1,2] In such compounds, the donor atoms are always phosphorus and arsenic together with either halogens or oxygen belonging to nitrate and perchlorate ions. It does not seem realistic to assume that these donor atoms have much larger μ values than those found for compounds I and II ($\mu \approx 5$ D. in this scheme). Most probably in this type of diamagnetic compounds spin pairing is favored by extensive formation of covalent bonds between the nickel and donor atoms. Indeed, the large molar absorbancies of the d–d bands in these low-spin compounds have been interpreted in such terms.[2] In these cases, perhaps, a molecular orbital approach would be necessary since the crystal field approach is inadequate.

Stabilities of Square-Pyramidal and Trigonal-Bipyramidal Configurations.—Many factors are responsible for the difference between the stability of trigonal-pyramidal and square-pyramidal configurations. Some of these, besides entropy factors, are metal–ligand attractions, ligand–ligand repulsions, crystal field stabilization energy (C.F.S.E.), and solvation or crystal-packing effects. Metal–ligand attractions should be nearly the same for both coordinations in a strictly electrostatic bonding scheme. This is not necessarily true if metal–ligand bonds are largely covalent in character. On the other hand, ligand–ligand repulsions are expected to be smaller for a trigonal-bipyramidal than for a square-pyramidal configuration.[15]

As far as C.F.S.E. is concerned, the calculated values are of course dependent upon the assumed model. Nevertheless, a comparison between the predicted values for both coordinations is reasonable since the same approximations have been made in both cases. In the present scheme, the slopes of the ground states energies *vs.* μ are -1685 cm.$^{-1}$ for a trigonal bipyramid and -2700, -2385, and -1585 cm.$^{-1}$ for square pyramids with β = 90, 100, and 110°, respectively. Hence C.F.S.E. is larger for the square-pyramidal configuration with β = 90 and 100° than for the trigonal-bipyramidal configuration. The reverse holds true for a square-pyramidal configuration with β = 110°. For instance, when μ = 5 D., the C.F.S.E. favors the square-pyramidal arrangement by *ca.* 5200 cm.$^{-1}$ = 15 kcal./mole, when β = 90°, and by *ca.* 3500 cm.$^{-1}$ = 10 kcal./mole, when β = 100°. With β = 110°, a trigonal-bipyramidal arrangement is favored instead by *ca.* 1.5 kcal./mole. Anyhow, for square pyramids it appears that the C.F.S.E. tends to act against values of β which deviate appreciably from 90°.

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(15) Nevertheless, a square-pyramidal configuration with β = 104° is expected to be energetically only a little less favorable than the trigonal-bipyramidal configuration; see J. Zemann, *Z. anorg. allgem. Chem.*, **324**, 241 (1963).