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# Applications of High-Field (W-Band) EPR to M–M Bonded Units (M = Cr, Mo): The First Confirmed Oxidation of a $Cr_2^{4+}$ Paddlewheel Complex to a Stable Isostructural $Cr_2^{5+}$ Product

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The EPR spectra of $\{Cr_2[(PhN)_2CN(CH_2)_4]_4\}PF_6$ and $[Mo_2(TiPB)_4]PF_6$ (TiPB = anion of 2,4,6-triisopropylbenzoic acid) at W-band are shown to have *g* values significantly lower than 2.00 and exhibit parallel and perpendicular components (not resolved at X-band). Therefore the unpaired electrons of the $M_2^{5+}$ units must reside on metal-based (not ligand-based) orbitals. Thus, the chromium compound must be considered as the first confirmed oxidation product of a $Cr_2^{4+}$ paddlewheel complex comparable to the $Mo_2^{5+}$ compounds.

Recently we reported the first structures of compounds containing the cations $Mo_2(carboxylate)_4^+$ (carboxylate = triisopropylphenylcarboxylate (TiPB) and pivalate)[1] and also described the first example of a stable structurally characterized oxidation product of a $Cr_2^{4+}$ paddlewheel compound.[2] Unfortunately, in both reports there were some questions that remained unanswered by low-field X-band EPR data (vide infra). In particular, in both cases the main signal was a single peak, with a *g* value close to 2.00. This was unexpected because of the cylindrical or even lower symmetry of the $M_2^{5+}$ bond. In order to obtain additional clues to the nature of the unpaired electron orbital we report EPR measurements at W-band (95 GHz). We can now report that in one case there is confirmation of the previous interpretation that oxidation of the $Mo_2^{4+}$ unit is metal-based, while in the other there is overwhelming evidence for the existence of a $Cr_2^{5+}$ unit, meaning that the unpaired electron resides on the $Cr_2$ core, contrary to the previous proposal that it was ligand-based.

For the $Mo_2(carboxylate)_4^+$ species we also reported on the electrochemistry and electronic spectra.[1] These data were consistent with an electronic configuration of $\sigma^2\pi^4\delta$ and a bond order of 3.5 between the metal atoms. However, X-band EPR spectra at 9.42 GHz and 70 K for $Mo_2(TiPB)_4X$, X = $BF_4$ or $PF_6$, were devoid of the expected splitting of the main peak due to the $g_\parallel$ and $g_\perp$ components, while the isotropic *g* value close to $g = 1.936$ was indicative of the unpaired electron being metal-based. This was similar to the observations for $Mo_2(butyrate)_4^+$.[3] Thus, it remained desirable to observe the *g*-component splitting commensurate with the axial or lower symmetry of the $Mo_2^{5+}$ environment.

Now we show that the W-band EPR spectrum of $[Mo_2(TiPB)_4]PF_6$ at room temperature (Figure 1) is consistent with our previous results. The clear separation of the signals from the dimetal unit from that of the organic radical 2,2-diphenyl-1-picrylhydrazyl, DPPH ($g = 2.0037$), strongly supports the idea that the unpaired electron resides on the $Mo_2$ unit. Upon cooling to 10 K the line width decreases and therefore the signal splits, thus allowing the quantification of $g_{zz}$ of 1.9427, $g_{yy}$ of 1.9358, and $g_{xx}$ of 1.9310. The *g* values were obtained via spectral simulation, which gave a near-perfect fit to Figure 1, lower panel. It is therefore certain that oxidation of the quadruply bonded $Mo_2(carboxylate)_4$ compounds leads to $Mo_2^{5+}$ units with bond orders of 3.5. This conclusion is in accord with more recent studies that have shown that for the two series of compounds $M_2(hpp)_4^{n+}$, $n = 0, 1, 2$, M = Mo,[4] W,[5] and hpp = the guanidinate-type anion of 1,3,4,6,7,8-hexahydro-2*H*-pyrimidol[1,2-*a*]pyrimidine, the removal of one $\delta$ electron from the neutral compounds having $\sigma^2\pi^4\delta^2$ electronic configurations increases the M−M bond lengths by ca. 0.05 Å, comparable to the increase of 0.06 Å observed for $Mo_2(carboxylate)_4^{0,+}$ couples.[1]

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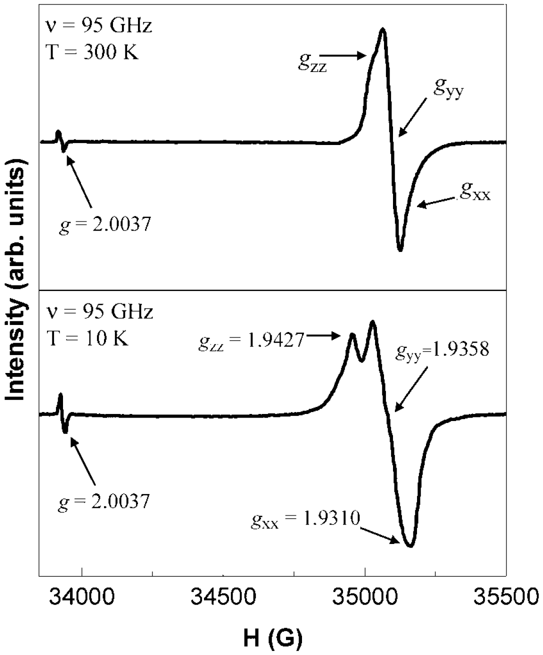
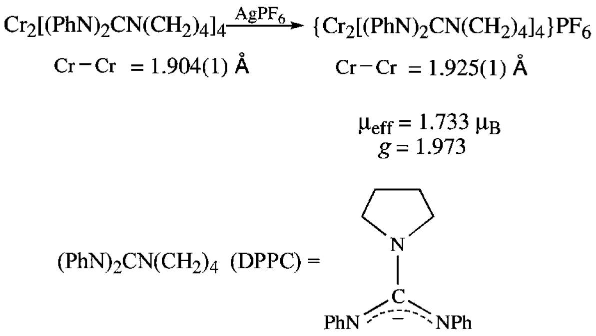


**Figure 1.** The W-band (95 GHz) EPR spectra of $[Mo_2(TiPB)_4]PF_6$ at 300 and 10 K.

**Scheme 1**



For the chromium compound the key chemical facts previously reported are recapitulated in Scheme 1, where DPPC represents the guanidinate anion $(Ph_2N)_2CN(CH_2)_4^-$. The increase of ca. 0.021 Å in the Cr−Cr bond length seemed consistent with, but, because it is relatively small, not conclusively diagnostic of the loss of a $\delta$ electron; however, the X-band EPR signal at a $g$ value of 1.973 was featureless and close to that expected for an organic radical. Moreover, there was some precedent for oxidation on the ligands of paddlewheel complexes[6] and no $Cr_2^{4+}$ complex with smaller ligands had ever previously been oxidized without decomposition. Thus, it was concluded that the oxidized product resulted from an oxidation process that was essentially ligand-based.

Therefore, we also carried out EPR experiments at higher frequencies to see if $g$-tensor components could be separated. Indeed, the new data provide definitive evidence that the $g$-values are sufficiently far away from 2.000 ± 0.005 (that expected for an organic radical), and reveal additional splittings and $g$-value features that enable us to reinterpret the earlier EPR conclusions and to infer that the oxidized product can be unambiguously described as having the $Cr_2^{5+}$ core.

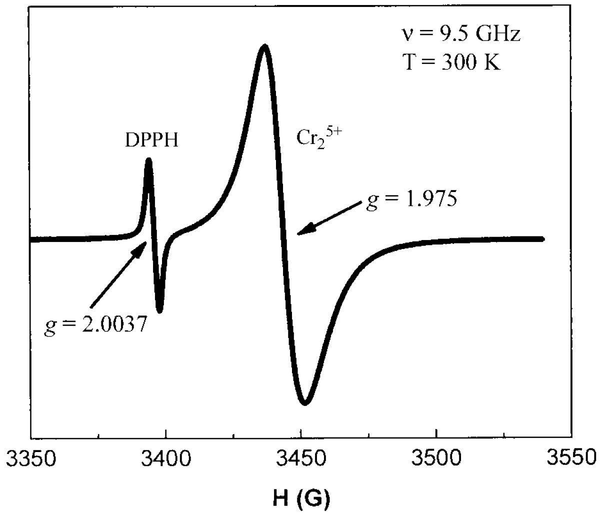


**Figure 2.** The X-band (9.5 GHz) EPR spectrum of $[Cr_2(DPPC)_4]PF_6$ appears as a single, nearly isotropic peak centered at $g = 1.975$ and that of the organic radical, DPPH, at $g = 2.0037$.

The new EPR measurements, both at X-band (9.5 GHz) and W-band (95 GHz), were made on crystalline $[Cr_2(DPPC)_4]PF_6$ from which interstitial solvent had been removed. As shown in Figure 2, the X-band spectrum is a single featureless peak, labeled $Cr_2^{5+}$, at $g = 1.975$, in good agreement with our earlier reported value of 1.973.[2] However, the $Cr_2^{5+}$ peak can be seen to be separated from that of DPPH, which has a $g$ of 2.0037, indicating that the signal is perhaps from a metal-containing unpaired electron species, but with the $g$-tensor components within the 14 G line width. Due to the low resonance frequency of this measurement it is impossible to resolve the components of the $g$-tensor expected to be present for a $Cr_2^{5+}$ system with intermediate symmetry. However, further evidence to support the presence of the unpaired electron in metal-based molecular orbitals comes from measurements at 95 GHz, which resolved the signal into two components (Figure 3) as expected from the approximate cylindrical symmetry of the unpaired electron delocalization on the $Cr_2^{5+}$ moiety. The $g$ values calculated from the 95 GHz spectrum correspond to $g_{\parallel} = 1.9701 \pm 0.0005$ and $g_{\perp} = 1.9767 \pm 0.0005$. These values are consistent with the X-band value of $g_{iso} = \frac{1}{3}(g_{\parallel} + 2g_{\perp}) = 1.975$.

The measured $g_{\parallel}$ and $g_{\perp}$ can be analyzed in terms of the unpaired electron being localized in an orbital with appreciable chromium d character. As a simple model for this, consider a 3d ion in a tetrahedral field with a tetragonal distortion. In this case (of an elongated tetrahedron), the $g$ values are given by[7,8]

$$g_{\parallel} \approx 2.0023 - 8\lambda/\Delta E_{xy}$$

$$g_{\perp} \approx 2.0023 - 2\lambda/\Delta E_{xz}$$

where $\lambda$ is the spin−orbit coupling constant for the Cr ion, and $E_{xy}$ and $E_{xz}$ are energy separations between the ground state ($d_{x^2-y^2}$) orbital and the $d_{xy}$ and $d_{xz}$ orbitals, respectively.

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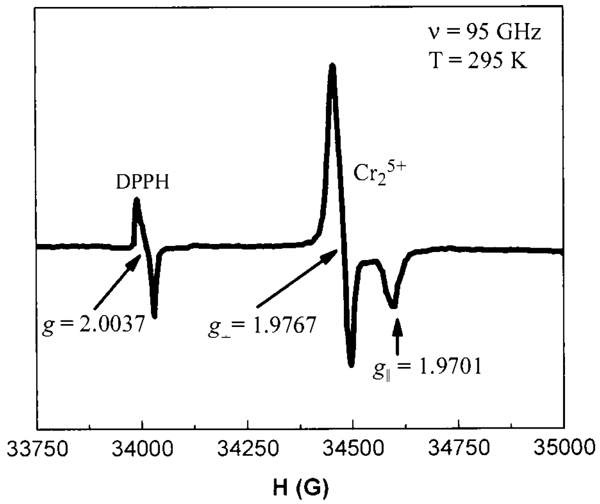

**Figure 3.** The W-band (95 GHz) EPR spectrum of $[Cr_2(DPPC)_4]PF_6$. The parallel and perpendicular components of the *g*-tensor are clearly resolved, and their positions resemble those of other spin doublet Cr systems, which are shown in Table 1. The field calibration sample, DPPH, was slightly over-modulated to obtain the best looking $Cr_2^{5+}$ peak.

**Table 1.** *g*-Tensor Components of $[Cr_2(DPPC)_4]PF_6$ in Comparison to Those of $Cr^{5+}$-Containing Species Also Obtained through High-Frequency EPR

| compound | $g_\parallel$(±0.0005) | $g_\perp$(±0.0005) |
|---|---|---|
| $[Cr_2(DPPC)_4]PF_6$ | 1.9701 | 1.9767 |
| $Li_3CrO_8 \cdot 10H_2O$ | 1.9533 | 1.9834 |
| $Cs_3CrO_8 \cdot 3H_2O$ | $g_z = 1.9546$ | $g_x = 1.9817$<br>$g_y = 1.9702$ |
| $Na_3CrO_8$ | $g_z = 1.9544$ | $g_x = 1.9848$<br>$g_y = 1.9802$ |
| $K_3CrO_8$ | 1.9431 | 1.9852 |
| $K_2NaCrO_8$ | $g_z = 1.9851$ | $g_x = 1.9636$<br>$g_y = 1.9696$ |
| $Rb_3CrO_8$ | 1.9426 | 1.9825 |
| $Rb_2NaCrO_8$ | $g_z = 1.9849$ | $g_x = 1.9633$<br>$g_y = 1.9688$ |

Using $\lambda = 380$ cm$^{-1}$ for a free $Cr^{5+}$ ion[8] and the literature values[9] of $\Delta E_{xy} = 35000$ cm$^{-1}$ and $\Delta E_{xz} = 18000$ cm$^{-1}$ for the well-studied $Cr^{5+}$ ion in $K_3CrO_8$, we obtain $g_\parallel = 1.92$ and $g_\perp = 1.96$. These values are in reasonable agreement with the measured values, considering that we have neglected the covalent bonding present in this system.

For comparison, the 95 GHz *g* values, together with those of several well-characterized $Cr^{5+}$-containing solids,[10] are collected in Table 1. A close similarity of the data in Table 1 also supports our new interpretation that for $Cr_2(DPPC)_4$ the oxidation involves the $Cr_2^{4+}$ core.

It will be noted that all *g* components for both compounds are lower than the free-electron value of 2.0023 but also that those for $Mo_2^{5+}$ are lowered twice as much (~0.059 for $g_\parallel$) as those for $Cr_2^{5+}$ (0.03). This is in proportion to their spin−orbit coupling constants, 750 cm$^{-1}$ for $Mo^{3+}$ vs 350 cm$^{-1}$ for $Cr^{3+}$.[7] However, $g_\parallel$ is greater than $g_\perp$ for $Mo_2^{5+}$ but the reverse is the case for $Cr_2^{5+}$. Such reversals have been observed in mononuclear species where they are related to the type of atomic orbital in which the unpaired electron resides.[10c] Unfortunately, further interpretation will have to wait for new theoretical calculations and expansion of the number of compounds having $M_2^{5+}$ cores for Cr and Mo. These studies are currently underway. Additional evidence for the unpaired electron residing on the $Cr_2^{5+}$ core should be obtainable by measurements of the $^{53}Cr$ hyperfine structure. As mentioned earlier,[2] no $^{53}Cr$ hyperfine structure was resolved despite measurements on frozen dilute samples (concentration 0.2−1 mM). This can be rationalized by noting that the unpaired electron is delocalized over both Cr atoms, and hence splitting is reduced to half that for the other compounds listed in Table 1. The isotropic value of $^{53}Cr$ hyperfine coupling for $K_3CrO_8$ is about 15 G. We would thus not expect a small intensity quartet of about 5−7 G to be resolved for the $Cr_2^{5+}$ case.

In conclusion, high-frequency EPR measurements demonstrate that the oxidation of $Cr_2(DPPC)_4$ to $[Cr_2(DPPC)_4]PF_6$ should be interpreted as involving the conversion of the core to $Cr_2^{5+}$ rather than the oxidation primarily localized on the ligands. The electronic structure of the oxidation products of $Mo_2(O_2CR)_4$ has also been revealed in more detail. The role of high-frequency EPR measurements in settling questions like these is clearly illustrated in metal−metal bonded systems. Without it the assignment of oxidation from the $Cr_2^{4+}$ to the $Cr_2^{5+}$ core is very difficult and ambiguous.

In view of the very great stability and kinetic inertness of the $Cr^{3+}$ ion, and its nearly exclusive predilection for octahedral coordination, the ability of the $Cr_2^{5+}$ core to diffuse the additional charge over both metal atoms and thus avoid fission in this compound (but not, so far as is known, in any of the several hundred other $Cr_2^{4+}$ complexes)[11] is presumed to be due to the character of the guanidinate anions present. Most particularly, guanidinate anions are extremely basic, in both the $\sigma$ and $\pi$ senses.[4,12] Therefore, while the guanidinate ions do not cause the unpaired spin density to diffuse off of the $Cr_2^{5+}$ core to the extent previously believed, they doubtless help to mitigate the buildup of positive charge on the $Cr_2^{5+}$ core.

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