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TRIGONAL PRISMATIC vs. OCTAHEDRAL STEREOCHEMISTRY IN COMPLEXES DERIVED FROM INNOCENT LIGANDS

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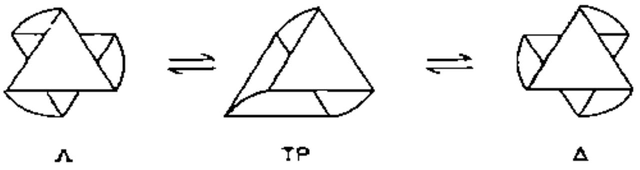
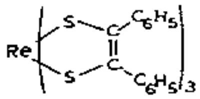
A. INTRODUCTION

Although the octahedral stereochemistry of certain metal complexes has been known since the time of Werner, trigonal-prismatic (TP) stereochemistry was reported first[1] only in 1923 for the indefinitely extended lattices of the minerals MoS_2 and WS_2. Without any examples of this stereochemistry in molecular complexes, Bailar was led in 1958 to propose that the isomerization and racemization of certain octahedral complexes could proceed by a trigonal twist through a TP intermediate[2], i.e.



However, through the ensuing years it was assumed that a six-coordinate complex in its ground state must have octahedral stereochemistry without much regard for a ligand's composition or possible conformations. This assumption proved to be warranted in all but a few cases. The report[3] that a dithiolato complex



had been shown by X-ray methods to have a near perfect TP stereochemistry was thus received with a great deal of surprise. This report engendered further structural determinations which definitely established TP coordination for $Mo(S_2C_2H_2)_3$ (ref. 4) and near-TP coordination for $V[S_2C_2(C_6H_5)_2]_3$ (ref. 5). Isomorphism and spectroscopic studies suggested TP or near-TP stereochemistries for many other dithiolato complexes of these metal atoms and those of Cr and W as well. A two-electron reduction of the neutral complexes was found to cause a twist about the three-fold axis toward octahedral coordination in the cases of $M[S_2C_2(CN)_2]_3{}^{2-}$ (M = V (ref. 6), Mo (ref. 7) and Fe (ref. 8)).

Since twisting about the three-fold axis does occur, it is not only convenient but appropriate to relate octahedral, TP, and intermediate stereochemistries by the magnitude of the twist as well as the approximate energetics of the twist. A generalized energy diagram for the racemization of octahedral complexes according to Bailar's trigonal twist appears in Fig. 1(a). The energy is shown as a function of the twist angle, α, which describes the rotation of one triangular face of the prism with respect to the other. Also appearing (Fig. 1(b)) is a diagram for twisting a complex in which the TP stereochemistry ($\alpha = 0°$) is more stable than the octahedral donor atom environment ($\alpha = 60°$) as is the case with complexes such as $Re[S_2C_2(C_6H_5)_2]_3$ or $Mo(S_2C_2H_2)_3$. The final diagram (Fig. 1(c) applies to complexes such as $Mo[S_2C_2(CN)_2]_3{}^{2-}$, in which the equilibrium stereochemistry lies between that of a trigonal prism and an octahedron. The dithiolato complexes of known structures are listed in Table 1 according to the twist angle. An excellent review[9], which describes the structural systematics of these and other dithiolato complexes, has appeared already. It is not the intent of this review to duplicate the other but to examine the systematics of complexes derived from so-called innocent ligands and metal atoms from the first transition series. Criteria for octahedral or TP stereochemistries with innocent ligands will be derived and complexes with known structures will be examined in the light of these criteria.

TABLE 1

Stereochemistry of some $M(S_2C_2R_2)_3^{n-}$ complexes

M	R	*n*	α (deg)	Ref.
V	C_6H_5	0	8.5 [a]	5
V	CN	2	Twisted [b]	6
Mo	H	0	0	4
Mo	CN	2	27	7
Re	C_6H_5	0	< 1	3
Fe	CN	2	~60	8

[a] Calculated from the atomic coordinates.

[b] Neither the twist angle nor the atomic coordinates are given in ref. 6.

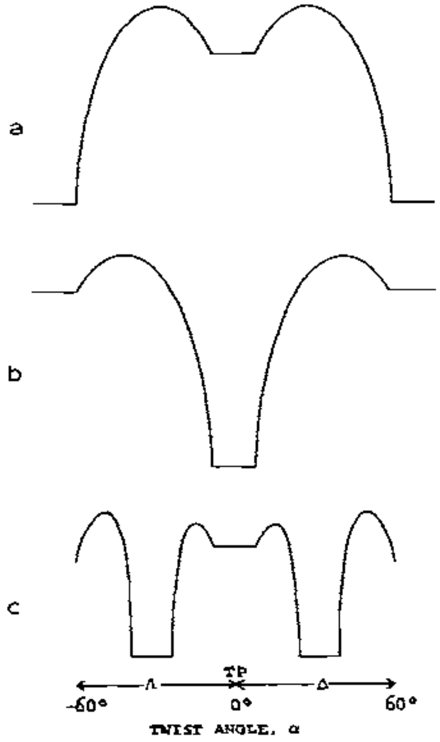
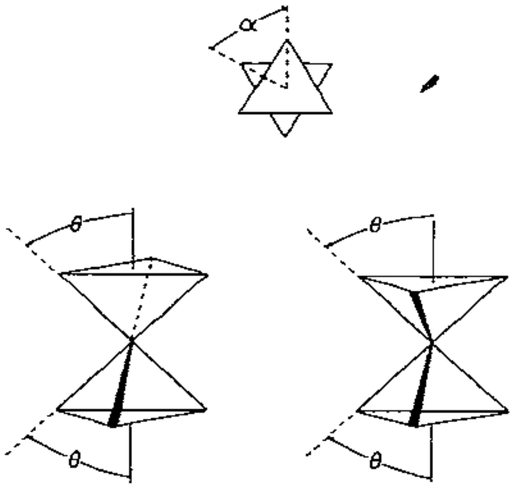


Fig. 1. Generalized energy profiles for twisting six-coordinate polyhedra about their three-fold axes. (a) The trigonal prism is less stable than the octahedral enantiomers. (b) The trigonal prism is more stable than the octahedral enantiomers. (c) Enantiomeric polyhedra with $0° < \alpha < 60°$ are more stable than either the octahedral counterparts or the trigonal prism.

B. LIGAND AND METAL STEREOCHEMICAL PREFERENCES

The stabilization of one six-coordinate geometry with respect to another will be the result of (*a*) maximizing bonding interactions between the atoms of the ligand itself; (*b*) minimizing all non-bonded contacts, and (*c*) maximizing the metal–ligand bonding interactions. With reference to condition (*c*), detailed calculations of the metal–ligand bonding energy in either geometry would be virtually impossible. However, if all contributions to the bonding energy, other than ligand field effects, are assumed to be roughly constant for both geometries, then a comparison of the ligand field stabilization energies (LFSE), which are readily calculated, ought to indicate the preferred stereochemistry.

It is now an easy matter to see that octahedral stereochemistry is favored over TP coordination in most cases. Twisting the octahedron shown in Fig. 2 about the three-fold axis will maintain the polar angle, θ (which we define for our purposes as the angle between the three-fold axis and the nearest metal–ligand internuclear distances), of $\cos^{-1}\sqrt{1/3}$. (54.73°) in the trigonal prism. The twisting will result also in eclipsed ligand donor atoms whose internuclear separation is only $\sqrt{2/3}$ of its value in the octahedron. Consequently,

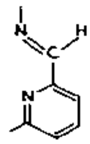


α=60° α=0°

Fig. 2. The relationship between an octahedron and a trigonal prism. It should be noted that the definition of the polar angle differs from the usual one: θ and $\pi-\theta$ measured from the positive z axis.

condition (*b*) is violated. This situation could be alleviated by lengthening the metal—ligand bond distance which in turn violates condition (*c*), or by a trigonal elongation which will increase the non-bonded contacts along the three-fold axis, a violation of condition (*b*) again. Because of this, the relationship between octahedral and TP stereochemistries in most six-coordinate complexes is that depicted in Fig. 1(a). Entirely equivalent results can be obtained by allowing six point charges on the surface of a sphere to find positions of minimum potential energy[10].

If a TP coordination geometry which is more stable than its octahedral counterparts is to be attained (Fig. 1(b)), a ligand is required which will maximize all bonding interactions and minimize all non-bonded contacts when the donor atoms are in TP array. A high degree of success has been achieved by the syntheses of rigid, hexadentate ligands which can either partially or completely encapsulate a metal atom. One or both of the trigonal faces of the prism are capped by the ligand, while three, rigid side chains emanate from one cap and terminate at the other if it is present. A particularly useful side chain is the pyridine-2-carboxaldimino moiety



which finds a maximum stability when conjugated and completely planar. Providing the caps are rigid, the natural conformation of the ligand becomes one in which the donor atoms occupy the vertices of a trigonal prism.

The equilibrium stereochemistry of the complex, however, will not be determined solely by the conformation of the ligand but by the stereochemical preference of the metal atom as well. Consider the cases which result from the interaction of a ligand whose preference is TP coordination with a series of metal atoms with differing preferences. With little or no preference for octahedral stereochemistry, the metal atom will not be able to overcome the conformational preference of the ligand, so that the equilibrium geometry of the complex will be TP. If the metal atom has an overwhelming preference for octahedral coordination, the final result will be an octahedral complex (assuming that the ligand is able to span the donor sites of an octahedron without undue perturbations of normal intraligand bond distances and angles). Alternatively, the preference of the metal atom may lie between these two extremes. In that case, the competition between the opposite preferences of the ligand and the metal atom will result in an equilibrium geometry for the complex which lies between that of an octahedron and a trigonal prism (Fig. 1(c)).

The preference of the metal atom can be determined to a first approximation by a comparison of its octahedral LFSE with that of a trigonal prism. This comparison is easier if it is established that the defined octahedral polar angle of $\cos^{-1}\sqrt{1/3}$ remains fixed in the trigonal prism, although it need not do so. Further justification for this assumption arises because the average polar angles in the complexes with known structures do not differ markedly from this value. A general ligand field potential can be derived in terms of this constant polar angle and a variable twist angle.

$$V_{\mathrm{LF}} = 14eq\sqrt{\pi}\{-Y_4^0-\sqrt{5/14}[(1-\mathrm{e}^{-i3\alpha})Y_4^3-(1-\mathrm{e}^{i3\alpha})Y_4^{-3}\}\,(r^4/R^5)/9$$

where e and r are the electronic charge and radius while q and R are the effective charge and metal–ligand distance, respectively, and the Y_l^m are spherical harmonics. (Note that V_{LF} contains a sign error in ref. 11.) The calculated orbital energies appear as a function of the twist angle in Fig. 3.

At $\alpha = 0°$, the energies become

$$E(e'') \equiv E(d_{xz}, d_{yz}) = 8/3\ Dq$$

$$E(e') \equiv E(d_{x^2-y^2}, d_{xy}) = -2/3\ Dq$$

$$E(a_1') \equiv E(d_{z^2}) = -4Dq$$

Since the energy span of the d orbitals in the trigonal prism ($20/3\ Dq$) is considerably less than that in the octahedron ($30/3\ Dq$), it is clear that in most cases the LFSE of a TP complex will be less than that of an octahedral complex. Exceptions exist at d^0, d^1, low-spin d^2, high-spin d^5 and d^{10} where no preferences are found. The results of a detailed comparison of the LFSE values associated with octahedral and TP coordination for the various d^n electronic configurations are shown in Fig. 4. Translating these results to real, divalent metal atoms from the first transition series shows that the tendency toward octahedral geometry should decrease according to: low spin $\mathrm{Fe^{II}} > \mathrm{Ni^{II}} >$ high-spin $\mathrm{Co^{II}} >$ high-spin $\mathrm{Mn^{II}} > \mathrm{Zn^{II}}$. Within a given electronic configuration where an octahedral preference is observed, the preference is expected to increase as the charge on the metal atom increases.

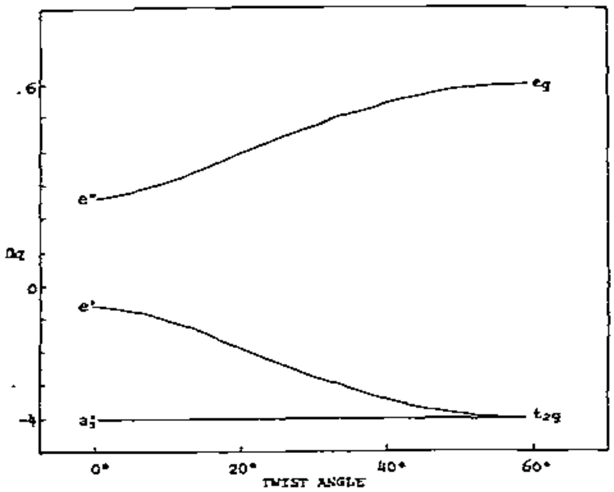


Fig. 3. Variation of the energies of the d orbitals as a function of the twist angle. The polar angle was taken to be $\cos^{-1}\sqrt{1/3}$.

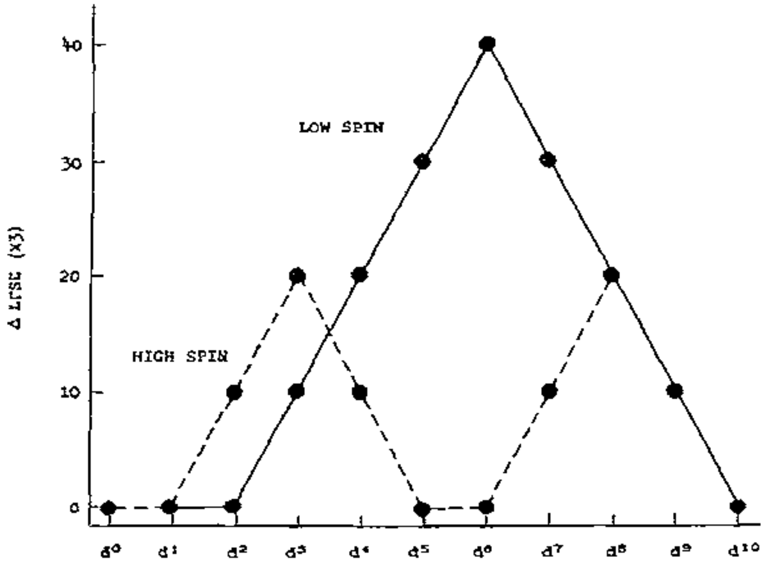


Fig. 4. Variation of ΔLFSE with the d orbital occupation number, where ΔLFSE = LFSE(octahedron) −LFSE(trigonal prism).

Thus, low-spin $\mathrm{Co^{III}}$ should have a greater tendency for octahedral stereochemistry than low-spin $\mathrm{Fe^{II}}$. These results actually tend to exaggerate the octahedral preference of a high-spin d^7 system with respect to the preferences of the d^8 and low-spin d^6 systems.

More complete calculations include the effects of repulsions between electrons occupying the d orbitals. The difference in energy between the occupied d orbitals in the two geometries then becomes (for d^5 through d^{10})

$$\begin{array}{lllll}
d^5: & E[(t_{2g})^3(e_g)^2] & - & E[(a_1')^1(e')^2(e'')^2] = 0 \\
d^6: & E[(t_{2g})^6] & - & E[(a_1')^2(e')^4] = -40/3\ Dq - 10B \\
d^7: & E[(t_{2g})^5(e_g)^2] & - & E[(a_1')^2(e')^3(e'')^2] = -10/3\ Dq + 3B \\
d^8: & E[(t_{2g})^6(e_g)^2] & - & E[(a_1')^2(e')^4(e'')^2] = -20/3\ Dq - 3B \\
d^9: & E[(t_{2g})^6(e_g)^3] & - & E[(a_1')^2(e')^4(e'')^3] = -10/3\ Dq \\
d^{10}: & E[(t_{2g})^6(e_g)^4] & - & E[(a_1')^2(e')^4(e'')^4] = 0
\end{array}$$

Thus, both LFSE and electronic repulsive energy favor octahedral stereochemistry for the d^8 and low-spin d^6 systems, but the stability of an octahedral, high-spin d^7 system due to LFSE is partially canceled by an increase in electronic repulsive energy.

The effect of these contributions to the total energy[12] can be appreciated more fully by imagining that it is possible to twist the octahedral $M(\text{bipy})_3^{2+}$ (M = Fe, Co, or Ni and bipy = 2, 2′-bipyridine) complexes until $\alpha = 0°$, but without altering the known values of Dq and B. The TP complexes of Fe^{II} and Ni^{II} are then found to be less stable than their octahedral counterparts by 75–95 and 30 kcal/mole, respectively. (The range of energies for the Fe^{II} complex exists because of uncertainties in the values of Dq and B.) The TP complex of Co^{II}, however, is less stable by only 5 kcal/mole. Consequently, there is virtually no octahedral preference in a high-spin Co^{II} atom and it is reasonable to place this system on a near par with the Zn^{II} and high-spin Mn^{II} systems where absolutely no preference exists.

C. KNOWN COMPLEXES

The structural principles which were discussed in the preceding paragraphs are exemplified by the stereochemistries of the following complexes.

(i) Schiff base condensates of cis,cis-*1, 3, 5-triaminocyclohexane*

Lions and Martin[13] reported the preparation of complexes of *cis, cis*-1, 3, 5-tris(pyridine-2-carboxaldimino)cyclohexane (or $(\text{py})_3$tach) of Fe^{II}, Co^{II} and Co^{III} which are derived from the condensation of pyridine-2-carboxaldehyde with the triaminocyclohexane (*cis, cis*-tach). Octahedral coordination was assigned to each, presumably because of the tendency to equate that stereochemistry with six-coordinate complexes. However, molecular models of the triaxial conformation of this ligand indicate that the donor atoms occupy the vertices of a trigonal prism in the absence of a metal atom. According to the previous arguments based on simple ligand field theory, the Zn^{II} complex would be

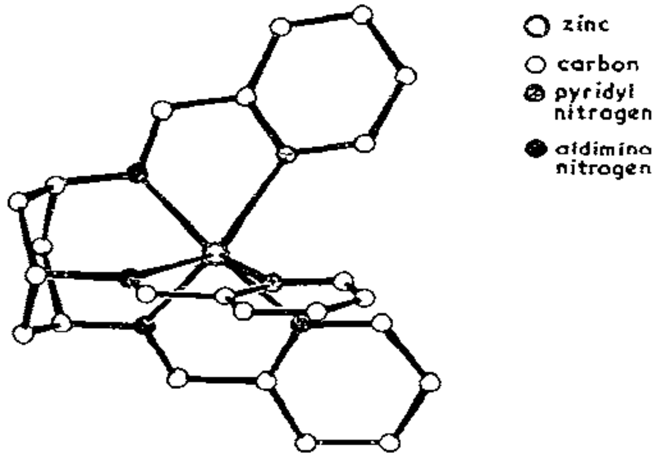


Fig. 5. The structure of the $Zn[(py)_3tach]^{2+}$ ion in the anhydrous perchlorate salt (courtesy of *Chem. Commun.*).

expected to preserve this stereochemistry. The structure of $Zn[(py)_3tach]^{2+}$, determined by an X-ray diffraction study[14] and shown in Fig. 5, consists of a slightly tapered trigonal prism with an average twist angle of only 4°. The slight deviation from the ideal TP geometry was attributed to the relief of non-bonded contacts which would result otherwise between the hydrogen atoms of the pyridine ring which are directed toward the three-fold axis. The average of the polar angles, which are 48° and 56°, is within 3° of $\cos^{-1}\sqrt{1/3}$. Isomorphism studies[11] indicated that the high-spin Mn^{II} and Co^{II} complexes were probably isostructural. The Ni^{II} and low-spin Fe^{II} complexes were neither mutually isomorphous nor isomorphous with the Zn^{II} complex. The arguments based on ligand field theory suggested that the d^8 and low-spin d^6 complexes were probably twisted toward an octahedron. The recent determination[15] of the structure of $Ni[(py)_3tach]^{2+}$ showed that the average twist angle is about 32° while the average polar angle is about 54°. A comparison of the interatomic distances and angles within the coordination polyhedra of the Zn^{II} and Ni^{II} complexes is given in Table 2.

The electronic spectrum[11] of the Co^{II} complex can be interpreted apparently according to a D_{3h} model. A complete diagram of the energies of the ligand field states is given in Fig. 6. The interpretation is aided by a comparison with the complex of another α-diimine, octahedral $Co(bipy)_3^{2+}$, which has $Dq = 1267$ cm^{-1} and $B = 791$ cm^{-1}. The energies of the various electronic states for D_{3h} and O_h complexes, having these Dq and B values, are compared in Fig. 7 to the observed spectrum. The manifold of the first, second and third excited states ($^4E'' + {}^4A_1''$, $^4A_2'' + {}^4A_2'$) is closely spaced and could result in the broad, unresolved band that is observed. The electric dipole selection rules in D_{3h} symmetry indicate that the only transitions which are formally allowed are $E' \rightarrow E''$, $E' \rightarrow A_1''$, and $E' \rightarrow A_2''$ while the $E' \rightarrow A_2'$ transition is forbidden. However, the coordination symmetry of the complex must be closer to C_{3v} where the selection rules permit all transitions which are possible in this case. The correlation between the two symmetries is

D_{3h}	C_{3v}
A_1', A_2''	A_1
A_1'', A_2'	A_2
E', E''	E

TABLE 2

Interatomic distances and angles in the coordination polyhedra[a] of Zn[(py)$_3$tach]$^{2+}$ and Ni[(py)$_3$tach]$^{2+}$

	Bond lengths (Å)		Bond angles (°)	
	M = Zn	M = Ni[b]	M = Zn	M = Ni[b]
M–N$_{ald}$	2.14–2.17	2.00–2.12, 1.96–2.08		
M–N$_{py}$	2.21–2.27	2.08–2.15, 2.09–2.16		
N$_{ald}$–M–N$_{ald}$			82–84	84–86, 82–87
N$_{py}$–M–N$_{py}$			89–95	92–93, 92–94
N$_{ald}$–M–N$_{py}$			73–75	77–80, 77–80

[a] N$_{ald}$ is the carboxaldimino nitrogen atom and N$_{py}$ is the pyridyl nitrogen atom.

[b] Two sets of bond distances and bond angles for Ni[(py)$_3$tach]$^{2+}$ are the result of two complex ions, not related by symmetry, within the unit cell.

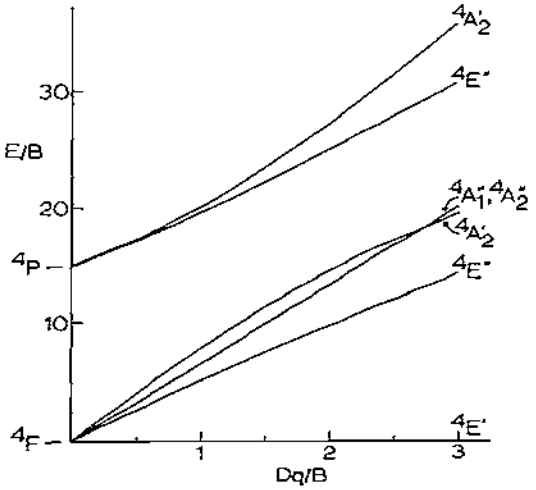


Fig. 6. Energy level diagram for a d^7 TP complex. Note that the symmetry labels given in ref. 11 are incorrect.

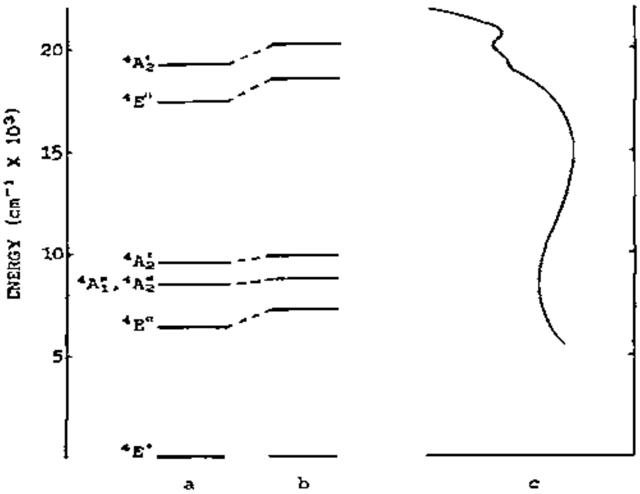


Fig. 7. Energy levels and electronic spectrum of Co[(py)$_3$tach]$^{2+}$. (a) Energy levels calculated at $\alpha = 0°$ from $Dq = 1267$ cm^{-1} and $B = 791$ cm^{-1}, i.e. those appropriate to Co(bipy)$_3^{2+}$, where α is assumed to be 60°. (b) Energy levels calculated at $\alpha = 0°$ from $Dq = 1290$ cm^{-1} and $B = 860$ cm^{-1}. (c) The reflectance spectrum of Co[(py)$_3$tach](ClO$_4$)$_2$.

In addition, vibrational contributions to the intensity cannot be discounted. Whatever the source of the intensity of the observed bands, it is evident that the spectrum of Co[(py)$_3$tach]$^{2+}$, whose twist angle is expected to be close to 0°, resembles the predicted spectrum of a hypothetical Co(bipy)$_3^{2+}$ complex which has a twist angle of 0°. Better agreement between the observed and calculated energies can be obtained with $Dq = 1290$ cm^{-1} and $B = 860$ cm^{-1}, as shown in Fig. 7.

The spectrum of Ni[(py)$_3$tach]$^{2+}$ has also been compared to that of a hypothetical Ni(bipy)$_3^{2+}$ with a twist angle of 30° (Fig. 8). The near-infrared band is then assigned to the transitions $^3A_2 \rightarrow {}^3A_1$, $^3A_2 \rightarrow {}^3E$, and $^3A_2 \rightarrow {}^1E$, while the band at shorter wavelengths is due to the $^3A_2 \rightarrow {}^3E$ transition. This model also predicts a $^3A_2 \rightarrow {}^3A_2$ transition which has not been observed, presumably because of its low intensity. The D_3 selection rules forbid this transition, while all others are allowed. The actual symmetry of the complex must be close to C_3, where all transitions become allowed. Nevertheless, the intensity of the $^3A_2 \rightarrow {}^3A_2$ transition would be expected to be weaker than the others, and it could be buried in the tail of the absorption at shorter wavelengths. Better agreement with the observed spectrum can be obtained by choosing $Dq = 1490$ cm^{-1} and $B = 830$ cm^{-1}, as shown in Fig. 8. This interpretation is only tentative, since the transitions terminating in the $^3A_2$ and ^1E states have not been identified. A low-temperature spectrum might aid the interpretation.

Magnetic susceptibility data have been of little stereochemical value[11]. The ground states of the high-spin d^5, low-spin d^6, and d^8 complexes are orbital singlets with any twist angle and magnetic moments close to $2[S(S+1)]^{1/2}$ are expected. Furthermore, detailed calculations for TP, high-spin d^7 complexes have shown that the magnetic moment to be

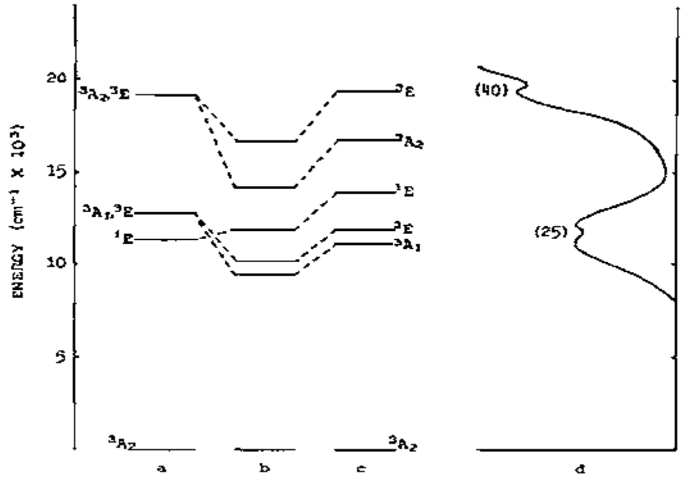


Fig. 8. Energy levels and spectrum of Ni[$(py)_3$tach]$^{2+}$. (a) Energy levels appropriate to Ni(bipy)$_3^{2+}$, with α assumed to be 60° and $Dq = 1280$ cm^{-1}, $B = 710$ cm^{-1}, and $C/B = 4.18$. (b) Energy levels calculated at $\alpha = 30°$ but with $Dq = 1490$ cm^{-1}, $B = 830$ cm^{-1}, and $C/B = 4.18$. (d) The aqueous solution spectrum of Ni[$(py)_3$tach]$(ClO_4)_2$. Extinction coefficients are given in parentheses.

expected for the $(a_1')^2(e')^3(e'')^2$ configuration, corresponding to the $^4E'$ ground state, should be about 5.1 ± 0.2 B.M. regardless of the magnitude of the spin–orbit coupling constant. These values also fall within the accepted ranges of the magnetic moment for octahedral complexes. Consequently, the value of 5.0 B.M. which was found for Co[$(py)_3$tach]$^{2+}$ does not indicate which stereochemistry is present.

When the Mn^{II}, Co^{II}, Ni^{II} and Zn^{II} complexes are treated with BH_4^- in aqueous solution, hydrogenation of the acyclic C=N double bond occurs[16]. The resulting complexes no longer have a TP conformational preference due to the ligand since the extended conjugation has been removed. The chiral nature of the Zn^{II} complex has been demonstrated using proton NMR, while the electronic spectra of the isomorphous Co^{II} and Ni^{II} complexes are compatible in all respects with those expected for octahedral complexes.

The reaction of glyoxal with Zn(*cis, cis*-tach)$_2^{2+}$ produces a monocondensate whose proton NMR spectrum indicates TP stereochemistry[17]. A dicondensate with the same stereochemistry could be obtained on some occasions, but no evidence for the desired tricondensate could be found.

(ii) 1, 1′, 1″-Tris(pyridine-2-carboxaldiminomethyl)ethane

Since this ligand ($(py)_3$tame) is far more flexible than $(py)_3$tach, a greater twist angle would be expected. Indeed, the structure[18] of Zn[$(py)_3$tame]$^{2+}$ shows that this angle is 28°, while the Mn^{II}, Co^{II} and Ni^{II} complexes are isomorphous and probably have similar structures. The Fe^{II} complex is not isomorphous, however, and has a twist angle[18] of 43°.

The proton NMR spectrum of Zn[$(py)_3$tame]$^{2+}$ between room temperature and −47°

contains a sharp singlet due to the methylene protons[19]. If the stereochemistry of the complex in the crystalline state is also present in solution, these results must mean that the complex is undergoing rapid racemization which averages the environment of these non-equivalent protons. The spectra of the Fe^{II} and Co^{III} complexes at room temperature contain *AB* multiplets due to these protons which coalesce at about 95° and 145°, respectively. The activation energies and frequency factors are in accord with those generally associated with twisting mechanisms. Furthermore, the rate of racemization for $Fe[(py)_3tame]^{2+}$ is independent of pH, in contrast to the acid-dependent racemization of $Fe(bipy)_3^{2+}$ which proceeds by a bond rupture mechanism.

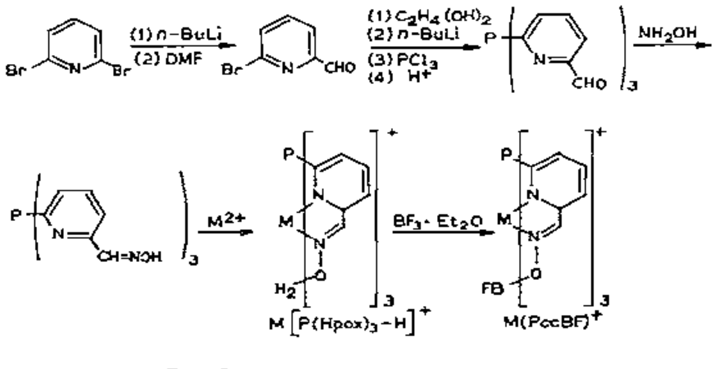
The electronic spectrum of $Ni[(py)_3tame]^{2+}$ can be interpreted according to an octahedral model, but the intensities of the ligand field bands are greater than those normally found in that stereochemistry. Consequently, some distortion from that geometry appears to be present in solution[19].

(iii) Tris(pyridine-2-carboxaldiminoethyl)amine

Greater flexibility is expected in this ligand than in either $(py)_3tach$ or $(py)_3tame$. Thus, it is not surprising that the twist angle[20] in the Fe^{II} complex is 54°. In fact, it may be that this angle represents the maximum angle which can be afforded without severe deformations to the normal bond angles and bond distances within the ligand. The electronic spectrum of the Ni^{II} complex is very similar in band position and intensity to those found with octahedral complexes of α-diimines with that metal atom[21].

(iv) Holm's clathro-chelates

Holm and his co-workers have devised an ingenious and elegant synthesis of a ligand which totally encapsulates a metal atom and simultaneously restricts the coordination environment to being one of TP or near-TP stereochemistry[22, 23].



$M = Fe^{II}, Co^{II}, Zn^{II}$ and Ni^{II}

The high-spin Co^{II}, Ni^{II} and Zn^{II} PccBF complexes are isomorphous. The average twist angle in the Ni^{II} complex, which is shown in Fig. 9, has been shown[24] to be only 1.5° while the average polar angle is about 51°. The low-spin Fe^{II} complex, which is not isomorphous, has an average twist angle of about 21° (Fig. 10). This distortion results in a loss of planarity of each of the ligand side chains including the pyridine rings[25]. The equilibrium stereochemistry of this complex can be viewed as a compromise between the very different stereochemical requirements of the ligand and metal atoms. The bond distances and angles within the coordination polyhedra of the Fe^{II} and Ni^{II} complexes are compared in Table 3.

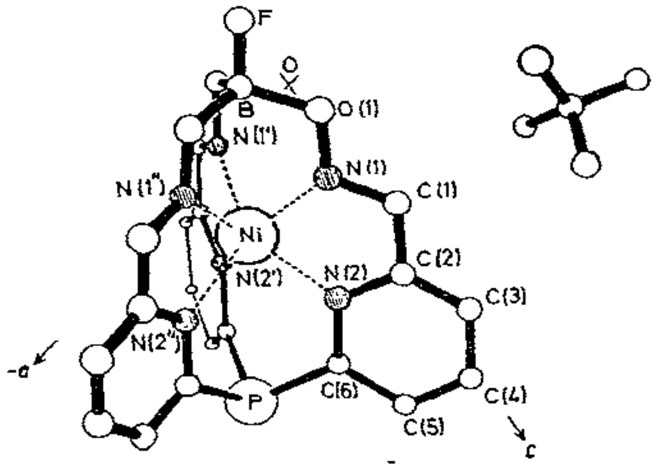


Fig. 9. The structure of $Ni(PccBF)BF_4$ (courtesy of *Chem. Commun.*).

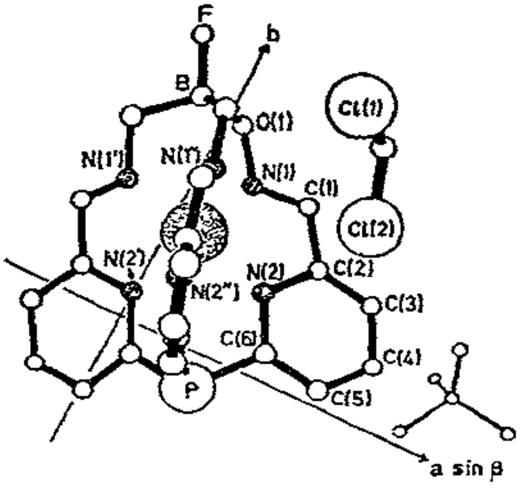


Fig. 10. The structure of $Fe(PccBF)BF_4 \cdot CH_2Cl_2$; the solvent of crystallization is not shown (courtesy of *Chem. Commun.*).

TABLE 3

Average interatomic distances and angles in the coordination polyhedra[a] of Fe(PccBF)$^+$ and Ni(PccBF)$^+$

	Bond length (Å)		Bond angle (°)	
	M = Fe	M = Ni	M = Fe	M = Ni
M–N_{ox}	1.94	2.03		
M–N_{py}	1.97	2.04		
N_{ox}–M–N_{ox}			84	83
N_{py}–M–N_{py}			88	88
N_{ox}–M–N_{py}			79	77

[a] N_{ox} is the oxime nitrogen atom and N_{py} is the pyridyl nitrogen atom.

The electronic spectrum of Co(PccBF)$^+$ is complicated by the possible presence of a Co^I impurity[23], making interpretation impossible at this time. The spectrum[23] of Ni(PccBF)$^+$ is slightly shifted from that of Ni[(py)$_3$tach]$_3^{2+}$ and an additional band appears at higher wavenumbers (Fig. 11). A complete diagram for the ligand field states is provided in Fig. 12. It becomes clear, upon attempting to fit the spectrum to that diagram, that an exact or near-exact duplication is impossible. However, the average polar angle in Ni(PccBF)$^{2+}$ differs from $\cos^{-1}\sqrt{1/3}$ considerably more than in Ni[(py)$_3$tach]$^{2+}$ (51° vs.

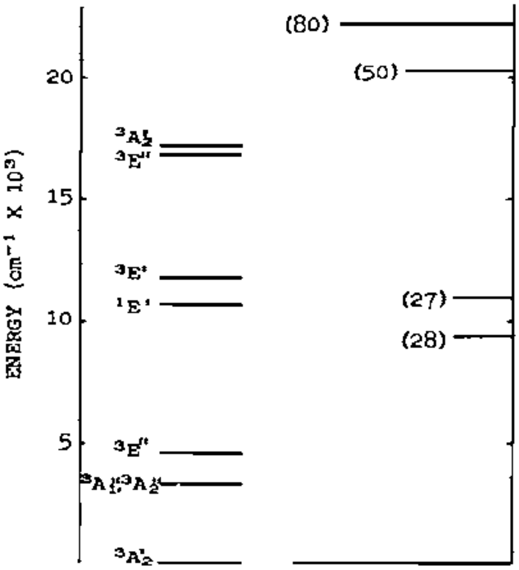


Fig. 11. Energy levels and spectrum of Ni(PccBF)$^+$. (a) Energy levels at $\alpha = 0°$ with Dq, B and C/B taken from Ni(bipy)$_3^{2+}$. (b) The solution spectrum of Ni(PccBF)BF$_4$. Extinction coefficients are given in parentheses.

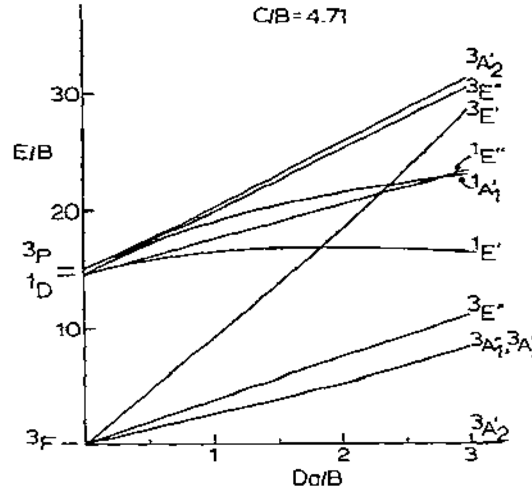


Fig. 12. Energy level diagram for a d^8 TP complex. Note that some of the symmetry labels given in ref. 11 are incorrect.

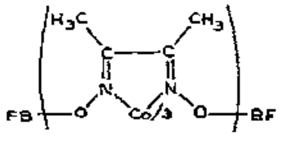
54°). Thus, additional perturbations to the energies of the electronic states are to be expected. Calculations which are now under way indicate that duplication of the observed spectrum is possible, providing this axial distortion is included. Furthermore, the similarity of the spectra of Ni(PccBF)$^{2+}$ and Ni[(py)$_3$tach]$^{2+}$ appears to be fortuitous, in that the transitions terminate in excited states whose origins are vastly different.

Magnetic moments of all of the PccBF complexes^{23} parallel those found for the corresponding complexes of (py)$_3$tach.

Similarities in the ligand field spectra and magnetism suggest that Co[P(Hpox)$_3$–H]$^+$ has a TP or near-TP stereochemistry^{23}. Magnetic and proton NMR studies of the Ni^{II} complex indicate the existence of solvent-dependent diamagnetic ⇌ paramagnetic ($S=1$) equilibrium. The paramagnetic complex is undoubtedly six-coordinate but the nature of the diamagnetic form is uncertain.

(v) Rose's clathro-chelates

The reaction of K$_3$Co(DMG)$_3$ (DMG = dimethylglyoximato di-negative anion) with BF$_3$·(CH$_3$CH$_2$)$_2$O yields^{26} a clathro-chelated complex of Co^{III}.



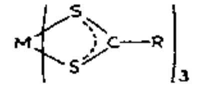
Reduction with NaI in CH_3CN produces the neutral Co^{II} complex[27]. Although both complexes were originally believed to have octahedral stereochemistries, the structures of the complexes, determined by X-ray techniques, are actually closer to TP stereochemistry[28]. The average twist angle in the Co^{II} complex is only 8.6°, while that of the Co^{III} complex is about 22°. An explanation for the interesting change in stereochemistry caused by a simple change in oxidation state can be couched in terms of the general ligand field argument. As shown in Fig. 4, an atom with a low-spin d^6 electronic configuration would have a far greater tendency for octahedral coordination than one with a high-spin d^7 configuration. This tendency would be further amplified by the increased formal charge on the Co^{III} atom.

The electronic spectrum of the Co^{III} complex is dominated by a very intense absorption which masks the ligand field bands[26].

(vi) Miscellany

The twist angle about the central Co^{II} atom in $[Co(NH_2CH_2CH_2O)_3]Co^{2+}$ (where the central atom is bonded to six oxygen atoms) is nearly 0°, while the terminal Co^{III} atoms have octahedral stereochemistries with identical chirality[29]. The TP stereochemistry is apparently caused by the unfavorable non-bonded contacts that would otherwise result if the $Co(NH_2CH_2O)_3$ moieties had opposing, rather than identical, chiralities.

Dithiocarbamato and xanthato ligands, unlike the dithiolates, permit well-defined oxidation states for the metal atom. Three structures which are available show an intermediate twist angle



M = Fe; R = $(n\text{-}C_4H_9)_2N$; $\alpha = 32°$ (ref. 30)
M = Co; R = $(C_2H_5)_2N$; $\alpha = 31°$ (ref. 31)
M = Fe; R = C_2H_5O; $\alpha = 41°$ (ref. 32)

The magnetic properties of the Fe^{III} complexes have excited considerable interest. Both complexes are characterized by the spin-state equilibrium $S = 1/2 \rightleftharpoons S = 5/2$, but at room temperature the equilibrium lies far to the right with $R = (n\text{-}C_4H_9)_2N$, while the $S = 1/2$ state is predominantly occupied with $R = C_2H_5O$. A decrease of about 0.1 Å in the Fe—S bond distance accompanies the change from $S = 5/2$ to $S = 1/2$.

Each of these ligands is unable to span the donor sites of an octahedron due to the chelate ring size. Metal—ligand bond distance requirements as well as optimum intra-ligand distances and angles appear to be far more important in determining the equilibrium geometry of the complex than the preference of the metal atom. Thus, the twist angles for the Fe^{III} and Co^{III} complexes are virtually identical despite the superior ligand field preference of the latter.

Similar reasoning must also be applied to a number of other complexes, for example $Cr(ox)_3^{3-}$ (ox = oxalate dianion) with $\alpha = 50°$ (ref. 33) or $Fe(acac)_3$ (acac = acetylacetonate anion) with $\alpha = 54°$ (ref. 34). In fact, it is probably true there are a large number of tris chelate complexes which have twist angles slightly less than 60° owing to the requirements of the ligand. These may include the $M(bipy)_3^{2+}$ complexes, which were assumed tacitly to have $\alpha = 60°$ in the previous paragraphs.

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