

Trapping Tetramethoxyzincate and -cobaltate(II) between Mo₂⁴⁺ Units

F. Albert Cotton,* Chun Y. Liu, Carlos A. Murillo,* and Xiaoping Wang

Department of Chemistry and Laboratory for Molecular Structure and Bonding, P.O. Box 30012, Texas A&M University, College Station, Texas 77842-3012

Received February 14, 2003

Two compounds of a new type, [Mo₂](CH₃O)₂M(CH₃O)₂[Mo₂] where [Mo₂] is an abbreviation for Mo₂[(*p*-MeOC₆H₄)-NCHN(*p*-MeOC₆H₄)₃] and M = Zn (**1**) and Co (**2**), are reported. Discrete [M(OR)₄]²⁻ ions, either as such or in the μ_2, η^4 role, have not heretofore been described. In these compounds they have distorted tetrahedral structures and bridge two [Mo₂] groups in much the same way as did SO₄²⁻, MoO₄²⁻, and WO₄²⁻ ions in other recently reported compounds (Cotton, F. A.; Donahue, J. P.; Murillo, C. A. *Inorg. Chem.* **2001**, *40*, 2229). The ¹H NMR spectrum of **1** and the visible spectrum and magnetic properties of **2** are consistent with these structures. The M(OCH₃)₄ bridges are moderately effective in coupling the two [Mo₂] redox centers. Compounds **1** and **2** may also be viewed as having Zn^{II} and Co^{II} centers tetrahedrally coordinated by the bidentate ligand [Mo₂[(*p*-MeOC₆H₄)NCHN(*p*-MeOC₆H₄)₃-(OMe)₂]⁻. From that point of view they may be compared with Zn(DPM)₂ and Co(DPM)₂ (**3**), where DPM is the anion of dipivaloylmethane. For purposes of comparison, **3** has been fully characterized structurally, spectroscopically, and magnetically. Close analogies between **2** and **3** are shown to exist.

1. Introduction

The fundamental understanding of the various aspects of molecular mediated metal–metal interactions is essential in chemistry and in living processes, such as communication and electron transport in proteins, and an enormous amount of effort has been put forth to find appropriate answers.¹ An early example of a system that has been extensively studied and continues to generate a great deal of excitement is that in which two single-metal units are linked by a bidentate ligand, e.g., two Ru(NH₃)₅²⁺ units joined by a pyrazine linker, **I**. Of course, this is the precursor of the so-called Creutz–Taube ion which has served as the prototype for hundreds of compounds for which the most varied techniques have been used to probe the electronic communication between the two metal units and how the linker affects such processes.²

In our laboratory, we have found that one could gain further insight by looking at systems in which the metal centers are composed of dinuclear metal–metal bonded units

rather than single metal centers since these units have probes present only in such dinuclear systems. For example, one such unique probe is the $\delta \rightarrow \delta^*$ transition in quadruply bonded complexes which is so well-understood in compounds having only one Mo₂⁴⁺ unit.³

Early attempts at using dicarboxylate anions to link (carboxylate)₃Mo₂⁺ units failed at providing isolable compounds that could be structurally characterized, although these have been characterized by other means and have been subject to many other studies mainly by the Chisholm group.⁴ In our laboratory, success in isolation and structural characterization has been accomplished by using less labile (formamidinate)₃Mo₂⁺ species which have been linked by various types of linkers such as dicarboxylate anions which

* To whom correspondence should be addressed. E-mail: cotton@tam.u.edu (F.A.C.); murillo@tam.u.edu (C.A.M.).

(1) See for example: (a) Lippard, S. J.; Berg, J. M. *Principles of Bioinorganic Chemistry*; University Science Books: Mill Valley, CA, 1994. (b) Schuster, G. B. *Acc. Chem. Res.* **2000**, *33*, 253. (c) Endicott, J. F.; Kumar, K.; Ramasami, T.; Rotzinger, F. P. *Prog. Inorg. Chem.* **1983**, *30*, 141. (d) Barigelletti, F.; Flamigni, L. *Chem. Soc. Rev.* **2000**, *29*, 12. (e) Pletneva, E. V.; Crnogorac, M. M.; Kostic, N. M. *J. Am. Chem. Soc.* **2002**, *124*, 14342.

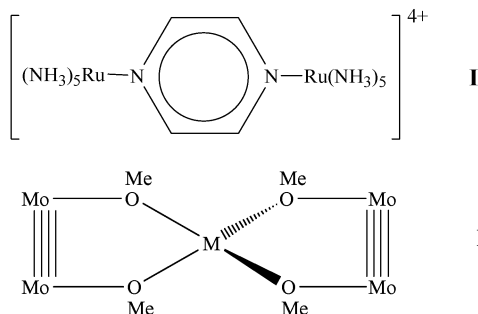
(2) See for example: (a) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1. (b) Brunshwig, B. S.; Creutz, C.; Sutin, N. *Chem. Soc. Rev.* **2002**, *31*, 168. (c) Demadis, K. D.; Hartshorn, C. M.; Meyer, T. J. *Chem. Rev.* **2001**, *101*, 2655. (d) Chen, P.; Meyer, T. J. *Chem. Rev.* **1998**, *98*, 1439. (e) Kaim, W.; Klein, A.; Gloeckle, M. *Acc. Chem. Res.* **2000**, *33*, 755. (f) Ferretti, A.; Lami, A.; Murga, L. F.; Shehadi, I. A.; Ondrechen, M. J.; Villani, G. *J. Am. Chem. Soc.* **1999**, *121*, 2594. (3) Cotton, F. A.; Nocera, D. G. *Acc. Chem. Res.* **2000**, *33*, 483. (4) (a) Chisholm, M. H. *J. Organomet. Chem.* **2002**, *641*, 15. (b) Bursten, B. E.; Chisholm, M. H.; Hadad, C. M.; Li, J.; Wilson, P. J. *Chem. Commun.* **2001**, 2382. (c) Bursten, B. E.; Chisholm, M. H.; Clark, R. J. H.; Firth, S.; Hadad, C. M.; MacIntosh, A. M.; Wilson, P. J.; Woodward, P. M.; Zaleski, J. M. *J. Am. Chem. Soc.* **2002**, *124*, 3050. (d) Bursten, B. E.; Chisholm, M. H.; Clark, R. J. H.; Firth, S.; Hadad, C. M.; Wilson, P. J.; Woodward, P. M.; Zaleski, J. M. *J. Am. Chem. Soc.* **2002**, *124*, 12244.

give compounds in which the two Mo_2^{4+} units are typically parallel to each other,⁵ or EO_4^{2-} anions (E = S, Mo, W) that provide complexes with the two Mo_2^{4+} units almost perpendicular to one another.⁶ This difference in the relative arrangement of the Mo_2 units is expected to provide very different communication pathways.

In the course of extending the range of linkers that can be used to probe electronic communication and to study how such communication is affected, diamidate anions were also considered. However, a new synthetic approach had to be devised since those applicable to dicarboxylate units did not work.⁷ This method involved reduction of $\text{Mo}_2(\text{DAniF})_3\text{Cl}_2$ ($\text{DAniF} = N,N'$ -di-*p*-anisylformamidinate) with zinc and then reaction with sodium methoxide before addition of the diamide, the NaOCH_3 being used as a deprotonating agent. During such reactions, some intermediates were observed. Therefore, we decided to investigate this process but found it more helpful to use $\text{Mo}_2(\text{DAniF})_3(\text{O}_2\text{CCH}_3)$ as starting material.

We report here the unexpected but interesting occurrence of the previously unknown tetramethoxyzincate ion, $[\text{Zn}(\text{OCH}_3)_4]^{2-}$, as a bridging tetradentate μ_2 - η^4 ligand. We also show that the method of preparation is more general by replacing the tetrahedrally coordinated Zn^{2+} ion by a tetrahedral Co^{2+} species. The molecules reported here have the core structure shown schematically as **II**, which is similar to those of reported molecules with SO_4^{2-} , MoO_4^{2-} , and WO_4^{2-} ions as the linkers.⁶

It is noteworthy that although polymeric zinc alkoxides are well-known, their capacity to attract additional alkoxide ions to form mononuclear alkoxyzincates, $\text{Zn}(\text{OR})_4^{2-}$, is not documented.⁸ For cobalt(II) there does not appear to be any report of a $[\text{Co}(\text{OR})_n]^{2-n}$ ion. As far as we know, these are the first such units reported for zinc and cobalt.



2. Experimental Section

2.1. 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 material, $\text{Mo}_2(\text{DAniF})_3\text{Cl}_2$ ($\text{DAniF} = N,N'$ -di-*p*-anisyl-

Table 1. X-ray Crystallographic Data for **1**, **2**, and **3**

	1 ·3.83 CH_2Cl_2	2 ·3.76 CH_2Cl_2	3
empirical formula	$\text{C}_{97.83}\text{H}_{109.66}\text{Cl}_{7.66}\text{Mo}_4\text{N}_{12}\text{O}_{16}\text{Zn}$	$\text{C}_{97.76}\text{H}_{109.52}\text{Cl}_{7.52}\text{CoMo}_4\text{N}_{12}\text{O}_{16}$	$\text{Co}(\text{C}_{11}\text{H}_{19}\text{O}_2)_2$
fw	2430.1	2417.89	425.45
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$I4_1/a$ (No. 88)
<i>a</i> , Å	13.8172(9)	23.929(1)	10.5256(6)
<i>b</i> , Å	15.226(1)	18.1747(9)	10.5256(6)
<i>c</i> , Å	27.319(2)	26.367(1)	21.807(3)
α , deg	90.332(1)	90	90
β , deg	102.897(1)	110.711(1)	90
γ , deg	104.118(1)	90	90
<i>V</i> , Å ³	5422.2(6)	10726(1)	2415.9(3)
<i>Z</i>	2	4	4
<i>T</i> , K	213	213	213
λ , Å	0.7103	0.7103	0.7103
<i>d</i> _{calc} , g/cm ³	1.49	1.497	1.17
μ , mm ⁻¹	0.923	0.859	0.731
<i>R</i> 1 ^a (<i>wR</i> 2) ^b	0.069 (0.135)	0.078 (0.140)	0.030 (0.075)

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$. $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$.

formamidinate), was prepared by following a published method;⁶ $\text{Mo}_2(\text{DAniF})_3(\text{O}_2\text{CCH}_3)$ was prepared by a procedure which will be reported separately. Commercially available chemicals were used as received.

2.2. Physical Measurements. ¹H NMR spectra were recorded on a Mercury 300 spectrometer with chemical shifts (δ) referenced to CD_2Cl_2 . The cyclic voltammograms were recorded on a BAS 100 electrochemical analyzer with Pt working and auxiliary electrodes, Ag/AgCl reference electrode, scan rate of 100 mV/s, and 0.1 M Bu_4NPF_6 as electrolyte, and in CH_2Cl_2 solution.

2.3. X-ray Structure Determinations. Crystals of **1**·3.83 CH_2Cl_2 and **2**·3.76 CH_2Cl_2 were obtained by layering hexanes over the corresponding dichloromethane solutions. Large yellow crystals of **1**·3.83 CH_2Cl_2 were collected after a period of two weeks. For **2**·3.76 CH_2Cl_2 , crystal growth was much faster; large reddish-brown crystals were collected after one week. Crystals of **3** were prepared by slow sublimation under vacuum at ca. 90 °C. Crystals were mounted on the tips of quartz fibers attached to the goniometer head. Data for **1**·3.83 CH_2Cl_2 , **2**·3.76 CH_2Cl_2 , and **3** were collected on a BRUKER SMART 1000 CCD area detector system. The structures were solved by direct methods using the SHELXS-97 program⁹ and refined using the SHELXL-97 program.¹⁰ Non-hydrogen atoms, except for those of disordered solvent molecules, were refined with anisotropic displacement parameters. Hydrogen atoms were added in calculated positions. Crystallographic data are presented in Table 1.

2.4. Preparation of $[\text{Mo}_2(\text{DAniF})_3]_2\text{Zn}(\text{OCH}_3)_4$, **1. Method A.**

To a mixture of dark brown $\text{Mo}_2(\text{DAniF})_3\text{Cl}_2$ (0.514 g, 0.500 mmol) and a large excess of Zn dust (3.5 g) was added 25 mL of acetonitrile. After stirring at room temperature for 1.5 h, the excess Zn dust was removed by filtration. Then, 6.0 mL of a NaOCH_3 solution (0.5 M in CH_3OH) was added to the yellow filtrate. A yellow precipitate formed in a few minutes, and this mixture was stirred at room temperature for 3 h. The solid was isolated by filtration. To this was added CH_2Cl_2 (ca. 10 mL), which was followed by filtration via a Celite-packed column that removed a small amount of insoluble material. After the volume of the filtrate was reduced under vacuum to ca. 5 mL, addition of hexanes (40 mL) by syringe produced a light yellow precipitate. The solid was

(5) (a) Cotton, F. A.; Lin, C.; Murillo, C. A. *Acc. Chem. Res.* **2001**, *34*, 759. (b) Cotton, F. A.; Lin, C.; Murillo, C. A. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4810.

(6) Cotton, F. A.; Donahue, J. P.; Murillo, C. A. *Inorg. Chem.* **2001**, *40*, 2229.

(7) Cotton, F. A.; Daniels, L. M.; Donahue, J. P.; Liu, C. Y.; Murillo, C. A. *Inorg. Chem.* **2002**, *41*, 1354.

(8) Bradley, D. C.; Mehrotra, R. C.; Rothwell, I. P.; Singh, A. *Alkoxo and Aryloxo Derivatives of Metals*; Academic Press: New York, 2001.

(9) Sheldrick, G. M. SHELXS-97. Program for crystal structure solution. *Acta Crystallogr.* **1990**, *A46*, 467.

(10) Sheldrick, G. M. SHELXL-97. Program for Crystal Structure Analysis; University of Göttingen: Göttingen Germany, 1997.

Trapping Tetramethoxyzincate and -cobaltate(II)

separated by filtration, washed with hexanes (1×10 mL), and dried under vacuum. Yield: 0.412 g, 78.4%. $^1\text{H NMR}$ δ (ppm in CD_2Cl_2): 8.36 (s, 4H, NCHN), 8.32 (s, 2H, NCHN), 6.49 (d, 32H, aromatic), 6.40 (d, 8H, aromatic), 6.18 (d, 8H, aromatic), 3.66 (s, 24H, OCH_3), 3.62 (s, 12H, OCH_3), 3.42 (s, 12H, OCH_3). UV-vis: λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 406 (5000), 470 (2000). Anal. Calcd for $\text{C}_{94}\text{H}_{102}\text{Mo}_4\text{N}_{12}\text{O}_{16}\text{Zn}$: C, 53.60; H, 4.89; N, 7.99. Found: C, 53.44; H, 4.73; N, 7.97.

2.5. Method B. $\text{Mo}_2(\text{DAniF})_3(\text{O}_2\text{CCH}_3)$ (0.203 g, 0.200 mmol) was mixed with anhydrous ZnCl_2 (0.020 g, 0.15 mmol) in 25 mL of acetonitrile. To the stirred suspension was added dropwise 2.0 mL of a NaOCH_3 solution (0.5 M in CH_3OH). This resulted in the formation of a flocculent yellow precipitate in about 30 min. Stirring was continued for 3 h; the yellow solid was then separated by filtration and washed with acetonitrile (1×10 mL). To the solid was added CH_2Cl_2 (15 mL) and the mixture filtered through a Celite-packed column. Hexanes were introduced by syringe into the filtrate to produce a pale yellow precipitate, which was isolated by filtration, washed with hexanes, and dried under vacuum. Yield: 0.134 g, 63.8%.

2.6. Preparation of $[\text{Mo}_2(\text{DAniF})_3]_2\text{Co}(\text{OCH}_3)_4$, **2.** This compound was prepared following method B as described but using CoCl_2 instead of ZnCl_2 . To a stirred suspension of $\text{Mo}_2(\text{DAniF})_3(\text{O}_2\text{CCH}_3)$ (0.506 g, 0.500 mmol) and anhydrous CoCl_2 (0.033 g, 0.25 mmol) in 25 mL of acetonitrile was added dropwise 3.2 mL of a NaOCH_3 solution (0.5 M in CH_3OH). The color changed from green to yellow, and a flocculent greenish-yellow precipitate formed. After another 4 h of stirring, the solid was separated by filtration and washed with acetonitrile (1×10 mL). Addition of CH_2Cl_2 to the solid, followed by filtration through a Celite-packed column, produced a red-brown solution. Addition of hexanes (50 mL) to the filtrate gave a brown precipitate which was isolated by filtration, washed with hexanes, and dried under vacuum. Yield: 0.295 g, 56.3%. UV-vis: λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 410 (5500), 480 (2500), 568 (74). Anal. Calcd for $\text{C}_{94}\text{H}_{102}\text{Mo}_4\text{N}_{12}\text{O}_{16}\text{Co}$: C, 53.80; H, 4.90; N, 8.01. Found: C, 53.90; H, 4.91; N, 8.03.

2.7. Preparation of $\text{Co}(\text{DPM})_2$, **3.** A modification of the procedure developed by Roger Soderberg was used.¹¹ To a stirred solution of dipivaloylmethane (2.50 g, 13.7 mmol) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.97 g, 6.85 mmol) in methanol (30 mL) was added 5 mL of an aqueous solution of NaOH (0.540 g, 13.5 mmol) dropwise. A reddish-pink precipitate formed immediately. The reaction mixture was stirred and heated to reflux for 2 h. The reddish-pink solid was isolated by filtration and extracted with diethyl ether (20 mL). A small amount of insoluble material was removed by filtration through a Celite-packed frit. When the volume of the filtrate was reduced under reduced pressure to ca. 5 mL, the product began to crystallize. After overnight storage in a refrigerator, large ruby-red crystals were collected by filtration. Yield: 2.45 g, 84.2%. UV-vis: λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 554 (70).

3. Results and Discussion

We have previously reported¹² many compounds in which $\text{Mo}_2(\text{DAniF})_3$ units are linked by dicarboxylate anions, and many more with long unsaturated linkers have since been prepared.¹³ Three compounds having Mo_2^{4+} units linked by

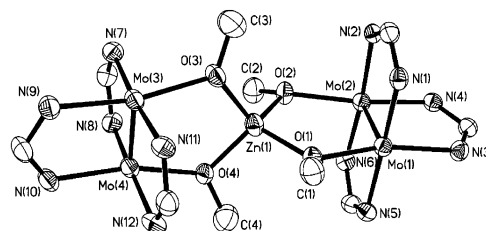


Figure 1. View of the core of **1** in $1 \cdot 3.83\text{CH}_2\text{Cl}_2$ drawn with 40% probability ellipsoids. All *p*-anisyl groups and solvent molecules have been omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1** and **2**

	$1 \cdot 3.83\text{CH}_2\text{Cl}_2$ (M = Zn)	$2 \cdot 3.76\text{CH}_2\text{Cl}_2$ (M = Co)
Mo(1)–Mo(2)	2.1169(7)	2.1162(7)
Mo(3)–Mo(4)	2.1113(8)	2.1142(9)
M–O(1)	1.946(4)	1.943(4)
M–O(2)	1.961(4)	1.956(4)
M–O(3)	1.942(4)	1.948(4)
M–O(4)	1.950(4)	1.942(4)
Mo(1)–N(1)	2.165(5)	2.155(5)
Mo(1)–N(3)	2.129(5)	2.120(5)
Mo(1)–N(5)	2.172(5)	2.162(5)
Mo(2)–N(2)	2.140(5)	2.153(5)
Mo(2)–N(4)	2.142(5)	2.125(5)
Mo(2)–N(6)	2.149(5)	2.142(5)
Mo(3)–N(7)	2.146(5)	2.181(5)
Mo(3)–N(9)	2.152(5)	2.098(7)
Mo(3)–N(11)	2.152(5)	2.163(5)
Mo(4)–N(8)	2.161(5)	2.151(5)
Mo(4)–N(10)	2.118(5)	2.139(6)
Mo(4)–N(12)	2.176(5)	2.149(5)
Mo(1)–O(1)	2.116(4)	2.139(4)
Mo(2)–O(2)	2.147(4)	2.130(4)
Mo(3)–O(3)	2.149(4)	2.110(4)
Mo(4)–O(4)	2.140(4)	2.139(4)
O(1)–M–O(2)	103.7(2)	103.2(2)
O(1)–M–O(4)	110.5(2)	108.5(2)
O(3)–M–O(1)	114.0(2)	117.1(2)
O(3)–M–O(4)	104.6(2)	103.4(2)
O(3)–M–O(2)	112.8(2)	106.2(2)
O(4)–M–O(2)	111.4(2)	119.2(2)

tetrahedral anions have also previously been reported,⁶ in which the bridging tetrahedral anions are SO_4^{2-} , MoO_4^{2-} , and WO_4^{2-} . For these, the independent existence of the anions allowed preparation by the obvious method of adding the anions, as tetraalkylammonium salts, to a solution of $[\text{Mo}_2(\text{DAniF})_3(\text{CH}_3\text{CN})_2]^+$ ions, but in the present work, the bridging anions were formed in situ from Zn^{2+} ions or Co^{2+} ions and methoxide ions.¹⁴

The first compound to be made had $\text{M} = \text{Zn}$; its core structure is shown in Figure 1. The principal bond lengths and angles are presented in Table 2. The dimensions of the $\text{Mo}_2(\text{DAniF})_3$ moieties are essentially the same as they have been in the many other compounds in which they are linked by other bridging groups such as dicarboxylate anions^{12,13} and EO_4^{2-} ions ($\text{E} = \text{S}, \text{Mo}, \text{W}$).⁶

(14) An attempt has been made to prepare the ethoxide analogue of **1** but without complete success. The compound obtained (by method A similar to that used for **1**) had a structure similar to that of **1**, but it appeared that some hydrolysis had occurred so that some μ -OEt groups were replaced by μ -OH groups. This compound also had electrochemistry very similar to that of **1** with reversible oxidation processes at -192 and $+42$ mV versus Ag/AgCl . Satisfactory refinement of the structure was not achieved, and no further work has been done on this compound.

(11) Soderberg, R. H. Ph.D. Thesis, Massachusetts Institute of Technology, 1962.

(12) Cotton, F. A.; Donahue, J. P.; Lin, C.; Murillo, C. A. *Inorg. Chem.* **2001**, *40*, 1234.

(13) Cotton, F. A.; Donahue, J. P.; Murillo, C. A. *J. Am. Chem. Soc.* **2003**, *125*, 5436.

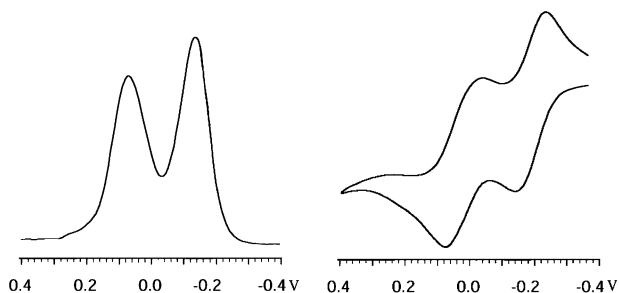


Figure 2. Electrochemistry of **1**. The DPVs are shown on the left and the CVs on the right. The electrochemistry of **2** is very similar to that of **1**.

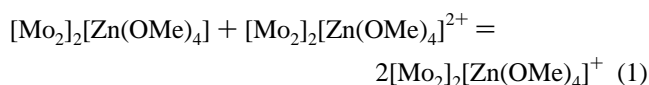
Table 3. Some Oxidation Potentials and Comproportionation Constants, K_C 's, for $[\text{Mo}_2](\text{linker})[\text{Mo}_2]^a$

linker	$E_{1/2}$ (1) mV	$E_{1/2}$ (2) mV	$\Delta E_{1/2}$ mV	K_C	ref
$\text{Zn}(\text{OME})_4^{2-}$	-208	4	212	3.8×10^3	this work
$\text{Co}(\text{OME})_4^{2-}$	-211	-4	207	3.2×10^3	this work
SO_4^{2-}	93	321	228	7×10^3	6
MoO_4^{2-}	81	392	311	2×10^5	6
WO_4^{2-}	102	387	285	7×10^4	6
$\text{O}_2\text{CCO}_2^{2-}$	294	506	212	3.8×10^3	13
$\text{O}_2\text{C}\equiv\text{CCO}_2^{2-}$	325	433	108	6.7×10	13

^a In all cases, the ratio of the anodic and cathodic current was nearly 1. Under similar experimental conditions, the Fc/Fc^+ couple had an $E_{1/2}$ of 450 mV.

The central portion of **1** has a zinc ion surrounded by four OCH_3 groups to give a distorted ZnO_4 tetrahedron. The distortion takes two forms. First, the $\text{O}-\text{Zn}-\text{O}$ angles that form part of the $\overline{\text{Zn}-\text{O}-\text{Mo}-\text{Mo}-\text{O}}$ rings are about 104° while the other four range from 110.6° to 113.9° . The variation in the latter corresponds to a slight tilting (ca. 3°) of the $\text{O}(15)-\text{Zn}-\text{O}(16)$ plane away from the S_4 axis that would be present in idealized D_{2d} symmetry. The chelate rings themselves deviate very little from planarity. Compound **1** has a ^1H NMR spectrum showing two methine signals in a ratio of 1:2 and other features in accord with the structure observed in the crystal.

The cyclic voltammogram (CV) and the differential pulse voltammogram (DPV) of **1** both show two reversible oxidation processes at 4 and -208 mV versus the Ag/AgCl reference electrode, as shown in Figure 2. This separation corresponds to a comproportionation constant,¹⁵ K_C , of 3.8×10^3 for reaction 1 (where $[\text{Mo}_2]$ represents the entire Mo_2 - $(\text{DAniF})_3$ moiety). From these results, it must be concluded that the efficiency of the $[\text{Zn}(\text{OME})_4]^{2-}$ bridging group in coupling the two $[\text{Mo}_2]$ units is comparable to that of several of the dicarboxylates and the SO_4^{2-} , MoO_4^{2-} , or WO_4^{2-} ion. It should be noted, however, that the redox potentials are negatively shifted by more than 300 mV, as shown in Table 3, relative to those of the EO_4^{2-} analogues.⁶ This probably reflects the increased basicity of $\text{M}(\text{OCH}_3)_4^{2-}$ linkers. For this reason the oxidized compounds are expected to be more robust.



In view of the fact that the tetrahedral complexes of cobalt(II) are very well-known,¹⁶ we were prompted to

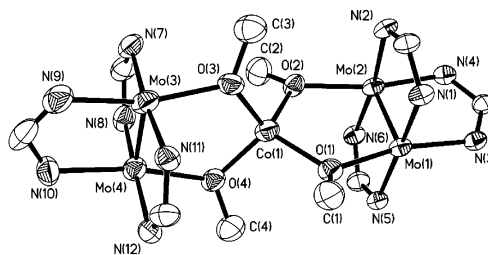


Figure 3. View of the core of **2** in $2 \cdot 3.76\text{CH}_2\text{Cl}_2$ drawn with 40% probability ellipsoids. All *p*-anisyl groups and solvent molecules have been omitted for clarity.

attempt the preparation of a cobalt analogue of **1**. This effort was successful and resulted in compound **2**. This molecule, Figure 3, is qualitatively isostructural with **1**, and the metrical parameters are listed in Table 2 for comparison with those of **1**. Since the crystals of **1** and **2** are not isomorphous, the molecules are not subject to the same packing forces in each case. As a result, the distortions of the CoO_4 “tetrahedron” are different from those of the ZnO_4 “tetrahedron”. The intraring $\text{O}-\text{Co}-\text{O}$ angles are quite similar, namely, ca. 103° , and the average value of the other four angles (112.8°) is also similar to that for **1** (112.2°). In the CoO_4 case there is a twist about what would be an S_4 axis in idealized D_{2d} symmetry such that the symmetry is reduced to only D_2 . It is quite possible that **1** and **2** both crystallize in both the $P\bar{1}$ and $P2_1/n$ forms and it is by pure chance that we happen to have chosen a crystal of **1** in the former and a crystal of **2** in the latter for X-ray study. We presume that in solution molecules of both compounds would have idealized D_{2d} symmetry.

Although the molecular structure of **2** *grosso modo* mimics that of **1**, the incomplete 3d-shell of the cobalt(II) ion affords access to spectroscopic and magnetic data not available for **1**, all of which may be compared with the voluminous data in the literature¹⁷ for the many well-characterized tetrahedral complexes of cobalt(II). The only disadvantage for **2** compared to **1** is that the ^1H NMR spectrum cannot be obtained. The situation here is very reminiscent of the way in which numerous enzymes which naturally have tetrahedrally coordinated zinc at the active site have been further studied by replacing the Zn^{2+} ion by a Co^{2+} ion.¹⁸

The electrochemistry of **2** closely resembles that of **1** (see Table 3). Again there are two successive oxidation processes, due to the oxidation of one Mo_2 unit and then the second

- (15) (a) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278. (b) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.
- (16) (a) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; John Wiley & Sons: New York, 1999; p 814. (b) *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, England, 1987; Vol. 1, p 254.
- (17) (a) Holm, R. H.; Cotton, F. A. *J. Chem. Phys.* **1959**, *31*, 788. (b) Holm, R. H.; Cotton, F. A. *J. Chem. Phys.* **1960**, *32*, 1168. (c) Cotton, F. A.; Goodgame, D. M. L.; Goodgame, M.; Sacco, A. *J. Am. Chem. Soc.* **1961**, *83*, 4157. (d) Cotton, F. A.; Goodgame, D. M. L.; Goodgame, M. *J. Am. Chem. Soc.* **1961**, *83*, 4690. (e) Cotton, F. A.; Soderberg, R. H. *J. Am. Chem. Soc.* **1962**, *84*, 872.
- (18) (a) Maret, W.; Vallee, B. L. *Methods Enzymol.* **1993**, *226*, 52. (b) Landro, J. A.; Schimmel, P. *Proc. Natl. Acad. Sci. U.S.A.* **1993**, *90*, 2261. (c) Auld, D. S. *Method Enzymol.* **1993**, *226*, 553. (d) Brown, D. C.; Collins, K. D. *J. Biol. Chem.* **1991**, *266*, 1597. (e) Schimmel, P.; Landro, J. A.; Schmidt, E. *J. Biomol. Struct. Dyn.* **1993**, *11*, 571.

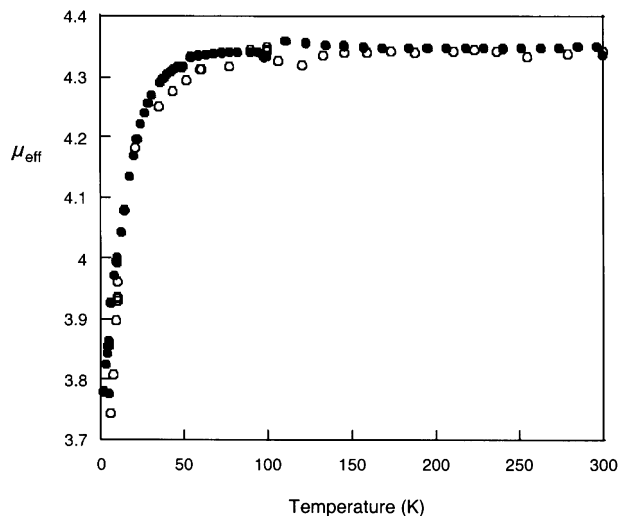


Figure 4. Plot of μ_{eff} vs $T(\text{K})$ for $2 \cdot 3.76\text{CH}_2\text{Cl}_2$ (○) and **3** (●).

one. The exact positions are slightly different, but the separation and hence the K_C values are nearly the same. Thus, the tetramethoxyzinc and tetramethoxycobalt bridges differ very little in their ability to mediate the coupling (as measured by electrochemistry) between the two.

Tetrahedrally coordinated cobalt(II) has three d–d transitions, only one of which occurs in the visible,^{16,17} with the other two in the near-infrared. For **2**, the visible d–d transition has been observed in the expected region. Because of its low intensity, its profile is not sharply defined, but it appears to have the shape generally observed for the ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{P})$ transition.^{17d} The position and low intensity of this band are fully in accord with the previously established correlations.^{17e} No effort was made to observe the other transitions because, on the basis of what is known,¹⁷ the prospects for success would be very low. The magnetic susceptibility of **2** (Figure 4) was measured from 5 to 300 K. The overall behavior is as expected, with the value of μ_{eff} being constant from 100 to 300 K at $4.34 \pm 0.02 \mu_{\text{B}}$.

It is possible to view compounds **1** and **2** as tetrahedral bis-chelate complexes of Zn^{2+} and Co^{2+} , with the chelating ligands being $[(\text{DAniF})_3\text{Mo}_2(\text{OMe})_2]^-$. This is a valid alternative to formulating them as two $[(\text{DAniF})_3\text{Mo}_2]^+$ ions linked by a $[\text{M}(\text{OMe})_4]^{2-}$ bridge. This point of view suggests comparison with the previously known $\text{M}(\text{DPM})_2$ (DPM represents the anion of dipivaloylmethane) compounds. Accordingly, we have done further work with both $\text{Co}(\text{DPM})_2$ (**3**)^{11,17e} and its isomorphous analogue $\text{Zn}(\text{DPM})_2$. Structural characterization of $\text{Zn}(\text{DPM})_2$ was reported¹⁹ in 1964, but the structure of the cobalt isomorph was never directly determined. We have now done that, with the results

(19) Cotton, F. A.; Wood, J. S. *Inorg. Chem.* **1964**, *3*, 245.

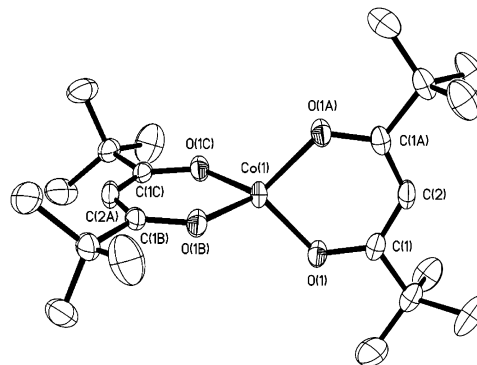


Figure 5. View of **3** drawn with 40% probability ellipsoids.

Table 4. Geometric Parameters of Tetrahedral Moieties of **1**, **2**, and Mononuclear Complexes $\text{M}(\text{DPM})_2$ ($\text{M} = \text{Zn}, \text{Co}$)

	1	2	$\text{Zn}(\text{DPM})_2$	$\text{Co}(\text{DPM})_2$ (3)
M–O (Å, av)	1.950[5] ^a	1.947[5]	1.962(7)	1.931(1)
O–M–O (close) (deg, av)	104.2[2]	103.3[2]	114.2(6)	116.90(4)
O–M–O (open) (deg, av)	112.2[3]	112.6[3]	94.7(6)	95.46(6)

^a Numbers in square brackets refer to errors in average values.

presented in Tables 1 and 4, and the comparison of the numerical data for molecules of **3** and $\text{Zn}(\text{DPM})_2$ can be seen in Table 4. A drawing of molecule **3** is shown in Figure 5. Both have strict D_{2d} symmetry for crystallographic reasons, and the dimensions are very similar. The visible spectrum of **3**, which, like **2**, is a bright red compound, is similar to that of **2**. Moreover, as shown in Figure 4, the magnetic susceptibilities of **2** and **3** are practically identical from 5 to 300 K.

It is also pertinent to recall that even though no $\text{Co}(\text{OR})_4^{2-}$ species have been described in the literature, there is evidence^{17d} for the existence of what is probably a mixture of $\text{Co}(\text{OH})_4^{2-}$ and $\text{Co}(\text{OH})_3(\text{H}_2\text{O})^-$ in solutions obtained by dissolving $\text{Co}(\text{OH})_2$ in concentrated aqueous alkali metal hydroxides. However, no solid compound containing such species has ever been described, and the characterization of the species in solution is sketchy.

Acknowledgment. We thank the National Science Foundation, the Robert A. Welch Foundation, and Texas A&M University (through the Laboratory for Molecular Structure and Bonding) for financial support. We also thank Prof. R. H. Soderberg for some information and J. F. Berry and D. Villagrán for help with magnetic measurements.

Supporting Information Available: UV–vis spectrum of **2** in PDF format and X-ray crystallographic data in CIF format for **1**· $3.83\text{CH}_2\text{Cl}_2$, **2**· $3.76\text{CH}_2\text{Cl}_2$, and **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC034167F