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On the electron delocalization in the radical cations formed by oxidation of MM quadruple bonds linked by oxalate and perfluoroterephthalate bridges†‡

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Electron paramagnetic resonance, electronic absorption, and resonance Raman spectroscopy reveal that in the oxalate-bridged compounds, $[[(^tBuCO_2)_3M_2]_2(\mu\text{-}O_2C\text{-}CO_2)]^+[PF_6]^-$, the unpaired electron is delocalized over four metal centers (M = Mo or W) as a result of M_2 δ to bridge π conjugation, but in the related cationic perfluoroterephthalate-bridged species, the tungsten complex is delocalized and the molybdenum analogue valence trapped.

Cotton,[1] Walton[2] and others[3,4] have shown that dinuclear units with multiple bonds can be linked through the agency of dicarboxylate ligands to give dimers of "dimers" and cyclic trimers and tetramers of "dimers". Cotton and coworkers have furthermore shown that these can be linked through the agency of neutral ligands to give supramolecular coordination polymers. There is here some parallel with the work of Stang *et al.*,[5] who have developed an extensive chemistry of polynuclear "polygons" based on the linking of square-planar d^8-metal fragments, most notably where $M = Pt^{2+}$ and Pd^{2+}. A significant difference between the Cotton and Stang molecular assemblies is that the former are neutral and the latter are in general cationic. Also, the linking of dinuclear units with MM multiple bonds involves redox active M_2 centers. We describe here our preparation and characterization of oxalate- and perfluoroterephthalate-bridged dimolybdenum and ditungsten radical cations supported by pivalate ligands according to the reaction shown in eqn. (1), performed in 1:1 THF/CH_2Cl_2.

$$M_4OXA \text{ (or } M_4PFT) + Cp_2Fe^+PF_6^- \longrightarrow M_4OXA^+PF_6^- \text{ (or } M_4PFT^+PF_6^-) + Cp_2Fe. \quad (1)$$

where $M_4OXA = [(^tBuCO_2)_3M_2]_2(\mu\text{-}O_2CCO_2)$, $M_4PFT = [(^tBuCO_2)_3M_2]_2(\mu\text{-}O_2CC_6F_4CO_2)$ and M = Mo or W.

Although efforts in this regard are currently underway, none of the new compounds prepared in reaction **1** has been isolated and fully characterized in the solid state (*e.g.*, by single crystal X-ray diffraction), but the following characterization data can leave little doubt concerning the nature of the radical cationic tetranuclear complexes.

1. By ESI-TOF-MS^+, the ions M_4OXA^+ and M_4PFT^+ are seen from THF/CH_2Cl_2 solutions. These ions are not detectable by ESI-TOF-MS^+ for the neutral species, M_4OXA and M_4PFT, when dissolved in the same solvent mixture. (For both the neutral and oxidized species, the molecular ions M_4OXA^+ and M_4PFT^+ are observed by LDI-MS.)

2. The radical cations show EPR spectra indicative of metal-based delocalized electrons. The EPR spectra for the Mo_4OXA^+ and Mo_4PFT^+ radicals are shown in Fig. 1 along with a comparison of the simulated spectra. We can conclude that the unpaired electron is delocalized over all four molybdenum atoms in the oxalate-bridged compound but only over two in the case of the perfluoroterephthalate; *i.e.* one Mo_2 center is oxidized and the other not. This is evident from a statistical analysis of the intensity distribution of the hyperfine lines, and from the simulations. It also correlates well with related previous work, that has demonstrated the manner in which the degree of electron delocalization over multiple molybdenum atoms influences the relative magnitude of the hyperfine coupling constants.[6] The Mo_4OXA^+ species is not kinetically persistent at room temperature and in solution, over 30 min, the EPR spectrum shown in Fig. 1 is transformed to that observed for $Mo_2(O_2C^tBu)_4^+$: $g_{av} = 1.942$, $A_{av} = 27.2$ G. Evidence for the formation of the latter ion is found in the ESI-TOF-MS and by the appearance of the $^2\delta \rightarrow {}^2\delta^*$ transition at 767 nm (see data in the ESI†). This degradation presumably arises from facile ligand scrambling.[7] In contrast, the tungsten species are kinetically more persistent in solution and both the oxalate and perfluoroterephthlate complexes reveal electron delocalization over all four W atoms. These spectra are depicted in Fig. 2.

3. The compounds $M_4OXA^+PF_6^-$ are blue and their electronic absorption spectra in THF are remarkably similar, and notably different from those of the neutral complexes. The blue colors arise from intense absorptions at $\lambda_{max} = 666$ nm (M = W) and 639 nm (M = Mo) which have $\varepsilon \sim 25{,}000$ L mol^{-1}

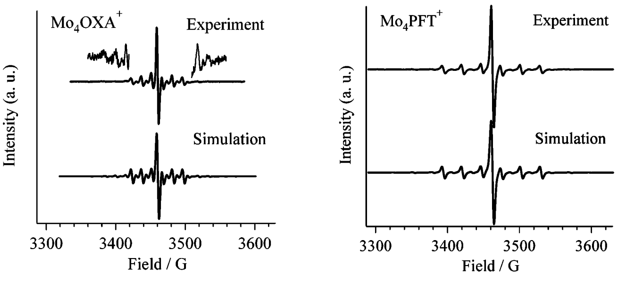

Fig. 1 X-Band EPR spectra in 2:1 THF/CH_2Cl_2 at 210 K, and spectral simulations performed using Bruker SimFonia. ^{95}Mo, ^{97}Mo: $I = 5/2$; $\Sigma_{abund} = 25.4\%$. ^{9x}Mo: $I = 0$; $\Sigma_{abund} = 74.6\%$. (left) $Mo_4OXA^+PF_6^-$: $g_{av} = 1.937$, $A_{av} = 14.8$ G. The intensity scale of the inset is magnified by 40×. (right) $Mo_4PFT^+PF_6^-$: $g_{av} = 1.942$, $A_{av} = 27.2$ G.

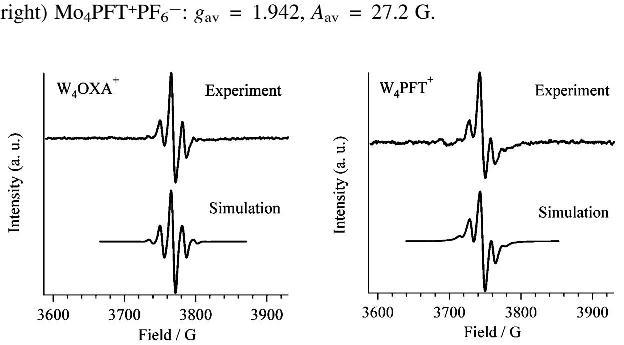

Fig. 2 X-Band EPR spectra in 2:1 THF/CH_2Cl_2 at 210 K, and spectral simulations performed using Bruker SimFonia. ^{183}W: $I = 1/2$; abund. = 14.3%. ^{18x}W: $I = 0$, abund = 85.7%. (left) $W_4OXA^+PF_6^-$: $g_{av} = 1.786$, $A_{av} = 31.0$ G. (right) $W_4PFT^+PF_6^-$: $g_{av} = 1.795$, $A_{av} = 29.6$ G.

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† Electronic Supplementary Information (ESI) available: experimental procedures; details of instrumentation; electronic absorption spectra of $Mo_2(O_2C^tBu)_4^+$ and Mo_4OXA^+; tabulation of selected Raman data. See http://www.rsc.org/suppdata/cc/b2/b202344j/

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cm^{-1}. In addition, there are low energy transitions at λ_{max} = 1700 nm (M = W) and 2500 nm (M = Mo), of lesser intensity (see Fig. 3, and spectra in the ESI†). These can be correlated with the electronic transitions expected for fully delocalized, Class III, mixed valence compounds for which $\Delta\tilde{\nu}_{1/2} < [2310\tilde{\nu}_{max}]^{1/2}$ cm^{-1}, $E_{op} = 2H_{AB}$.[8] For W_4OXA^+, H_{AB} = 2980 cm^{-1} is calculated from the experimental spectrum and for Mo_4OXA the experimental H_{AB} = 2000 cm^{-1}. These may be compared with H_{AB} = 5647 cm^{-1} (M = Os) and 3146 cm^{-1} (M = Ru) for the now-classical pyrazine-bridged dinuclear cations $[(NH_3)_5M(pz)M(NH_3)_5]^{5+}$. It has been generally found that H_{AB} < 1000 cm^{-1} for class II complexes, however. The W_4PFT^+ ion shows an even lower energy transition centered at λ_{max} = 2700 nm, also of a width appropriate for a class III complex. In contrast, no NIR transition is present for $Mo_4PFT^+PF_6^-$.

4. Further evidence for the electronic delocalization of Mo_4OXA^+ comes from resonance Raman spectroscopy. The neutral compounds show strong resonance enhancement of the totally-symmetric oxalate modes in the order $\nu_1 \gg \nu_2 \sim \nu_3$, where ν_1, ν_2 and ν_3 are the normal modes depicted in Fig. 4, and, to a lesser extent, ν(MoMo), with excitation within the envelope of the Mo_4 $\delta(b_{2g})$ to oxalate $\pi^*(b_{3u})$ electronic transition.[9] With excitation at 647 nm, the Mo_4OXA^+ ion shows similar resonance enhancements although the spectrum is notably different from that of the neutral counterpart. As shown in Fig. 5, ν_1 is shifted to lower wavenumber (Δ = 60 cm^{-1}) and is broadened. In contrast, ν_2 is shifted to slightly higher wavenumber and is sharpened and exhibits even greater resonance enhancement, as does the Raman band at 393 cm^{-1}, assignable to ν(MoMo). By contrast, the perfluoroterephthalate-based vibrational modes of Mo_4PFT are virtually unaffected by one-electron oxidation.

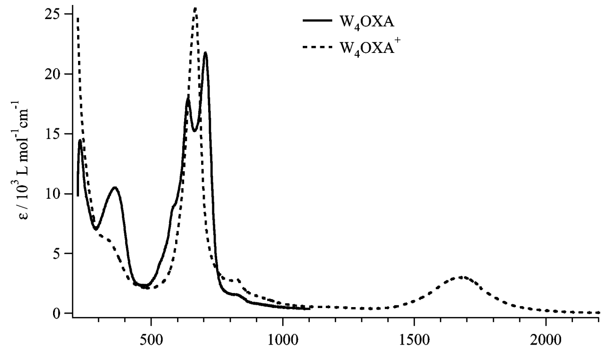

Fig. 3 Electronic absorption spectra of W_4OXA and $W_4OXA^+PF_6^-$ in THF at room temperature.

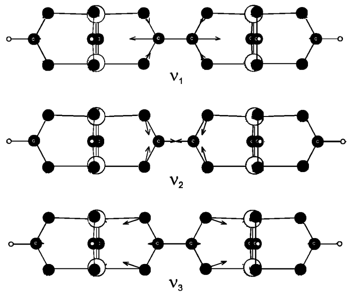

Fig. 4 Representations of the oxalate-based $\nu_1(a_{1g})$, $\nu_2(a_{1g})$ and $\nu_3(a_{1g})$ normal modes of Mo_4OXA.[9]

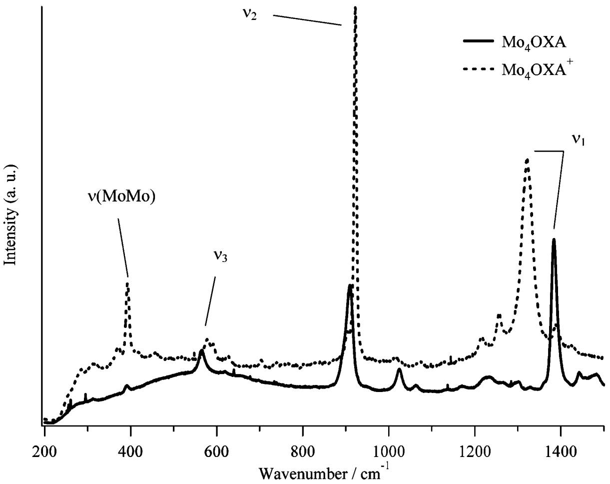

Fig. 5 Raman spectra of Mo_4OXA and $Mo_4OXA^+PF_6^-$, in THF at 210 K: 647.1 nm (225 mW) excitation was employed.

In conclusion, the data obtained from this work indicate that MM quadruple bonded complexes of molybdenum and tungsten in chains or cyclic structures should be delocalized in their single electron oxidized forms when linked by oxalate bridges, and thereby provide examples of conducting molecular wires and loops. In the case of perfluoroterephthalate-bridged complexes, the single electron radical cations should be valance-trapped for molybdenum, but delocalized for tungsten. These results complement recent calculations on neutral oxalate and perfluoroterephthalate model compounds, $[(HCO_2)_3M_2]_2$-(bridge) and $[(HCO_2)_2M_2bridge]_4$, and underscore the significance of M_2 δ to bridge π conjugation in assemblies containing MM quadruple bonds.[10]

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