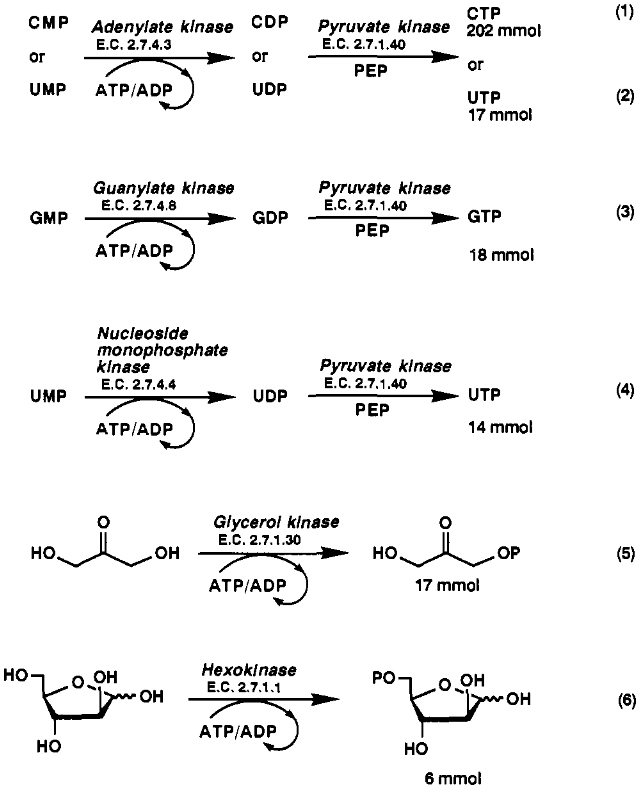
**Scheme II.** Reactions Tested by Using the 3-PGA Method To Regenerate ATP According to Scheme I[a]



[a] Amount refers to quantity isolated. P = phosphate; CTP = cytidine 5′-triphosphate; UTP = uridine 5′-triphosphate; GTP = guanosine 5′-triphosphate.

the solution was stirred at 22–24 °C under a positive pressure of $N_2$. Addition of 3 M HCl using a pH stat controlled the pH at 7.5–7.8. After 48 h, consumption of HCl had ceased but $^1H$ NMR spectroscopy indicated that the reaction was not complete. An additional 32 g of 3-PGA (barium salt, 84 mmol) was converted to the $K^+$ salt as described and added to the reaction mixture. After an additional 24 h, $^1H$ NMR spectroscopy indicated that the reaction was complete. A total of 130 mL of 3 N HCl had been consumed.

To isolate CTP, ~150-mL portions of the clear, pale-yellow reaction mixture were transferred into 12 500-mL polypropylene centrifuge tubes and 150 mL of absolute ethanol was added to each tube. A white precipitate formed immediately. The tubes were cooled in an ice bath for 15 min and then centrifuged (4 °C, 10000g, 10 min). The combined, sticky pellets were dissolved in 600 mL of water, the resulting solution was divided among six 250-mL centrifuge tubes, and 100 mL of absolute ethanol was added to each tube. The tubes were again cooled and centrifuged. Lyophilization of the combined pellets provided 145 g of an off-white powder containing 202 mmol of CTP according to enzymatic analysis[16] (92% yield; 90% purity for $CTP{\cdot}K_3$).[17]

The primary advantage of the PGA method as a route to PEP is that it requires less time, produces less organic waste, and is more convenient than the chemical synthesis. Its starting materials are commercially available. It is, however, more expensive. The convenience outweighs the difference in cost for reactions carried out on a scale <1 mol. The convenience of the PGA method, along with its reliance on commercially available reagents, recommends it as a general technique for the in situ regeneration of ATP.

**Acknowledgment.** We thank M. J. Kim (Chief of Trade Section, Miwon Foods Co., Ltd., Seoul, Korea) for providing us with CMP and GMP.

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[15] All enzymes were from Sigma: adenylate kinase (10 000 units, lyophilized powder from chicken muscle), pyruvate kinase (5000 units, lyophilized powder from rabbit muscle), enolase (4000 units, lyophilized powder from yeast), and phosphoglycerate mutase (5000 units, suspension in ammonium sulfate from rabbit muscle). In this example, we used an excess of the enzymes because their cost is low compared with the value of the product.

[16] Keppler, D. In *Methods of Enzymatic Analysis*, 3rd ed.; Bergmeyer, H. U., Bergmeyer, J., Grassl, M., Eds.; VCH: Weinheim, 1985; Vol. VII, p 432.

[17] The water content (7.14%) was determined by the Karl Fischer method. Thin-layer chromatography [poly(ethylenimine)-cellulose, eluant: 2.0 N HCOOH/2.0 N LiCl, 1:1, v/v] indicated that ATP was present in addition to CTP; neither CMP nor CDP was detected. Comparison of the $^1H$ and $^{31}P$ NMR spectra with those of authentic CTP from Sigma indicated the presence of ~1% each of ATP, dipyruvate, 3-PGA, inorganic phosphate, and ethanol.

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# Electronic Coupling between Covalently Linked Metal–Metal Quadruple Bonds of Molybdenum and Tungsten

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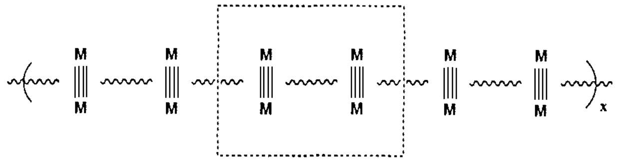
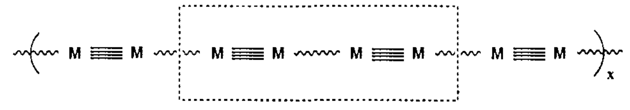
Chemical and physical properties of one-dimensional materials that contain electronically coupled, redox-active transition-metal centers are of interest.[1] We report herein the synthesis and preliminary characterization of tetranuclear compounds of molybdenum and tungsten containing covalently linked M–M quadruple bonds. These compounds represent models for the dimeric subunits in hypothetical one-dimensional polymers of type I and II that may too show interesting electronic, optical, and magnetic properties.



I



II

The new tetranuclear compounds were synthesized according to the stoichiometric reaction shown in eq 1.[2] The tetranuclear

$$2M_2(O_2C\text{-}t\text{-}Bu)_4 + HO_2C(R)CO_2H \rightarrow [M_2(O_2C\text{-}t\text{-}Bu)_3]_2(\mu\text{-}O_2C(R)CO_2) + 2t\text{-}BuCO_2H \quad (1)$$

$$M = Mo, W$$

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[1] See, for example: (a) Marks, T. J. *Science* **1985**, *227*, 881. (b) Miller, J. S.; Epstein, A. J. *Prog. Inorg. Chem.* **1976**, *20*, 1. (c) Whangbo, M.-H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 6093.

[2] A typical procedure involves the reaction between $M_2(O_2C\text{-}t\text{-}Bu)_4$ (ca. 500 mg), dissolved in dry toluene (10–15 mL) under an oxygen-free $N_2$ atmosphere, and the dicarboxylic acid (0.5 equiv). The solution is stirred at room temperature for ca. 1–3 days, during which time a finely divided microcrystalline precipitate forms. The precipitate is collected by filtration, washed with hexane (2 × 10 mL), and dried in vacuo to yield the crude compounds of type III or IV. Yields are ca. 90–95% for M = Mo and ca. 50–80% for M = W. Purification of the linked dinuclear compounds involves either recrystallization from pyridine or chromatography through Bio-Beads (Bio-Rad, S-X8) with THF eluent. The compounds reveal two types of $O_2C\text{-}t\text{-}Bu$ ligands in the ratio of 1:2 in both $^1H$ and $^{13}C$ NMR spectra assignable to pivalate ligands that are trans and cis to the bridging ligand, respectively. Satisfactory elemental analyses have been obtained for all compounds.

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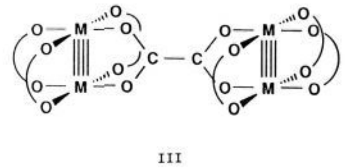
**Table I**. Comparison of Electrochemical Data for Selected Covalently Linked Mononuclear Systems with Those of Carboxylate-Bridged M–M Quadruply Bonded Compounds and the Parent $M_2(O_2CR)_4$ Compounds

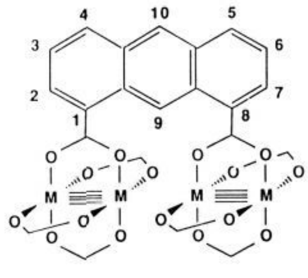
| compound | $E_{1/2}^1$,[a] V | $E_{1/2}^2$,[a] V | $\Delta E_{1/2}$,[a] mV | $K_c$ |
|---|---|---|---|---|
| $[Mo_2(O_2C\text{-}t\text{-}Bu)_3]_2(\mu\text{-}C_2O_4)$ | +0.86 | +1.14 | 280 | $5.4 \times 10^4$ |
| $[W_2(O_2C\text{-}t\text{-}Bu)_3]_2(\mu\text{-}C_2O_4)$ | −0.36 | +0.36 | 717 | $1.3 \times 10^{12}$ |
| $[(NH_3)_5Ru]_2(\mu\text{-pyrazine})^{4+}$[b] | −0.45[c] | −0.06[c] | 390 | $3.9 \times 10^6$ |
| $[(NH_3)_5Os]_2(\mu\text{-pyrazine})^{4+}$[d] | −1.24[c] | −0.48[c] | 760 | $7.0 \times 10^{12}$ |
| $[Mo_2(O_2C\text{-}t\text{-}Bu)_3]_2(\mu\text{-}1,4\text{-}C_6F_4(CO_2)_2)$ | +0.96 | +1.02 | 65 | 13 |
| $[W_2(O_2C\text{-}t\text{-}Bu)_3]_2(\mu\text{-}1,4\text{-}C_6F_4(CO_2)_2)$ | +0.24 | +0.52 | 285 | $6.6 \times 10^4$ |
| $[(NH_3)_5Ru]_2(\mu\text{-}1,4\text{-}C_6H_4(CN)_2)^{4+}$[e] | −0.30[c] | −0.22[c] | 72 | 16 |
| $[Mo_2(O_2C\text{-}t\text{-}Bu)_3]_2(\mu\text{-}1,8\text{-}C_{14}H_8(CO_2)_2)$ | +0.92 | *f* | | |
| $[W_2(O_2C\text{-}t\text{-}Bu)_3]_2(\mu\text{-}1,8\text{-}C_{14}H_8(CO_2)_2)$ | +0.23 | +0.39 | 156 | $4.3 \times 10^2$ |
| $[Mo_2(O_2C\text{-}t\text{-}Bu)_3]_2(\mu\text{-}1,8\text{-}C_{14}H_{10}(CO_2)_2)$ | +0.87 | +0.97 | 106 | 62 |
| $[W_2(O_2C\text{-}t\text{-}Bu)_3]_2(\mu\text{-}1,8\text{-}C_{14}H_{10}(CO_2)_2)$ | +0.20 | +0.34 | 146 | $2.9 \times 10^2$ |
| $Mo_2(O_2C\text{-}t\text{-}Bu)_4$ | +0.86 | | | |
| $W_2(O_2C\text{-}t\text{-}Bu)_4$ | +0.19 | | | |

[a] The half-potentials $E_{1/2}^1$ and $E_{1/2}^2$ refer to one-electron-redox couples vs Ag wire reference in 0.2 M $Bu_4NPF_6$/THF at a scan rate of 100 mV/s, and the term $\Delta E_{1/2} = |E_{1/2}^2 - E_{1/2}^1|$. [b] Lim, H. S.; Barclay, J.; Anson, F. C. *Inorg. Chem.* **1972**, *11*, 1460. [c] In aqueous solution with $E_{1/2}$ values converted to the Ag/Ag$^+$ reference. [d] Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1. [e] Reference 7. [f] At potentials greater than +1.00 V, the anthracene π electrons are oxidized.

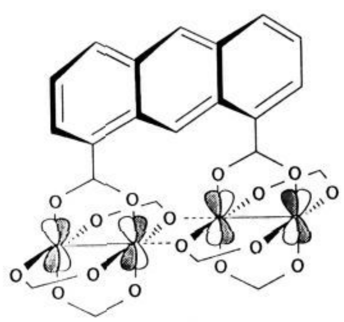
complexes are notably less soluble than the $M_2(O_2C\text{-}t\text{-}Bu)_4$ compounds in common organic solvents. If the carboxylate exchange reaction is carried out with the diacids $HO_2CCO_2H$ or *p*-$HO_2CC_6F_4CO_2H$, the resulting carboxylate-bridged tetranuclear species provide soluble models for dimeric units in the perpendicular[3] polymer, I, as shown in III, whereas 1,8-anthracenedicarboxylic acid and its 9,10-dihydro derivative yield carboxylate-linked compounds that because of the structural constraints of the anthracene moiety, are forced to adopt an orientation similar to the dimeric subunits in parallel polymer II (see IV). In these latter compounds, rotation about the aryl C to carboxylate C bond may allow M···O bonding (see V), as is found in the "laddered" structures of $[M_2(O_2CR)_4]_\infty$ in the solid state.[4] In addition to providing O→M bonding, this orientation also allows an interaction *between* the M–M δ orbitals of the two subunits, the lowest energy combination of which is depicted in V.



III

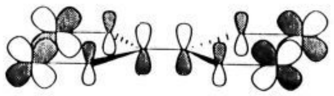


IV



V

The electronic delocalization in the oxalate-bridged complexes, $[M_2(O_2C\text{-}t\text{-}Bu)_3]_2(\mu\text{-}O_2CCO_2)$, of Mo and W have been examined in greater detail by UV–vis spectroscopy and Fenske–Hall MO calculations.[5] Assuming a planar oxalate bridge, the calculations indicate extensive mixing of the M–M δ bonding combinations with the $C_2O_4$ π orbitals. In particular, the lowest unoccupied $C_2O_4$ π orbital is significantly lower in energy than the empty *t*-$BuCO_2$ π orbitals. The oxalate LUMO interacts with, and accepts electron density from, the M–M δ bonding orbitals, as shown in VI (Mulliken population of the lowest energy $C_2O_4$ π orbital = 0.12 e (M = Mo) and 0.18 e (M = W)). Excitation from one of the M–M δ combinations ($b_{3g}$) into this low-lying oxalate orbital ($b_{2u}$) (MLCT) is allowed ($B_{1u}$ under $D_{2h}$ symmetry) and would be expected to occur at lower energy relative to the δ → $CO_2$ π* transitions associated with the *t*-$BuCO_2$ ligands. Consistent with this prediction is the appearance of absorptions at 464 nm (ε = 14 240) and 704 nm (ε = 36 360) for the Mo and W compounds, respectively. These mask the δ → δ* (singlet) transitions and are assigned to δ → $C_2O_4$ π*.



VI

Previous electrochemical studies, particularly by cyclic voltammetry (CV), on the $M_2(O_2CR)_4$ systems have provided direct observation of the reversible removal of an electron from the δ orbital: $M_2(O_2CR)_4$, $\sigma^2\pi^4\delta^2 \rightleftarrows M_2(O_2CR)_4^+$, $\sigma^2\pi^4\delta^1 + e^-$.[6] We

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(3) The terms perpendicular and parallel (vide infra) refer to the orientation of the M–M bond with respect to the propagation direction of the polymer.

(4) See, for example: Chisholm, M. H.; Chiu, H. T.; Huffman, J. C. *Polyhedron* **1984**, *3*, 759.

(5) The oxalate-bridged complexes were modeled by $[M_2(O_2CH)_3]_2(\mu\text{-}O_2CCO_2)$ for M = Mo and W by using the interatomic distances and angles found in the crystal structure of $Mo_2(O_2C\text{-}t\text{-}Bu)_4$ (Cotton, F. A.; Extine, M.; Gage, L. D. *Inorg. Chem.* **1978**, *17*, 172) for the dinuclear moieties and assuming a C–C distance of 1.50 Å. The calculations were performed according to the method of Fenske and Hall (Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768).

(6) (a) Chisholm, M. H.; Clark, D. L.; Huffman, J. C.; Van Der Sluys, W. G.; Kober, E. M.; Lichtenberger, D. L.; Bursten, B. E. *J. Am. Chem. Soc.* **1987**, *109*, 6796. (b) Santure, D. J.; Huffman, J. C.; Sattelberger, A. P. *Inorg. Chem.* **1985**, *24*, 371. (c) Cotton, F. A.; Pedersen, E. *Inorg. Chem.* **1975**, *14*, 399. (d) Zietlow, T. C.; Klendworth, D. D.; Nimry, T.; Salmon, D. J.; Walton, R. A. *Inorg. Chem.* **1981**, *20*, 947.

have carried out similar CV studies on the carboxylate-bridged compounds in order to investigate the degree of electronic coupling between the two dinuclear centers. A summary of the electrochemical data is given in Table I together with comparative data for related bridged mononuclear complexes.

Using the electrochemical data for reversible oxidations of linked mononuclear complexes of the formula $[(NH_3)_5M]_2(\mu\text{-}L)^{4+/5+/6+}$, where M = Ru and Os and L = $N_2$, pyrazine, and other bidentate donor ligands, Taube and co-workers[7] have determined values of $K_c$ (conproportionation equilibrium constant) for the equilibrium reaction 2. The greater the magnitude of $K_c$, the greater the

$$[M\text{-}L\text{-}M]^{4+} + [M\text{-}L\text{-}M]^{6+} \overset{K_c}{\rightleftharpoons} 2[M\text{-}L\text{-}M]^{5+} \qquad (2)$$

degree of charge delocalization in the mixed-valence state and the greater the electronic coupling of the two redox centers.

For the dicarboxylate-linked dinuclear systems we observed two successive one-electron-oxidation processes,[8] the first of which is reversible and the second essentially irreversible.[9] By analogy with Taube's work, we define a conproportionation equilibrium constant $K_c$ for the mixed valence state of the linked quadruply bonded compounds in eq 3.

$$[M_2\sim\sim\sim M_2] + [M_2\sim\sim\sim M_2]^{2+} \overset{K_c}{\rightleftharpoons} 2[M_2\sim\sim\sim M_2]^{1+} \qquad (3)$$

As seen in Table I, the electronic coupling in the carboxylate-bridged tetranuclear compounds is greater for M = W than for M = Mo and directly parallels the trend in Taube's pentaamine system where coupling for the third-row element Os is greater than for the second-row element Ru. As expected, the shorter perpendicular link (oxalate) exhibits greater electronic coupling than the longer perfluorophenyl dicarboxylate bridge, and their magnitudes are similar to those obtained for pyrazine and 1,4-dicyanobenzene bridged pentaamine systems, respectively.

The $K_c$ values for the parallel-linked systems are similar for both the 1,8-anthracenedicarboxylate bridged species and the saturated 9,10-dihydro-1,8-anthracenedicarboxylate bridged species. Thus the electron transfer is probably occurring directly between the metals of the subunits rather than through the carboxylate bridge, and in any event the contribution to these $K_c$ values from direct $M_2\cdots M_2$ electron delocalization in the mixed-valence state is likely to be small compared to contributions arising from electrostatic factors.[10]

The preliminary results reported here indicate that strong electronic coupling between covalently linked M-M multiple bonds is possible and that this coupling should be tunable by choice of metal (e.g., Mo versus Rh), the covalent link, and the orientation of the $M_2$ axes. This is encouraging with respect to achieving electronic communication along one-dimensional polymer chains of either type I or II.[11]

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(7) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278.

(8) The one-electron nature of the redox couples was established by comparing the magnitude of the current flow with that measured for equimolar concentrations of the corresponding $M_2(O_2C\text{-}t\text{-}Bu)_4$ compound under identical CV conditions.

(9) For well-separated redox couples (i.e., >250 mV), the ratio of the anodic peak current to the cathodic peak current for the first couple was found to be unity. For successive redox couples separated by <250 mV, such criteria could not be applied.

(10) For a discussion of factors influencing the relative stability of mixed-valence species, see: Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984**, *60*, 114-119. We thank Professor Taube for bringing this matter to our attention.

(11) We gratefully acknowledge the National Science Foundation for a postdoctoral fellowship for R.H.C.

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# Detection of EPR Spectra in *S* = 2 States of Trivalent Manganese Complexes

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The presence of trivalent manganese is implicated in a number of redox-active metalloenzymes, including the photosynthetic oxygen-evolving complex,[2] superoxide dismutase,[3] pseudocatalase,[4] and ribonucleotide reductase.[5] Considerable effort has been focused on the synthesis and characterization of inorganic complexes as structural models for these biological metal centers.[6] However, EPR spectroscopy has rarely been applied to study the electronic structure of trivalent manganese complexes. This is perhaps a result of a prevalent assumption that the non-Kramers spin states of such systems would be EPR silent, as a result of either large zero-field splittings or fast spin relaxation processes. Although a few EPR studies of trivalent manganese impurity ions in solid-state systems have been reported,[7] these have relied largely on indirect detection methods or very high observation frequencies.

In this communication, we present X-band EPR spectra of $S = 2$ spin states of three trivalent manganese complexes, including the mononuclear manganese(III) tris(acetylacetonate) and tris(picolinate) coordination complexes and the weakly antiferromagnetically exchange coupled binuclear complex $Mn_2^{III,III}O(O_2CCH_3)_2(HB(pz)_3)_2$ ($HB(pz)_3$ = hydrotris(1-pyrazolyl)borate).[8] In all cases, stronger signals were obtained with a geometry in which the microwave magnetic field was polarized parallel to the applied magnetic field, in contrast to the conventional EPR method in which the microwave field is polarized perpendicular to the applied field. The parallel microwave polarization induces magnetic dipole transitions with the selection rule $\Delta m = 0$, which can become partially allowed in spin systems with $S > {}^1/_2$ when zero-field Hamiltonian terms mix the Zeeman basis states. The zero-field interaction $D[S_z^2 - {}^1/_3S(S + 1)] - E(S_x^2 - S_y^2)$ splits the levels of an $S = 2$ spin system into two doublets, one comprised of linear combinations of the $m_s = |\pm 2\rangle$ states and the other of the $m_s = |\pm 1\rangle$ states, and a singlet corresponding to the $m_s = |0\rangle$ state.[9] EPR transitions may be observed between the levels of

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(1) (a) Department of Physics. (b) Department of Chemistry. (c) Chemical Biodynamics Division, Lawrence Berkeley Laboratory, University of California, Berkeley. (d) Present address: Department of Chemistry, Emory University, Atlanta, GA.

(2) (a) Kirby, J. A.; Goodin, D. B.; Wydrzynski, T.; Robertson, A. S.; Klein, M. P. *J. Am. Chem. Soc.* **1981**, *103*, 5537-5542. (b) Yachandra, V. K.; Guiles, R. D.; McDermott, A. E.; Cole, J. L.; Britt, R. D.; Dexheimer, S. L.; Sauer, K.; Klein, M. P. *Biochemistry* **1987**, *26*, 5974-5981.

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(9) Abragam, A.; Bleaney, B. *Electron Paramagnetic Resonance of Transition Metal Ions*; Clarendon Press: Oxford, 1970; pp 209-211.

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