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On the Failure To Observe Isotropic Electron Paramagnetic Resonance Spectra for Certain Chromium(I) Carbonyl Complexes

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Despite extensive efforts using in situ electron paramagnetic resonance (EPR) and voltammetric techniques[1] or chemical oxidation at temperatures down to 200 K, isotropic EPR spectra are not observed for *fac*-$[\mathrm{Cr(CO)_3L_3}]^+$ [2,3] (L is a phosphine, phosphite, or phosphonite ligand), *fac*-$[\mathrm{Cr(CO)_3}(\eta^2\text{-LL})(\eta^1\text{-LL})]^+$ (LL = $\mathrm{Ph_2P(CH_2)}_n\mathrm{PPh_2}$, $n = 1$, 2, or pompom = $\mathrm{(MeO)_2PCH_2CH_2P(OMe)_2}$,[4,5] $[\mathrm{Cr(CO)_3}(\eta^6\text{-arene})]^+$, *cis*-$[\mathrm{Cr(CO)_2L_4}]^+$, *cis*-$[\mathrm{Cr(CO)_2}(\eta^2\mathrm{LL})_2]^+$,[6] or $\mathrm{Cr(CO)_3}(\eta^5\text{-}\mathrm{C_5Ph_5})$).[7] This is in contrast with generally well-resolved spectra recorded for *cis*-$[\mathrm{Cr(CO)_4L_2}]^+$,[8] *mer*-$[\mathrm{Cr(CO)_3L_3}]^+$,[2,3] *mer*-$[\mathrm{Cr(CO)_3}(\eta^2\text{-LL})(\eta^1\text{-LL})$,[4,5] *trans*-$[\mathrm{Cr(CO)_2L_4}]^+$,[2,3] and *trans*-$[\mathrm{Cr(CO)_2}(\eta^2\text{-LL})_2]^+$ [4,5] and the reasonably well-resolved frozen solution spectra of *fac*-$[\mathrm{Cr(CO)_3(triphos)}]^+$ (triphos = $\mathrm{(Ph_2P)_3CH}$,[3] *fac*-$[\mathrm{Cr(CO)_3}(\eta^2\text{-pompom})(\eta^1\text{-pompom})]^+$,[5] and $\mathrm{Cr(CO)_3}(\eta^5\text{-}\mathrm{C_5Ph_5})$).[7] We have sought an explanation for these apparent discrepancies for some years. In this note, we present the (almost certainly) correct answer,

In octahedral symmetry, the low-spin d^5 configuration is degenerate and a Jahn−Teller distortion of the $^2\mathrm{T}_{2g}$ ground state is expected; the epikernel principle[9] suggests that the distortion is to one of three equivalent D_{2h} structures. Rapid interconversion among these structures—the dynamic Jahn−Teller effect—provides a mechanism for spin−lattice relaxation. Classic examples of this phenomenon are the EPR spectra of the benzene, triphenylene, and coronene radical anions, which have unusally broad lines.[10] Liquid solution EPR spectra of organometallic radicals subject to Jahn−Teller distortion may be so broad as to be undetectable. Thus, the EPR spectrum of $\mathrm{V(CO)_6}$ could only be observed at low temperature in a rigid matrix where the Jahn−Teller distorted form is sufficiently long-lived.[11] The case of $[\mathrm{Cr(CO)_6}]^+$ is somewhat unclear. The early report by Pickett and Pletcher[12] was almost certainly of an acetonitrile solvate, but careful work by Mleczko[1] led to a broad signal (with ^{53}Cr satellites) similar to that reported by Bagchi et al.,[13] which might well have been the expected Cr(I) complex. Interconversion of the epikernel states could be much slower for the charged Cr(I) radical than for the uncharged V(0) species.

Substitution of a weaker π-acceptor ligand, L, for CO gives $[\mathrm{M(CO)_5L}]^+$ (C_{4v}) or *trans*-$[\mathrm{M(CO)_4L_2}]^+$ (D_{4h}). In both cases, d_{xy} interacts with four CO ligands and thus is lower in energy than d_{xz} and d_{yz}, which interact with three or two CO's. Thus, the expected ground state is ^{2}E (C_{4v}) or $^2\mathrm{E_g}$ (D_{4h}). An EPR spectrum has been reported for *trans*-$[\mathrm{V(CO)_4(PMe_3)_2}]$ diluted into a single crystal of the Cr(0) analogue,[14] but the spectrum could only be detected at very low temperature. A broad, weak spectrum ($\langle g \rangle = 2.027$, $\langle a^{\mathrm{P}} \rangle = 18 \pm 2$ G), observed for *trans*-$[\mathrm{Cr(CO)_4(PPh_3)_2}]^+$ at room temperature, was found to improve slightly at lower temperatures.[15] The epikernel principle suggests a Jahn−Teller distortion from D_{4h} to one of two equivalent D_{2h} structures, but interconversion is apparently sufficiently slow that the isotropic spectrum is detectable.

A similar analysis for *cis*-$[\mathrm{Cr(CO)_4L_2}]^+$ (C_{2v}), *mer*-$[\mathrm{Cr(CO)_3L_3}]^+$ (C_{2v}), and *trans*-$[\mathrm{Cr(CO)_2L_4}]^+$ (D_{4h}) leads to the unambiguous prediction of nondegenerate ground states well separated from excited states—$^2\mathrm{A}_1$, $^2\mathrm{A}_2$, and $^2\mathrm{B}_{2g}$, respectively—consistent with the reported isotropic EPR spectra of such species.[2−5,16]

The cases of *cis*-$[\mathrm{Cr(CO)_2L_4}]^+$, *cis*-$[\mathrm{Cr(CO)_2}(\eta^2\text{-LL})_2]^+$, *fac*-$[\mathrm{Cr(CO)_3L_3}]^+$, *fac*-$[\mathrm{Cr(CO)_3}(\eta^2\text{-LL})(\eta^1\text{-LL})]^+$, and $[\mathrm{Cr(CO)_3}(\eta^6\text{-arene})]^+$, where no isotropic EPR signals have been detected, are less obvious. While these species are usually unstable with respect to isomerization to *trans*-$[\mathrm{Cr(CO)_2L_4}]^+$ and *mer*$[\mathrm{Cr(CO)_3L_3}]^+$, extensive electrochemical studies have shown concentrations of the *cis*-dicarbonyl or *fac*-tricarbonyl cations, which should have been EPR-detectable, but no isotropic spectrum could be found. A ligand-field argument for *cis*-$[\mathrm{Cr(CO)_2L_4}]^+$ suggests that, with the CO ligands along the x- and y-axes, the d_{xy} orbital, which interacts with both CO ligands, will lie lower in energy than d_{xz} or d_{yz}, which interact with only one CO each. On this basis, the d_{xz}- and d_{yz}-based MO's should be nearly degenerate. A closer analysis, taking into account the (at least approximate) C_{2v} symmetry, shows that the highest-energy doubly occupied MO (HOMO) and the singly occupied MO (SOMO) should belong to the b_2 ($d_{xz} + d_{yz}$) and a_2 ($d_{xz} - d_{yz}$) representations. In other words, there is no symmetry-

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imposed requirement of degeneracy, and neither the Jahn−Teller theorem nor the epikernel principle apply. Similar analysis of *fac*-$[\mathrm{Cr(CO)_3L_3}]^+$ with CO ligands along the *x*-, *y*-, and *z*-axes suggests that because each of the t_{2g} orbitals interacts with two CO ligands, the three orbitals will remain nearly degenerate. However, when C_{3v} symmetry is imposed, the t_{2g} orbitals split into a_1 and e, and again, there is no symmetry-imposed requirement of a degenerate ground state. Of course, in the case of *fac*-$[\mathrm{Cr(CO)_3}(\eta^2\text{-LL})(\eta^1\text{-LL})]^+$, the symmetry is at most C_s, and all levels are expected to be nondegenerate.

Extended Hückel MO calculations[17] suggest that the a_2 and b_2 orbitals are indeed nearly degenerate for *cis*-$[\mathrm{Cr(CO)_2(PH_3)_4}]^+$ with the $^2B_2$ state 0.052 eV lower than $^2A_2$, an energy difference comparable to a vibrational quantum for a ligand bending mode, suggesting a mechanism for spin−lattice relaxation. Similarly, EHMO calculations for *fac*-$[\mathrm{Cr(CO)_3(PH_3)_3}]^+$ predict a ^2A ground state 0.068 eV lower in energy than ^2E.

Interestingly, a low-temperature isotropic EPR spectrum was reported for *fac*-$[\mathrm{V(CO)_3(PMe_3)_3}]$.[20] EHMO calculations were repeated for this complex, keeping bond lengths and angles fixed at the values used for the Cr calculations. The $^2A/^2E$ energy difference is predicted to increase to 0.084 eV, a direct result of the larger 3d orbitals for V and consequent better overlap with the CO π^* orbitals.[21]

EHMO calculations for *fac*-$[\mathrm{Cr(CO)_3(PH_3)_3}]^+$ also employed C−Cr−C bond angles ranging from 82° to 92°, holding the trans P−M−C bond angles constant at 180°. The $^2A/^2E$ energy difference decreased to 0 when the C−Cr−C bond angle was decreased to 84.6°. Thus, to the extent that increasing the P−M−P bond angles leads to a decrease in the C−M−C angles, we might expect the $^2A/^2E$ energy difference to decrease with increasing steric bulk of the phosphorus ligands.

Energy differences obtained from EHMO calculations should never be taken very seriously. However, the qualitative EHMO results follow directly from overlap integrals calculated using Slater-type orbitals and thus are independent of the EHMO formalism. Consider *cis*-$[\mathrm{Cr(CO)_2L_4}]^+$ with CO ligands along the *x*- and *y*-axes. The symmetry-adapted combinations of carbonyl π_z and metal $3d_{xz}$, $3d_{yz}$ orbitals are

$$\psi_{\mathrm{d,a_2}} = \frac{1}{\sqrt{2}}(\mathrm{d}_{xz} - \mathrm{d}_{yz}) \qquad \psi_{\pi,\mathrm{a_2}} = \frac{1}{\sqrt{2(1 - S_{\|})}}(\pi_{z1} - \pi_{z2})$$

$$\psi_{\mathrm{d,b_2}} = \frac{1}{\sqrt{2}}(\mathrm{d}_{xz} + \mathrm{d}_{yz}) \qquad \psi_{\pi,\mathrm{b_2}} = \frac{1}{\sqrt{2(1 + S_{\|})}}(\pi_{z1} + \pi_{z2})$$

where $S_{\|}$ is the overlap integral for the π_z orbitals of $\mathrm{CO_1}$ and $\mathrm{CO_2}$. Overlap of d_{xz} with π_{z1} is identical to that of d_{yz} with π_{z2} (S_{big}); the overlap of d_{xz} with π_{z2} and the overlap of d_{yz} with π_{z1} are also identical ($S_{\mathrm{small}} = 0$ if the bond angles are exactly 90°). The overlap integrals critical to the MO energies then are

$$S_{\mathrm{d}\pi,\mathrm{a_2}} = \frac{S_{\mathrm{big}} - S_{\mathrm{small}}}{\sqrt{1 - S_{\|}}}, \quad S_{\mathrm{d}\pi,\mathrm{b_2}} = \frac{S_{\mathrm{big}} + S_{\mathrm{small}}}{\sqrt{1 + S_{\|}}}$$

Thus, the difference in energy between $^2A_2$ and $^2B_2$ is due to $S_{\|}$, small but nonzero, and possibly to S_{small}, which is significant for distorted conformations.

Analysis of the a_1/e energy gap for *fac*-$[\mathrm{Cr(CO)_3L_3}]^+$ is qualitatively similar, albeit somewhat more complex. With $\mathrm{CO_1}$, $\mathrm{CO_2}$, and $\mathrm{CO_3}$ along the *x*-, *y*-, and *z*-axes, respectively, the a_1 symmetry-adapted combinations are

$$\psi_{\mathrm{d,a_1}} = \frac{1}{3}(\mathrm{d}_{xz} + \mathrm{d}_{yz} + \mathrm{d}_{xy})$$

$$\psi_{\pi,\mathrm{a_1}} = \frac{1}{\sqrt{6(1 + S_{\perp} + S_{\|})}}(\pi_{y1} + \pi_{z1} + \pi_{x2} + \pi_{z2} + \pi_{x3} + \pi_{y3})$$

where $S_{\perp}$ (e.g., between π_{y1} and π_{x2}) > $S_{\|}$ (e.g., between π_{z1} and π_{z2}). We have ignored $\pi-\pi$ overlap integrals, which are zero for 90° bond angles (e.g., between π_{y1} and π_{z2}). The relevant dπ overlap integral then is

$$S_{\mathrm{d}\pi,\mathrm{a_1}} = \frac{2(S_{\mathrm{big}} + 2S_{\mathrm{small}})}{\sqrt{2 + 2S_{\perp} + 2S_{\|}}}$$

The corresponding e combinations are

$$\psi_{\mathrm{d,e_1}} = \frac{1}{\sqrt{6}}(2\mathrm{d}_{xy} - \mathrm{d}_{yz} - \mathrm{d}_{xz}),$$

$$\psi_{\pi,\mathrm{e_1}} = \frac{1}{\sqrt{6(2 + 2S_{\perp} - S_{\|})}}(2\pi_{y1} + 2\pi_{x2} - \pi_{z1} - \pi_{z2} - \pi_{x3} - \pi_{y3})$$

$$\psi_{\mathrm{d,e_2}} = \frac{1}{\sqrt{2}}(\mathrm{d}_{yz} - \mathrm{d}_{xz}),$$

$$\psi_{\pi,\mathrm{e_2}} = \frac{1}{\sqrt{2(2 + 2S_{\perp} - S_{\|})}}(\pi_{z2} + \pi_{y3} - \pi_{x3} - \pi_{z1})$$

and for either set of functions

$$S_{\mathrm{d}\pi,\mathrm{e}} = \frac{2(S_{\mathrm{big}} - S_{\mathrm{small}})}{\sqrt{2 + 2S_{\perp} - S_{\|}}}$$

Again, the a_1/e energy gap is due to $S_{\|}$ and S_{small}. (The Slater-type orbitals used by the EHMO program give $S_{\mathrm{big}} = 0.1517$, $S_{\perp} = 0.0664$, $S_{\|} = 0.0218$.) As the C−Cr−C bond angles are changed, we expect changes in S_{small}, which lead to variations in the $^2A/^2E$ energy difference. In particular, $S_{\mathrm{d}\pi,\mathrm{a}}$ decreases weakly with increasing C−Cr−C bond angle while $S_{\mathrm{d}\pi,\mathrm{e}}$ increases strongly with increasing angle. The EHMO result—degenerate ground state for angles less than 84.6°—thus is consistent.

In summary, the calculations predict that a Jahn−Teller distortion per se is not expected for Cr(I) *cis*-$\mathrm{(CO)_2}$ and *fac*-$\mathrm{(CO)_3}$ complexes. However, the energy gap is so small and is so sensitive to bond angle that rapid spin−lattice relaxation is expected, especially for complexes in liquid solutions. Spectra observable in frozen solutions are likely to result from a solvation state that removes the degeneracy, either by a symmetric increase in the C−Cr−C bond angle(s) or by departure from C_{2v} or C_{3v} symmetry.

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