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Notes

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Is There a Hole in the t_{2g} Subshell in the Chromium(III) Doublets?

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At least some participation by the doublet states in the photoreactions of Cr(III) complexes has now been experimentally established in several quarters.[1,2] Considerably less certain is the mechanistic pathway for doublet photoreactions, assuming that direct photochemistry does occur, and how this may differ from that of the excited quartets or the ground state. An idea that once had some currency was that several of the doublet states had a vacant t_{2g} orbital, which could become the focal point for an associative reaction.[3-5] An examination of Griffith's wave functions for the t_{2g}^3 doublets, however, shows equal orbital occupancy for all of them, even for those belonging to the $^2T_{1g}$ and $^2T_{2g}$ states, which comprise functions of the type a^2b, where a and b are distinct t_{2g} orbitals.[6] Ceulemans et al. have elegantly demonstrated that this holds for any alternative basis set; i.e., it is impossible in O_h symmetry to create a t_{2g}^3 wave function with a hole.[7]

Taube first introduced the proposition that a vacant t_{2g} orbital greatly enhanced the lability of octahedral transition-metal complexes.[8] He suggested that the vacancy made a competitive associative pathway possible. Many of the reactions on which Taube based his analysis are now thought to be primarily dissociative, and other reasons for enhanced lability have been advanced, for example, crystal field stabilization energies. The notion that an empty t_{2g} orbital might promote association is not entirely discredited, however. It appears from time to time in discussions of both ground-state and excited-state reactivity.[9]

Ceulemans et al. have examined the question of how the t_{2g} orbital occupancies of the Cr(III) doublet states are changed in tetragonal and trigonal symmetries.[10] They concluded that a partial hole can occur in two of the $^2T_{1g}$ component states to the extent that the octahedral $^2T_{1g}$ and $^2T_{2g}$ states are mixed by the lower symmetry field.

Several investigators have noted that a large asymmetry in the π-donor or -acceptor properties of the ligands in a tetragonal (CrA_5B or CrA_4B_2 Cr(III) complex can cause a $^2T_{1g}$ component to become the lowest lying doublet.[11-13] Forster and Kirk have demonstrated a correlation between the width of the solution emission spectrum and the nature of the emitting state: a (relatively) large bandwidth implies $^2T_{1g}$ emission; a narrow bandwidth implies ^2E_g emission.[14]

Table I. Calculated Orbital Occupancies in the Lowest Energy $^2T_{1g}$ Component for CrA_4B_2 Complexes with Isotropic Ligands[a]

$e_{\pi B}$, cm^{-1}	(xy)	(xz)	(yz)	ΔE_D,[b] cm^{-1}
-2000	0.30	1.34	1.34	0
-1500	0.41	1.29	1.29	0
-1000	0.56	1.21	1.21	141
0	0.99	0.99	0.99	537
1000	1.44	0.77	0.77	133
1500	1.59	0.70	0.70	0
2000	1.69	0.64	0.64	0

[a] Other parameters (cm^{-1}): $e_{\sigma A} = 6500$, $e_{\pi A} = 0$, $e_{\sigma B} = (19\,500 + 4e_{\pi B})/3$ (to maintain constant Δ), $B = 650$, $C = 3200$, $\zeta = 0.1$. [b] Energy relative to lowest doublet.

The existence of a sizable number of complexes with a $^2T_{1g}$ component as lowest excited state offers cause to reopen the question of whether an associative photoreaction pathway involving that $^2T_{1g}$ component might be competitive for some of them, or, rather, more competitive, since there is fairly good evidence that some Cr(III) photosubstitution reactions proceed associatively, at least that portion reacting through a doublet state.[15] If the question is to be examined experimentally, it is important to have some idea which complexes are most likely to exhibit a substantial vacancy in the lowest doublet state, or in one that is thermally accessible from the lowest excited state.

In this note this question is explored for several kinds of complexes, containing both isotropic and anisotropic ligands, the latter being those in which π-interaction with the metal is not cylindrically symmetric. Ligand field calculations were performed within the full 120 × 120 d^3 configuration as previously described,[16] and the angular overlap model was used to parametrize the ligand field.

Relative Electron Densities

One way to approach the problem is to determine the occupation numbers of the three t_{2g} orbitals for the lowest energy $^2T_{1g}$ eigenfunction, the one that mixes most strongly with the $^2T_{2g}$ state. An occupation number significantly below 1.0 constitutes a partial vacancy and should make it more likely that a nucleophilic attack will occur. But where it might occur may not be obvious. The d_{xy}, d_{xz}, and d_{yz} orbitals will be scrambled in most ligand geometries (tetragonal geometry is the exception). The new t_{2g} orbitals are the eigenfunctions of the one-electron ligand field operator, and the form of the orbital with the vacancy may not immediately reveal where an actual reduction in electron density occurs and how substantial that reduction is.

What we have also done, therefore, is to calculate electron densities, relative to those in a complex with O_h symmetry, at certain fixed positions, specifically the centers of the twelve edges and the eight faces of the coordination octahedron. This presupposes that a unique Cartesian axis system can be drawn, even when the coordinating atoms are not 90° apart. This can be done for all the examples below, and many others. Even when it is impossible, however, a reasonable approximation usually results by orienting the axis system to minimize the squares of the displacements of the six coordinated atoms from the axes.

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Table II. Occupation Numbers for the t_{2g} Orbitals and Relative Edge and Face Electron Densities in $Cr(A-A)_3$ Complexes

bite angle,[a] deg	state	energy, cm^{-1}	occupation nos.		edges[b]		faces[c]	
			a_1	e	ρ_A	ρ_B	ρ_A	ρ_B
5.7	$^4A_2(^4A_{2g})$	0	1.00	1.00	0.70	0.80	1.00	0.99
	$^2E(^2E_g)$	14381	0.83	1.07	0.69	0.80	0.83	1.04
	$^2A_1(^2T_{1g})$	14726	0.99	1.00	0.70	0.80	0.99	0.99
	$^2E(^2T_{1g})$	15170	0.96	1.01	0.69	0.80	0.96	1.00
11.3	$^4A_2(^4A_{2g})$	0	1.00	1.00	0.63	0.85	0.97	1.00
	$^2E(^2E_g)$	13949	0.59	1.19	0.61	0.87	0.59	1.10
	$^2A_1(^2T_{1g})$	14353	0.99	1.00	0.63	0.85	0.99	0.97
	$^2E(^2T_{1g})$	15242	0.96	1.00	0.63	0.85	0.96	0.98

[a] Cartesian bite angle, the angular displacement of the ligands from the Cartesian axes. [b] Densities relative to faces in O_h ground state; ρ_A refers to edges spanned by ligands and to the opposite three edges; the B set includes the remaining six edges. [c] Densities relative to faces in O_h ground state; ρ_A refers to the two faces centered on the C_3 axis; the B set includes the remaining six faces.

In terms of the usual real d-orbital basis, $\{d_i\}$, the one-electron eigenfunctions, $\{\xi_i\}$, can be expressed as

$$\xi_i = \sum_{j=1}^{5} W_{ji} d_j \qquad (1)$$

The 120-term three-electron basis set, $\{\omega_i\}$, can be developed from the $[\xi_i]$ basis, $\omega_i = \omega_{jkl} = (\xi_j,\xi_k,\xi_l)$. $\{\xi_i\}$ occupation numbers, n_i, can then be calculated for any eigenfunction expressed in the $\{\omega\}$ basis.

The electron density at a point (x, y, z) for a function ψ that can be expressed in terms of the natural orbitals $\{\xi_i\}$ is given by[17]

$$\rho(x,y,z) = \sum_{i=1}^{5} n_i[\xi_i(x,y,z)]^2 \qquad (2)$$

Maintaining a common distance from the metal, we calculated the densities at the centers of the edges and faces of the octahedron for the lowest energy $^2T_{1g}$ component of the several examples below. In O_h symmetry, ρ is four-thirds as large at the face centers as at the edge centers. Densities in the complexes discussed below are expressed as a fraction of the face center density in O_h.

Isotropic Ligands. Two cases will be considered: a $Cr(A-A)_3$ complex, to assess the effect of a trigonal ligand field distortion, and a trans CrA_4B_2 complex, to assess a tetragonal distortion (I have used the symbols A and B for ligands interacting isotropically with the metal and L for anisotropic ligands).

In the CrA_4B_2 complexes, the ligands were assumed to be positioned exactly on the Cartesian axes. A summary of the results appears in Table I. The calculated t_{2g} orbital populations are presented for the lowest lying component of the octahedral $^2T_{1g}$ state. The energy gap between this state and the lowest doublet state is also indicated in Table I for the particular set of parameters employed. The ligand field of A was set at $e_\sigma = 6500$ cm^{-1} and $e_\pi = 0$, which is typical of some amines. For ligand B, the crystal field energy, $\Delta = 3e_\sigma - 4e_\pi$, was held constant while e_π was varied.

In these D_{4h} molecules, the d_{xy}, d_{xz}, and d_{yz} orbitals are already eigenfunctions of the ligand field operator. The eight faces of the octahedron remain equivalent, while the edges are split into a group of four (those in the *xy* plane) and a group of eight. The electron densities at the face centers are virtually unchanged in any of the $(t_{2g})^3$ doublet states. The edge densities change in exact proportion to the orbital occupancies, which can therefore be used directly to show where and how extensive any vacancies are.

Ceulemans et al.[10] developed a perturbation formula based on the splitting of the t_{2g} orbitals under the ligand field distortion, from which occupation numbers could be calculated. Their results are confirmed quite well by the more complete calculation presented here. A particular example was *trans*-$[Cr(NH_3)_4F_2]^+$. With parameters $e_{\sigma N} = 7180$, $e_{\pi N} = 0$, $e_{\sigma F} = 7630$, $e_{\pi F} = 1880$, $B = 700$, and $C = 2800$ (all in cm^{-1}), Ceulemans et al. calculated $n(xy) = 1.74$ and $n(xz) = n(yz) = 0.63$. Our 120 × 120 calculation yielded 1.69 and 0.64, respectively.

The *trans*-CrA_4B_2 results in Table I are also in agreement with Figure 2 of Ceulemans et al.[10] Both show that a very low population can be achieved for the d_{xy} orbital in the lowest $^2T_{1g}$ component when the π-asymmetry is large and the more π-electron-withdrawing (or less π-donating) ligands are on the unique axis. Table I also shows that this component becomes the lowest excited doublet state near $\Delta e_\pi = \pm 1200$ cm^{-1}. This is in broad agreement with Forster and Kirk's experimental classification of ^2E and $^2T_1$ emitters.[14]

Unlike the tetragonal case, electron densities are not as easily altered by trigonal perturbations, at least within the typical range of such perturbations in transition-metal complexes. Tris complexes with bidentate ligands are common examples of trigonal distortions. Two $Cr(A-A)_3$ geometries were examined. The Cartesian bite angles (the angular displacements of the coordinated atoms from the Cartesian axes) were 5.7 and 11.3° in the two cases, and the Cartesian twist angles (the angular displacement of the A–Cr–A plane from the Cartesian plane) were zero. This corresponds to a moderately strained ring (bite angle of 78.6° by the common definition) and a severely strained ring (67.4° bite). The ligand field parameters were the same as for A in the CrA_4B_2 complexes. The CrA_6 skeleton has D_3 symmetry, which divides the edges into two groups of six and divides the faces into a group of two and a group of six equivalent faces.

The results of the calculation are shown in Table II. In trigonal symmetry, the (O_h) ^2E_g state mixes with ^2E states from the $^2T_{1g}$ and $^2T_{2g}$ states and a moderate vacancy does occur when the A–Cr–A angle is small enough. This translates into a concomitant lowering of electron density on the two faces perpendicular to the C_3 axis. The edge densities also depend on how strained the rings are, but the effect occurs in the ground state and is not altered significantly in any of the $(t_{2g})^3$ excited states. Even in the more strained example from Table II, the density on the perpendicular faces in the $^2E(^2E_g)$ state is still predicted to be about equal to that on six of the edges: the three spanned by the chelates (where attack is presumably unlikely) and the three opposite to them. The extent of the vacancy can be enhanced by using π-withdrawing ligands, but π-bonding in chelates is normally anisotropic.

Anisotropic Ligands. When one π-symmetry orbital per coordinated atom, rather than two or none, is interacting with the metal d orbitals, the symmetry of the ligand field is often not the same as that for the σ-system. Just as for the σ-system, it is the holohedrized symmetry[18] (the symmetry of the molecule superimposed on its inversion image) that is important. In analogy to the thought processes for isotropic interactions, we are concerned both with the actual holohedrized molecular symmetry and with the approximate holohedrized symmetry that would obtain if each coordinated atom were located at the corner of an octahedron.

Consider the approximate symmetry in a $Cr(L-L-L)_2$ complex in which the tridentate ligand is coordinated meridionally. In each case, the L atom can be presumed to π-bond through a p orbital perpendicular to the Cr–L–X plane, where X is the ring atom adjacent to L. If the rings in $Cr(L-L-L)_2$ are confined to the Cartesian planes and the L atoms are located on the axes, the σ-system has O_h symmetry, assuming that the middle L is

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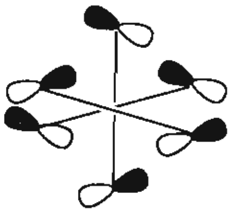
Table III. Calculated Orbital Occupancies in the Lowest Energy $^2T_{1g}$ Component for a Meridionally Coordinated $Cr(L-L-L)_2$ Complex with Anisotropic Ligands[a]

$e_{\sigma L}$	$e_{\pi L}$	(xy)	(xz)	(yz)	ΔE_D,[b] cm^{-1}
5833	−2500	1.87	0.55	0.55	0
6167	−2000	1.84	0.56	0.56	0
6833	−1000	1.71	0.63	0.63	0
7167	−500	1.59	0.69	0.69	0
7500	0	1.37	0.80	0.80	388
7833	500	1.07	0.96	0.96	674
8167	1000	0.74	1.12	1.12	563
8833	2000	0.32	1.33	1.33	0
9167	2500	0.22	1.37	1.37	0

[a] All ligands were assumed to π-bond through one orbital only; $3e_\sigma - 2e_\pi$ was held constant. Other parameters (cm^{-1}): $B = 750$, $C = 2900$, $\zeta = 0$. The geometry of Cr in $Rb[Cr(PDC)_2]$ was assumed (PDC = pyridinedicarboxylate).[18] [b] Energy relative to lowest doublet.

equivalent to the terminal L's. The orientation of the ligand p orbitals is shown in I. The actual symmetry of the π-system is



I

D_{2d} (ignoring phases), while the holohedrized symmetry is D_{4h}. This means that, even in its approximate geometry, the Cr t_{2g} orbitals will be split in $Cr(L-L-L)_2$. Furthermore, this splitting can be substantial. The d_{xy} orbital, which interacts with the four terminal atoms, is perturbed 4 times as strongly as the d_{xz} and d_{yz} orbitals, each of which interacts with just one central ligand p orbital. This mimics isotropic CrA_4B_2 complexes with strong π-asymmetry. These are the conditions that can lead to the ^2E state from $^2T_{1g}(O_h)$ becoming the lowest doublet and also developing a partial vacancy.

The molecular symmetry of the system is not lowered if the bite angle is less than 90°, as long as the coordinated ligands remain in a plane. The actual and the holohedrized symmetries remain D_{2d} and D_{4h}, respectively. The symmetry of the σ-system is lowered, but this does not greatly affect the $(t_{2g})^3$ doublet states. The ligand field symmetry is lowered, however, if the rings are puckered rather than confined to a plane. The ligand p orbitals would then be tilted relative to the reference plane. This would destroy the symmetry planes but could leave the S_4 axis intact (the point group would then be S_4). The effect on the energies and orbital occupancies of the doublet states depends on the amount of pucker.

Table III illustrates the effects of π-asymmetry in the $Cr(L-L-L)_2$ complex more quantitatively. The coordination geometry of the pyridinedicarboxylate (PDC) ligand was used.[19] When PDC coordinates to Cr(III), a meridional plane (Cr–O–N–O) is established, with the oxygens displaced 11° toward the nitrogens from the reference axes. The p-orbital tilt is 1.3° on the oxygens and 2.7° on the nitrogens, a relatively small degree of pucker. Even though the terminal L groups are not on the Cartesian axes, the d_{xy}, d_{xz}, and d_{yz} orbitals are eigenfunctions of the ligand field operator. The face densities are all equal and scarcely affected by changes in orbital occupancy. The edge densities reflect exactly the occupancies of the corresponding t_{2g} orbitals. The calculated orbital occupancies for the $^2E(^2T_{1g})$ state are listed for a range of ligand e_π values. The average t_{2g}–e_g splitting was held approximately constant for these calculations by adjusting e_σ so that $3e_\sigma - 2e_\pi$ was constant, as is appropriate for a ligand that π-bonds through just one orbital.

Table III shows that, with strongly π-donating ligands, quite small occupation numbers are predicted for the $^2E(^2T_{1g})$ state of $Cr(L-L-L)_2$. Electron-withdrawing ligands stabilize higher occupation numbers in the d_{xy} orbital, which is subject to the largest π-interaction with the ligands. For the system illustrated, the $^2E(^2T_{1g})$ state becomes the lowest doublet excited state at e_π values below −400 and above 1600 cm^{-1}.

When π-bonding occurs in a trigonal $Cr(L-L)_3$ complex, the "hole" that arises in the $^2E(^2E_g)$ state on the A faces (the two faces perpendicular to the C_3 rotation axis) may be enhanced or diminished. Enhancement occurs with π-withdrawing ligands, while π-donating ligands reduce the extent of the vacancy. This effect is attributable not to the anisotropy of the bonding but to the geometry of the coordinating atoms. The distortion from the Cartesian axes is in the direction away from the A faces. When π-withdrawing ligands are present, they stabilize higher electron densities in the metal d orbitals, favoring the faces closest to the coordinating atoms (the B faces). In the ligand field model, the total metal d-electron density stays constant, so the calculation predicts that the A faces will be depleted.

Conclusions

Ceulemans et al. established that a tetragonal distortion could lead, for the ^2E state derived from the octahedral $^2T_{1g}$, to a fairly large vacancy in one of the t_{2g} orbitals.[10] We have now shown that anisotropic π-bonding can also cause a substantial vacancy. When this occurs, it is because one of the t_{2g} orbitals interacts considerably more (or less) with the ligands than the other two t_{2g} orbitals do. This mimics an isotropic tetragonal perturbation and, in fact, can be anticipated by examining the holohedrized symmetry of the entire molecule, not just the chromophore skeleton. Ligands that are π-donating (positive e_π) favor smaller occupation numbers in the metal d orbitals with which they interact, while ligands that are π-withdrawing (negative e_π) favor higher occupation numbers. Of course, the higher electron density in the latter case presumably winds up shared with the ligand through MO formation, but ligand field models do not normally try to quantify this.

Putting these several conclusions together, we can develop strategies to construct a molecule with a nearly complete hole. One approach would be to withdraw as much electron density as possible from the d_{xz} and d_{yz} orbitals by placing isotropic π-withdrawing ligands on the axial positions (interacting with both the d_{xz} and d_{yz} orbitals) and anisotropic out-of-plane π-withdrawing ligands on the equatorial positions (each interacting with either the d_{xz} or the d_{yz} orbital). Planar chelates would be the ideal model to achieve the latter condition. This would achieve high occupation numbers in the d_{xz} and d_{yz} orbitals, leaving the d_{xy} orbital depleted. The *trans*-$[Cr(bpy)_2CN_2]^+$ complex might be a good model for this. For this molecule a calculation (using $e_{\pi C} = -290$[21] and $e_{\pi N} = -2300$ cm^{-1} [22]) predicts an orbital occupancy of around 0.17 in the $^2E(^2T_{1g})$ state, which is also predicted to be the lowest lying doublet. This ignores phase coupling in the bipyridines.

Whether such complexes would actually favor an associative route and lead to measurably different photochemistry remains to be seen. But the principle to apply in constructing test cases is to place the maximum degree of π-withdrawal on two of the t_{2g} orbitals (as naturally defined by the σ-system) and, if possible, the maximum degree of π-donation on the other one.

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