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Is the Axial Zero-Field Splitting Parameter of Tetragonally Elongated High-Spin Manganese(III) Complexes Always Negative?

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Despite being strongly tetragonally elongated, the $S = 2$ ground term of [Mn(cyclam)I$_2$]I exhibits an axial anisotropy of the opposite sign as that predicted by classical ligand field theory (LFT).

Recent high-field and frequency electron paramagnetic resonance (EPR) and inelastic neutron scattering studies[1] of high-spin manganese(III) complexes have without exception and in agreement with all predictions made by classical LFT,[2] confirmed that the spin Hamiltonian parameter D is negative. D is the axial zero-field splitting (ZFS) parameter in the spin Hamiltonian

$$\hat{H} = D\left[\hat{S}_z^2 - \frac{1}{3}S(S+1)\right] + E(\hat{S}_x^2 - \hat{S}_y^2) + \mu_B\hat{\mathbf{S}}\cdot\mathbf{g}\cdot\mathbf{B} \quad (1)$$

where E represents rhombicity of the system and g_x, g_y, and g_z are the Zeeman parameters. According to LFT, a negative D value is associated with a tetragonally elongated ligand environment.[2] All the studied complexes are tetragonally elongated, and accordingly D values in the range -1.168 to -4.524 cm^{-1} have been reported.[1] E values are much smaller, in agreement with the predominant axial distortions. A positive D parameter is associated with either tetragonal compression or with trigonal bipyramidal five-coordination.[3]

trans-[Mn(cyclam)I$_2$]I precipitates quantitatively by addition of iodide to an aqueous solution of *trans*-[Mn(cyclam)(H$_2$O)$_2$](CF$_3$SO$_3$)$_3$·H$_2$O.[4] The magnetic susceptibility measurement of *trans*-[Mn(cyclam)I$_2$]I in the temperature range 50−300 K exhibits a temperature independent effective magnetic moment of 4.95, consistent with an $S = 2$ ground term. The crystal structure[4] of *trans*-[Mn(cyclam)I$_2$]I which is isomorphous with that of *trans*-[Mn(cyclam)Br$_2$]Br[5] reveals neither five-coordination nor a tetragonally compressed ligand environment. The cation exhibits tetragonally elongated six-coordination with four equal Mn−N and two equal Mn−I distances of 2.028 and 2.9416 Å, respectively. Surprisingly, 95 GHz (Figure 1) and 230 GHz (not shown) EPR spectra of this compound recorded at 5 and 15 K unambiguously allow us to conclude that D is positive, The experimental spectrum was simulated[6] using eq 1 with the parameters $D = 0.604$ cm^{-1}, $E = 0.034$ cm^{-1}, $g_x = g_y = 2.00$ and $g_z = 1.99$ where g_x, $g_y > g_z$ was chosen in agreement with Griffith[2]. From the positive D parameter, we conclude that the LFT predictions mentioned above do not hold for this compound.

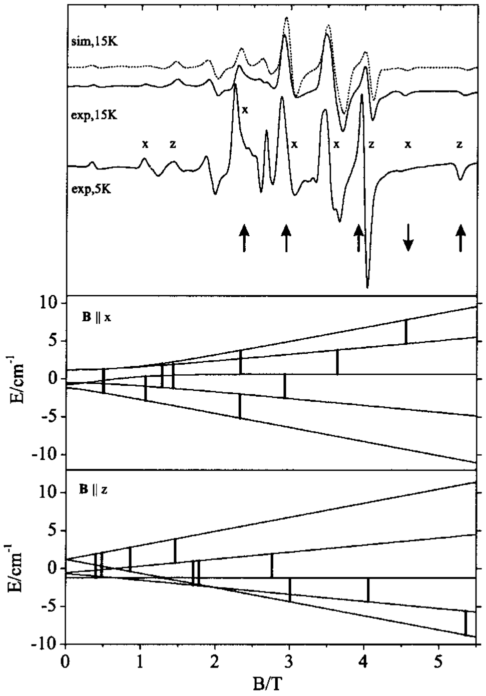

Figure 1. Experimental (solid lines) and simulated (dotted line) EPR spectra of *trans*-[Mn(cyclam)I$_2$]I at 95 GHz. The arrows indicate lines which clearly increase (up) and decrease (down) in intensity upon cooling. The energy level diagrams below are included to illustrate the determination of the sign of D. Transitions originating from the lowest and highest levels gain and loose, respectively, intensity upon cooling.

A necessary prerequisite for LFT to be successful in this respect is that the low-energy excitations are of d−d character. This is not fulfilled by the present compound. Big crystals are black, smaller ones being dark red, indicating the presence of low-lying ligand-to-metal charge transfer (LMCT) states in the visible spectral region.[7] This is anticipated on the basis of the oxidizing and reducing character of manganese(III) and iodide, respectively. In comparison all the known congeners *trans*-[Mn(cyclam)X$_2$]$^+$ (X$^-$ = Cl$^-$, Br$^-$, NCS$^-$, NCO$^-$, NO$_2^-$, NO$_3^-$, ClO$_4^-$, N$_3^-$) and *trans*-[Mn(cyclam)(H$_2$O)$_2$]$^{3+}$ [4,5,8] are weakly colored.

To account for the sign of D in this system we suggest application of the valence bond configuration interaction (VBCI) model,[9] which explicitly takes into account the interaction between the ground term and these low-energy LMCT terms. We adapt the VBCI model to our specific situation, but to begin with we consider but one Mn−I bond and we assume C_{4v} symmetry. In the ground state iodide has the electron configuration 5p^6 giving rise to the ^{1}S (R_3 notation) term, whereas the manganese(III) ion has the electron configuration $d_{xy}^1\, d_{yz}^1\, d_{zx}^1\, d_{z^2}^1$ the ground term of which is ^{5}B$_1$. Hence, the ground (GR) electron configuration of the Mn−I moiety is (5p^6)($d_{xy}^1\, d_{yz}^1\, d_{zx}^1\, d_{z^2}^1$). Transferring an electron from the iodide to the metal d_{z^2} orbital yields the pd_{z^2}-LMCT electron configuration (5p^5)($d_{xy}^1\, d_{yz}^1\, d_{zx}^1\, d_{z^2}^2$), giving rise to the ^{2}P ground term of iodine and a ^{5}B$_1$ term of manganese(II).

The relevant terms arising from the GR and the pd_{z^2}-LMCT configurations are illustrated in Figure 2. The terms arising from

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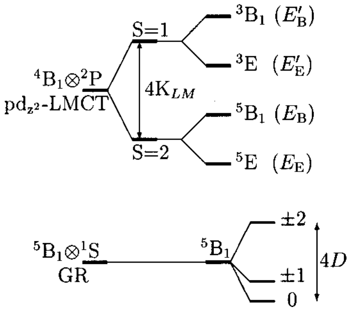

Figure 2. The terms arising from the GR and pd_{z^2}-LMCT electron configurations. Symbols in parentheses designate the energies of the LMCT terms relative to the ground term. The splittings drawn are not to scale.

the LMCT configuration are split in first order by three effects. First, the spin quintet and triplet terms are separated by two-center two-electron exchange integrals of which one is $\langle p_z(1)d_{zx}(2)|1/r_{12}|d_{zx}(1)p_z(2)\rangle$. This triplet-quintet splitting is designated as $4K_{LM}$ where K_{LM} is an average (positive) exchange integral. Second, the quintet terms are split into ^5E and $^5B_1$ by the ligand field splitting of the p orbitals and similarily with the triplet terms. Finally, the four terms $^3B_1$, ^3E, $^5B_1$, and ^5E further split and mix due to the large spin−orbit interaction between the six 5p spin−orbitals. The ground term interacts with the LMCT $^5B_1$ terms via the hybridization matrix element $\langle d_{z^2}|\hat{h}|p_z\rangle = V_\sigma$, where $\hat{h}$ is the appropriate one-electron Hamiltonian.

The terms from Figure 2 represent the basis functions in our VBCI model. The 29 basis functions can be generated using standard methods,[10] and the matrix elements can be calculated. The lowest five eigenvalues of the Hamiltonian matrix so obtained will now be examined using perturbation theory up to 4th order. We get

$$D = \frac{1}{16}\frac{V_\sigma^2\zeta^2}{E_B^2}\left[\frac{1}{E_E} - \frac{1}{E_E{}'}\right] = \frac{1}{4}\frac{V_\sigma^2\zeta^2}{E_B^2 E_E E_E{}'}K_{LM} \tag{2}$$

where ζ is the spin−orbit coupling parameter relevant for the ^2P ground term of iodine. Equation 2 is valid as long as we consider the σ ligand−metal interaction only for one Mn−I bond. However, the p_x and p_y ligand orbitals can interact with the d_{yz} and d_{zx} metal orbitals, respectively, via the one-electron matrix element $V_\pi = \langle p_x|\hat{h}|d_{yz}\rangle = \langle p_y|\hat{h}|d_{zx}\rangle$. To account for this interaction, we must, in addition to the pd_{z^2}-LMCT, also consider the pd_{yz}- and the pd_{zx}-LMCT electron configurations and the terms arising from them. Augmenting the model by these terms and introducing the second iodide ligand results in the following expression for D

$$D = \frac{1}{2}\frac{\zeta^2 K_{LM}}{E_{av}^4}(V_\sigma^2 - V_\pi^2) \tag{3}$$

Here we have assumed the terms arising from the pd_{yz}-, pd_{zx}-, and the pd_{z^2}-LMCT electron configuration have similar energies E_{av}. This is justified because the pronounced tetragonal elongation makes the energies of the d_{yz}, d_{zx}, and d_{z^2} orbitals roughly equal. Equation 3 represents the VBCI contribution to D. Since K_{LM} is positive and σ interactions are larger than π interactions, $V_\sigma > V_\pi$, we conclude that this contribution is positive. The magnitude of the contribution eq 3 is estimated as follows. From ref 11 we find $\zeta = 5070$ cm^{-1}. From the color of the compound we estimate the CT energies E_{av} in the visible spectral region, that is, 15000−30000 cm^{-1}. The VBCI model has been successfully applied to account for magnetic properties and UV/vis spectral features of oxo-bridged iron(III) dimers.[12] In that report the following values of hybridization matrix element for the iron−oxide bond were used: $V_\sigma \approx 18000$ cm^{-1} and $V_\pi \approx 11000$ cm^{-1}. Iodide has significantly weaker donor properties as compared to the oxide ligand. We therefore estimate V_σ(iodide) ≈ V_π(oxide), and $V_\sigma/2 \geq V_\pi \geq V_\sigma/3$. Finally, metal−ligand two-electron exchange integrals, K_{LM}, have been estimated to be $K_{LM} \approx 100-400$ cm^{-1}.[13] Inserting these parameter value ranges in eq 3 we find that the VBCI model contribution to D is in the range 0.2 cm^{-1} < D < 10 cm^{-1}. This is of the same magnitude but of the opposite sign as the ZFS calculated by LFT.[2] We conclude, that for the present compound the VBCI model contribution to D is numerically larger than the LFT contribution.

The broad lines in the experimental spectra did not allow us to determine the g values to a better accuracy than 1−2%. However, abnormally high g values, as those found for copper(II) iodo complexes[14] were not observed. LFT also failed to account for the sign of the D parameter in $FeCl_4^-$ and $Fe(SR)_4^-$ (R = 2,3,5,6-Me_4-C_6H).[15] In these high-spin d^5 systems the sign of D depends on the sign of the low-symmetry splittings of excited ligand field states, whereas for the present d^4 system, the splittings of excited ligand field states only influence the magnitude but not the sign of D.[2]

In summary, we have shown that the zero-field splitting parameter D of tetragonally elongated manganese(III) complexes can be positive. In addition to considering the interaction between the ground state and LMCT states, this implies accounting for the ligand-centered spin−orbit interaction in the LMCT states.

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