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A mixed-valence compound with one unpaired electron delocalized over four molybdenum atoms in a cyclic tetranuclear ion

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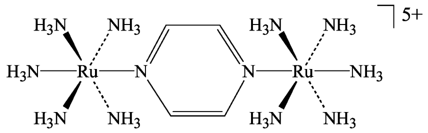
The first oxidation of a species derived from a compound having two linked, quadruply-bonded Mo_2 units has been performed and [[*cis*-$Mo_2(DAniF)_2]_2(\mu\text{-}Cl)_4]PF_6$, 2, has been isolated and characterized in many ways; it has one unpaired electron and a fully delocalized structure where the Mo–Mo distances increase from 2.1191(4) Å in the reduced species to 2.1453(3) Å in 2 and the K_c of 1.3×10^9 is three orders of magnitude larger than that of the Creutz–Taube ion.

Electronic communication between two metal centers is of fundamental importance in chemical processes ranging from simple light absorption in photochemical reactions to the propagation of stimuli in complex systems such as photosynthetic processes.[1] Communication can be modulated by the nature of the linkers uniting the metal centers. A very well studied group of compounds is that related to the so-called Creutz–Taube ion, **I**, which has two ruthenium units linked by a pyrazine molecule and the formal oxidation numbers are +2 for one of the ruthenium atoms and +3 for the other.[2] By replacing the metal atoms by others such as osmium and by modifying the chemical composition of the linker, an enormous amount of literature has been generated concerning the electronic communication between metal centers. This has been accomplished in many ways, *e.g.*, by studying the intervalence band in the mixed-valent system[3] or by studying the electrochemical properties[4] In the latter, the ΔE between redox processes serves as a probe, with larger values indicating better communication. In this way, these compounds can be grouped using the Robin–Day classification in three classes: I (poor), II (intermediate) and III (good communication).[5]



I

In our laboratory, we have been studying electronic communication between pairs of metal–metal bonded dinuclear and electrochemically active centers by electrochemical means. Examples are those with quadruply bonded species $[Mo_2(DAniF)_3]^+$ or *cis*-$[Mo_2(DAniF)_2]^{2+}$, abbreviated as $[Mo_2]$, where DAniF = *N,N′*-di-*p*-anisylformamidinate.[6] We have determined that when dicarboxylate units are used as linkers, communication depends on the distance between the midpoints of the dimetal units and also in whether there is conjugation in the linkers.[6a,d] Even though cyclovoltammograms show that such dicarboxylate-linked units can be oxidized by one or two electrons, none of the oxidized species have yet been isolated and characterized structurally.

Here we report the isolation, structural and spectroscopic characterization of the first oxidized compound containing two Mo_2 units in brown [[*cis*-$Mo_2(DAniF)_2]_2(\mu\text{-}Cl)_4]PF_6$, **2**. This was obtained† in 80% yield by reaction at low temperature of $FeCp_2PF_6$ and the previously described wine-red cyclic compound [*cis*-$Mo_2(DAniF)_2]_2(\mu\text{-}Cl)_4$, **1**,[7] which has been made† in very high yield (*ca.* 86%) using a modified synthesis, in which *cis*-$[Mo_2(DAniF)_2(MeCN)_4](BF_4)_2$[8] reacts with $Bu^n{}_4NCl$. For **1**, there are two absorption bands resolved in the electronic spectrum in the visible region which are attributable to transitions within the $[Mo_2]$ units: a shoulder at λ_{max} = 390 nm ($\varepsilon = 3.2 \times 10^3\ M^{-1}\ cm^{-1}$) and a well resolved band at λ_{max} = 495 nm ($\varepsilon = 4.3 \times 10^3\ M^{-1}cm^{-1}$). Compound **2** is intensely colored and has two broad absorption bands in the visible region, one at 434 nm ($\varepsilon = 8.5 \times 10^3\ M^{-1}cm^{-1}$) and the other at 600 nm ($\varepsilon = 1.2 \times 10^4\ M^{-1}cm^{-1}$).

The cyclovoltammogram (CV) of **1** measured in CH_2Cl_2 using $Bu^n{}_4NPF_6$ as electrolyte and referenced to Ag/AgCl is presented in Fig. 1. It shows two reversible waves resulting from two successive one-electron oxidation processes. There is a very large separation between the two features giving a potential difference, $\Delta E_{1/2}$, of 540 mV. A comproportionation constant, K_c, of 1.3×10^9, for the equilibrium involving the species $[Mo_2]^{1+}[Mo_2]^{1+}$, $[Mo_2][Mo_2]$ and $[Mo_2]^{1+}[Mo_2]$ can be calculated using the relationship $K_c = e^{\Delta E/25.69}$.[4a] This value of 540 mV for $\Delta E_{1/2}$ is remarkably large and indicates that there is strong electronic coupling between the two dimetal centers. From the magnitude of K_c, the mixed-valence species $[Mo_2]^{1+}[Mo_2]$ can be assigned to Class III in terms of the Robin–Day classification.[5] This electronic coupling is three orders of magnitude larger than that in the Creutz–Taube ion.[2b,9] It should be noted that the largest K_c for species containing two quadruply-bonded Mo_2 units linked by dicarboxylate anions is only 6×10^3 for $[(DAniF)_3Mo_2]_2(O_2C\text{-}CO_2)$[6a] and it is 2×10^5 for $[(DAniF)_3Mo_2]_2MoO_4$,[10] where the two $[Mo_2]$ units are linked by the tetrahedral ion $MoO_4{}^{2-}$. Although the separation between the midpoints of the Mo_2 units (see below) becomes shorter for the chloride linker than for the oxalate and molybdate linkers, it is surprising that the chloride ions in **2** favor the mixed-valence species by so much and it is clear that the delocalized unit $[Mo_2]^{0.5+}[Mo_2]^{0.5+}$ is the best description of the oxidized form in solution.

Except for the presence of the $PF_6{}^-$ anion, the structure of the cation in **2**, shown in Fig. 2 is quite similar to that of the neutral molecule **1**. Both possess an inversion center that renders the two Mo_2 units equivalent but there are some subtle differences in the bond distances and angles as highlighted in Fig. 3. As oxidation occurs the Mo–Mo distance increases from 2.1191(4)

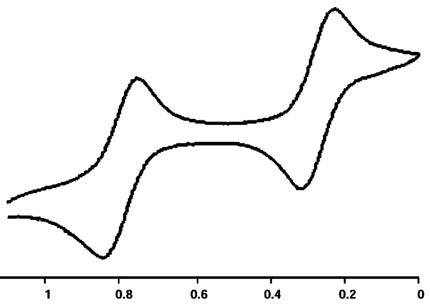


Fig. 1 Cyclic voltammogram of **1** in CH_2Cl_2 recorded using Pt working and auxiliary electrodes, Ag/AgCl reference electrode, scan rate of 100 mV sec^{-1}, and 0.1 M Bu_4NPF_6 as electrolyte. The $E_{1/2}(0/+1)$ and $E_{1/2}(+1/+2)$ are 0.26 V and 0.80 V, respectively. Under the same conditions the $E_{1/2}$ for Fc/Fc^+ couple appeared at 0.44 V.

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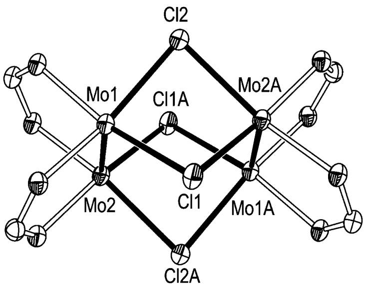

Fig. 2 The core of the cation in **2**, $[Mo_2(DAniF)_2]_2(\mu\text{-}Cl)_4]PF_6$, showing displacement ellipsoids at the 40% probability level.

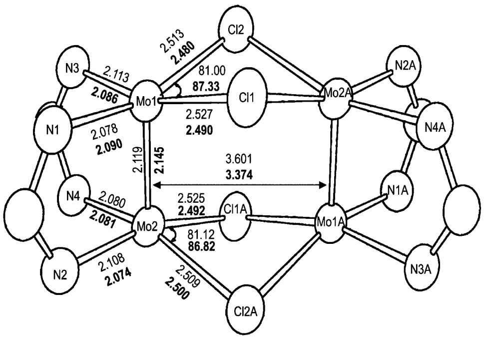

Fig. 3 Selected bond distances (Å) and angles (deg) for **1** and **2**. The bold numbers are for **2**, the others are for **1**.

to 2.1453(3) Å which is consistent with a decrease in bond order from 4 in **1** to an average of 3.75 in **2**. The average Mo–N distances show a small decrease from 2.095[4] to 2.083[3] Å as expected for an increase in positive charge upon oxidation. The Mo–Cl bond lengths decrease from 2.518[9] to 2.490 [6] Å. Also, the distance between the midpoints of the Mo_2 units decreases by more than 0.2 Å from 3.601 in **1** to 3.374 Å in **2**. These changes are consistent with the presence of fully delocalized units in the solid state for **2**. While equivalence of the two Mo_2 units cannot be asserted without reservation because of the possibility of crystallographic disorder, the displacement ellipsoids are not in the least suggestive of this. For the Creutz–Taube ion, the structural results were decidedly ambiguous.[11]

Further evidence of the electron delocalization over both Mo_2 units is obtained from the X-band EPR spectrum of the singly-charged cation as determined in frozen solution which exhibits a single broad signal with a g_{iso} of 1.912, that is consistent with an electronic ground state of $S = \frac{1}{2}$. This g value is significantly different from that expected for a free electron and thus indicative of the unpaired electron residing in a metal orbital. The broadness of the signal is expected from the coupling of four Mo and four Cl atoms, all of which would be expected to give rise to hyperfine structure.

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Notes and references

† Syntheses. **1**. To a mixture of *cis*-$[Mo_2(DAniF)_2(NCCH_3)_4](BF_4)_2$, 0.624 g (0.600 mmol), and an excess amount of $(n\text{-}C_4H_9)_4NCl$, 0.554 g (2.00 mmol), was added 5.0 mL of CH_3CN, giving a red solution. While stirring, 50 mL of ethanol was added slowly. A red–brown precipitate formed in about 10 min. The mixture was stirred at room temperature for 5 h. Then, the solid was separated by filtration, washed with ethanol (2 × 10 mL) and dried in vacuum. Yield: 0.400 g, 86.3%. Large red–brown crystals of $\mathbf{1}\cdot 2CH_2Cl_2$ were obtained by slow diffusion of hexanes into a CH_2Cl_2 solution of the product. ^1H NMR (δ in $CDCl_3$): 8.68 (s, 4H, –NC*H*N–), 6.74 (d, 16H, aromatic C–*H*), 6.62 (d, 16H, aromatic C–*H*), 3.69 (s, 24H, –OC*H*$_3$).

For **2**, a solution having one equivalent of ferrocenium hexafluorophosphate, 0.080 g (0.240 mmol), in 10 mL of CH_2Cl_2 was transferred using a cannula to a cold (−78 °C) solution prepared by dissolving crude **1** (0.370 g, 0.240 mmol), in 20 mL of CH_2Cl_2. Upon mixing, the color of the solution turned dark brown. The reaction mixture was stirred at low temperature for 30 min; then pre-cooled hexanes (50 mL) was added to form a precipitate. After washing with 20 mL of hexanes, the solid was dissolved in 20 mL of CH_2Cl_2; the resultant solution was layered with 45 mL of hexanes. Large, dark-brown crystals, 0.324 g (79.8%) were obtained after a period of one week . Anal. Calcd for $C_{60}H_{60}Cl_4F_6Mo_4N_8O_8P$: C, 42.60; H, 3.58; N, 6.62. Found: C, 42.69; H, 3.67; N, 6.56%.

Single-crystal X-ray data for both $\mathbf{1}\cdot 2CH_2Cl_2$ and **2** were collected at 213(2) K on a BRUKER-SMART 1000 CCD area detector system. Structure determination and refinement were carried out using the SHELXS-97 and SHELXL-97 programs. Crystal data for $\mathbf{1}\cdot 2CH_2Cl_2$: $C_{62}H_{64}Cl_8Mo_4N_8O_8$, $M = 1716.57$, monoclinic, space group $P2_1/n$, $a = 11.7836(7)$, $b = 12.3312(7)$, $c = 23.867(1)$ Å, $\beta = 98.773(1)°$, $Z = 2$, $V = 3427.4(3)$ Å^3. The structure was refined on F^2 and converged for 6023 unique reflections and 382 parameters to give $R1 = 0.038$ and $wR2 = 0.086$ and a goodness-of-fit = 1.049. This structure is similar to that in ref. 7. Crystal data for **2**: $C_{60}H_{60}Cl_4F_6Mo_4N_8O_8P$, $M = 1691.69$, triclinic, space group $P\bar{1}$, $a = 10.8175(8)$, $b = 13.015(1)$, $c = 14.260(1)$ Å, $\alpha = 69.115(1)$, $\beta = 68.231(1)$, $\gamma = 67.478(1)°$, $Z = 1$, $V = 1667.7(2)$ Å^3. The structure was refined on F^2 and converged for 6432 unique reflections and 422 parameters to give $R1 = 0.0286$ and $wR2 = 0.0618$ and a goodness-of-fit = 1.046. CCDC 212254 and 212255. See http://www.rsc.org/suppdata/cc/b3/b306822f/ for crystallographic data in .cif or other electronic format.

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