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Fully Localized Mixed-Valence Oxidation Products of Molecules Containing Two Linked Dimolybdenum Units: An Effective Structural Criterion

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Abstract: Two previously reported compounds $[Mo_2](CH_3O)_2M(CH_3O)_2[Mo_2]$ (Cotton, F. A.; Liu, C. Y.; Murillo, C. A.; Wang, X. *Inorg. Chem.* **2003**, *42*, 4619), in which $[Mo_2]$ is an abbreviation for the quadruply bonded Mo_2^{4+} unit embraced by three (*p*-anisyl)NC(H)N(*p*-anisyl) anions and M = Zn (**1**) or Co (**2**), have been chemically oxidized. One-electron oxidation products $[Mo_2](CH_3O)_2M(CH_3O)_2[Mo_2](PF_6)$ (**3**, M = Zn; **4**, M = Co) and the two-electron oxidation product $[Mo_2](CH_3O)_2Zn(CH_3O)(OH)[Mo_2](PF_6)_2$ (**5**) have been isolated and structurally characterized. As expected, oxidations occur at the dimolybdenum units. The mono-charged cations in **3** and **4** have asymmetric molecular structures with two distinct $[Mo_2]$ units. In each case, one of the $[Mo_2]$ units has a lengthened Mo–Mo bond distance of 2.151[1] Å, as expected for one-electron oxidation, whereas the other remains unchanged at 2.115[1] Å. These correspond to bond orders of 3.5 ($\sigma^2\pi^4\delta^1$) and 4.0 ($\sigma^2\pi^4\delta^2$), respectively. The crystallographic results thus show unambiguously that in the crystalline state, the mixed-valence compounds (**3** and **4**) are electronically localized and the unpaired electron is trapped on one $[Mo_2]$ unit. These results are supported by the EPR spectra. The doubly oxidized compound **5** has two equivalent $[Mo_2]$ units, both with a Mo–Mo bond distance of 2.149[1] Å. EPR and magnetic susceptibility measurements for **5** indicate that there is no significant ferromagnetic or antiferromagnetic spin coupling and the species is valence-trapped.

Introduction

The question of electronic communication between transition metal units having different oxidation states, and linked by bridging ligands, is a topic of great interest as these mixed-valence species play important roles in chemistry, physics, and biology.[1] For example, a $Mn^{II} Mn^{III}Mn^{IV}$ aggregate is believed to be a part of the S_0 state in photosystem II,[2] mixed-valence iron–sulfur clusters are notable in enzymatic electron-transfer reactions,[3] and multicopper centers with metal atoms in mixed oxidation states are found in cytochrome *c* oxidase as part of the purple Cu_A centers.[4]

The issue of how to evaluate the electronic communication is pertinent, and it has been the subject of many studies[5] (which are still continuing),[6] mainly with single metal ion sites, for example, diruthenium (II, II), -(II, III), and -(III, III) complexes, of which the Creutz–Taube, C–T, complex is the classic paradigm.[7] In the system of three complexes, of which the Creutz–Taube ion (**I**), $[(NH_3)_5Ru(pyrazine)Ru(NH_3)_5]^{5+}$, is the central member, a key question is whether this ion has a localized electronic structure (i.e., an Ru^{II} ion at one end and an Ru^{III} at the other) or a delocalized one. Many techniques employing electrochemical, spectroscopic, and magnetic measurements have been used to evaluate the so-called *coupling* between metal units and the effect of the linker and have been

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‡ Florida State University.

(1) See, for example: (a) Prassides, K. Ed. *Mixed Valency Systems: Applications in Chemistry, Physics and Biology*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991. (b) Kitagawa, H.; Onodera, N.; Sonoyama, T.; Yamamoto, M.; Fukawa, T.; Mitani, T.; Seto, M.; Maeda, Y. *J. Am. Chem. Soc.* **1999**, *121*, 10068. (c) Dinda, R.; Sengupta, P.; Ghosh, S.; Mak, T. C. W. *Inorg. Chem.* **2002**, *41*, 1684. (d) Hagadorn, J. R.; Que, L., Jr.; Tolman, W. B. *J. Am. Chem. Soc.* **1999**, *121*, 9760. (e) Nelsen, S. F. *Chem.-Eur. J.* **2000**, *6*, 581.

(2) (a) Pecoraro, V. L.; Hsieh, W.-Y. In *Manganese and its Role in Biological Processes*; Sigel, A., Siegel, H., Eds.; Marcel Dekker: New York, 2000; Vol. 37. (b) Alexiou, M.; Dendrinou-Sumara, C.; Karagianni, A.; Biswas, S.; Zaleski, C. M.; Kampf, J.; Yoder, D.; Penner-Hahn, J. E.; Pecoraro, V. L.; Kessissoglou, D. P. *Inorg. Chem.* **2003**, *42*, 2185.

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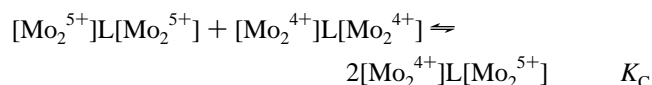
(4) (a) Robinson, H.; Ang, M. C.; Gao, Y.-G.; Hay, M. T.; Lu, Y.; Wang, A. H.-J. *Biochemistry* **1999**, *38*, 5677. (b) Wilmmans, M.; Lappalainen, P.; Kelly, M.; Sauer-Eriksson, E.; Saraste, M. *Proc. Natl. Acad. Sci. U.S.A.* **1995**, *92*, 11955.

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(6) (a) Demadis, K. D.; Hartshorn, C. M.; Meyer, T. J. *Chem. Rev.* **2001**, *101*, 2655. (b) Brunschwig, B. S.; Creutz, C.; Sutin, N. *Chem. Soc. Rev.* **2002**, *31*, 168. (c) Kaim, W.; Klein, A.; Glöckle, M. *Acc. Chem. Res.* **2000**, *33*, 755.

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used in evaluating the metal−metal interactions. Because of the variability in the time-resolution of the various techniques, the answer might not always be the same and some uncertainty is often present.

Another way in which such a question might, *in principle*, be answered is by a structure determination that would show either distinct structural differences between one end of the molecule and the other or an average of the oxidized and reduced forms. However, this method has not been used extensively as preparation of crystalline samples of mixed-valence species is often difficult and even when crystals can be made uncertainties sometimes prevail. For example, for two crystalline forms of **I**,[8] one with chloride counterions and one with tosylate anions, the detectable structural differences between the [(NH$_3$)$_5$Ru^{II}-(pyrazine)Ru^{II}(NH$_3$)$_5$]$^{4+}$ entities and those of the singly oxidized C−T ion are negligible. These admirably careful studies led to the conclusion that "the sum of structural and spectroscopic evidence does not allow one to decide the question whether the odd electron in the C−T ion is trapped on one Ru(atom) or delocalized equally over both." The authors then suggested that "resolution of this issue has to await a fuller understanding of the electronic structure of this ion."[8a]
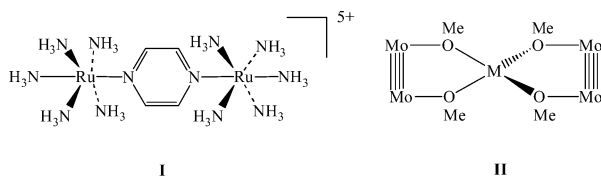
We believe that this methodology has been underutilized owing to the lack of appropriate systems with multiple structural probes that would improve the chances of obtaining a definite answer. Work in this laboratory[9] has shown that [Mo$_2$] units (in which [Mo$_2$] is an abbreviation for the quadruply bonded Mo$_2$$^{4+}$ unit embraced by three (*p*-anisyl)NC(H)N(*p*-anisyl) anions can be linked by a great variety of linkers, L, to form [Mo$_2$]L[Mo$_2$] molecules, most of which undergo reversible electrochemical oxidation to ([Mo$_2$]L[Mo$_2$])$^+$ and ([Mo$_2$]L-[Mo$_2$])$^{2+}$ ions. Useful information has been obtained from solution studies. In general, the extent of coupling, as indicated by the separation between the two $E_{1/2}$ values, $\Delta E_{1/2}$, can be associated with the comproportionation constant,[10] $K_C = e^{\Delta E_{1/2}/25.69}$:

$$[Mo_2^{5+}]L[Mo_2^{5+}] + [Mo_2^{4+}]L[Mo_2^{4+}] \rightleftharpoons$$
$$2[Mo_2^{4+}]L[Mo_2^{5+}] \qquad K_C$$

It is usually accepted that comproportionation constants above 10^6 (for which a $\Delta E_{1/2}$ of 355 mV would be required) justify

the assumption that delocalization occurs.[6c] The C−T ion barely meets this criterion ($\Delta E_{1/2} = 390$ mV; $K_C = 3.9 \times 10^6$).[6a,11]

Studies have already been focused on the oxidation of compounds having only one quadruply bonded Mo$_2$$^{4+}$ or W$_2$$^{4+}$ core and the determination of the structural changes resulting from oxidation to the corresponding M$_2$$^{5+}$ cores.[12] Removing an electron from the M$_2$$^{4+}$ core decreases the bond order to 3.5, and, in every case, it has been found that the bond distance lengthens by 0.04−0.06 Å.[12a,b,d] Furthermore, the increase in positive charge shortens the M−ligand distances.

Therefore, we felt we have a solid basis to study the chemical oxidation of [Mo$_2$]L[Mo$_2$] species. The idea behind this work is to employ the structural change that we know occurs when an Mo$_2$$^{4+}$ unit is oxidized to Mo$_2$$^{5+}$ to monitor structurally the localization (or delocalization) of charge. The change in the Mo−Mo distance of 0.04−0.06 Å from Mo$_2$$^{4+}$ to Mo$_2$$^{5+}$, *in the same ligand environment*, can be precisely and unambiguously measured by X-ray crystallography. A second structural probe is the shortening of the metal−ligand bonds that is generally associated with an increase in oxidation state. It is not our contention that this a perfect criterion, nor even that it is necessarily the best. However, it appears to be as valid as any other, convenient to use, and, when applicable, to have the advantage of giving hard numbers and thus an unequivocal answer, at least for the molecule in its crystalline environment.

The specific concern of this paper is the isolation and characterization of the oxidation products of the two recently reported compounds[13] [Mo$_2$](CH$_3$O)$_2$M(CH$_3$O)$_2$[Mo$_2$] (**II**), M = Zn (**1**) or Co (**2**). These have oxidation potentials more favorable than those of the dicarboxylate analogues[9a,d] and provide the first series of chemically oxidized [Mo$_2$]L[Mo$_2$]$^{n+}$ species in three compounds: {[Mo$_2$]Zn(OCH$_3$)$_4$[Mo$_2$]}PF$_6$, **3**, {[Mo$_2$]Co(OCH$_3$)$_4$[Mo$_2$]}PF$_6$, **4**, and {[Mo$_2$]Zn(OCH$_3$)$_3$(OH)-[Mo$_2$]}(PF$_6$)$_2$, **5**. In each of the first two, one of the previously reported neutral [Mo$_2$]M(OCH$_3$)$_4$[Mo$_2$] molecules has been oxidized once, and in **5**, the tetramethoxyzincate bridged molecule has been oxidized twice.[14] We had predicted from the $\Delta E_{1/2}$ values for **3** and **4** that they would have localized oxidation. In **5**, the important question was whether coupling between the two oxidized ends would be significant and, if so, whether it would be ferromagnetic or antiferromagnetic. This work conclusively answers these questions and advances our knowledge of how molecules with two linked, equivalent redox sites behave when subjected to one- and two-electron oxidations.

Experimental Section

Materials and Methods. Solvents used were freshly distilled under N$_2$ by employing standard procedures. All synthetic operations were conducted under N$_2$ using Schlenk line techniques. The starting

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(11) Other species such as [(NC)$_5$M(μ-pyrazine)M(CN)$_5$]$^{5-}$, M = Fe, Ru, Os, have smaller K_C values and are considered valence-localized on the time scale of 10^{-12} s. See: Schering, T.; Kaim, W.; Olabe, J. A.; Parise, A. R.; Fiedler, J. *Inorg. Chim. Acta* **2000**, *300−302*, 125.

(12) See, for example: (a) Cotton, F. A.; Hillard, E. A.; Murillo, C. A. *Inorg. Chem.* **2002**, *41*, 1639. (b) Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Wilkinson, C. C. *J. Am. Chem. Soc.* **2002**, *124*, 9249. (c) Cotton, F. A.; Daniels, L. M.; Liu, C. Y.; Murillo, C. A.; Schultz, A. J.; Wang, X. *Inorg. Chem.* **2002**, *41*, 4232. (d) Cotton, F. A.; Huang, P.; Murillo, C. A.; Timmons, D. J. *Inorg. Chem. Commun.* **2002**, *5*, 501. (e) Cotton, F. A.; Huang, P.; Murillo, C. A.; Wang, X. *Inorg. Chem. Commun.* **2003**, *6*, 121. (f) Cotton, F. A.; Gruhn, N. E.; Gu, J.; Huang, P.; Lichtenberger, D. L.; Murillo, C. A.; Van Dorn, L. O.; Wilkinson, C. C. *Science* **2002**, *298*, 1971.

(13) Cotton, F. A.; Liu, C. Y.; Murillo, C. A.; Wang, X. *Inorg. Chem.* **2003**, *42*, 4619.

(14) We found it impossible to carry out the preparation of **5** without the replacement of one CH$_3$O$^-$ by OH$^-$.

Table 1. X-ray Crystallographic Data for **3**, **4**, and **5**

	3·4CH$_2$Cl$_2$	**4·4CH$_2$Cl$_2$**	**5·3.44CH$_2$Cl$_2$**
empirical formula	C$_{98}$H$_{110}$Cl$_8$F$_6$Mo$_4$N$_{12}$O$_{16}$PZn	C$_{98}$H$_{110}$Cl$_8$CoF$_6$Mo$_4$N$_{12}$O$_{16}$P	C$_{96.44}$H$_{109.88}$Cl$_{6.88}$F$_{12}$Mo$_4$N$_{12}$O$_{16}$P$_2$Zn
fw	2589.68	2583.24	2675.88
space group	$P4_1$ (No. 76)	$P4_1$ (No. 76)	$C2/c$ (No. 15)
a, Å	13.8487(3)	13.8316(3)	34.473(2)
b, Å	13.8487(3)	13.8316(3)	15.2086(7)
c, Å	57.189(2)	57.273(2)	44.285(2)
β, deg	90	90	105.497(1)
V, Å^3	10 968.1(6)	10 957.2(6)	22 373(2)
Z	4	4	8
T, K	213	213	213
λ, Å	0.7103	0.7103	0.7103
d_{calcd}, g/cm^3	1.568	1.566	1.589
μ, mm^{-1}	0.947	0.880	0.926
R1^a (wR2^b)	0.079(0.169)	0.048(0.102)	0.086(0.140)

^{a} R1 $= \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} wR2 $= [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

materials, [Mo$_2$(DAniF)$_3$]$_2$M(OCH$_3$)$_4$ (M = Zn, Co and DAniF = *N,N′*-di-*p*-anisylformamidinate), were prepared by following a published method;[13] commercially available chemicals were used as received.

Physical Measurements. Elemental analyses were performed by Canadian Microanalytical Service, Delta, British Columbia, Canada. Electronic spectra of **3**, **4**, and **5** were measured in dichloromethane over a range of 300−800 nm on a Cary 17 spectrophotometer.[15] The electrochemical measurements were recorded on a BAS 100 electrochemical analyzer with Pt working and auxiliary electrodes, an Ag/AgCl reference electrode, a scan rate of 100 mV/s, and 0.1 M Bu$_4$NPF$_6$ (in CH$_2$Cl$_2$) as electrolyte. Measurement of magnetic susceptibility was performed on a SQUID magnetometer. Variable temperature X-band (9.5 GHz) EPR spectra were obtained on a Bruker E-500 spectrometer outfitted with a liquid helium cryostat. The field was calibrated with an NMR gaussmeter, and the organic free radical diphenylpicryl-hydrazyl (DPPH, $g = 2.0037$) was used as a standard. The frequency was measured with a digital frequency counter (Bruker ER 049x microwave bridge). EPR simulations were done using the XSophe program of Bruker.

General Procedure for Preparation of 3, 4, and 5. Dichloromethane solutions of the neutral complexes, [Mo$_2$(DAniF)$_3$]$_2$-M(OCH$_3$)$_4$, M = Zn or Co (0.100 mmol in 10 mL of CH$_2$Cl$_2$), and ferrocenium hexafluorophosphate (dissolved in 20 mL of CH$_2$Cl$_2$ and having 1 equiv for the singly oxidized species or 2 equiv for the doubly oxidized **5**), were prepared separately and cooled to −78 °C. The two solutions were mixed by transferring the oxidizing reagent to the complex at low temperature through a cannula, giving a dark-brown solution. After the resultant solution was stirred at low temperature for 30 min, hexanes (50 mL) were added by a syringe to produce a dark-brown precipitate. The solvent was then decanted, and the solid residue was washed with 20 mL of precooled hexanes. The solid was dissolved in dichloromethane, and the solution was layered with hexanes to obtain a crystalline product.

3·4CH$_2$Cl$_2$. [Mo$_2$(DAniF)$_3$]$_2$Zn(OCH$_3$)$_4$ (0.211 g, 0.100 mmol) reacted with 1 equiv of ferrocenium hexafluorophosphate (0.033 g). After the general procedure described above was followed, large dark-brown crystals of **3·4CH$_2$Cl$_2$** were collected. Drying the crystals under vacuum resulted in partial loss of the solvent molecules. Yield of **3·**CH$_2$Cl$_2$: 0.165 g (71%). λ_{max} (nm) (ϵ, M^{-1} mol^{-1}): 465 (2.7 × 10^3). Anal. Calcd for C$_{95}$H$_{104}$Cl$_2$F$_6$Mo$_4$N$_{12}$O$_{16}$PZn (**3·**CH$_2$Cl$_2$): C, 48.80; H, 4.49; N, 7.20. Found: C, 49.23; H, 4.38; N, 7.22.

4·4CH$_2$Cl$_2$. [Mo$_2$(DAniF)$_3$]$_2$Co(OCH$_3$)$_4$ (0.210 g, 0.100 mmol) reacted with 1 equiv of ferrocenium hexafluorophosphate (0.033 g). After the general procedure described above was followed, large dark-brown crystals of **4·4CH$_2$Cl$_2$** were collected. Drying the crystals under vacuum resulted in partial loss of the solvent molecules. Yield of **4·**CH$_2$Cl$_2$: 0.172 g (74%). λ_{max} (nm) (ϵ, M^{-1} mol^{-1}): 460 (2.8 × 10^3). Anal. Calcd for C$_{95}$H$_{104}$Cl$_2$F$_6$CoMo$_4$N$_{12}$O$_{16}$P (**4·**CH$_2$Cl$_2$): C, 48.97; H, 4.50; N, 7.22. Found: C, 49.12; H, 4.41; N, 7.39.

5·3.44CH$_2$Cl$_2$. [Mo$_2$(DAniF)$_3$]$_2$Zn(OCH$_3$)$_4$ (0.211 g, 0.100 mmol) reacted with 2 equiv of ferrocenium hexafluorophosphate (0.066 g). After the general procedure described above was followed, dark-brown needle-shaped crystals of **5·3.44CH$_2$Cl$_2$** were collected. Drying the crystals under vacuum resulted in partial loss of the solvent molecules. Yield of **5·**CH$_2$Cl$_2$: 0.155 g (63%). λ_{max} (nm) (ϵ, M^{-1} mol^{-1}): 460 (3.1 × 10^3). Anal. Calcd for C$_{94}$H$_{102}$Cl$_2$F$_{12}$Mo$_4$N$_{12}$O$_{16}$P$_2$Zn (**5·**CH$_2$-Cl$_2$): C, 45.79; H, 4.12; N, 6.82. Found: C, 45.43; H, 4.40; N, 6.61.

X-ray Structure Determinations. A single crystal suitable for X-ray diffraction analysis of each compound was mounted on the tip of a quartz fiber with a small amount of silicone grease and attached to a goniometer head. Data for **3**, **4**, and **5** were collected at 213 K on a Bruker SMART 1000 CCD system equipped with a low-temperature controller cooled by liquid nitrogen. In each case, 20 frames were collected first to determine the orientation matrix. The cell parameters were then calculated through an autoindexing routine, and a hemisphere of data was collected. During the course of data collection, no crystal decay was observed. Data reduction and integration were performed with the software package SAINT,[16] which corrects for Lorentz and polarization effects, while absorption corrections were applied by using the program SADABS.[17] Positions of non-hydrogen atoms were found by direct methods using the Bruker SHELXTL software package.[18] Subsequent cycles of least-squares refinement followed by difference Fourier syntheses revealed the positions of the remaining non-hydrogen atoms. Hydrogen atoms were placed in calculated positions. Crystal data and structural refinement information for **3**, **4**, and **5** are given in Table 1.

Results and Discussion

In a prior study, it was shown that two [Mo$_2$] units, defined above, can be linked by a tetramethoxy metal dianion, thereby building complexes with a general formula [Mo$_2$]M(OCH$_3$)$_4$-[Mo$_2$] (M = Zn, **1** and Co, **2**).[13] An electrochemical study revealed both one- and two-electron oxidations at −208 and 4 mV for **1** and −211 and −4 mV for **2**, respectively. These potentials are significantly more favorable toward oxidation than those in analogues with dicarboxylate linkers; for example, for the oxalate complex, the $E_{1/2}$'s are 294 and 506 mV. Thus, it appeared that chemical oxidations, which up to now have eluded all attempts of synthesis for the dicarboxylate complexes, could

(15) Efforts are currently in progress to study the electronic spectra in the near-infrared region.
(16) *SMART. Data Collection Software. Version 5.618*; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2000.
(17) *SAINT. Data Reduction Software*. V*ersion 6.28A*; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2001.
(18) Sheldrick, G. M. *SHELXTL. Version 6.10*; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2000.
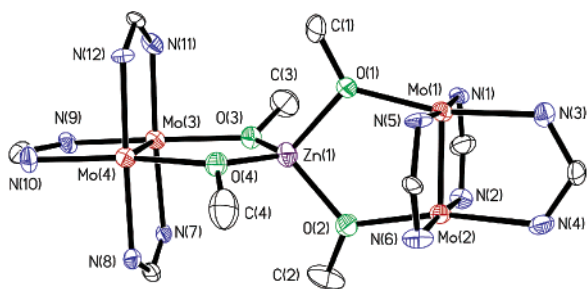
Figure 1. The core of the monocation in **3·**4CH$_2$Cl$_2$ showing the tetrahedral [Zn(OMe)$_4$]$^{2-}$ linkers and the perpendicular arrangement of the Mo−Mo bonds. All *p*-anisyl groups and hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 40% probability level. The structure of the Co analogue is similar, and a figure is given in the Supporting Information.

be accessible for those with tetramethoxy zincate and cobaltate linkers. Indeed, this has been accomplished by employing ferrocenium hexafluorophosphate as an oxidizing reagent because it has a reduction potential of 0.45 V (vs Ag/AgCl), which is higher than the potentials of the first ($E_{1/2}^{1+/0}$) as well as the second ($E_{1/2}^{2+/1+}$) redox couples of **1** and **2**.

As is well known, in mixed-valence chemistry, when starting with the reduced form, the use of just 1 equiv of an oxidizing reagent does not guarantee the generation of only the singly oxidized species. Thermodynamic stability of the one-electron oxidized compound is an important issue that needs to be taken into account as it might disproportionate. However, the disproportionation constant will be the reciprocal of the comproportionation constant, K_C, which can be derived from the electrochemical measurement of $\Delta E_{1/2}$ values. For both **1** and **2**, the magnitudes of K_C are on the order of 10^3.[13] Thus, the disproportionation constants are ca. 10^{-3}, which suggests that the isolation of the one-electron oxidized complexes might be possible. Of course, preparation of a doubly oxidized product should in any case result from the use of 2 equiv of a suitable oxidizing agent.

Compounds **3**, **4**, and **5** have been prepared in good yields by reactions of the corresponding neutral precursors **1** or **2** with stoichiometric amounts of ferrocenium hexafluorophosphate. Reactions and purification were conducted at low temperature to reduce the risk of decomposition because of the air and moisture sensitivities of the precursors. For **3** and **4**, the complex cores are maintained in the course of preparation, while in **5**, one of the methoxy groups on the linker is replaced by a hydroxy group, even though the reactions were handled as carefully as possible.[19]

The singly oxidized compounds **3** and **4** are isomorphous and crystallize, in the given solvent system, in tetragonal space group *P*4$_1$, in which the molecules reside on general positions. The overall structures of the cations of **3** and **4** are similar and resemble those of their precursors in having two [Mo$_2$] units linked by a tetrahedral linker and having Mo−Mo bonds that are essentially perpendicular to each other. The core of **3** is shown in Figure 1. The common and most important structural feature of **3** and its cobalt analogue, **4**, is that there are two structurally distinct dimolybdenum units in the molecules. As seen in Table 2, for both compounds, the bond length of Mo-(3)−Mo(4) falls in the range which is typical for a quadruply

(19) Using reaction conditions similar to those for the preparation of **5**, we did not isolate a doubly oxidized Co analogue.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **3**, **4**, and **5**

	3·4CH$_2$Cl$_2$	4·4CH$_2$Cl$_2$	5·3.44CH$_2$Cl$_2$
Mo(1)−Mo(2)	2.151(1)	2.1509(7)	2.147(1)
Mo(3)−Mo(4)	2.116(1)	2.1130(7)	2.151(1)
Mo(1)−O(1)	2.048(9)	2.045(4)	2.070(5)
Mo(2)−O(2)	2.045(9)	2.053(4)	2.063(5)
Mo(3)−O(3)	2.145(9)	2.140(4)	2.057(5)
Mo(4)−O(4)	2.145(8)	2.136(4)	2.074(5)
M(1)−O(1)	1.970(8)	1.974(4)	1.938(5)
M(1)−O(2)	1.969(9)	1.961(4)	1.956(6)
M(1)−O(3)	1.917(9)	1.922(4)	1.939(6)
M(1)−O(4)	1.908(8)	1.930(4)	1.944(5)
Mo(1)−N(1)	2.121(8)	2.132(4)	2.131(6)
Mo(1)−N(3)	2.09(1)	2.095(5)	2.093(6)
Mo(1)−N(5)	2.123(8)	2.138(5)	2.134(6)
Mo(2)−N(2)	2.153(8)	2.137(5)	2.140(6)
Mo(2)−N(4)	2.11(1)	2.117(6)	2.100(6)
Mo(2)−N(6)	2.081(9)	2.113(5)	2.163(6)
Mo(3)−N(7)	2.181(8)	2.167(4)	2.141(7)
Mo(3)−N(9)	2.13(1)	2.132(5)	2.094(6)
Mo(3)−N(11)	2.156(8)	2.154(4)	2.128(6)
Mo(4)−N(8)	2.175(8)	2.161(5)	2.137(6)
Mo(4)−N(10)	2.14(1)	2.129(5)	2.135(6)
Mo(4)−N(12)	2.158(7)	2.151(4)	2.121(6)
O(2)−M(1)−O(1)	98.0(4)	97.68(19)	97.1(2)
O(3)−M(1)−O(1)	112.8(3)	112.39(17)	113.8(2)
O(4)−M(1)−O(1)	110.6(3)	109.62(17)	120.2(2)
O(3)−M(1)−O(2)	114.1(3)	114.99(18)	113.4(2)
O(4)−M(1)−O(2)	114.9(3)	115.65(18)	115.2(2)
O(4)−M(1)−O(3)	106.5(4)	106.41(19)	98.1(2)

Table 3. Comparison of Important Bond Distances (Å) along with the Distances between the Two [Mo$_2$] Units[a]

	1	2	3	4	5
Mo−Mo	2.1169(7)	2.1162(7)	2.116(1)	2.1130(7)	2.147(1)
Mo−Mo	2.1113(8)	2.1142(9)	2.151(1)	2.1509(7)	2.151(1)
Mo−O	2.131[4]	2.135[4]	2.145[9]	2.138[4]	2.067[5]
Mo−O	2.145[4]	2.125[4]	2.047[9]	2.049[4]	2.066[5]
M−O	1.954[4]	1.950[4]	1.913[9]	1.926[4]	1.947[6]
M−O	1.946[4]	1.945[4]	1.970[9]	1.968[4]	1.942[6]
[Mo$_2$]−[Mo$_2$]	6.547	6.562	6.526	6.529	6.596

[a] For **3** and **4**, bolded atoms are oxidized or attached to an oxidized species.

bonded dimolybdenum unit, whereas in the other unit, the Mo-(1)−Mo(2) bond is significantly lengthened, being consistent with a bond distance expected for a dimolybdenum unit in which there has been a decrease from a bond order of 4 to a bond order of 3.5.[12a,b,d] This can be made clearer by direct comparison with the corresponding neutral precursors, **1** and **2**, and the doubly oxidized compound **5**, as listed in Table 3. Further support can be obtained as we examine closely other related bond lengths. For example, for both **3** and **4**, there are two sets of Mo−O bond distances. The shorter ones (2.047 Å) are found in the [Mo$_2$] unit in which the Mo−Mo bond distance is lengthened upon oxidation, while the longer ones (2.145 Å) are found in the [Mo$_2$] unit which remains unchanged after oxidation. Also, there are two sets of M−O distances (Table 3) caused by the uneven distribution of charge over the two [Mo$_2$] units. It is evident that when 1 equiv of oxidizing reagent is applied, only one of the dimetal units is oxidized and the oxidized products, **3** and **4**, are unequivocally structurally unsymmetrical.[20]

In view of the preceding discussion of the structures of **3** and **4**, we have no problem in understanding the structure of the doubly oxidized compound, **5**. As we might have anticipated,
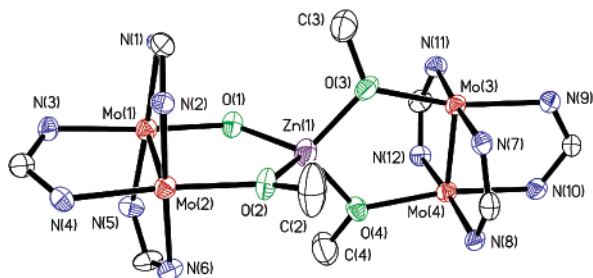
Figure 2. A view of the core of the dication in **5**·3.44CH₂Cl₂. Displacement ellipsoids are drawn at the 40% probability level.

in **5** (Figure 2), the two [Mo₂] units have Mo—Mo bond distances that are equal within experimental error. Upon oxidation, both have been lengthened to a magnitude corresponding to a dimolybdenum unit with a bond order of 3.5. As shown in Table 3, upon oxidation, all of the related bond distances vary reasonably in the expected directions. Interestingly, oxidation also causes a small but noticeable change in the distance between the two [Mo₂] units. The one-electron oxidation shrinks the molecules slightly; as a result, the nonbonding separations between the two [Mo₂] centers, [Mo₂]—[Mo₂], for **3** (6.526 Å) and **4** (6.529 Å) are slightly shorter than those for **1** (6.547 Å) and **2** (6.562 Å). This is because both Mo—O and M—O bond distances change, one being shortened and the other lengthened, but without complete compensation. However, two-electron oxidation changes [Mo₂]—[Mo₂] in the opposite direction. The distance between the two [Mo₂] units in **5** (6.596 Å) is longer than those in **3** (6.526 Å) and **1** (6.547 Å). This might be attributed to the electrostatic repulsion between the two [Mo₂] units bearing one unit of positive charge each.

Because our structural results clearly establish that both **3** and **4** are electronically localized, the structural uncertainty about the extent of electron delocalization for the C—T ion does not exist here.[8a] Therefore, it is appropriate to describe the two dimetal mixed-valence compounds using a symmetrical double-well potential.[21] The odd electron in **3** or **4** is trapped on one [Mo₂] unit, essentially as an isolated unpaired δ electron. One difference from single metal, binuclear systems that should be made clear is that in these compounds, valences are trapped on dimetal units, instead of on individual metal atoms because of electronic delocalization within the dimetal unit. In other words, the two molybdenum atoms in the same [Mo₂] units are undistinguishable. For the valence trapped compounds **3** and **4**, the electronic structures for the two distinct [Mo₂] units are $\sigma^2\pi^4\delta^2$ (bond order 4.0) and $\sigma^2\pi^4\delta^1$ (bond order 3.5), respectively.

The comproportionation constants for both **3** and **4** are on the order of 10^3, indicating that the two dimetal centers are only weakly coupled and both compounds belong at best to Class II of mixed-valence compounds in terms of the Robin—Day

classification.[22] A pertinent issue raised here is how reliable electrochemical measurements can be to assess the extent of electronic delocalization for a system. While it is known that medium effects resulting from solvent and electrolyte may lead to considerable systematic deviations,[23] for the systems **1**/**3** and **2**/**4**, the electrochemical measurements in solution and the molecular structures in crystalline material are completely consistent.

Because a tetrahedral unit serves as a linker and the two [Mo₂] units are perpendicular to each other, similar to previously reported [Mo₂]O₂EO₂[Mo₂] (E = S, Mo, and W),[9b] appreciable π orbital overlaps are unlikely. Thus, the electrostatic interactions due to the relatively short distance (ca. 6.5 Å) between the two dimetal centers are thought to be the main contributors to the values of the comproportionation constant K_C. Mechanistically, the situation here is quite different from unsaturated dicarboxylate linked dimolybdenum analogues[9d,e] and Creutz—Taube type complexes, where a conjugated linker that can facilitate π/π coupling spans the two metal centers. These π interactions between δ orbitals of [Mo₂] units and π* orbitals of the dicarboxylate anion in the dimolybdenum compounds,[9d,e] and between d orbitals (e.g., d_{xz}, d_{yz}) and pyrazine π* orbitals for C—T complex,[7b,24] are believed to play significant roles in electron delocalization of the metal centers. Other work in this laboratory has shown that efficient π interaction between the two dimetal centers through a suitable linker enhances the communication.[9e]

Magnetism. Compounds **3**, **4**, and **5** are paramagnetic, and magnetic measurements provide further support for the valence-trapped description. At room temperature, the X-band (9.5 GHz) EPR spectrum of the powder of **3** shows one very prominent symmetric peak around $g = 1.9426 \pm 0.0003$, which is assigned to the singly oxidized Mo₂ unit from the ^{96}Mo ($I = 0$) isotope, based on earlier data on [Mo₂(C₃H₇O₂)₄]⁺ [25] and [Mo₂(2,4,6-triisopropylbenzoate)₄]⁺.[26] Eight or so smaller peaks flanking the main signal were assignable to hyperfine structure from the ^{95,97}Mo ($I = \frac{5}{2}$) isotopes (natural abundance of about 25%).[25,26] Because lowering the temperature to 5 K did not improve the hyperfine resolution, powder EPR simulation techniques were used to calculate the hyperfine parameters. The spin Hamiltonian was the same as that employed for [Mo₂(C₃H₇O₂)₄]⁺ and [Mo₂-(TiPB)₄]⁺:[26]

$$H = \beta[g_{\|}H_{\|}S_z + g_{\perp}H_{\perp}S_{\perp}] + A_{\|}S_zI_z + A_{\perp}S_{\perp}I_{\perp} \quad (1)$$

where the symbols ‖ and ⊥ refer to the tensor components along and perpendicular to the main molecular symmetry directions. As shown in Figure 3, spectral simulation showed satisfactory agreement with the experimental data. The best fit parameters for the zinc species **3**, which are listed in Table 4, are $g_{iso} = 1.9426 \pm 0.0003$, $A_{\|} = 37.7 \pm 3$ G, and $A_{\perp} = 15.6 \pm 2$ G. The small sharp peak on the low field side of the hyperfine peaks, denoted by an asterisk, is attributed to an impurity.

At room temperature, the spectra for the cobalt analogue **4** contain the same features as those of **3**. However, as shown in

(20) While the present manuscript was bring reviewed, the characterization of the singly oxidized compound [[*cis*-Mo₂(DAniF)₂]₂(μ-Cl)₄]PF₆ was accomplished. It has two crystallographically equivalent Mo—Mo distances of 2.1453(3) Å which are longer than those in the unoxidized form of 2.1191(4) Å. The K_c of 1.3×10^9 for this compound implies it is delocalized. Thus, the data are consistent with those presented here. See: Cotton, F. A.; Liu, C. Y.; Murillo, C. A.; Wang, X. *Chem. Commun.* **2003**, 2190.

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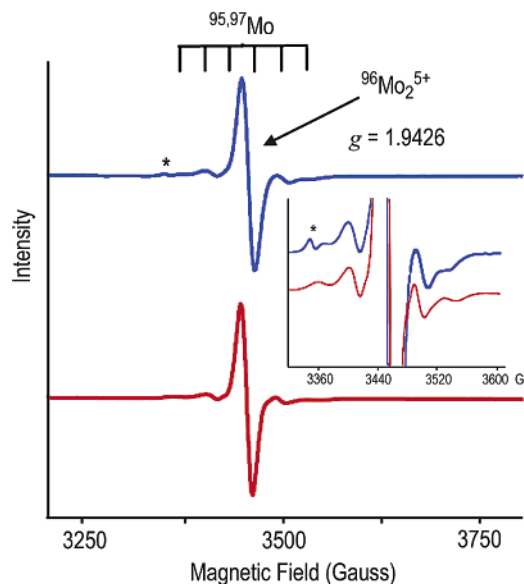
Figure 3. X-band EPR spectrum at room temperature of a powdered sample of **3** (top). The simulated spectrum using a g_{iso} of 1.9426, $A_{||}$ = 37.7 G, and $A_{\perp}$ = 15.6 G is given below the experimental spectrum. The inset shows an enlargement to clarify the hyperfine peaks. The weak signal with an asterisk is due to an impurity.

Table 4. Mo g and Hyperfine Parameters for Some Compounds with Mo_2^{5+} Units

compound[a]	$g_{||}$	$g_{\perp}$	$A_{||}$ (Gauss)	$A_{\perp}$ (Gauss)	ref
3	1.9426 ± 0.0003	1.9426 ± 0.0003	37.7 ± 3	15.6 ± 2	this work
4	1.9426 ± 0.0003	1.9426 ± 0.0003	37.7 ± 3	15.6 ± 2	this work
$[Mo_2(C_3H_7OO)_4]^+$	1.941	1.941	39.3	19.7	25
$[Mo_2(TiPB)_4]^+$	1.936	1.936	39.5	20.2	26

[a] For **5**, g_{iso} = 1.9463 ± 0.0003.

Figure 4, upon lowering the temperature to ca. 25 K an additional signal appears. This very broad and asymmetric peak has been assigned to the Co^{2+} unit in the compound because it is absent in the spectrum of **3** which has the EPR silent Zn^{2+} ion and because it appears in the same region of the spectrum of the precursor **2**, which has a $g_{\perp}$ of 5.8810 and a $g_{||}$ of 4.9706.[27] The peak at g of 2.165 denoted by the double asterisk (**) is from an impurity.[28] A simulated spectrum using the spin Hamiltonian in eq 1 compares well with the experimental data and gave the best fit parameters of g_{iso} = 1.9426 ± 0.0003, $A_{||}$ = 37.7 ± 3 G, and $A_{\perp}$ = 15.6 ± 2 G (see Table 4). The results for both **3** and **4** are consistent with those for the singly oxidized Mo_2 species in $[Mo_2(C_3H_7OO)_4]^+$ [25] and $[Mo_2(TiPB)_4]^+$.[26]

To detect any interaction between the magnetic centers of the Co and the oxidized Mo_2 subunits, the peak-to-peak line width, commonly called ΔH_{pp},[29] of the main ^{96}Mo transition (g = 1.9426) was monitored as a function of decreasing temperature. For comparison, similar measurements were made on **3**

(27) The assumption can be made that only the perpendicular component is observed and the parallel component is too broad to see because of strong exchange with the Mo_2^{5+} unit. Therefore, the $g_{\perp}$ component can be measured at the top of the peak and has a value of ~5.57, similar to that of the precursor **2**.

(28) The inset to Figure 4 shows that the impurity is the same as that in the zinc analogue. Therefore, it rules out the possibility of it belonging to the Co^{2+} unit.

(29) See, for example: (a) Rast, S.; Borel, A.; Helm, L.; Belorizky, E.; Fries, P. H.; Merbach, A. E. *J. Am. Chem. Soc.* **2001**, *123*, 2637. (b) Setifi, F.; Golhen, S.; Ouahab, L.; Miyazaki, A.; Okabe, K.; Enoki, T.; Toita, T.; Yamada, J. *Inorg. Chem.* **2002**, *41*, 3786.
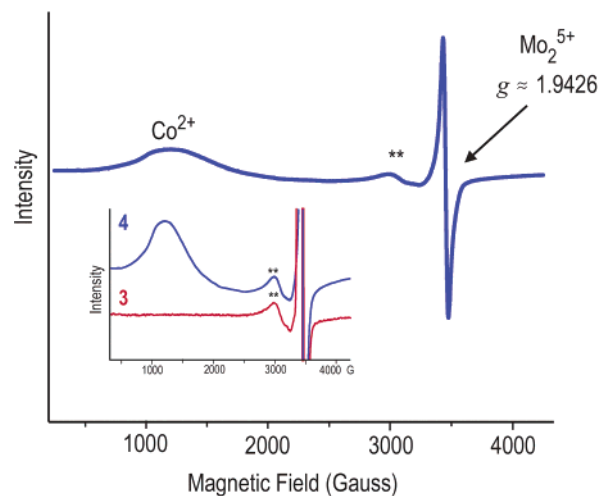
Figure 4. X-band EPR spectrum of powdered **4** at 5 K showing signals for the Mo_2^{5+} unit and the Co^{2+} species. The inset compares the spectra of **4** and **3**. The signal denoted with ** is due to an impurity.
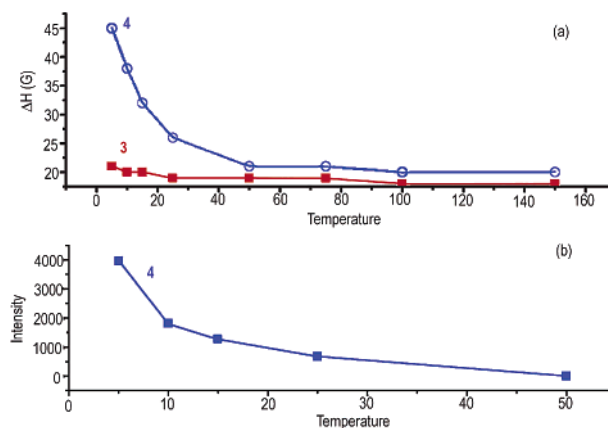

Figure 5. (a) Line-to-line peak separation, ΔH_{pp}, for the g of 1.9426 signal as a function of temperature for **3** and **4**. (b) Intensity of peak corresponding to the Co^{2+} signal at $g \approx 5.57$ as a function of temperature.

in which such interactions should be absent because the Zn^{2+} species is diamagnetic. The results are summarized in Figure 5. As can be seen from the dotted line in Figure 5a which corresponds to data for **3**, as the temperature is lowered from 150 to 5 K, the ΔH_{pp} of the peak at g = 1.9426 increases only slightly by 3 G from 18.2 to 21.5 G. In contrast, the ΔH_{pp} for **4** exhibited a much larger change, as shown by the continuous line in Figure 5a, increasing from 21 G at 50 K to about 45 G at 5 K. A clue to the cause of this broadening is provided by the observation that the line width change for **4** coincides with the onset of the appearance of the broad Co^{2+} peak. Figure 5b shows a plot of intensity versus temperature for the Co^{2+} signal. Clearly, the signal from the oxidized Mo_2 unit (g = 1.9426) does not begin to broaden until the Co^{2+} signal begins to appear. Thus, the broadening of the $[Mo_2]^{5+}$ transition is evidence for a rapid cross-relaxation process between the Co^{2+} and $[Mo_2]^{5+}$ centers. It seems that the spin−lattice relaxation process of Co^{2+} is too fast at temperatures above about 25 K when the corresponding EPR peak is broadened beyond detection. Further support of the exchange interaction between the $[Mo_2]^{5+}$ and Co^{2+} units is provided by the presence of a narrow signal in the precursor **2**. Similar cross-relaxation processes have been reported earlier in a system containing the *m-N*-methylpyri-
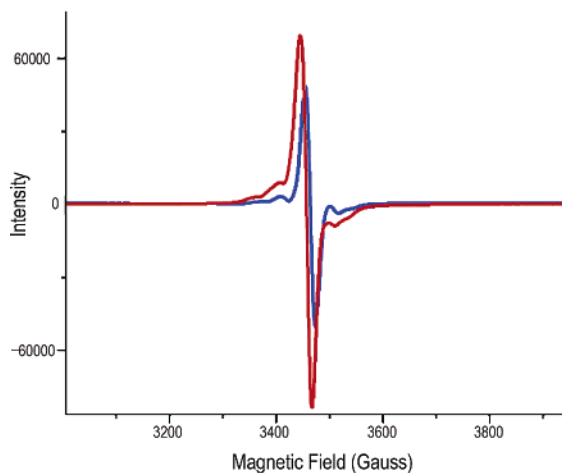
Figure 6. Superposition of the spectra of **3** as a powder (blue) and **5** in a frozen glass (red) at 5 K. The similarity is evidence that the two Mo₂ units do not interact.

dinium nitronylnitroxide (*m*-MPYNN⁺) radical cation and an anionic Mn₁₂ aggregate.[30]

In the hope of further resolving the broad transition attributed to the Co²⁺ unit, a dilute frozen glass sample was studied. However, at 5 K the resolution of the Co²⁺ peak did not improve. This lack of spectral enhancement supports the idea that the relaxation process is intramolecular. Because such a process does not depend on intermolecular interactions, there is no change upon dilution of the molecules.

The doubly oxidized compound **5** has one unpaired electron residing at each of the two [Mo₂] units which are separated by the linker. Thus, it offers an excellent opportunity to study the magnetic behavior of a system with two spatially separated odd electrons. For such a compound, the possible spin coupling patterns include: (1) no coupling; (2) ferromagnetic coupling; and (3) antiferromagnetic coupling. The first case is simply the combination of its parts; it possesses only local spins, each with $S = \frac{1}{2}$. Ferromagnetic coupling would generate a triplet ground state, $S = 1$, and antiferromagnetic coupling would yield a singlet ground state, $S_T = 0$. Calculated values of $\chi_m T$ (emu K mol⁻¹) in the limit $T \rightarrow 0$ K, using in each case a spin-only model with $g = 2.00$, are 0.75, 1, and 0 for the three cases, respectively. A variable temperature study of the bulk suscep- tibility of **5** shows a value of $\chi_m T$ of 0.62 emu K mol⁻¹ that is independent of T. This is conclusive evidence that there is no significant spin coupling, either ferromagnetic or antiferromag- netic, in the system and favors the no-coupling hypothesis.

Additional support for the no-coupling hypothesis is obtained from the EPR spectrum at room temperature of a powdered sample of **5**. This exhibits a fairly broad peak centered around $g_{iso} = 1.9463 \pm 0.0003$. Better resolution is obtained from a dilute frozen glass spectrum. A comparison of the frozen glass spectrum of **5** with the powder spectrum of **3**, which has only one of the Mo₂ units oxidized, shows little difference, as shown in Figure 6. If the two Mo₂ units were interacting, there should be at least 11 peaks due to the ⁹⁵,⁹⁷Mo isotopes. Instead, the spectrum appears very similar to the spectrum of the singly oxidized **3**. Thus, no evidence for interaction between the Mo₂ units is observed in the EPR spectrum of a frozen glass.

The magnetic results for **3**, **4**, and **5** can be compared to those on the Creutz−Taube system in which the counterpart of **5** is the fully oxidized [(NH₃)₅Ru(pyrazine)Ru(NH₃)₅]⁶⁺ ion and that of **3** and **4** is the C−T ion itself, **II**. For the former, one study showed that there is no antiferromagnetic exchange interaction between the two Ru(III) units, each having one unpaired electron. Interestingly, the EPR spectra of the mixed-valence species and the fully oxidized complex have the same *g* values, and both are almost identical to that of the mononuclear Ru- (III) complex. These led to the conclusion that C−T ion, **I**, belongs to a mixed-valence complex of Class II, being electronically localized, even though there was no confirmation of this from the structural studies.[8] However, a single-crystal EPR showed that in the mixed-valence species,[31] the unpaired electron is predominantly in an orbital perpendicular to the plane of the pyrazine ligand, thus allowing for the possibility of delocalization of the odd electron over the two ruthenium ions via the π* system of the pyrazine linker.

In our system, the EPR and magnetic susceptibility results are in complete accord with the positive results of structural characterization and the electrochemical measurements of the mixed-valence complexes, which show that the odd electron in **3** and **4** is electronically localized in the δ orbital of one of the [Mo₂] units and that the two unpaired electrons, one in each dimetal unit in **5**, are localized also.

Concluding Remarks

The system [Mo₂](CH₃O)₂M(OCH₃)₂[Mo₂]ⁿ⁺, where $n = 0$, 1, and 2, [Mo₂] is the quadruply bonded Mo₂⁴⁺ unit embraced by three (*p*-anisyl)NC(H)N(*p*-anisyl) anions, and M = Zn or Co, has been characterized structurally, magnetically, and otherwise. In these compounds, the configuration around the M atom is tetrahedral, and therefore the metal−metal bonds are almost perpedicular to each other. The species with $n = 1$ provides the first example of fully localized complexes in which the odd electron resides in only one of the two dimetal units where it is expected to be fully delocalized in one of the molecular orbitals of the oxidized [Mo₂] unit. These conclusions are supported by electrochemical and EPR measurements and confirmed by X-ray crystallography. The latter offers an excellent criterion for establishing without a doubt if a species is valence-trapped for systems having metal−metal bonded units. The doubly oxidized, $n = 2$, complex is also fully localized and, along with complexes with $n = 0$, serves as a structural probe for the compounds with $n = 1$, in which one [Mo₂] unit resembles those for $n = 0$ and the other resembles those with $n = 2$.

Recent results from our laboratory indicate that by using oxamidate ligands,[32] the first oxidation potentials are similar to those of **1** and **2**, and thus it is likely that oxidation products can be isolated for such a system. Furthermore, some of the oxamidate-linked [Mo₂]L[Mo₂] compounds can be obtained in two isomeric forms, one in which the two Mo₂ units are perpendicular to each other and the other having two parallel Mo−Mo bonds. These open the possibility of using the techniques described here to study the electronic communication

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between [Mo₂] units in different conformations but with an identical coordination environment. This work is in progress now.

Supporting Information Available: Cyclic voltammograms and DPVs of **3** and **4**, the core structure of **4**, and EPR spectra for **2**−**5** (PDF). X-ray crystallographic data in CIF format for **3**·4CH₂Cl₂, **4**·4CH₂Cl₂, and **5**·3.44CH₂Cl₂. This material is available free of charge via the Internet at http://pubs.acs.org.

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