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Structure and Chemistry of $[RhX(ttp)]^{n+}$ Complexes: Trans Influence and Steric Distortion Effects on Rhodium–Phosphorus Coupling Constants and Bond Distances

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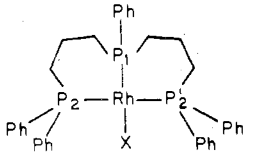
Polyphosphine ligands have been synthesized with two primary aims:[1] First, the chelate effect has been used to reduce complications in studies of catalytic properties of the metal complexes by eliminating substitution equilibria of labile monodentate phosphine ligands.[2] Second, linking the phosphines in an open chain arrangement would eliminate steric interactions of the attendant R groups in otherwise bulky phosphines and permit the metal atom to assume an undistorted but defined coordination geometry. Complexes of Rh(I) and other metals with the linear tridentate triphosphine ligand $PhP(CH_2CH_2CH_2PPh_2)_2$ (ttp) should provide excellent probes with which to study catalytic hydrogenation, substrate displacement reactions, and metal-induced activation of small molecules (e.g., O_2, SO_2, H_2). Since the intramolecular steric forces are expected to be small, this system should also serve well to probe the trans influence of a variety of ligands upon the central phosphorus–metal bond. As the ttp chelate ensures that the ligand field about the rhodium is enforced, this system has the advantage that a homologous series RhX(ttp), I, can be prepared, wherein the geometrical configuration is fixed for differing ligands, X.



I

The ttp ligand has been found, however, to endow its Rh(I) complexes with somewhat different reactivity than its tris(triarylphosphine) monodentate counterparts. For example, the rhodium atom in RhCl(ttp) is a much stronger nucleophile than that in the $RhCl(PPh_3)_3$ analogue, reacting readily with neutral and cationic acids (SO_2, BF_3, CO, Cl_2, CH_3I, NO^+, N_2Ph^+, CH_3^+, CH_3CO^+, and H^+) to yield stable five-coordinate complexes.[1,3] The apparent basicity of the metal center is in fact more akin in its behavior to that of $IrCl(PPh_3)_3$ complexes.[4] Studies on the five-coordinate SO_2 adducts of $[RhX(ttp)]^{n+}$ (n = 0, X^- = Cl^-, N_3^-, CN^-; n = 1, X = CH_3CN, $PPhMe_2$, CO, and PEt_3)[5] suggest that the environment at the fourth coordination site of the parent $[RhX(ttp)]^{n+}$ may actually be somewhat sterically hindered and thus may contribute to that site's reactivity. In $[Rh(ttp)(PEt_3)(SO_2)]$, it is the equatorial PEt_3 group rather than the normally more weakly bound SO_2 that is the more labile.[5b]

Table I. ^{31}P NMR Data for $[Rh(ttp)X]^{n+}$ Complexes

complex[a]	J_{Rh-P_1}, Hz	J_{Rh-P_2}, Hz	cone angle,[b] deg	PA(X)[i]
Rh(OH)(ttp)	166.5	127.7	90	390[c]
RhCl(ttp)	162.5	128.7	102	333[d]
$Rh(N_3)(ttp)$	152.2	131.6	95–110	
$[Rh(ttp)(CH_3CN)]PF_6$	151.5	123.0	95	186[e]
Rh(NCS)(ttp)	149.3	127.4		
$[Rh(ttp)(py)]BF_4$	139.7	129.7	119	225[f]
Rh(CN)(ttp)	122.6	134.5	95	349[d]
$Rh(CH_3)(ttp)$	113.3	152.8	90	405[e]
$[Rh(ttp)(CO)]PF_6$	113.3	114.3	95	143[f]
$[Rh(ttp)(PEt_3)]AsF_6$	113.2	137.9	132	~220[g]
$[Rh(ttp)P(OMe)_3]AsF_6$	111.6	124.7	107	218[h]

[a] P_1 is the central, P_2 the terminal phosphorus atom. [b] From ref 15; some values for the smaller ligands (e.g., CH_3CN) have been estimated from models. [c] S. A. Sullivan and J. L. Beauchamp, *J. Am. Chem. Soc.*, **99**, 5017 (1977). [d] S. A. Sullivan and J. L. Beauchamp, *ibid.*, **98**, 1160 (1976). [e] J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971). [f] D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, **94**, 4726 (1972). [g] Estimated from values of other phosphines. [h] R. V. Hodges, T. J. McDonnell, and J. L. Beauchamp, *J. Am. Chem. Soc.*, in press. [i] Gas-phase proton affinity in kcal/mol.

In order to explain this behavior and to gather data for trans influence studies, we have synthesized and characterized an extended series of $[RhX(ttp)]^{n+}$ complexes, examined their ^{31}P NMR spectra, and determined the structures of the X = py and X = PEt_3 derivatives.[6]

In Table I we have assembled some of the ^{31}P NMR results for a number of the neutral and cationic four-coordinate complexes $[RhX(ttp)]^{n+}$, arranged in the order of decreasing rhodium–phosphorus coupling constant, J_{Rh-P_1}.[7] We find, as has been found for Pt(II) complexes,[8] that the neutral and cationic complexes can be considered together; the range of rhodium–phosphorus coupling constant values, particularly of J_{Rh-P_2}, are indistinguishable. As for the platinum complexes, the rhodium–phosphorus coupling constants (J_{Rh-P_1}) can be used similarly to establish a trans influence series for the ligands. Our observed ordering, in part, is $OH^- < Cl^- < N_3^- \sim CH_3CN \sim NCS^- < py < CN^- < CH_3^- \sim CO \sim PEt_3 \sim P(OMe)_3$, which is considerably different from that found (using J_{Pt-P}) for Pt(II):[8,9] $CH_3CN < Cl^- < py < SCN^- < OH^- < PhS^- < CO < CN^- < P(OPh)_3 \sim PPh_3 \sim CH_3$. That the ordering of the ligands is different is not surprising, because the trans influence of a ligand depends not only upon the nature and properties of the ligand itself but as well on the particular metal, its oxidation state, the other ligands, and the degree of coordination of the metal.[10] We do, however, find the placement of some of the ligands in this series inconsistent with bonding arguments which should hold a priori for these complexes and which have well rationalized the trans influence series observed for some other metal systems.[10,11]

Equation 1 is appropriate for discussion of the rhodium–

$$J_{Rh-P} \propto \gamma_{Rh}\gamma_{P}\alpha_{Rh}{}^2|\psi_{Rh(5s)}(0)|^2\alpha_{P}{}^2|\psi_{P(3s)}(0)|^2(^3\Delta E)^{-1} \quad (1)$$

phosphorus coupling constants:[12] γ_A is the appropriate gy-

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romagnetic ratio, α_A the fraction of atom A's s character in the bond, $|\psi_A(0)|^2$ the s-electron density at the nucleus of A, and $^3\Delta E$ is the singlet–triplet splitting for the metal. Usually one assumes, for a given series of complexes wherein only certain of the ligands or substituents are varied, that most of these terms are constant and that changes in the coupling constant can be related almost completely to variation in the values for α_{metal} and $|\psi_{\text{metal}(ns)}(0)|^2$. Because of the constancy of the ttp chelate, these same assumptions should hold particularly well for the compounds in Table I. As well as relating $J_{\text{Rh-P}_1}$ to changes in the nature of X in the ttp complexes, we can also observe any cis influence of X upon $J_{\text{Rh-P}_2}$.[13,14] It must be remembered that the coupling constants are unusual measures of the bonding in that by eq 1 they reflect primarily s-orbital contributions to the bond order of the Rh–P bond and are only secondarily sensitive to the total bond order or bond strength, which may also contain some π components.

Strictly σ-donor ligands (OH^-, Cl^-, CH_3^-) should present trans influence strengths roughly in the order of their σ basicity; however, $J_{\text{Rh-P}_1}$ (Table I) clearly does not decrease smoothly with increasing gas-phase proton afinity (PA) of X. Generally accepted weak-field ligands do constitute those in the upper third of Table I, but it is apparent that some very weak σ donors have the largest effects on $J_{\text{Rh-P}_1}$; CO, perhaps the weakest σ donor of the ligands in Table I, produces the same $J_{\text{Rh-P}_1}$ as a methyl group, the strongest σ base. This can be qualitatively rationalized if one considers that CO and the phosphines are π acids and compete with the trans P_1 phosphine for rhodium d-orbital density. As the Rh–P_1 bond is weakened on changing from X = Cl^- to PR_3, it is expected to lengthen. This will reduce the total orbital overlap and thus the s-electron bond order. The superior competition of CH_3^- for the rhodium s orbital achieves the same result in $J_{\text{Rh-P}_1}$ but the mechanism is of course different. The placement of hydroxide ion in our series is as yet inexplicable. The same argument for OH^- as for CH_3^- (high PA) should yield a higher placement in the series; for Pt(II), OH^- is comparable to the sulfur donors PhS^- and SCN^-.[8]

In general, one would expect that cis effects of the ligand X on the strength of the Rh–P_2 bonds to be smaller than the trans influence. Several rationalizations of the origins of cis influence have been advanced. Syrkin's original trans-influence theory predicts that ligands of strong trans influence should yield a slight strengthening of the cis bonds by rehybridization of the σ-bond framework.[15] However, a definite correlation between weakening of Pt–P_{cis} bonds in $PtCl_2(PEt_3)X$ complexes with increasing π acidity of X has been noted and attributed to π-orbital competition between X and P_{cis} for the Pt(II) d orbital density.[13] Alternatively, steric effects and ligand size have been suggested to play a significant role in controlling metal–phosphorus distances.[16] It is likely that all three mechanisms are actually operative in varying degrees in any given case. With the prominent exceptions of X = CH_3^-, CO, and PEt_3, our $J_{\text{Rh-P}_2}$ values seem *relatively* insensitive to the nature of X. If we choose a small subset, for example of X = CO, $P(OMe)_3$, and PEt_3, there appears to be a weak correlation of $J_{\text{Rh-P}_2}$ with the increasing cone angle of X, suggestive of rehybridization at the rhodium caused by cis steric interactions. Such direct correlations may only be observable if all but one of the several contributory factors are held constant. In this case the $J_{\text{Rh-P}_1}$ values for the three ligands are nearly identical, suggesting that their Rh s-orbital demands are constant, but the order of increasing $J_{\text{Rh-P}_2}$ is the same as that expected for the decreasing π acidity of CO, $P(OMe)_3$, and PEt_3. As the rhodium–phosphorus coupling constants reflect but one aspect of the Rh–P bond, much care must be taken to corroborate such observations with other measures of the Rh–P bond strength.

Table II. Structural Data for Rh(ttp) Complexes

	RhCl(ttp)[a]	[Rh(ttp)-(py)]HF$_4$[b]	[Rh(ttp)-(PEt$_3$)]-AsF$_6$[c]
Rh–P$_1$, Å	2.201 (2)	2.221 (2)	2.269 (2)
Rh–P$_2$, Å	2.288 (1)	2.288 (2) 2.295 (2)	2.276 (2) 2.303 (2)
Rh–X, Å	2.381 (2)	2.158 (5)	2.359 (2)
P$_1$–Rh–X, deg	178.8	169.6	162.1
P$_2$–Rh–P$_2$′, deg	171.1	158.7	147.4
P$_1$–Rh–P$_2$, deg	90.7	93.1 92.5	89.8 88.5
P$_2$–Rh–X, deg	89.2	88.8	95.5
rms deviation from LS plane RhP$_1$P$_2$P$_2$′X, Å	0.099	0.279	0.444
dihedral angle,[d] deg	8.9	23.3	36.2

[a] Reference 18. [b] $[Rh(ttp)(py)]BF_4$: $a = 13.674$ (8) Å, $b = 17.16$ (1) Å, $c = 17.70$ Å, $\beta = 104.84$ (6)°, $P2_1/n$, No. 14, $Z = 4$, ρ_{exptl} 1.40 (1) g/cm^3, $\rho_{\text{calcd}} = 1.375$ g/cm^3. For all 7113 unique reflections ($3893 \geqslant 3\sigma(I)$) $R = 9.2\%$, $R_w = 10.1\%$, and GOF = 1.42. [c] $[Rh(ttp)(PEt_3)]AsF_6$: $a = 10.520$ (2) Å, $b = 20.385$ (4) Å, $c = 20.127$ (4) Å, $\beta = 93.82$ (1)°, $P2_1/c$, No. 14, $Z = 4$, $\rho_{\text{exptl}} = 1.53$ (1) g/cm^3, $\rho_{\text{calcd}} = 1.519$ g/cm^3. For 7635 unique reflections ($4586 \geqslant 3\sigma(I)$) $R = 7.5\%$, $R_w = 9.3\%$, and GOF = 1.44. [d] The dihedral angle is defined as the angle between the planes X-Rh-P$_2$′ and P$_2$-Rh-P$_1$. The limiting values are 0° for a square-planar geometry and 90° for tetrahedral.

The crystal structure analyses of the chloro,[18] pyridine, and triethylphosphine complexes have been completed; Table II presents pertinent results and Figure 1 shows the increasing tetrahedral distortion from planar geometry as the X ligand increases in bulk. Surprisingly, it is the P$_2$–Rh–P$_2$′ rather than the P$_1$–Rh–X angle which is the more distorted from linearity in each of these complexes. In the PEt_3 complex the Rh–P_2 bonds are in fact significantly inequivalent as a consequence of intramolecular contacts between the triethylphosphine moiety and the phenyl groups on the terminal phosphines of the ttp ligand. Presumably the steric interactions also force slightly different hybridization upon the terminal phosphorus atoms. On an NMR time scale the terminal phosphines are equivalent, and it is of interest that the average of the two Rh–P_2 distances (2.290 (9) Å) is nearly identical with those in the chloro and pyridine complexes. In contrast to this constancy, the Rh–P_1 bond length increases smoothly from 2.201 Å for the chloro complex to 2.221 Å for py and 2.269 Å for PEt_3, in good agreement both with the usual trans influence strength of these ligands and with the $J_{\text{Rh-P}_1}$ observations.

In Figure 2 these results are plotted against the angles between the appropriate trans bonds. Two features of these plots are of interest: First, although $J_{\text{Rh-P}_1}$ and d(Rh–P_1) appear to be correlated with the P$_1$–Rh–X angle, they are in fact strongly correlated only with each other. It is only because Cl^-, py, and PEt_3 happen to increase in steric bulk and in trans influence in the same order that the plot has the appearance of a functional dependence. Clearly, both CO and CH_3^-, similar to Cl^- in size, have very strong trans influences, comparable to PEt_3, but would not give rise to the steric interactions or distortions attendant with a ligand the size of PEt_3. Their points would fall far from the dashed curve for $J_{\text{Rh-P}_1}$. The observed variation in $J_{\text{Rh-P}_1}$ can be explained simply by considering the bond lengthenings caused by successively stronger ligands X. If there is a component to the change in $J_{\text{Rh-P}_1}$ due to rehybridization as a consequence of steric adjustment of the P$_1$–Rh–X angle, it would tend to increase $J_{\text{Rh-P}_1}$ (increasing s character) with increasing angle, in the opposite direction from the plotted changes. The rehybridization

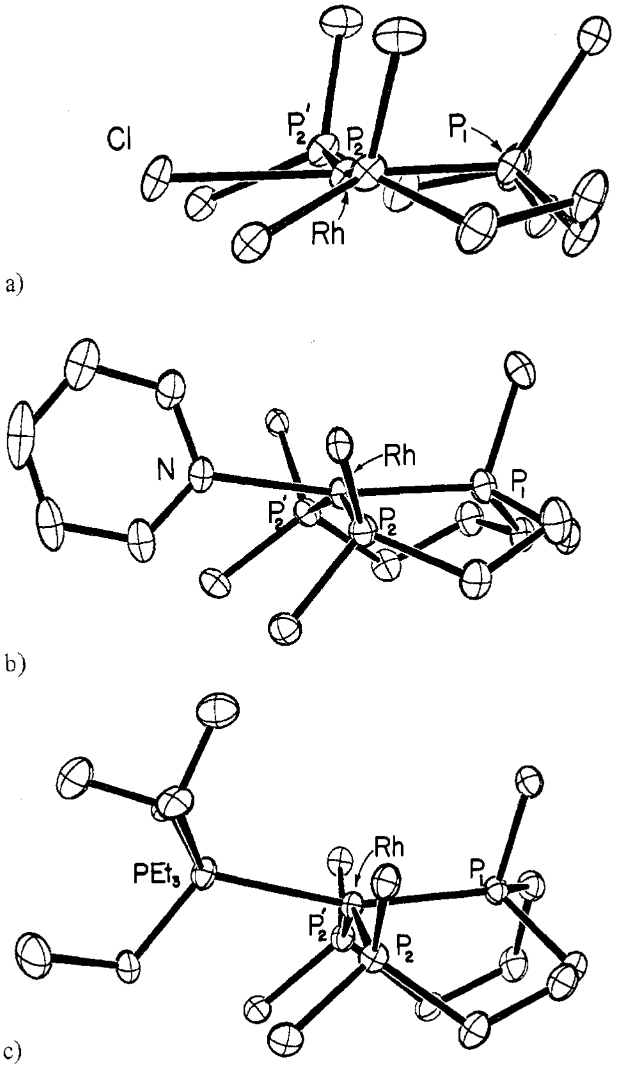

Figure 1. ORTEP views of (a) RhCl(ttp), (b) $[Rh(ttp)(py)]^+$, and (c) $[Rh(ttp)(PEt_3)]^+$. All but the α-carbon atoms of the phenyl groups have been eliminated for clarity. Thermal ellipsoids are drawn at the 30% probability level. Changes in the P_1–Rh–X and P_2–Rh–P_2' angles are apparent, as are substantial conformational adjustments of the ttp ligand, with increasing trans influence and steric bulk of the X ligand.

component thus must be the smaller contributor to the change in J_{Rh-P_1}.

This conclusion is affirmed by the second feature of interest, which is that although the small increases in J_{Rh-P_2} values smoothly reflect the changes in the P_2–Rh–P_2' angle, the Rh–P_2 distances vary not at all in length and presumably not in strength. Because two independent factors are involved, namely steric interactions and electronic cis influence, one could argue that the effect of the former on the Rh–P_2 bond is compensated by a weakening effect of the latter. The results noted above for $PtCl_2(PEt_3)X$ complexes suggest that PEt_3, as a π acceptor, should weaken a cis M–P bond rather than strengthen it.[13] It is thus probable that we in fact see in the J_{Rh-P_2} and d(Rh–P_2) values the consequences of both angle distortion and cis influence which leave the net bond strength unchanged. Attempts to correlate Cu–P distances with P–Cu–P angles in an extended series of complexes[19,20] show only a small dependence; Cu–P decreases approximately 0.0015 Å per degree of increase in the P–Cu–P angle, in spite of differing electronegativities of the remaining ligands. Presumably, if corrections for these other components could be made, one would find both a more significant and larger dependence of M–P distance upon the interbond angles at the metal.

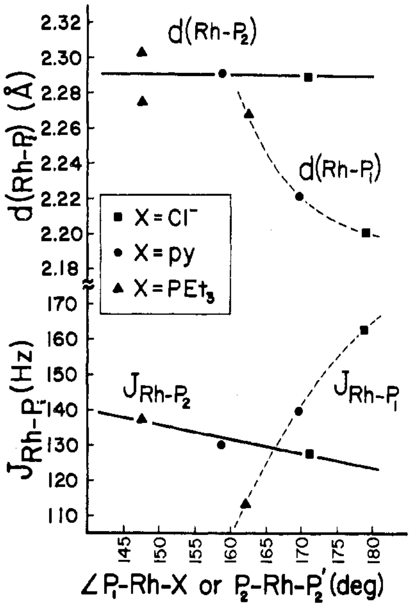

Figure 2. Values of the Rh–P_j bond distances and J_{Rh-P_j} coupling constants as functions of the trans interbond angles. The solid lines refer to parameters for the terminal phosphorus atoms, P_2, while the dashed lines refer to those for P_1.

The J_{Rh-P} values for X = CO and CH_3^- in the present series of complexes suggest that the bond distances in these compounds would be most valuable in sorting out the relative magnitudes of the several factors that give rise to cis and trans influence effects. The structure analyses of these complexes are planned.

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Registry No. Rh(OH)(ttp), 69069-21-2; RhCl(ttp), 34964-03-9; $Rh(N_3)(ttp)$, 69069-22-3; $[Rh(ttp)(CH_3CN)]PF_6$, 50700-90-8; Rh(NCS)(ttp), 69069-23-4; $[Rh(ttp)(py)]BF_4$, 69069-25-6; Rh(CN)(ttp), 69069-26-7; $Rh(CH_3)(ttp)$, 69069-27-8; $[Rh(ttp)(CO)]PF_6$, 36480-96-3; $[Rh(ttp)(PEt_3)]AsF_6$, 69069-29-0; $[Rh(ttp)P(OMe)_3]AsF_6$, 69069-31-4.

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(6) The details of the X-ray structure determinations and of the syntheses and characterizations will be reported elsewhere: G. G. Christoph, A. Elia, and W. C. Liu, manuscript in preparation; P. Blum and D. W. Meek, manuscript in preparation.
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Correspondence

Photochemistry of $Cr(NH_3)_5F^{2+}$, *trans*-$Cr(en)_2(NH_3)F^{2+}$, and *trans*-$Cr(en)_2F_2^+$

Sir:

The development of ligand field photochemistry in coordination complexes[1,2] has been stimulated to a great extent by the formulation of Adamson's empirical rules[3] in 1967. Later on, these rules have been generalized and modified; moreover, they have been related to a theoretical understanding of the electronic structure of transition-metal complexes.[1,4]

Recently, Adamson[5] and Kirk[6] independently reported on the photolysis of fluoropentaamminechromium(III); their papers apparently intended to fill an important gap in Cr(III) photochemistry. It is well to stress that the importance of this gap is particularly obvious from the viewpoint of several theoretical models.[4,7–9]

However, the experimental data, reported for *trans*-$Cr(en)_2(NH_3)F^{2+}$ and $Cr(NH_3)_5F^{2+}$, are claimed[6] to be in complete disagreement with the theoretical predictions; it was suggested that the strong ionic character of the Cr(III)–F bond is responsible for this anomaly.[6] It is the purpose of the present paper to show that the new experimental data, on the contrary, contribute significantly to the corroboration of a ligand field model. At the same time, several theoretical features of the model will be discussed in more detail.

Let us briefly summarize the experimental results. It has been shown[6] that irradiation of *trans*-$Cr(en)_2(NH_3)F^{2+}$ in its lowest quartet band liberates NH_3:

$$trans\text{-}Cr(en)_2(NH_3)F^{2+} + H_2O \xrightarrow[546\ \text{nm}]{h\nu} cis\text{-}Cr(en)_2(H_2O)F^{2+} + NH_3$$

This experiment clearly demonstrates a strong preferential labilization effect of the heteroaxis NH_3–Cr–F over the equatorial ethylenediamine axes. Indeed, since the ground-state bond strengths should be nearly identical for the axial amine ligand and for the equatorial ethylenediamine ligands, the observed aquation directly reflects a specific, oriented destabilization effect of the absorbed photon energy.

$Cr(NH_3)_5F^{2+}$ also predominantly photoaquates NH_3, resulting in a cis product; in this case, the axial character of the labilization has not been proven unambiguously, but it is considered quite probable.[5]

It is interesting to compare these results to the photoaquation of *trans*-$Cr(en)_2F_2^+$, where the leaving ligand has been shown to be predominantly the equatorial amine.[10,11] Here, axial and equatorial labilizations necessarily result in chemically *different* leaving ligands (F^- and en, respectively). Therefore, in this case, the ground-state bond strengths are different to begin with, and the photochemical labilization will not be the *only* factor determining the dominant aquation mode.[4]

Application of the Ligand Field Model. Despite an earlier erroneous treatment by Rowley,[12] the energy ordering of the five d orbitals in $Cr(NH_3)_2F^{2+}$ and *trans*-$Cr(en)_2F_2^+$ seems quite well established by now.[6,13,14] If the heteroaxis containing the fluoride ligand(s) is taken to be the *z* axis, the relative ordering is given by the sequence

$$d_{xy} < d_{xz},\ d_{yz} \ll d_{x^2-y^2} < d_{z^2}$$

the three lowest orbitals being singly occupied. It reflects the stronger σ- and π-donor properties of fluoride relative to amine:

$$\sigma_F > \sigma_N \quad \text{and} \quad \pi_F > \pi_N$$

From this energy level ordering, it does *not* follow that the lowest excited quartet state should correspond to the $(xz, yz) \rightarrow (x^2 - y^2)$ excitation. Figure 1 shows the relevant state energies and their octahedral parentage.[15–17] In deriving the orbital composition of Figure 1, use was made of the matrix equation

$$(x^2 \quad y^2 \quad x^2-z^2 \quad y^2-z^2) = (z^2 \quad x^2-y^2)\begin{pmatrix} -1/2 & -1/2 & -3^{1/2}/2 & -3^{1/2}/2 \\ 3^{1/2}/2 & -3^{1/2}/2 & 1/2 & -1/2 \end{pmatrix} \qquad (1)$$

where z^2 stands for d_{z^2}, etc. The d_{x^2} orbital has the same functional form as d_{z^2}, but it is characterized by a rotational symmetry around the *x* axis; the $d_{x^2-z^2}$ orbital has the same functional form as $d_{x^2-z^2}$ and can be obtained from the latter by a rotation over 90° around the *x* axis.

The notation of eq 1 has the advantage that it shows immediately why the octahedral $^4T_{2g}$ wave functions are characterized by the same energy: each one of the three functions corresponds to an orbital excitation $pq \rightarrow p^2 - q^2$ (where *p* or *q* stand for *x*, *y*, or *z*). Both orbitals *pq* and $p^2 - q^2$ have their largest probability density in the same coordinate plane, perpendicular to the third coordinate axis *r* (*z*, *x*, or *y*); they can be transformed into each other by a rotation of 45° around the *r* axis. This explains why the $^4T_{2g}$ state is characterized by the same interelectronic repulsion energy as the ground state. Indeed, the $pq \rightarrow p^2 - q^2$ excitation leaves the *pr* and *qr* orbitals singly occupied; the electron density $[(pr)^2 + (qr)^2]$ exhibits axial symmetry around the *r* axis. Therefore the excitation—corresponding to the rotation of the remaining singly occupied orbital *pq* around the *r* axis—does not modify the interelectronic interactions, and $E(^4T_{2g}) - E(^4A_{2g}) = E(e_g) - E(t_{2g}) = 10Dq = 3\sigma - 4\pi$.

The $^4T_{1g}$ functions on the other hand are of the general type $pq \rightarrow r^2$; therefore, this excitation concentrates one electron

0020-1669/79/1318-0897$01.00/0