Ni[P(O-*o*-tolyl)$_3$]$_3$, 41716-77-2; N$_2$[Ni(PCy$_3$)$_2$]$_2$, 21729-50-0; Ni(PPh$_3$)$_3$, 25136-46-3; (ACN)$_2$Ni, 12266-58-9; (C$_2$H$_4$)Ni(PPh$_3$)$_2$, 23777-40-4; (S)NiL$_2$, 41685-58-9; (MA)NiL$_2$, 41813-01-8; (C$_2$H$_4$)Ni(PCy$_3$)$_2$, 41685-59-0; (COD)NiL$_2$, 41685-51-2; (ACN)NiL$_2$, 31666-48-5; (2-BN)NiL$_2$, 41685-61-4; (C$_2$H$_4$)NiL$_2$, 31666-47-4; (COD)$_2$Ni, 1295-35-8; K$_2$NiF$_6$, 17218-47-2; π-C$_4$H$_7$Ni[P(OEt)$_3$]$_2$PF$_6$, 32678-25-4; Ni(NO$_3$)$_2$, 13138-45-9; Ni(3-PN)$_6$(ZnCl$_3$)$_2$, 41685-63-6; Ni(NH$_3$)$_6$(ZnCl$_3$)$_2$, 41685-64-7; NiCl$_2$, 7718-54-9; (π-C$_5$H$_5$)$_2$Ni, 1271-28-9; K$_2$Ni(CN)$_4$, 14220-17-8; Ni[CH$_3$C(CH$_2$PPh$_2$)$_3$(NO)]BPh$_4$, 33789-62-7; [Ni(acac)$_2$]$_3$, 29090-30-0; Me$_2$Ni(dipy), 32370-42-6; ZnNi(CN)$_4$, 41685-66-9; Ni[PPh(OEt)$_2$]$_3$(CN)$_2$, 24419-45-2; Ni(PPh$_2$Et)$_2$Cl$_2$, 15633-29-1; Ni(PPh$_2$Et)$_2$I$_2$, 41685-69-2; Ni(PPh$_3$)$_2$(SCN)$_2$, 15709-62-3; Ni(PPh$_2$Et)$_2$Br$_2$, 41716-78-3; Me$_2$Ni(diphos), 31387-22-1; π-C$_3$H$_5$Ni(PPh$_3$)Br, 12336-45-7; PhNi(PEt$_3$)$_2$CN, 41685-72-7; Ni(PPh$_2$Et)$_2$Br$_2$, 15633-28-0; B, 7440-42-8; C, 7440-44-0; N, 7727-37-9; O, 7782-44-7; F, 7782-41-4; P, 7723-14-0; S, 7704-34-9; Cl, 7782-50-5; K, 7440-09-7; Ni, 7440-02-0; Zn, 7440-66-6; Br, 7726-95-6; I, 7553-56-2.

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Hindered Ligand Systems. VII. Crystal Field Spectrum of *cis,cis*-1,3,5-Tris(pyridine-2-carboxaldimino)cyclohexanenickel(II)

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The assignment of the spectrum of the titled compound, based on conventional crystal field calculations and averaged angular coordinates from X-ray structural data ($\phi = 32°$, $\theta_1 = 51°$, and $\theta_2 = 57°$), has not been successful. The criteria for failure include the necessity of choosing a value of Dq in large excess of those normally found for tris(α-diimine) complexes of Ni(II). A series of solutions which approximate the observed spectrum has been obtained with $\phi > 32°$ and θ(average) = 57 ± 1°. The solutions require Dq values which are only slightly larger than the normal range. A possible explanation for the increased value of ϕ is explored.

The existence and approximate formation criteria of a group of complexes whose stereochemistries range between trigonal prismatic and octahedral have been established and discussed in some detail.[1] Each complex can be classified according to its twist angle, ϕ, the angle which describes the rotation of one triangular face of donor atoms with respect to the other.[2] Sexadentate ligands which contain the pyridine-2-carboxaldimino group comprise a series of these complexes wherein equilibrium values of ϕ occur throughout the range between 0 and 60°. Complexes of one of these ligands, *cis,cis*-1,3,5-tris(pyridine-2-carboxaldimino)cyclohexane ((py)$_3$tach) have been investigated in this laboratory.[3] The structure of the Zn(II) complex is known[4] to have an average twist angle of about 4°, while the Mn(II) and Co(II) complexes are isomorphous and presumably isostructural.[3,4] The average twist angle in the Ni(II) complex has been shown[5] to be about 32°.

An interpretation of the spectrum of the Co(II) complex, assuming $\phi = 0°$, was seemingly straightforward,[3] but the spectrum of the Ni(II) complex, which was first recorded[6] in 1968, has not yet been interpreted with certainty. The purpose of this publication is to outline some of the problems associated with the interpretation according to crystal field theory.

Crystal Field Theory

The crystal field potential which was used for all calculations is

$$V = 7eq\pi^{1/2}\{3(1/5)^{1/2}(BY)_2{}^0(r^2/R^3) + ((3/4)(BY)_4{}^0 - 35(1/140)^{1/2}[(BY)_4{}^3 - (BY)_4{}^{-3}])(r^4/R^5)\}$$

with $(BY)_l{}^m = B_l{}^m(\theta_1,\theta_2)Y_l{}^m$ and

$$B_2{}^0(\theta_1,\theta_2) = (1/7)(3[\cos^2\theta_1 + \cos^2(\pi - \theta_2)] - 2)$$

$$B_4{}^0(\theta_1,\theta_2) = (1/7)((35/3)[\cos^4\theta_1 + \cos^4(\pi - \theta_2)] - 10[\cos^2\theta_1 + \cos^2(\pi - \theta_2)] + 2)$$

$$B_4{}^{\pm 3}(\theta_1,\theta_2) = (1/7)(\sin^3\theta_1\cos\theta_1 + \sin^3(\pi - \theta_2)\cos(\pi - \theta_2)e^{\mp i3\phi})$$

where θ_1 and θ_2 are polar angles and ϕ is the twist angle.[7] This potential is appropriate to D_{3h} ($\phi = 0°$) and D_3 ($0° < \phi < 60°$) symmetries if $\theta_1 = \theta_2$ and O_h ($\phi = 60°$) symmetry if $\theta_1 = \theta_2 = \cos^{-1}(1/3)^{1/2}$. It is also appropriate to C_{3v} ($\phi = 0°$) and C_3 ($0° < \phi < 60°$) symmetries if $\theta_1 \neq \theta_2$. The one-electron matrix elements are $\langle d_{\pm 2}|V|d_{\pm 2}\rangle = -3B_0{}^2\rho_2 + (3/8)B_4{}^0\rho_4$, $\langle d_{\pm 1}|V|d_{\pm 1}\rangle = (3/2)B_2{}^0\rho_2 - (3/2)B_4{}^0\rho_4$, $\langle d_0|V|d_0\rangle = 3B_2{}^0\rho_2 + (9/4)B_4{}^0\rho_4$, and $\langle d_{\pm 2}|V|d_{\mp 1}\rangle = \pm(35/4)B^{\pm 3}\rho_4$, where $\rho_n = eq\langle r^n/R^{n+1}\rangle$ and $B_l{}^m(\theta_1,\theta_2)$ is further abbreviated to $B_l{}^m$.

It is possible to express $B_l{}^0(\theta_1,\theta_2)$ in terms of its value at $\theta_1 = \theta_2 = \cos^{-1}(1/3)^{1/2}$ (the octahedral value) and a complicated, but easily derived, set of trigonometric functions of β_1 and β_2, the latter being the respective differences between the observed (or effective) polar angles and the octahedral

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[1] R. A. D. Wentworth, *Coord. Chem. Rev.*, 9, 171 (1972).

[2] This angle has also been denoted by α in ref 1.

[3] W. O. Gillum, R. A. D. Wentworth, and R. F. Childers, *Inorg. Chem.*, 9, 1825 (1970); 11, 1446 (1972).

[4] W. O. Gillum, J. C. Huffman, W. E. Streib, and R. A. D. Wentworth, *Chem. Commun.*, 843 (1969).

[5] E. B. Fleischer, A. E. Gebala, and D. R. Swift, *Chem. Commun.*, 1280 (1971); E. B. Fleischer, A. E. Gebala, D. R. Swift, and P. A. Tasker, *Inorg. Chem.*, 11, 2775 (1972).

[6] J. E. Sarneski and F. L. Urbach, *Chem. Commun.*, 1025 (1968).

[7] The bite angle (α) is sometimes used by other authors as a structural parameter. This angle, defined as the intraligand donor atom–metal atom–donor atom angle, is related to the polar and twist angles in a regular polyhedron ($\theta_1 = \theta_2 = \theta$) by $\cos\alpha = \sin^2\theta\cos\phi - \cos^2\theta$. Because of this relationship, if ϕ is allowed to vary from 0 to 60°, while holding θ at the normal octahedral value as in Figure 1, α will vary from 70° 32′ to 90°. Thus, it is clear that three-dimensional space is required ideally to depict the energy variation. If $\theta_1 \neq \theta_2$, then $\cos\alpha = \sin\theta_1\sin\theta_2\cos\phi - \cos\theta_1\cos\theta_2$ and four-dimensional space is required.

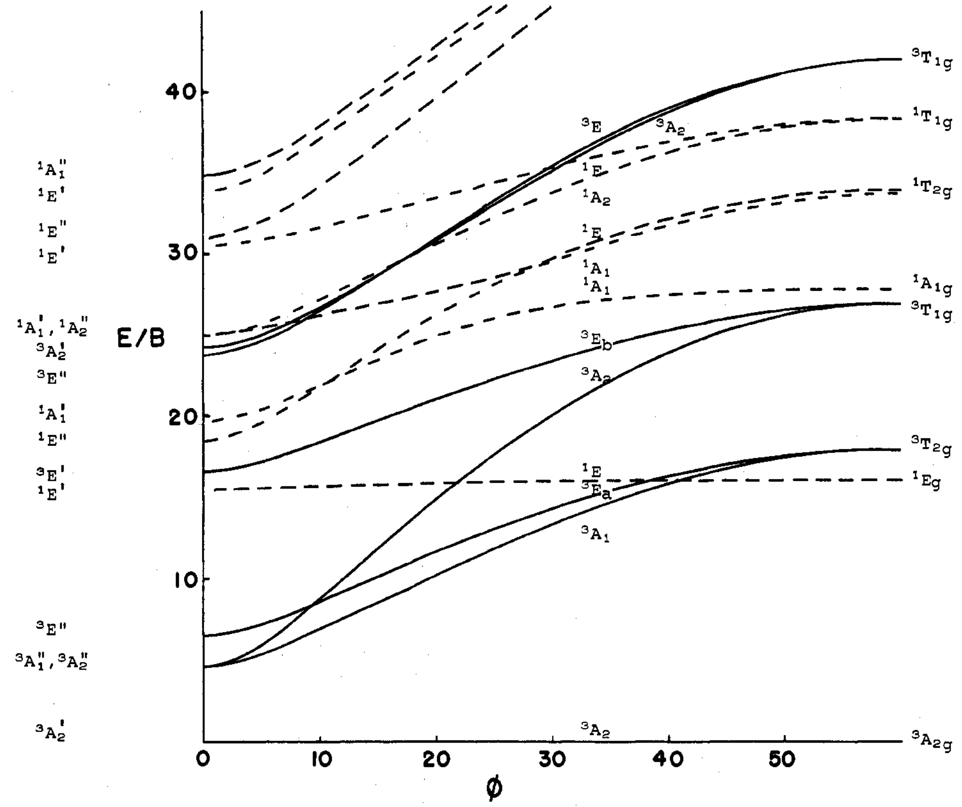

Figure 1. Triplet (——) and singlet (- - - -) energy levels for a d^8 complex as a function of ϕ with $\theta_1 = \theta_2 = \cos^{-1}(1/3)^{1/2}$, $Dq/B = 1.80$, and $C/B = 4.18$.

value.[8] This expansion is particularly appropriate with $B_4^0(\theta_1,\theta_2)$

$$B_4^0(\theta_1,\theta_2) = -{}^8/_{27} + f(\beta_1,\beta_2)$$

A new parameter is then defined as

$$Dr = -(9/16)B_4^0(\theta_1,\theta_2)\rho_4$$

When θ_1 and θ_2 assume the octahedral value, it can be seen that, in addition to $B_2^0(54.7,54.7°) = 0$, $Dr = Dq = (1/6)\rho_4$ where Dq is the conventional octahedral parameter. At other values of θ_1 and θ_2, Dq and Dr are related by

$$Dq = Dr + (9/16)f(\beta_1,\beta_2)\rho_4$$

An energy level diagram appropriate to twisting $Ni(bipy)_3^{2+}$ from $\phi = 60°$ to $\phi = 0°$ is shown in Figure 1. In this calculation, $\theta_1 = \theta_2 = \cos^{-1}(1/3)^{1/2}$, $Dr = Dq = 1280$ cm^{-1}, $B = 710$ cm^{-1}, and $C/B = 4.18$.[9] Several important features of the diagram are worthy of note. First, the energy of the ${}^1E$ state is virtually independent of the twist angle. Thus, each member of a series of Ni(II) complexes which have similar ligands but different twist angles should possess an absorption (corresponding to a transition to the ${}^1E$ state) at relatively constant wave numbers, provided that absorption is not masked by nearby spin-allowed absorptions. For example, transitions to the ${}^3A_1$ and ${}^3E_a$ states would probably overshadow and possibly completely obscure the transition to the singlet state in a complex with a twist angle near 40°. Another important feature of the diagram is that all transitional energies remain relatively constant near $\phi = 0°$ and again near $\phi = 60°$. Thus an "octahedral" complex may actually have a twist angle as low as 50° but have an absorption spectrum which can be evaluated according to strict O_h microsymmetry without appreciable error. Still another aspect of the diagram is the precipitous change in the triplet-to-triplet transitional energies that occur in the interval between $\phi = 10°$ and $\phi = 50°$. Consequently, small changes in the twist angle, whatever their cause, will bring about large changes in the transitional energies for the triplet states. It is also possible to anticipate another development. The electronic charge (lone pair) from the ligating atom in a constrained ligand, such as twisted $(py)_3$tach, will not necessarily lie on the metal atom–ligating atom internuclear vector. In that event, observed values of ϕ may need to be replaced by an effective value which describes the location of the electronic charge rather than the position of the ligating atom.

$Ni((py)_3tach)^{2+}$

The unit cell of the perchlorate salt of this complex contains two crystallographically independent complex ions with similar bond angles and bond distances.[5] The twist angles range between 30 and 34° while one polar angle (z axis–Ni–aldimino N) is 51–53° and the other is 56–58°. The Ni–aldimino N bond distances are found between 1.96 and 2.12 Å and the Ni–pyridine N bond distances range between 2.08 and 2.16 Å. The average value of the former is somewhat less than that of the latter but it is clear that some overlap exists between the two ranges. For the purpose of calculations, it has been assumed that all metal–ligand bond distances are identical and that the average angles are given by $\phi = 32°$, $\theta_1 = 51°$, and $\theta_2 = 57°$. The model polyhedron which results possesses C_3 symmetry. However, the symmetry labels which are used in the following discussion are appropriate to D_3 rather than C_3 symmetry in order to make Figure 1 more useful. The correlation between the two symmetries is

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[8] The set of trigonometric functions of β_1 and β_2 has the form $f(\beta_1,\beta_2) = 5[7(\sin^4\beta_1 + \sin^4\beta_2) - 4(\sin^2\beta_1 + \sin^2\beta_2) - 28(2)^{1/2}\cdot(\sin^3\beta_1\cos\beta_1 + \sin^3\beta_2\cos\beta_2) + 56(\sin^2\beta_1\cos^2\beta_1 + \sin^2\beta_2\cos^2\beta_2) + 8(2)^{1/2}(\sin\beta_1\cos\beta_1 + \sin\beta_2\cos\beta_2)]/189$.

[9] R. A. Palmer and T. S. Piper, *Inorg. Chem.*, 5, 864 (1966). The value of C/B was calculated from the data within this reference.

C_3	D_3
A	A_1, A_2
E	E

The solution spectrum, which appears in Table I, agrees closely with a solid-state spectrum (Nujol mull) taken at 80°K, so that no major changes in either bond angles or distances have occurred in solution. Furthermore, no new bands have been resolved.

Parameters[10] obtained from the spectra of a series tris(α-diimine) complexes of Ni(II), assuming O_h microsymmetry, have been used to provide reasonable estimates of these parameters in $Ni((py)_3tach)^{2+}$. The value of Dq in those complexes lies between 1040 and 1280 cm^{-1}, while the $^3A_{2g} \rightarrow {}^1E_g$ transition lies between 11,400 and 12,200 cm^{-1}. The value of B, calculated by us from the value of Dq and the wave number of the band which was assigned to the $^3A_2 \rightarrow {}^3T_1(F)$ transition, ranges with a few exceptions, between 740 and 880 cm^{-1}.[11] Unfortunately, values calculated in this manner are not as accurate generally as those calculated from the wave number of the $^3A_2 \rightarrow {}^3T_1(P)$ transition. However, this transition is not observed with this series of complexes. The expected range of ρ_2 is even less certain. Piper and Carlin[12] have estimated that ρ_2/ρ_4 should lie between 2 and 6 for first-row transition metal ions, but others[13] have used values as high as 10.

Using the average polar angles given above, $f(\beta_1,\beta_2)$ is only 0.000394 and Dr is virtually identical with Dq over the expected values of ρ_4 ($6 \times 1040 \leqslant 6Dq \leqslant 6 \times 1280$). In addition, $B_2{}^0(51,57°)$ is only 0.0115. A typical energy level diagram is shown in Figure 2. Thus there exists the possibility for three bands in the near-infrared region of the spectrum: $^3A_2 \rightarrow {}^3A_1$, $^3A_2 \rightarrow {}^3E_a$, $^3A_2 \rightarrow {}^1E$. This number can be reduced to 2 if the $^3A_1$ and ^3E_a states are degenerate (or nearly so) or if the transitions to the nondegenerate $^3A_2$ and ^3E_a states have sufficient intensity to mask the spin-forbidden transition. These possibilities lead to assignments I and II in Table I.[14,15] However, both assignments require two concomitant conditions: Dq values in excess of 1450 cm^{-1} and virtually no intensity in the $^3A_2 \rightarrow {}^3A_2$ transition. These conditions represent serious drawbacks to either assignment. The first condition requires Dq values far greater than that found in $Ni(bipy)_3{}^{2+}$ (1280 cm^{-1}). The second condition requires that the selection rules are *strictly* governed by D_3 symmetry, wherein $^3A_2 \nrightarrow {}^3A_2$, rather than C_3 symmetry where the transition is allowed. However, even under the best of circumstances, *strict* adherence to the electric dipole selection rules for a given symmetry is rarely, if ever, observed. These conditions, which must be simultaneously operative, would appear to make assignments I and II improbable.

One of the most disturbing features in the spectrum of $Ni((py)_3tach)^{2+}$ is the band at 19,200 cm^{-1} which exactly duplicates the position[9] of the $^3A_2 \rightarrow {}^3T_1(F)$ transition in $Ni(bipy)_3{}^{2+}$. Yet, according to Figure 1, energies for transitions to the $^3A_2$ and ^3E_b states at $\phi = 32°$ would be expected to lie far below that wave number. It was shown in the preceding paragraph that the observed deviations from the octahedral values of the polar angles do not cause sufficient perturbations to allow this band to appear at 19,200 cm^{-1}, unless Dq values in excess of 1450 cm^{-1} are used. A possible explanation is that *effective* values of the polar angles and the twist angle differ considerably from the values obtained from crystallography. The variables then become ϕ, θ_1, and θ_2, as well as ρ_2, ρ_4, B, and C, an alarming number to be determined from a spectrum containing only three bands, even though the rather narrow restrictions on ρ_4 and B will still be applicable, along with the broader restrictions on ρ_2. In order to decrease the number of variables (and the expense of the calculation), θ_1 and θ_2 have been replaced by $\bar{\theta}$, the average effective polar angle. This substitution can be justified in part since the effective polar angles, whatever their values, can be expressed in terms of the average polar angle ($\bar{\theta}$) as $\bar{\theta} + \gamma$ and $\bar{\theta} - \gamma$. If γ is no larger than a few degrees, then $B_l{}^m(\theta_1,\theta_2) \approx B_l{}^m(\bar{\theta},\bar{\theta})$. For example, if effective values of θ_1 and θ_2 are 51 and 57° respectively, $\bar{\theta}$ becomes 54°, $B_4{}^0(54,54°) = 0.30334$, and $B_4{}^0(51,57°) = 0.29575$. The overall effect of this approximation can be judged from the results in Table II, wherein eigenvalues are compared for each case, assuming $Dq/B = 1.80$, $\phi = 32°$, $\rho_2/\rho_4 = 10.0$, and $C/B = 4.00$.

Eigenvalues were obtained throughout the ranges given by $28° \leqslant \phi \leqslant 48°$ (in 2° intervals), $46° \leqslant \theta \leqslant 60°$ (in 2° intervals), $1.60 \leqslant Dq/B \leqslant 1.80$ (in intervals of 0.02), and $0 \leqslant \rho_2/\rho_4 \leqslant 10$ (in unit intervals). The effect of the value of the polar angle on the energies of the important ligand field states is shown in Figure 3. While the energies of $^3A_1$, ^3E_a, and ^3E_b states pass through a maximum as the polar angle is increased from 46 to 60°, the energy of the ^1E state remains relatively constant and that of the $^3A_2$ excited state increases steadily until it eventually exceeds the energy of the ^3E_b state. Increasing the value of either ϕ or Dq/B increases the energies of all states.

The intent of these calculations is to attempt to assign the transitions to the $^3A_1$ and ^3E_a states to the bands at 11,100 and 12,200 cm^{-1} while placing the transition to the $^3A_2$ state at 19,200 cm^{-1}. A series of solutions, rather than a unique solution, agrees approximately with the observed spectrum. All of these require twist angles in excess of 38° and polar angles of about 57 ± 1°. To fit the spectrum in each case, however, requires Dq values of 1330–1380 cm^{-1}, which are in moderate excess of the highest values found for other tris(α-diimine)nickel(II) complexes.[10] A typical example is given as assignment III in Table I. In view of the approximation involving the polar angle, the agreement appears to be good. Moreover, this approximation may be responsible for Dq values slightly larger than those within the acceptable range.

Still another assignment appears to be possible after inspecting the results of these calculations. The bands at 11,100, 12,200, and 19,200 cm^{-1} can be assigned to transitions to the $^3A_1$, ^1E, and ^3E_a states, respectively, if $\phi \geqslant 38°$, $\theta \approx 52°$, $Dq/B > 1.70$, and $\rho_2/\rho_4 > 5$. This assignment is improbable, however, since a Dq value in excess of 1400 cm^{-1} is required to fit the spectrum in each case.

Discussion

The calculations have indicated that a reasonable assignment for the spectrum of $Ni((py)_3tach)^{2+}$ cannot be obtained from the crystallographic data. The most plausible assignment obtained thus far requires major increases in the

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[10] M. A. Robinson, J. D. Curry, and D. H. Busch, *Inorg. Chem.*, 2, 1178 (1963).

[11] Values for B as low as 20 cm^{-1} and as high as 1980 cm^{-1} have also been obtained. It is not known whether these results are due to misprints, incorrect assignments, or the expected rhombic symmetry of the complexes which are involved.

[12] T. S. Piper and R. L. Carlin, *J. Chem. Phys.*, 33, 1208 (1960).

[13] M. Gerloch and P. N. Quested, *J. Chem. Soc.*, 3729 (1971).

[14] Placing the $^3A_2 \rightarrow {}^1E$ transition at 12,127 cm^{-1} in assignment II is rather arbitrary since it is the result of setting $C/B = 4.00$.

[15] No solutions were found which would simultaneously place the transitions to the $^3A_1$ and ^3E_a states under the band envelope centered at 11,100 cm^{-1} and the transition to the ^1E state at 12,200 cm^{-1}.

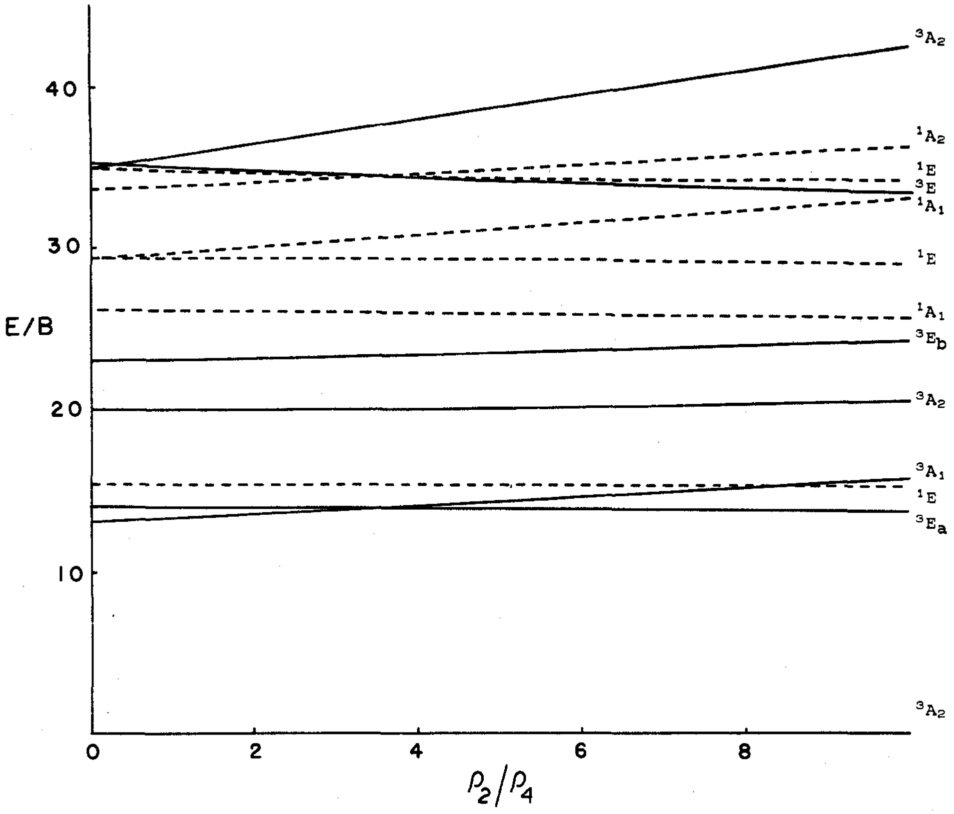

Figure 2. Triplet (——) and singlet (- - - -) energy levels for a d^8 complex as a function of ρ_2/ρ_4 with $\phi = 32°$, $\theta_1 = 51°$, $\theta_2 = 57°$, $Dq/B = 1.80$, and $C/B = 4.00$.

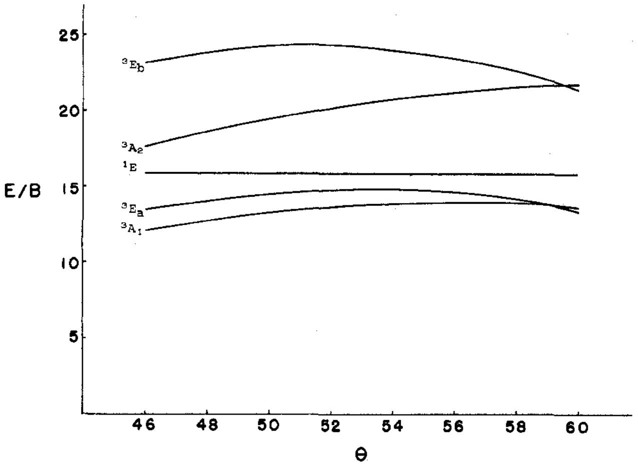

Figure 3. Spectroscopically important energy levels for a d^8 complex as a function of θ with $\phi = 32°$, $Dq/B = 1.80$, $\rho_2/\rho_4 = 0$, and $C/B = 4.18$.

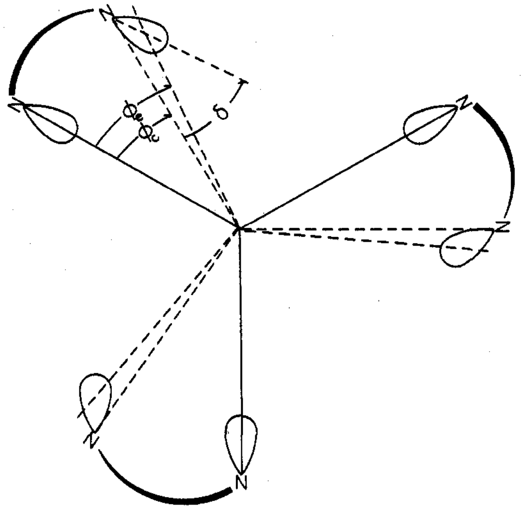

Figure 4. The projection of a half-twisted polyhedron down the C_3 axis which shows the possibility that the twist angle due to atomic distribution (ϕ_c) is less than the twist angle due to electron pair distribution (ϕ_e). The coincidence of ϕ_c and ϕ_e can only occur if $\delta = 0°$.

crystallographic twist angle and possibly slight increases in the average polar angle. Deviations between the crystallographic value of the polar angle and that required to fit observed data have been noted in the past for simple systems with pseudooctahedral coordination environments. For example, the magnetic properties[16] of $Fe(H_2O)_6SiF_6$ and the polarized crystal spectrum[17] of the tris(acetylacetonate) of Co(III) have been explained by a trigonal compression ($\theta > \cos^{-1} (1/3)^{1/2}$) rather than by the expected trigonal elongation (although in each case there are adequate reasons to question this expectation). There are no past examples of deviations in the twist angle and, indeed, it would seem fruitless to search for such deviations in pseudooctahedral complexes. The effective twist angle would have to be less than about 50° in order noticeably to influence the energies of the ligand field states (Figure 1). However, in the case of $Ni((py)_3tach)^{2+}$, this criterion is present and it would appear that the effective twist angle could be greater than is indicated by the distribution of N atoms.

This result is not entirely unreasonable. The natural conformation of a pyridine-2-carboxaldimino moiety ligated to a metal with little or no octahedral ligand field stabilization energy, such as Zn(II) or high-spin Mn(II), should

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[16] M. Gerloch, J. Lewis, G. G. Phillips, and P. N. Quested, *J. Chem. Soc.*, 1941 (1970).

[17] T. S. Piper and R. L. Carlin, *J. Chem. Phys.*, 36, 3330 (1962).

Table I. Ligand Field Spectrum of $Ni((py)_3tach)^{2+}$ (cm^{-1})

Obsd	Calcd		
	I[a]	II[b]	III[c]
19,200	$^3A_2 \rightarrow {}^3E_b$ 19,199	$^3A_2 \rightarrow {}^3E_b$ 19,212	$^3A_2 \rightarrow {}^3E_b$ 19,550[d] $^3A_2 \rightarrow {}^3A_2$ 19,195
	$^3A_2 \rightarrow {}^3A_2$ 16,715	$^3A_2 \rightarrow {}^3A_2$ 16,786	
12,200	$^3A_2 \rightarrow {}^3E_a$ 12,111 $^3A_2 \rightarrow {}^3A_1$ 11,974	$^3A_2 \rightarrow {}^1E$ 12,127 $^3A_2 \rightarrow {}^3E_a$ 11,996	$^3A_2 \rightarrow {}^3E_a$ 12,729
11,100	$^3A_2 \rightarrow {}^1E$ 11,102	$^3A_2 \rightarrow {}^3A_1$ 11,252	$^3A_2 \rightarrow {}^3A_1$ 11,038

[a] Calculated from $Dq = 1495$ cm^{-1}, $B = 712$ cm^{-1}, $\rho_2/\rho_4 = 3.00$, and $C/B = 4.00$. [b] Calculated from $Dq = 1476$ cm^{-1}, $B = 777$ cm^{-1}, $\rho_2/\rho_4 = 0$, and $C/B = 4.00$. [c] Calculated from $\phi = 40°$, $\theta = 56°$, $Dq = 1360$ cm^{-1}, $B = 782$ cm^{-1}, and $\rho_2/\rho_4 = 6.0$. Singlet levels were not considered. [d] Possibly masked by the tail of strong absorption at higher wave numbers.

Table II. Comparison of Eigenvalues[a]

	A[b]	B[c]
$[E(^3E_b) - E(^3A_2)]/B$	24.762	24.988
$[E(^3A_2) - E(^3A_2)]/B$	21.112	21.204
$[E(^3E_a) - E(^3A_2)]/B$	16.352	16.329
$[E(^1E) - E(^3A_2)]/B$	15.376	15.395
$[E(^3A_1) - E(^3A_2)]/B$	14.288	14.588

[a] Calculated from $Dq/B = 1.80$, $\phi = 32°$, $\rho_2/\rho_4 = 10.0$, and $C/B = 4.00$. [b] $\theta_1 = 51°; \theta_2 = 57°$. [c] $\theta_1 = \theta_2 = 54°$.

be planar.[1,4] If the polyhedron is capped with a rigid group, such as *cis,cis*-1,3,5-cyclohexyl, the resulting stereochemistry about the metal atom will be trigonal prismatic. Distortions toward octahedral stereochemistry can be induced by inserting a metal with a greater tendency toward octahedral coordination, such as Ni(II).[5] This distortional rotation must be accompanied by bond rotations which will cause the entire pyridine ring to rotate, but possibly with the electronic charge from the sp^2 ligating orbital advancing further than the pyridine N atom to which it belongs. Thus, the electron pair distribution about the metal atom could be more twisted than the atomic distribution as shown in Figure 4 wherein the crystallographic and electronic twist angles are denoted by ϕ_c and ϕ_e, respectively. Another angle, δ, is also included in the figure. This angle is the *projected* supplement of the angle made by the Ni-pyridine N vector and the vector between that N atom and the para C atom of the pyridine ring. The ligating orbital should lie along a line which contains the latter. The coincidence of ϕ_c and ϕ_e can only occur if $\delta = 0°$. The six values of δ (three for each nonequivalent complex ion) were calculated by projecting the N and para C atoms, whose atomic coordinates are known,[5] into a plane which was parallel with the least-squares plane of the cyclohexane ring and which contained the Ni atom. This plane is the plane of the paper in Figure 4 to a good approximation. All values of δ were found to be approximately zero, which requires that $\phi_c = \phi_e$. However, angular distortions, such as those sought and not found above, can also occur at the imino N atoms. These atoms unfortunately do not possess regular bond angles and no method of comparing ϕ_c and ϕ_e has been devised for these sites.

It is also possible that, in this case as well as the cases of $Fe(H_2O)_6SiF_6$ and $Co(acac)_3$, the apparent incompatibility of the observed angular parameters with the electronic spectrum may only indicate the shortcomings of a point charge model. It is noteworthy, however, that recently published calculations,[18] based on the angular overlap method and idealized angular coordinates from the known structure, failed to account satisfactorily for the spectrum of $Ni((py)_3tach)^{2+}$.

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