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Charge Transfer Spectroscopy in Low-Spin d^6 Pentacyano and Pentaammine Complexes

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Pentaammine- and pentacyano-L complexes of group 8 metals (L = pyridine (py), pyrazine (pz), and derivatives) have been widely used for systematic studies on structure and reactivity. The M^{II} compounds display intense charge transfer (CT) bands, whose number and origin have been used to probe their electronic structure.[1] Specific donor−acceptor interactions of the coligands with the solvent are observed, with significant shifts of the CT bands and the redox potentials at the metal site.[2] These MX$_5$ fragments also have been used to prepare mixed-valent dinuclear complexes, either symmetric or asymmetric,[3] suited for studying energy- and electron-transfer, and bridge-mediated metal−metal coupling.[4] Overall, they have played a key role in the understanding of electron-transfer processes.[5]

The $[\mathrm{Os^{II}(CN)_5L}]^{n-}$ compounds *in aqueous solution* show two CT bands (CT$_1$ and CT$_2$ for the high- and low-energy components), with the intensity ratio, *R*, close to 2:1 and the energy difference, ΔE_{CT}, around 4200 cm^{-1}. ΔE_{CT} remains roughly constant *independently* of L and, for most ligands, also of the solvent, as exemplified by $[\mathrm{Os^{II}(CN)_5pz}]^{3}$ (Figure 1a). We interpreted our results[1e] on the basis of a simplified model previously used for Os(II) compounds.[6] Although the low-spin d^6 configuration is not split under spin−orbit coupling effects, the excited-state d^5 configuration leads to A and E states. Two transitions should then be observed with a *constant* ΔE_{CT} of $3/2\lambda$ ($\lambda_{\mathrm{Os}} = 2800$ cm^{-1}),[7] and *R always* near 2:1. In a subsequent work[1f] we observed solvent-dependent ΔE_{CT} in the CT bands of the $[\mathrm{Os^{II}(CN)_5Mepz}]^{2-}$ complex and weakening of CT$_2$ (Figure 1b), as for the analogous $[\mathrm{Os^{II}(NH_3)_5L}]^{n+}$. Hence, the spin−orbit coupling-only model fails in providing a comprehensive description for the CT spectroscopy of all the osmium complexes.

In this Communication we report an interpretation, based on Magnuson and Taube's (MT) molecular orbital model for the $[\mathrm{Os^{II}(NH_3)_5L}]^{n+}$ CT spectroscopy.[8] Our present description, which introduces the effect of spin−orbit coupling, explains the CT pattern in *all* $[\mathrm{Os^{II}(CN)_5L}]^{n-}$ compounds, and questions the previous spectral assignment in the $[\mathrm{Os^{II}(NH_3)_5L}]^{n+}$ series. It provides simultaneously a straightforward methodology to evaluate the degree of metal−ligand coupling.

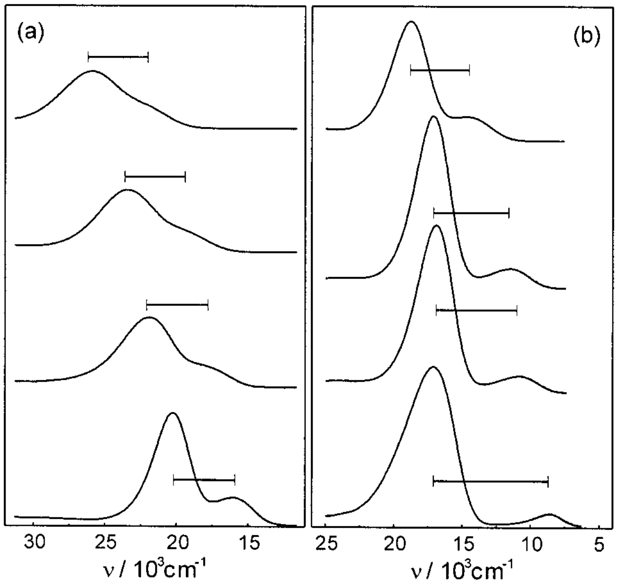

Figure 1. Electronic spectra of $[\mathrm{Os^{II}(CN)_5L}]^{n-}$ (L = pz (a), Mepz$^+$ (b)) in (from top to bottom) water, MeOH, EtOH, and acetonitrile.

Magnuson and Taube assumed that the two bands observed in $[\mathrm{Os^{II}(NH_3)_5L}]^{n+}$ compounds originated in different metal orbitals. Under C_{2v} symmetry, the t$_{2g}$ set splits into a$_1$(x^2−y^2), b$_1$(xz), and b$_2$(yz).[9] The b$_2$(yz) orbital interacts with the lowest b$_2$(π^*_{L}) orbital leading to the formation of two molecular orbitals: a lower lying $\varphi_{\mathrm{A}} = c_{\mathrm{M}}\mathrm{d}_{yz} + c_{\mathrm{L}}\pi^*_{\mathrm{L}}$ and a higher lying $\varphi_{\mathrm{B}} = c_{\mathrm{M}}\pi^*_{\mathrm{L}} - c_{\mathrm{L}}\mathrm{d}_{yz}$, while b$_1$($xz$) and a$_1$($x^2$−$y^2$) remain nonbonding and roughly degenerate. CT$_1$ and CT$_2$ of $[\mathrm{Os^{II}(NH_3)_5L}]^{n+}$ were assigned to the symmetry allowed b$_2$(φ_{A}) → b$_2$(φ_{B}) and a$_1$(x^2−y^2) → b$_2$(φ_{B}) transitions, respectively. The L-dependent ΔE_{CT} was taken as a measurement of M−L coupling. Quantitative relations were derived, affording the orbital energies and the ground state mixing coefficients c_{M} and c_{L} in terms of $\Delta_{\mathrm{ML}} = \langle\pi^*_{\mathrm{L}}|H|\pi^*_{\mathrm{L}}\rangle - \langle \mathrm{d}_{yz}|H|\mathrm{d}_{yz}\rangle$ and $H_{\mathrm{ML}} = \langle \mathrm{d}_{yz}|H|\pi^*_{\mathrm{L}}\rangle$ (see Supporting Information). These notably intuitive concepts were also applied to explain the solvent dependence of the two CT bands present as well in $[\mathrm{Ru^{II}(NH_3)_5Mepz}]^{3+}$.[2a] Further studies[10] on M−L coupling, though based on different methodologies, also rely on the MT spectral assignment.

Some crucial facts interfere with the MT assignment of the CT spectroscopy in the osmium compounds. As noted previously,[10] the poor overlap between the a$_1$(d$_{x^2-y^2}$) and b$_2$(φ_{B}) orbitals requires a low-energy transition of very low intensity. The low oscillator strength observed in CT$_2$ for $[\mathrm{Os^{II}(NH_3)_5L}]^{n+}$ and $[\mathrm{Ru^{II}(NH_3)_5Mepz}]^{3+}$ spectra might be consistent with an overlap-forbidden charge transfer. However, high intensity for CT$_2$ and constant ΔE_{CT} for many $[\mathrm{Os^{II}(CN)_5L}]^{n-}$ [1e] cannot be explained under the MT assignment, unless we depart from a one-electron description.

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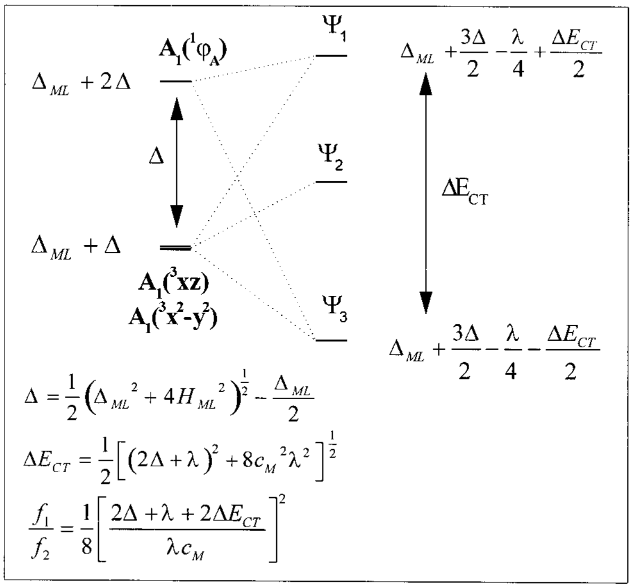

Figure 2. Effect of s−o coupling on the relevant excited states.

On the basis of their spatial symmetry properties, the CT excited configurations are $A_1 = (\varphi_A)^1(d_{xz})^2(d_{x^2-y^2})^2(\varphi_B)^1$, $A_2 = (\varphi_A)^2(d_{xz})^1(d_{x^2-y^2})^2(\varphi_B)^1$, and $B_2 = (\varphi_A)^2(d_{xz})^2(d_{x^2-y^2})^1(\varphi_B)^1$. One intense CT involving the A_1 configuration is expected if the symmetry-allowed but overlap-forbidden CT to B_2 is neglected. Electron repulsion resolves the A_1, A_2, and B_2 excited states arising from the MO description into singlets and triplets.[11] Now, the *twelve* CT microstates can mix due to spin−orbit coupling. The spin−orbit coupling operator H_{so} spans the totally symmetrical representation and only mixes states which share the same total spin−orbital symmetry designation. Only the totally symmetric triplet component $\mathbf{A_1(^3xz)} = {}^1/_2(|d_{xz}\varphi_B\rangle - |\varphi_B d_{xz}\rangle)(|\alpha\beta\rangle + |\beta\alpha\rangle)$ and $\mathbf{A_1(^3x^2{-}y^2)} = {}^1/_2(|d_{x^2-y^2}\varphi_B\rangle - |\varphi_B d_{x^2-y^2}\rangle)(|\alpha\alpha\rangle - |\beta\beta\rangle)$ states will mix with the orbitally and spin allowed $\mathbf{A_1(^1\varphi_A)}$ singlet ${}^1/_2(|\varphi_A\varphi_B\rangle + |\varphi_B\varphi_A\rangle)(|\alpha\beta\rangle - |\beta\alpha\rangle)$, providing *at most* three CT bands to states of total $\mathbf{A_1}$ symmetry. We can constrain the computation of the spin−orbit coupling matrix elements (see Supporting Information for details) to these three spin−orbitals.[12] The zero-order diagonal elements were estimated from the MT-MO energies, neglecting the electron repulsion terms. Thus Δ, the energy difference between the s−o uncoupled $\mathbf{A_1(^1\varphi_A)}$ and the triplet components $\mathbf{A_1(^3x^2{-}y^2)}$ and $\mathbf{A_1(^3xz)}$, becomes a direct measurement of π-back-bonding.

Figure 2 shows the effect of spin−orbit coupling and provides quantitative relations linking the observed CT with $|H_{ML}|$ and Δ_{ML}. $\Psi_2 = 2^{-1/2}(\mathbf{A_1(^3xz)} - \mathbf{A_1(^3x^2{-}y^2)})$ remains a pure triplet, and does not contribute to the observed spectrum. $\Psi_1 = c_S\mathbf{A_1(^1\varphi_A)} + 2^{-1/2} ic_T(\mathbf{A_1(^3xz)} + \mathbf{A_1(^3x^2{-}y^2)})$ (essentially a singlet excited state, containing at most 33% triplet character) and $\Psi_3 = ic_T\mathbf{A_1(^1\varphi_A)} - 2^{-1/2}c_S(\mathbf{A_1(^3xz)} + \mathbf{A_1(^3x^2{-}y^2)})$ (essentially triplet, owing intensity to its singlet character) are responsible for the CT_1 and CT_2 bands, respectively.[13] The expected ΔE_{CT} is in all cases larger than Δ (see Figure 2). One limiting case shows up when the magnitude of Δ becomes negligible compared to λ, making ΔE_{CT} reach its minimum value of $3/2\lambda$. This figure is consistent with the s−o coupling-only model depicted above and suggests a negligible degree of M−L coupling for most $[Os^{II}(CN)_5L]^{n-}$ in aqueous solution (i.e., $c_L^2 \approx 0$). For $[Os^{II}(CN)_5Mepz]^{2-}$, however, the situation changes. The greater ΔE_{CT} and R are indicative of Os-Mepz$^+$ mixing, as shown in Table 1. Variations with solvent arise largely because the electron-donor ability ($E^0(M^{III}/M^{II})$) of the $M(CN)_5$ moiety is very solvent dependent, while the acceptor ability of L is not.[14] This translates into larger Δ_{ML} in water than in organic media.

Table 1. Parameters Calculated for $[Os^{II}(CN)_5Mepz]^{2-}$

	CT_1[a]	CT_2[a]	Δ_{ML}[a]	$\lvert H_{ML}\rvert$[a]	c_L^2[b]	Δ[a]	c_T^2[c]	R_{calc} (R_{exp})[d]
water	18.8	14.5	16.8	2.5	0.02	0.4	0.29	2.5 (4.1)
MeOH	17.1	11.6	10.9	6.1	0.17	2.8	0.12	7.3 (8.1)
EtOH	16.9	11.0	9.7	6.6	0.20	3.3	0.10	9.0 (9.9)
AcN	17.1	8.7	4.0	8.2	0.38	6.4	0.04	24 (21)

[a] CT_1 and CT_2 stand for transitions to $\Psi_1 = c_S\mathbf{A_1(\varphi_A)} + i2^{-1/2}c_T(\mathbf{A_1(xz)} + \mathbf{A_1(x^2{-}y^2)})$ and $\Psi_3 = ic_T\mathbf{A_1(\varphi_A)} - 2^{-1/2}c_S(\mathbf{A_1(xz)} + \mathbf{A_1(x^2{-}y^2)})$, respectively. Energies in units of 10^3 cm^{-1} [b] Orbital mixing coefficient, $|c_L|^2 + |c_M|^2 = 1$. [c] Excited state mixing coefficient, $|c_S|^2 + |c_T|^2 = 1$. [d] Intensity ratio, $R = f_1/f_2$.

We estimated R by evaluating the mixing coefficients between the zero order singlet and triplets. For $\Delta = 0$, c_T^2 is 0.33 and R_{calc} simply becomes 2:1. For increasing π-mixing, the R_{calc} values agree with the experimental results, being good evidence for the correctness of the model and hence for the assignments of the CT transitions and the assumptions made in its derivation.

The $[Os^{II}(NH_3)_5L]^{n+}$ complexes show L-dependent ΔE_{CT} due to larger π-mixing (large Δ). The growth in Δ reduces the spin−orbit mixing, explaining the low intensity of CT_2. Despite the scarce intensity data found for the pentaammmine complexes in the literature, our preliminary estimations suggest consistent results and interpretation for the relevant parameters, as in Table 1. Pursuing a unified picture of CT spectroscopy in all the relevant d^6 systems, we are presently extending our analysis to the Ru and Fe analogues, using the appropriate λ values.[15] With $[Ru^{II}(NH_3)_5Mepz]^{3+}$, spin−orbit scrambling still occurs, so that CT_2, even with diminished singlet character, still bears appreciable intensity. The overall agreement is encouraging ($|H_{ML}| = 8.800$ cm^{-1}, $\Delta_{ML} = 5.700$ cm^{-1}, $c_L^2 = 0.35$, $\Delta = 6.400$ cm^{-1}, $c_T^2 = 0.01$, $R_{exp} = 93$, $R_{calc} = 99$).[16] For other less acceptor L ligands we propose that the absence of CT_2 should not be related to poor orbital overlap[2a] but to the smaller M−L and spin−orbit coupling. Thus, ΔE_{CT} becomes very small (and R too large), making difficult the observation of CT_2, which might be buried below the high-energy component. Detailed experimental and theoretical work is under way for assessing the above predictions and will be reported soon.

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Supporting Information Available: MT's model quantitative relations and detailed derivation of the s−o coupling equations (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[12] We discard spin−orbit mixing with other $\mathbf{A_1}$ states (including ground state, d → d, and M → CN$^-$ excited states), based on energy mismatch.

[13] The solvent and internal nuclear coordinates are frozen into the environment of the ground state. Upon CT, however, electronic relaxation might occur. We assume that the distribution of the remaining electrons in the excited state is adequately described by the ground-state wavefunctions.

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[16] In aqueous solution. Experimental values taken from ref 10.