2670 *J. Am. Chem. Soc.* **2001,** *123,* 2670−2671

Maximum Communication between Coupled Oxidations of Dimetal Units

F. Albert Cotton,*[,†] Chun Lin,[†] and Carlos A. Murillo*[,†,‡]

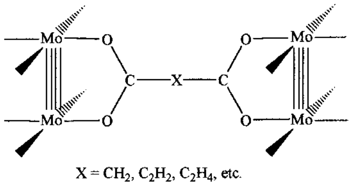
Department of Chemistry and Laboratory for
Molecular Structure and Bonding, PO Box 30012
Texas A&M University, College Station, Texas 77842-3012
Department of Chemistry, University of Costa Rica
Ciudad Universitaria, Costa Rica

Received December 4, 2000

Current interest in supramolecules in which moieties containing geometry-defining metal complex units that are linked by difunctional organic bridging units is widespread and still growing.[1] With but a few exceptions[1] the reported supramolecular species carry high positive charges and, because of the metal ions employed (typically, Pd^{2+}, Pt^{2+}, Zn^{2+}), do not allow for alteration of oxidation states by electrochemical or other means.

Several years ago we began work which demonstrates, for the first time, that properly designed *dimetal* units can also be used to fabricate, in a deliberate and controlled fashion, supramolecules that can be characterized not only by NMR in solution but also by X-ray crystallography. The structures of these supramolecules comprise pairs,[2] loops,[3] squares,[4] triangles,[4a,5] polyhedra,[6] tubes,[7] sheets,[7] and still more complex three-dimensional structures.[8] It may also be noted that a great variety of supramolecular structures formed by $Rh_2(O_2CCF_3)_4$ have recently been reported from this laboratory.[9]

In a recently published study[2b] of the class of compounds represented schematically by **I**, we noted that the connectors, $-O_2CXCO_2-$, varied widely in their ability to make the effect of oxidation of one Mo_2 moiety felt at the other one. We used as the measure of communication the separation of the successive oxidation potentials as others have also done before, for example, studies of ruthenium species linked by diamine groups[10] and similar studies of electronic communication between linked mononuclear centers.[11] Most likely, when communication is best, among the series of dicarboxylate-bridged $[Mo_2]_2$ pairs, it may be presumed that the charge created by the first oxidation is delocalized. Spectroscopic studies are currently being carried out to obtain direct evidence on that point, especially to determine where the borderline between localized and delocalized systems may lie. In the meantime, however, we have addressed the challenge of how to maximize communication.



I

In the series of compounds represented by **I** the best communication was found in the case that, strictly speaking, is not represented by **I**, namely when the connecting dicarboxylate, oxalate ion, has no X; the two carboxyl groups are linked directly to each other. Still, of course, there is a C−C bond between them. Is there any way to do even better and eliminate this as well? Obviously one cannot do exactly that, but there are two ways to do something like that. One of these, which we have recently reported,[2c] is to use dianions which have only one central atom instead of two, namely SO_4^{2-}, MoO_4^{2-}, and WO_4^{2-}. This is quite effective, giving peak-to-peak separations in the differential pulse voltammograms (DPV) of 321, 392, and 387 mV, respectively, compared to 212 mV for oxalate.

The other way to have a connector with only one central atom and at the same time have that atom be a carbon atom is to use the carbonate ion. The problem here, of course, is that no compound resembling the type **I** compounds can be made which has equivalent Mo_2 units. However, a system with equivalent Mo_2 units can be obtained by turning to the types called molecular squares or triangles, of which we have already reported the first examples with both Mo_2 units[4] and Rh_2 units.[4] Because of their cyclic nature it is possible to have unsymmetrical bridges while still having all dimetal units equivalent.

We have prepared[12] such a compound by the reaction of our usual precursor for a molecular square of Mo_2^{4+} units, $[(cis\text{-DAniF})_2Mo_2(CH_3CN)_4]^{2+}$ [13] (DAniF = *N,N′*-di-*p*-anisylformamidinate) with $(Bu^n{}_4N)_2CO_3$ in wet CH_3CN as solvent. The $(Bu^n{}_4N)_2CO_3$, as an aqueous solution was obtained by passing CO_2 gas into a commercially available solution of $Bu^n{}_4NOH$. The

---

[†] Texas A&M University.

[‡] University of Costa Rica.

(1) (a) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853, and references therein. (b) Fujita, M. *Chem. Soc. Rev.* **1998**, *27*, 417 and references therein. (c) Swiegers, G. F.; Malefetse, T. J. *Chem. Rev.* **2000**, *100*, 3843. (d) O'Keeffe, M.; Eddaoudi, M.; Li, H.; Reinike, T.; Yaghi, O. M. *J. Solid State Chem.* **2000**, *152*, 3. (e) Spinet, P.; Soulantica, K.; Charmant, J. P. H.; Orpen, A. G. *Chem. Commun.* **2000**, 915. (f) Navarro, J. A. R.; Lipper, B. *Coord. Chem. Rev.* **1999**, *185−186*, 653. (g) Whang, D.; Kim, K. *J. Am. Chem. Soc.* 1997, *119*, 451. (h) Mann, S.; Huttner, G.; Zsolnai, L.; Heinze, K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 5**,** 2808. (i) Scherer, M.; Caulder, D. L.; Johnson, D. W.; Raymond, K. N. *Angew. Chem., Int. Ed.* **1999**, *38*, 1588. (j) Benkstein, K. D.; Hupp, J. T.; Stern, C. L. *Inorg. Chem.* **1998**, *37*, 5404. (k) Lai, S.-W.; Chan, M. C.-W.; Peng, S.-M.; Che, C.-M. *Angew. Chem., Int. Ed.* **1999**, *38*, 669. (l) Jones, C. J. *Chem. Soc. Rev.* **1998**, *27*, 289. (m) Klausmeyer, K. K.; Wilson, S. R.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1999**, *121*, 1**,** 2705.

(2) (a) Cotton, F. A.; Lin, C.; Murillo *J. Chem. Soc., Dalton Trans.* **1998**, 3151. (b) Cotton, F. A.; Donahue, J. P.; Lin, C.; Murillo, C. A. *Inorg. Chem.* **2001**, *40*, in press. (c) Cotton, F. A.; Donahue, J. P.; Murillo, C. A. *Inorg. Chem.*, accepted.

(3) Cotton, F. A.; Lin, C.; Murillo, C. A. *Inorg. Chem.* **2001**, *40*, 472.

(4) (a) Cotton, F. A.; Daniels, L. M.; Lin, C.; Murillo, C. A. *J. Am. Chem. Soc.* **1999**, *121*, 4538. (b) Cotton, F. A.; Lin, C.; Murillo, C. A. *Inorg. Chem.* **2001**, *40*, 478. (c) Cotton, F. A.; Daniels, L. M.; Lin, C.; Murillo, C. A.; Yu, S.-Y. *J. Chem. Soc., Dalton Trans.*, in press.

(5) Cotton, F. A.; Lin, C.; Murillo, C. A. *Inorg. Chem.* **2001**, *40*, 575.

(6) Cotton, F. A.; Daniels, L. M.; Lin, C.; Murillo, C. A. *Chem. Comm.* **1999**, 841.

(7) Cotton, F. A.; Lin, C.; Murillo, C. A. *Chem. Commun.* **2001**, 11.

(8) Cotton, F. A.; Lin, C.; Murillo, C. A. *J. Chem. Soc., Dalton Trans.* in press.

(9) (a) Cotton, F. A.; Dikarev, E. V.; Stiriba, S.-E. *Inorg. Chem.* **1999**, *38*, 4877. (b) Cotton, F. A.; Dikarev, E. V.; Petrukhina, M. A.; Stiriba, S.-E. *Inorg. Chem.* **2000**, *39*, 1748. (c) Cotton, F. A.; Dikarev, E. V.; Petrukhina, M. A.; Stiriba, S.-E. *Organometallics* **2000**, *19*, 1402. (d) Cotton, F. A.; Dikarev, E. V.; Petrukhina, M. A.; Stiriba, S.-E. *Polyhedron*, **2000**, *19*, 1829.

(10) (a) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278. (b) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1. (c) Ito, T.; Hamaguchi, T.; Nagano, H.; Yamaguchi, T.; Kido, H.; Zavarine, I. S.; Richmond, T.; Washington, J.; Kubiak, C. P. *J. Am. Chem. Soc.* **1999**, *121*, 4625. (d) Kaim, W.; Klein, A.; Glöckle, M. *Acc. Chem. Res.* **2000**, *33*, 755.

(11) See, for example: (a) Flanagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* **1978**, *100*, 4248. (b) Cannon, R. D. *Electron-Transfer Reactions*; Butterworths: London, 1980.

(12) Compound **1** was prepared as follows: To a stirred solution of $[(cis\text{-DAniF})_2Mo_2(CH_3CN)_4](BF_4)_2$ (0.104 g, 0.100 mmol) in deoxygenated CH_3CN was added $(Bu^n{}_4N)_2CO_3$ (0.100 mmol) in a mixture of CH_3CN/H_2O (v:v, 1:1). After the mixture stirred at room temperature for 0.5 h, a yellow solid was obtained by filtration. This was washed with CH_3CN. Then it was dissolved in CH_2Cl_2 (10 mL), and the solution was layered with hexanes. After 1 week, yellow crystals of **1**$\cdot 2.58CH_2Cl_2\cdot 0.5H_2O$ suitable for X-ray structural analysis were collected by filtration. Yield (0.060 g, 76%). After elimination of the interstitial solvent molecules: Anal. for **1**, $C_{124}H_{120}Mo_8N_{16}O_{28}$, Calcd (Found): C, 48.83 (48.77); H, 3.97 (4.02); N, 7.35 (7.26). ^1H NMR δ (ppm, in CD_2Cl_2): 8.61 (s, 4H, $-NCHN-$), 8.31 (s, 4H, $-NCHN-$), 6.72−5.96 (m, 64H, aromatic), 4.47 (s, 8H, H_2O), 3.65 (s, 12H, $-OCH_3$), 3.62 (s, 12H, $-OCH_3$), 3.49 (s, 12H, $-OCH_3$), 3.15 (s, 12H, $-OCH_3$).

(13) Chisholm, M. H.; Cotton, F. A.; Daniels, L. M.; Folting, K.; Huffman, J. C.; Iyer, S. S.; Lin, C.; Macintosh, A. M.; Murillo, C. A. *J. Chem. Soc., Dalton Trans.* **1999**, 1387.

10.1021/ja004149m CCC: $20.00

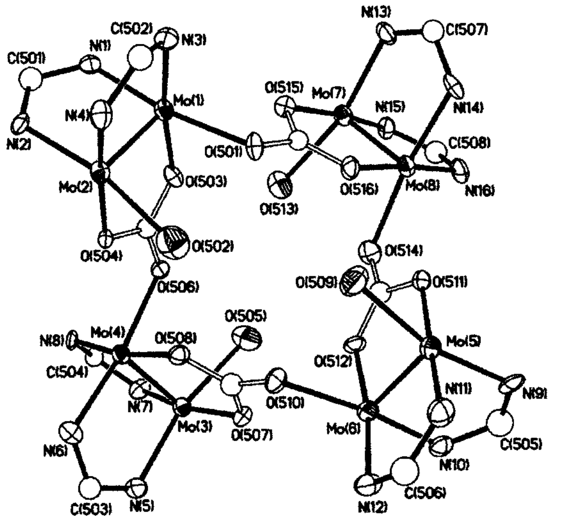


Figure 1. A view of the core of one of the two independent molecular squares in **1**·2.58CH$_2$Cl$_2$·0.5H$_2$O with displacement ellipsoids drawn at the 40% probability level for the non-carbon atoms. For clarity the *p*-anisyl groups attached to each of the 16 nitrogen atoms with the interstitial solvent molecules have been removed. Average distances are: Mo−Mo, 2.095[1]; Mo−O$_{\text{carbonate}}$, 2.135[5]; Mo−O$_{\text{water}}$, 2.256[2]; and Mo−N, 2.118[3] Å.

reaction affords [(*cis*-DAniF)$_2$Mo$_2$(CO$_3$)(H$_2$O)]$_4$, **1**, the structure[14] of which is shown in Figure 1. The bridging posture of the carbonate ions is at the least a very unusual one; we have not been able to find a prior example in the literature. To complete the set of eight equatorial ligands about each Mo$_2^{4+}$ unit there is a water molecule on each one. The whole arrangement has approximately S_4 symmetry. The Mo−Mo distances, in two crystallographically independent but structurally similar molecules present in the asymmetric unit, are in the range 2.092(2)−2.098(2) Å, in accord with the presence of quadruple bonds.[15]

A very interesting feature of this molecule is its electrochemistry. Its cyclic voltammogram and DPV are shown in Figure 2. The most remarkable feature is that five oxidation states are reversibly available for the first time in any dimolybdenum square. These are within a range of about 600 mV, corresponding to charges of 0 to +4 on the square. As shown in Figure 2, the first and second oxidations are barely separated, and presumably correspond to oxidizing Mo$_2$ units at opposite corners of the square. Presumably, charge delocalization does not occur over this distance. The third oxidation is considerably more difficult, and it is possible that delocalization does occur in the +2 ion. There is also a much larger gap between the +2/+3 and the +3/+4 oxidations than there was between the 0/+1 and +1/+2 oxidations, which would also be most easily explained by delocalization occurring in both the +2 and +3 ions. However, more direct evidence concerning delocalization must await the results of spectroscopic studies and structure determinations for the ions. Delocalization, if it occurs, might be reduced or suppressed if the oxidations were carried out in the presence of more strongly coordinating anions. This would appear to be the most interesting molecular square yet made with M$_2^{4+}$ units. There is also the possibility of obtaining a dirhodium analogue, since the analogous dirhodium starting material is available and the [Rh$_2$(O$_2$CO)$_4$]$^{4-}$ ion is known.[16]

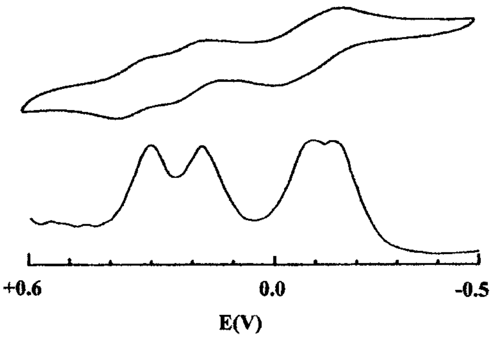
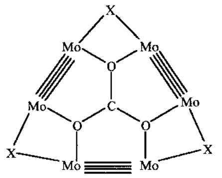


Figure 2. Cyclic and differential pulse voltammograms of **1** in oxygen free CH$_2$Cl$_2$. The DPV clearly supports the existence of five oxidation numbers, 0 to +4.

It is interesting to note here that there is another solution to the problem of coupling equivalent dimetal units via a carbonate ion, which was published about the time our work was being done. Our former co-worker, Jhy-Der Chen, and his group reported[17] compounds that may be schematically represented as **II**. They did not look at the electrochemical behavior of their compounds. It would be very interesting to see such data.



II

In conclusion, [(*cis*-DAniF)$_2$Mo$_2$(CO$_3$)(H$_2$O)]$_4$ is the first molecular square containing quadruply bonded Mo$_2^{4+}$ units that shows four oxidation processes corresponding to charges of 0 to +4 on the square. The maximum number of steps we have been able to observe before was three.[4a] This implies that the electronic communication through the carbonate ion is significantly higher than that possible from dicarboxylate linkers.

Acknowledgment. We are grateful to the National Science Foundation for support of this work.

Supporting Information Available: Tables of crystallographic data including atomic positional and displacement parameters for **1**·2.58CH$_2$Cl$_2$·0.5H$_2$O. Also included are plots of the core of the second molecule in the asymmetric unit and of each of the entire molecules (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA004149M

---

(14) Crystal data for **1**·2.58CH$_2$Cl$_2$·0.5H$_2$O at 213 K: MF = C$_{126.57}$H$_{134.15}$Cl$_{5.15}$Mo$_8$N$_{16}$O$_{32.50}$, MW = 3349.64, triclinic, *P*1, a = 20.941(4) Å, b = 22.403(4) Å, c = 34.096(7) Å, α = 108.69(1)°, β = 95.88(1)°, γ = 102.88(1)°, V = 14507(5) Å^3, Z = 4. The final R factor was 0.089 for 26254 reflections with $I_o > 2\sigma(I_o)$ (wR^2 = 0.186).

(15) Lin, C.; Protasiewicz, J. D.; Smith, E. T.; Ren, T. *Inorg. Chem.* **1996**, *35*, 6422 and references therein.

(16) Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1980**, *19*, 320.

(17) Suen, M.-C.; Tseng, G.-W.; Chen, J.-D.; Keng, T.-C.; Wang, J.-C. *Chem. Commun.* **1999**, 1185.