the available spectroscopic evidence suggests[4,37] the absence of sulfur and dominance of nitrogen in the copper coordination sphere.

Acknowledgment. For support of this work, we are indebted to the Natural Sciences and Engineering Research Council of Canada (L.K.T.) and Drexel University (A.W.A.) and thank the University of British Columbia Chemistry Department for the use of ESR facilities (L.K.T.).

Registry No. I, 75267-56-0; II, 75267-58-2; III, 75267-59-3; IV, 75330-96-0; V, 75267-61-7; VI, 75267-63-9; VII, 75284-08-1; VIII, 75267-65-1; IX, 75267-67-3; X, 75267-68-4; XI, 765299-13-7; XII, 75284-09-2; XIII, 75284-10-5; XIV, 75284-12-7; XV, 75284-13-8; XVI, 75284-14-9; XVII, 75420-67-6; XVIII, 75284-15-0; XIX, 75284-16-1; XX, 75267-70-8; $[Cu(NTB)(H_2O)](BF_4)_2$, 67269-67-4; $Cu(ClO_4)_2 \cdot 6H_2O$, 15333-31-0.

Contribution from the Department of Chemistry,
University of Leuven, 3030 Heverlee, Belgium

Photolabilization and Bond Indices in Hexacoordinated Transition-Metal Complexes: The D_{2h} Case

L. G. VANQUICKENBORNE* and A. CEULEMANS

Received March 4, 1980

Bond indices I(ML) are introduced for the ground and the excited states of hexacoordinated transition-metal complexes. The formalism is developed for the general case where the three orthogonal axes are characterized by different ligand field parameters. It is shown that photolabilization and photosubstitution reactions can be summarized by the simple rule that the leaving ligand is the one characterized by the smallest value of the bond index I^*(ML).

Introduction

Adamson's rules[1] on the photolabilization of hexacoordinated transition-metal complexes have been discussed extensively in the recent literature.[2-5] So far, all the complexes under consideration were characterized by a real or an effective D_{4h} symmetry. The bond-breaking process is accordingly classified either as axial labilization or as equatorial labilization. Recently, a few cases were reported[6-9] where the effective symmetry of the hexacoordinated species was only D_{2h} (three *different* orthogonal axes). It is the purpose of this work to extend the previously developed I^* model[4,5] to this class of complexes.

Definition of the Bond Indices I and I^*

Let V represent the ligand field Hamiltonian; let d_i and ϵ_i be the five eigenstates and eigenvalues of the one-electron perturbation matrix, constructed on the d-orbital manifold (i = 1–5). This means that $\epsilon_i = (d_i|V|d_i)$ are the d-orbital destabilization energies. In what follows, the ligand orbital stabilization is assumed to be equal to the corresponding metal d destabilization. Figure 1 shows the example of a schematic energy level diagram for an octahedral complex.

If the state function under consideration Ψ can be described by one single configuration (as in Figure 1), the total one-electron bonding energy is given by

$$I = -(\Psi|V|\Psi) = \sum_i h_i \epsilon_i \qquad (1)$$

where h_i is the number of holes in the ith d orbital.

Since the ligand field Hamiltonian can be written as a sum of individual ligand perturbations

$$V = \sum_L V_L$$

the contribution of the Lth ligand to I is given by

$$I(\mathrm{ML}) = \sum_i h_i (d_i|V_L|d_i) \qquad (2)$$

It should be stressed that the quantities I and I(ML) are not necessarily acceptable approximations for the thermodynamic bond energies. For instance, they should certainly not be used to compare the bond strength from one metal to another one (having a different number of d electrons). But they can be useful in a more limited context: for instance, the "bond indices" I(ML) might provide a comparative measure of the different bond strengths *within one given state of a complex*.

If the relevant state function is constructed on the basis of several configurations, the extension of eq 1 is quite straightforward. One particular case, that will be of some interest in the next section, arises when the state function is a linear combination of two determinants, differing in only one spin orbital. A wavefunction of this type can obviously be rearranged into one single determinant, whose spin orbitals are *not* diagonal in V. In this case, it is easy to show that the quantity I can still be obtained from eq 1, but now the summation does not run over the five eigenorbitals of V but over the orbitals in the determinant and their orthogonal counterparts.

For instance, consider the t_{2g}^3, $^4A_{2g}$ ground state and the $t_{2g}^2e_g^1$, $^4T_{2g}$ excited state of an octahedral d^3 system; the wave functions (corresponding to $M_S = {}^3/_2$ for instance) are given by eq 3. In O_h, $\epsilon(t_{2g}) = 4\pi$ and $\epsilon(e_g) = 3\sigma$; therefore, the

$$\Psi_0 = |xz\ yz\ xy|$$

$$\Psi_1 = |xz\ yz\ x^2 - y^2|$$

$$\Psi_2 = (3^{1/2}/2)|xz\ xy\ z^2| + (1/2)|xz\ xy\ x^2 - y^2|$$

$$\Psi_3 = (3^{1/2}/2)|yz\ xy\ z^2| - (1/2)|yz\ xy\ x^2 - y^2| \qquad (3)$$

ground state $I = 3\epsilon(t_{2g}) + 4\epsilon(e_g) = 12\sigma + 12\pi$, and each $I(\mathrm{ML}) = 2\sigma + 2\pi$. For $^4T_{2g}$ the three functions lead to the expression $I^* = 4\epsilon(t_{2g}) + 3\epsilon(e_g) = 9\sigma + 16\pi$, and all I^*(ML)

---

(1) A. W. Adamson, *J. Phys. Chem.*, **71**, 798 (1967).

(2) M. Wrighton, H. B. Gray, and G. S. Hammond, *Mol. Photochem.*, **5**, 164 (1973).

(3) J. I. Zink, *J. Am. Chem. Soc.*, **96**, 4464 (1974).

(4) L. G. Vanquickenborne and A. Ceulemans, *J. Am. Chem. Soc.*, **99**, 2208 (1977).

(5) L. G. Vanquickenborne and A. Ceulemans, *Inorg. Chem.*, **18**, 897 (1979).

(6) M. T. Gandolfi, M. F. Manfrin, A. Juris, L. Moggi, and V. Balzani, *Inorg. Chem.*, **13**, 1342 (1974); M. F. Manfrin, M. T. Gandolfi, L. Moggi, V. Balzani, *Gazz. Chim. Ital.*, **103**, 1189 (1973).

(7) L. Viaene, J. D'Olieslager, and S. De Jaegere, *J. Inorg. Nucl. Chem.*, **37**, 2435 (1975).

(8) L. H. Skibsted, D. Strauss, and P. C. Ford, *Inorg. Chem.*, **18**, 3171 (1979).

(9) S. F. Clark and J. D. Petersen, *Inorg. Chem.*, **18**, 1394 (1979).

0020-1669/81/1320-0110$01.00/0

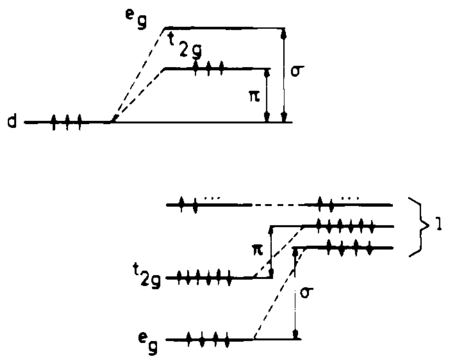

Figure 1. Schematic orbital energy level diagram of an octahedral d^3 system (ground state). Ligand orbital stabilization is assumed to be equal to the metal d-orbital destabilization. Therefore, the total stabilization resulting from the bonding interactions (l orbitals) is simply related to the distribution of the holes in the d orbitals.

$= {}^3/_2\sigma + {}^8/_3\pi$, where the asterisk refers to the bond indices in the excited state. As a consequence of the excitation, an isotropic bond weakening results to the extent that $I - I^* = {}^1/_2\sigma - {}^2/_3\pi = {}^1/_6(10Dq)$. If the symmetry is lowered from O_h to D_{4h}, the $^4T_{2g}$ state gives rise to $^4B_{2g}$ and ^4E_g; to first order in perturbation theory, the state functions remain Ψ_1 and (Ψ_2, Ψ_3), respectively (if C_4 is along the z axis). Let the five diagonal matrix elements in this case be denoted by $\epsilon(z^2) = 2\bar{\sigma}_{ax} + \bar{\sigma}_{eq}$, $\epsilon(xy) = 4\bar{\pi}_{eq}$, $\epsilon(x^2 - y^2) = 3\bar{\sigma}_{eq}$, and $\epsilon(xz) = \epsilon(yz) = 2\bar{\pi}_{ax} + 2\bar{\pi}_{eq}$, where $\bar{\sigma}_{ax} = {}^1/_2(\sigma_z + \sigma_{-z})$, $\bar{\sigma}_{eq} = {}^1/_4(\sigma_x + \sigma_{-x} + \sigma_y + \sigma_{-y})$, and $\sigma_x + \sigma_{-x} = \sigma_y + \sigma_{-y}$; ax stands for axial and eq for equatorial. Then, for Ψ_1, corresponding to the excitation $xy \rightarrow x^2 - y^2$

$$\begin{aligned} I^* &= \epsilon(xz) + \epsilon(yz) + \epsilon(x^2 - y^2) + 2\epsilon(z^2) + 2\epsilon(xy) \\ &= 4\bar{\sigma}_{ax} + 4\bar{\pi}_{ax} + 5\bar{\sigma}_{eq} + 12\bar{\pi}_{eq} \end{aligned}$$

and

$$\begin{aligned} I^*(ML_{ax}) &= 2\sigma_{ax} + 2\pi_{ax} \\ I^*(ML_{eq}) &= {}^5/_4\sigma_{eq} + 3\pi_{eq} \end{aligned} \tag{4}$$

For Ψ_2, the populated e_g orbital is $(3^{1/2}/2)d_{z^2} + (1/2)d_{x^2-y^2} = d_{z^2-y^2}$, while the vacant orthogonal orbital is given by $-(1/2)d_{z^2} + (3^{1/2}/2)d_{x^2-y^2} = d_{x^2}$. Therefore, $I^* = \epsilon(xz) + \epsilon(xy) + \epsilon(z^2 - y^2) + 2\epsilon(yz) + 2\epsilon(x^2)$. Since $(z^2|V|x^2 - y^2) = 0$ in D_{4h}, one has

$$\epsilon(z^2 - y^2) = (z^2 - y^2|V|z^2 - y^2) = {}^3/_4\epsilon(z^2) + {}^1/_4\epsilon(x^2 - y^2) = {}^3/_2\bar{\sigma}_{ax} + {}^3/_2\bar{\sigma}_{eq}$$

$$\epsilon(x^2) = (x^2|V|x^2) = {}^1/_4\epsilon(z^2) + {}^3/_4\epsilon(x^2 - y^2) = {}^1/_2\bar{\sigma}_{ax} + {}^5/_2\bar{\sigma}_{eq} \tag{5}$$

Therefore

$$\begin{aligned} I^*(ML_{ax}) &= {}^5/_4\sigma_{ax} + 3\pi_{ax} \\ I^*(ML_{eq}) &= {}^{13}/_8\sigma_{eq} + {}^5/_2\pi_{eq} \end{aligned} \tag{6}$$

Identical equations can be obtained for Ψ_3.

In a previous communication,[4] the same results were obtained in a more intuitive way. The corresponding anisotropic ligand labilization has been related to Adamson's empirical rules and to the relevant experimental data. In virtually all complexes, the labilization mode (axial or equatorial) was correctly predicted.[4,5]

Orthorhombic Labilization

If the effective symmetry of the complex is lowered from D_{4h} to D_{2h}, the matrix element $(z^2|V|x^2 - y^2)$ becomes nonzero. At the one-electron level, one obtains $\epsilon(xy) = 2\bar{\pi}_x + 2\bar{\pi}_y$, $\epsilon(xz) = 2\bar{\pi}_x + 2\bar{\pi}_z$, and $\epsilon(yz) = 2\bar{\pi}_y + 2\bar{\pi}_z$, and the a_g part of the perturbation matrix is given by (I). The roots of the resulting

$$\begin{array}{cc} z^2 & x^2 - y^2 \\ \hline 2\bar{\sigma}_z + (1/2)(\bar{\sigma}_x + \bar{\sigma}_y) & -(3^{1/2}/2)(\bar{\sigma}_x - \bar{\sigma}_y) \\ -(3^{1/2}/2)(\bar{\sigma}_x - \bar{\sigma}_y) & (3/2)(\bar{\sigma}_x + \bar{\sigma}_y) \end{array} \tag{I}$$

secular equation contain quadratic terms; therefore, the bond indices I(ML) can no longer be expressed as linear functions of σ_L and π_L *alone*. Apparently, I(ML) now becomes an explicit function of the σ and π parameters of the other ligands as well.

A formal treatment of this situation is most easily carried out by introducing

$$\tan 2\alpha = \frac{3^{1/2}(\bar{\sigma}_y - \bar{\sigma}_x)}{2\bar{\sigma}_z - \bar{\sigma}_x - \bar{\sigma}_y} \qquad \frac{\pi}{2} \le 2\alpha \le \frac{3\pi}{2} \tag{7}$$

where the angle α is a measure for the deviation from tetragonal symmetry.

We will adopt the conventions $\bar{\sigma}_y > \bar{\sigma}_x$ and $2\bar{\sigma}_z > \bar{\sigma}_x + \bar{\sigma}_y$, which correspond to a particular though not necessarily unique choice of the coordinate system. If so, the orbital of lowest energy d_l has a predominant $(x^2 - y^2)$ character, while d_h, the orbital of highest energy, has a predominant (z^2) character (see eq 8). The mixing coefficients sin α and cos α depend

$$\begin{gathered} d_l = (\sin\alpha)(x^2 - y^2) + (\cos\alpha)(z^2) \\ d_h = (\sin\alpha)(z^2) - (\cos\alpha)(x^2 - y^2) \\ \frac{\pi}{2} \le \alpha \le \frac{3\pi}{4} \end{gathered} \tag{8}$$

on the σ parameters of all the metal–ligand interactions.

If we want to extend our considerations to a many-electron system, the mixing coefficients of d_{z^2} and $d_{x^2-y^2}$ are further determined by the electron-repulsion parameters. Indeed, consider the D_{2h} states, resulting from a parent $^4T_{2g}$ (t_{2g}^2 e_g) state of the octahedral d^3 system, shown in Figure 2. If the orthorhombic perturbation $V_{o\text{-}rh}$ is small, the octahedral functions Ψ_1, Ψ_2, and Ψ_3 will still provide an adequate description for $^4B_{1g}$, $^4B_{3g}$, and $^4B_{2g}$, respectively. The energy of, e.g., $^4B_{1g}(xy \rightarrow x^2 - y^2)$ is given by $5(\overline{Dq}_x + \overline{Dq}_y)$, where $\overline{Dq}_x = {}^1/_2(Dq_x + Dq_{-x})$ etc. In what follows, we will adopt the convention that $^4B_{1g}$ is the lowest excited state; it is always possible to orient the coordinate system so as to realize this condition by simply making $\overline{Dq}_z$ the strongest field. Since the σ parameters are the most important contributors to Dq, the here proposed choice of coordinate system is generally compatible with the convention of the one-electron case: $2\bar{\sigma}_z > \bar{\sigma}_y + \bar{\sigma}_x$. In the rare cases, where it is not, the treatment should be modified—albeit only very slightly—at the appropriate places.[10]

If $V_{o\text{-}rh}$ increases, the second-order interactions—especially between $^4T_{1g}(pq \rightarrow r^2)$ and $^4T_{2g}(pq \rightarrow p^2 - q^2)$—become gradually more important (p, q, and r stand for x, y, or z). For the lowest $^4B_{1g}$ state, the excitation corresponds to

$$\begin{gathered} xy \rightarrow (\sin\theta)(x^2 - y^2) + (\cos\theta)(z^2) \\ \frac{\pi}{2} \le \theta \le \alpha \le \frac{3\pi}{4} \end{gathered} \tag{9}$$

where the angle θ is formally introduced in order to describe the appropriate mixing of z^2 and $x^2 - y^2$ under the combined action of both the interelectronic repulsion and the ortho-

---

(10) In these cases, one still lets $\overline{Dq}_z > \overline{Dq}_x$ or $\overline{Dq}_y$, but now $2\bar{\sigma}_z < \bar{\sigma}_x + \bar{\sigma}_y$ and $\bar{\sigma}_y > \bar{\sigma}_x$, so that $\tan 2\alpha < 0$. Therefore, $\pi/4 \le \alpha \le \pi/2$, and in eq 8, d_h becomes the lowest orbital while in eq 9 the excitation to the lowest $^4B_{1g}$ state corresponds to $xy \rightarrow (\sin\theta)(z^2) - (\cos\theta)(x^2 - y^2)$ ($\pi/4 \le \alpha \le \theta \le 3\pi/4$).

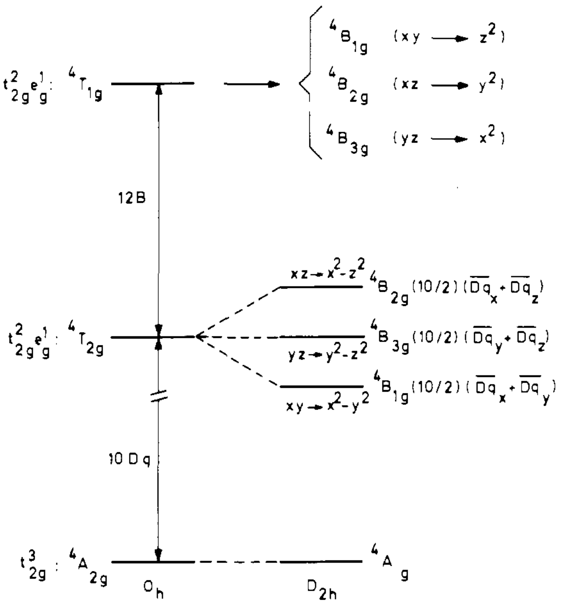

Figure 2. Partial state energy level diagram of an octahedral d^3 system with symmetry lowering to D_{2h}. The three states resulting from $^4T_{2g}$ correspond to excitations of the type $pq \rightarrow p^2 - q^2$; the three states resulting from $^4T_{1g}$ correspond to excitations of the type $pq \rightarrow r^2$, where p, q, or r stands for x, y, or z.

rhombic perturbation. When $\bar{\sigma}_y = \bar{\sigma}_x$, $\theta = \alpha = \pi/2$ and the D_{4h} functions are obtained; when $\bar{\sigma}_y$ increases with respect to $\bar{\sigma}_x$, θ increases much more slowly than α and only for large values of $\bar{\sigma}_y - \bar{\sigma}_x$, does θ approach α again. Indeed, the upper bound for the (z^2, $x^2 - y^2$) mixing is determined by the D_{2h} eigenorbitals of eq 8; this situation can only be realized when the orthorhombic crystal field becomes much larger than the interelectronic repulsion.

For any given complex, the numerical value of θ depends on the relative magnitude of the different σ parameters and the repulsion parameters B and C; it can be determined in each case by a complete numerical state calculation.

The bond indices, corresponding to the lowest $^4B_{1g}$ state, can be found from the previously derived equations; if the singly occupied σ orbital in eq 9 is denoted by $1a_g$, the corresponding orthogonal vacant orbital is given by

$$2a_g = (\sin\theta)(z^2) - (\cos\theta)(x^2 - y^2) \qquad (10)$$

Then one finds for $^4B_{1g}$

$$I^* = 2\epsilon(xy) + \epsilon(xz) + \epsilon(yz) + (1a_g|V|1a_g) + 2(2a_g|V|2a_g)$$

and

$$I^*(ML_z) = 2\pi_z + (2 - \cos^2\theta)\sigma_z$$

$$I^*(ML_y) = 3\pi_y + [2 - \cos^2(\theta - \pi/3)]\sigma_y$$

$$I^*(ML_x) = 3\pi_x + [2 - \cos^2(\theta + \pi/3)]\sigma_x \qquad (11)$$

These expressions obviously reduce to eq 4 for $\theta = \pi/2$. It is well to stress again at this point that the simple form of eq 11 does *not* imply that a given bond index $I^*(ML_p)$ should depend only on the parameters σ_p and π_p. Indeed, the value of θ depends on *all* the ligands and even on their relative position. The variation of the σ_p coefficients is shown in Figure 3; the effects of θ are obviously very large. For instance, for a given value σ_y and σ_x, the relative values of the bond indices $I^*(ML_x)$ and $I^*(ML_y)$ might interchange by increasing, e.g., σ_z!

It should also be noted that the coefficients of $I^*(ML_x)$ and $I^*(ML_y)$—being equal at the outset (1.25)—are very sensitive functions of θ; the effect is such that the bonds on the weaker σ axis ($\bar{\sigma}_x < \bar{\sigma}_y$) are weakened even more.

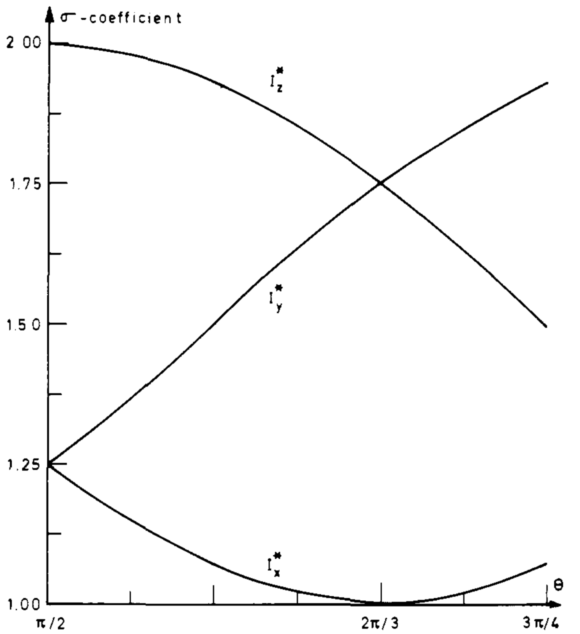

Figure 3. Variation of the coefficient of σ_p with angle θ (d^3 or d^6 system). For $\theta = \pi/2$, the occupied e orbital is simply $d_{x^2-y^2}$; for $\theta = 3\pi/4$, the occupied e orbital is an equal mixture of $d_{x^2-y^2}$ and d_{z^2} (eq 9). The functions shown are $(2 - \cos^2\theta)$ for $I^*(ML_z)$ and $[2 - \cos^2(\theta \pm \pi/3)]$ for $I^*(ML_x)$ and $I^*(ML_y)$ (eq 11).

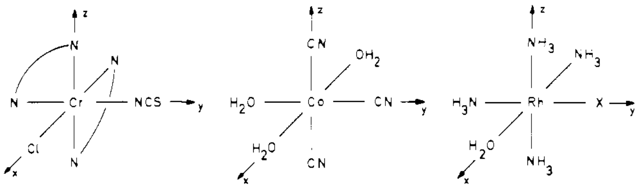

Figure 4. Coordinate system satisfying the conventions used in the text: $\bar{\sigma}_z > \bar{\sigma}_y > \bar{\sigma}_x$; $\overline{Dq}_z > \overline{Dq}_y$, $\overline{Dq}_x$.

Applications

To our knowledge, the only cases where D_{2h} labilization has been studied experimentally are the following.

1. *cis*-$Cr(en)_2(NCS)Cl^+$.[6] The coordinate system satisfying the conventions $\overline{Dq}_z > \overline{Dq}_y$, $\overline{Dq}_x$; $\bar{\sigma}_y > \bar{\sigma}_x$, and $\bar{\sigma}_z > {}^1/_2(\bar{\sigma}_y + \bar{\sigma}_x)$ is shown in Figure 4.

Using the parameters $\sigma_{en} = 0.718\ \mu m^{-1}$, $\sigma_{NCS^-} = 0.641\ \mu m^{-1}$, $\sigma_{Cl^-} = 0.558\ \mu m^{-1}$, $\pi_{en} = 0$, $\pi_{NCS^-} = 0.038\ \mu m^{-1}$, $\pi_{Cl^-} = 0.090\ \mu m^{-1}$, and $B = 0.07\ \mu m^{-1}$, one finds $\alpha = 105.62°$, $\theta = 92.44°$, and the $1a_g$ orbital is given by $1a_g = 0.999(x^2 - y^2) - 0.043(z^2)$. The I^* values are

$$I^*(ML_z) = 2\pi_z + 1.998\sigma_z \quad I^*(Cr\text{–}(en)_z) = 1.44\ \mu m^{-1}$$

$$I^*(ML_y) = 3\pi_y + 1.288\sigma_y \quad I^*(Cr\text{–}(en)_y) = 0.93\ \mu m^{-1}$$
$$I^*(Cr\text{–}NCS) = 0.94\ \mu m^{-1}$$

$$I^*(ML_x) = 3\pi_x + 1.214\sigma_x \quad I^*(Cr\text{–}(en)_x) = 0.87\ \mu m^{-1}$$
$$I^*(Cr\text{–}Cl) = 0.95\ \mu m^{-1}$$

Therefore, in a photosubstitution of this molecule, one expects the ethylenediamine ligand to be exchanged with a rather pronounced preference for bond breaking in a bond *trans* to Cl^-. This conclusion is also compatible with an extension of Adamson's empirical rules to D_{2h} molecules.

Experimentally, one observes virtually no photosolvation of Cl^- or NCS^- ($\phi \leq 10^{-3}$), while the en ligand photodissociates very efficiently ($\phi \approx 0.2$ or 0.3). It is unknown whether or not the en molecule is released preferentially from the x axis.

2. *trans*-Co(CN)$_3$(H$_2$O)$_3$.[7] Although the detailed examples in the previous sections were all concerned with d^3 systems, an extension to d^6 systems is quite straightforward.[11] The adequate coordinate system is shown in Figure 4. The ligand field parameters were taken from a detailed spectroscopic analysis of a number of mixed aquo–cyano–cobalt(III) complexes[12] (all values in μm^{-1}): σ_{CN^-}, 1.215; σ_{H_2O}, 0.66; C, 0.360; π_{CN^-}, 0.039; π_{H_2O}, 0.108; B, 0.053; $10Dq_{CN^-}$, 3.489; $10Dq_{H_2O}$, 1.547. In this complex, $\bar{\sigma}_y = {}^1/_2(\bar{\sigma}_z + \bar{\sigma}_x)$, which implies that $\tan 2\alpha = 1/3^{1/2}$ and $\alpha = 105°$. Calculating the combined effect of the orthorhombic field and the interelectronic repulsion, one obtains $\theta = 100.83°$ and $1a_g \simeq 0.982(x^2 - y^2) - 0.188(z^2)$.

The lowest excited $^3B_{1g}$ state ($xy \rightarrow 1a_g$) is characterized by

$$I^* = \epsilon(xy) + (1a_g|V|1a_g) + 2(2a_g|V|2a_g)$$

$$I^*(ML_z) = 1.96\sigma_z \qquad I^*(Co\text{–}(CN)_z) = 2.39\ \mu m^{-1}$$

$$I^*(ML_y) = 1.43\sigma_y + \pi_y \qquad I^*(Co\text{–}(CN)_y) = 1.77\ \mu m^{-1}$$
$$I^*(Co\text{–}(H_2O)_y) = 1.05\ \mu m^{-1}$$

$$I^*(ML_x) = 1.11\sigma_x + \pi_x \qquad I^*(Co\text{–}(H_2O)_x) = 0.84\ \mu m^{-1}$$

Therefore, one expects the solvent ligands on the x axis to be preferentially exchanged upon ligand field irradiation. This is again compatible with an application of Adamson's rules to the D_{2h} case. The experimentally observed photoinertness of *trans*-Co(CN)$_3$(H$_2$O)$_3$ in aqueous solution is compatible with the predictions, but so far the possibility of $(H_2O)_y$ labilization cannot be excluded.

3. *cis*-Rh(NH$_3$)$_4$(H$_2$O)Cl^{2+},[8] *cis*-Rh(NH$_3$)$_4$(H$_2$O)Br^{2+},[8] and *cis*-Rh(en)$_2$(H$_2$O)Br^{2+}.[9] For the Rh(III) parameters, the following numbers have been derived from a spectral analysis[12] (all values in μm^{-1}): σ_{NH_3}, 1.14; σ_{Cl^-}, 0.88; σ_{Br^-}, ~0.93; π_{NH_3}, 0; π_{CL^-}, 0.21; π_{Br^-}, 0.29; B, ~0.04.

The water parameters are less well-known, except for the fact that $10Dq \approx 2.2\ \mu m^{-1}$. We will assume $\pi_{H_2O} \simeq 0.05$ and $\sigma_{H_2O} = 0.8\ \mu m^{-1}$. Adopting the coordinate system of Figure 4, one can readily obtain the relevant quantities $\alpha = 96.5$ and 102° and $\theta \simeq 96.2$ and 100.7° for Cl$^-$ and Br$^-$, respectively. The $1a_g$ orbitals are given by $1a_g(Cl^-) \simeq 0.994(x^2 - y^2) - 0.107(z^2)$ and $1a_g(Br^-) \simeq 0.983(x^2 - y^2) - 0.186(z^2)$, and for the $^3B_{1g}$ state ($xy \rightarrow 1a_g$) in the chloro complex one finds

$$I^*(ML_x) = 1.988\sigma_z \qquad I^*(Rh\text{–}(NH_3)_z) = 2.27\ \mu m^{-1}$$

$$I^*(ML_y) = \pi_y + 1.347\sigma_y \qquad I^*(Rh\text{–}(NH_3)_y) = 1.54\ \mu m^{-1}$$
$$I^*(Rh\text{–}Cl^-) = 1.40\ \mu m^{-1}$$

$$I^*(ML_x) = \pi_x + 1.163\sigma_x \qquad I^*(Rh\text{–}(NH_3)_x) = 1.33\ \mu m^{-1}$$
$$I^*(Rh\text{–}H_2O) = 0.98\ \mu m^{-1}$$

In the bromo complex, one obtains nearly the same bond indices[13] for NH$_3$ and H$_2$O, while $I^*(Rh\text{–}Br^-) = 1.54\ \mu m^{-1}$. Clearly, the photoactive $^3B_{1g}$ state will most readily release its H$_2$O ligand—the uncertainty on the H$_2$O parameters is definitely smaller than the differences between the I^* values.[14] This conclusion is in agreement with the observation that ligand field excitation of *cis*-Rh(NH$_3$)$_4$(H$_2$O)X^{2+} leads to *trans*-Rh(NH$_3$)$_4$(H$_2$O)X^{2+}. These results have been interpreted[8] in terms of a dissociative reaction mechanism, where the isomerization of the pentacoordinated intermediate Rh(NH$_3$)$_4$X^{2+} is held responsible for the observed stereomobility. It should also be stressed that an extension of Adamson's rules leads to the wrong predictions: the strongest ligand on the weakest axis is $(NH_3)_y$.

Conclusions

The bond index formalism is a versatile tool in the comparative study of the different metal–ligand bond strengths within any one given electronic state.

It is possible to adapt this formalism to D_{2h} molecules; the results are sometimes, but not always, similar to Adamson's rules. When the conclusions are divergent, the bond index formalism appears to lead to the correct answers. The reason for deviations from Adamson's rules are twofold:

(i) As shown earlier, Adamson's rules are equivalent to postulating that the leaving ligand is the one that absorbs the most energy and is therefore characterized by the maximal value of $\Delta I(ML) = I(ML) - I^*(ML)$. In fact, the relevant quantity appears to be $I^*(ML)$, not $\Delta I(ML)$.

(ii) In some cases, the role of the *other* ligands may be important in determining $I(ML)$; the relative position and ligand field parameters of the "inert" ligands determine the numerical value of α and θ to a significant extent.

Registry No. *cis*-Cr(en)$_2$(NCS)Cl$^+$, 25125-67-1; *trans*-Co(CN)$_3$(H$_2$O)$_3$, 58918-76-6; *cis*-Rh(NH$_3$)$_4$(H$_2$O)Cl^{2+}, 71424-38-9; *cis*-Rh(NH$_3$)$_4$(H$_2$O)Br^{2+}, 71382-14-4; *cis*-Rh(en)$_2$(H$_2$O)Br^{2+}, 53368-48-2.

---

[11] Such an extension is carried out in detail for D_{4h} in ref 4. It is also shown there how the I^* model can accommodate π-acceptor ligands.

[12] L. G. Vanquickenborne, A. Ceulemans, and D. Beyens, to be submitted for publication.

[13] More specifically, one obtains $I^*(Rh\text{–}(NH_3)_z) = 2.24\ \mu m^{-1}$, $I^*(Rh\text{–}(NH_3)_y) = 1.54\ \mu m^{-1}$, $I^*(Rh\text{–}(NH_3)_x) = 1.33\ \mu m^{-1}$, and $I^*(Rh\text{–}H_2O) = 0.98\ \mu m^{-1}$.

[14] Even with $\pi_{H_2O} = 0.1\ \mu m^{-1}$, one still obtains $I^*(Rh\text{–}Cl) - I^*(Rh\text{–}H_2O) > 0.1\ \mu m^{-1}$.

Contribution from the Department of Chemistry,
North Carolina State University, Raleigh, North Carolina 27650

Electronic Structures of [PtL$_4$·PtL$_4$X$_2$]$^{4+}$ and NbX$_4$ Chains

MYUNG-HWAN WHANGBO* and MARY J. FOSHEE

Received April 11, 1980

The band structures of the singly bridged [Pt(NH$_3$)$_4$·Pt(NH$_3$)$_4$X$_2$]$^{4+}$ chain (X = Cl, Br) and the doubly bridged NbX$_4$ chain (X = Cl, I) were obtained by employing the tight-binding scheme based upon the extended Hückel method. The band gaps and the stabilities of these chains were examined as a function of distortion in their unit cell geometries. In contrast to the case of the singly bridged [Pt(NH$_3$)$_4$·Pt(NH$_3$)$_4$X$_2$]$^{4+}$ chain, the doubly bridged NbX$_4$ chain leads to partially filled overlapping bands even if the metal-bridging halide bonds are not exactly the same in length.

Metal–ligand–metal bridging is an important structural pattern leading to numerous chain and net compounds of transition-metal ions.[1-3] In connection with recent interest in low-dimensional conducting materials, a number of lig-

0020-1669/81/1320-0113$01.00/0 © 1981 American Chemical Society