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MIXED-LIGAND SYSTEMS CONTAINING QUADRUPLE BONDS. CAPTURE AND STRUCTURAL CHARACTERIZATION OF AN INTERMEDIATE IN THE LIGAND EXCHANGE PROCESS LEADING TO NEW CARBOXYLATES OF THE DIMOLYBDENUM(4+) UNIT. SYNTHESIS AND X-RAY CRYSTALLOGRAPHIC AND ELECTROCHEMICAL STUDIES OF $Mo_2[(\eta^5\text{-}C_5H_4CO_2)Fe(\eta^5\text{-}C_5H_5)]_2(O_2CCH_3)_2(C_5H_5N)_2$ AND $[Mo_2[(\eta^5\text{-}C_5H_4CO_2)Fe(\eta^5\text{-}C_5H_5)]_4(ax\text{-}CH_3CN)(ax\text{-}DMSO)](DMSO)_2$

F.A. COTTON, L.R. FALVELLO, A.H. REID, Jr. and J.H. TOCHER

Department of Chemistry and the Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station TX 77843 (U.S.A.)

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Summary

The compounds $Mo_2[(\eta^5\text{-}C_5H_4CO_2)Fe(\eta^5\text{-}C_5H_5)]_2(O_2CCH_3)_2(C_5H_5N)_2$ and $[Mo_2[(\eta^5\text{-}C_5H_4CO_2)Fe(\eta^5\text{-}C_5H_5)]_4(ax\text{-}CH_3CN)(ax\text{-}DMSO)](DMSO)_2$ have been prepared by ligand exchange on $Mo_2(O_2CCH_3)_4$ by ferrocenemonocarboxylic acid. The first compound, an intermediate in the complete carboxylate exchange process used in the synthesis of more exotic carboxylates of the quadruply-bonded dimolybdenum(4+) unit crystallizes in the orthorhombic system, space group *Pbca* (no. 61), with a 8.063(1), b 20.653(2), c 21.095(1) Å, V 3513(3) Å^3 and $Z = 4$. The structure was refined to discrepancy indices $R_1 = 0.057$ and $R_2 = 0.068$. The compound is (a) the first reported tetracarboxylate of dimolybdenum(4+) possessing two different carboxylate ligands; (b) an example of the relatively rare *trans* geometry seen only infrequently in dimers containing a mixture of bridging ligands. The second compound is the final product for the ligand exchange process. It crystallizes in the triclinic system, space group $P\bar{1}$ (no. 2), with a 11.877(7), b 13.491(11), c 9.922(12) Å, α 105.57(2), β 105.62(2), γ 101.86(2)°, V 1407(6) Å^3 and $Z = 1$. The compound possesses both eclipsed and staggered ferrocene moieties. The structure was refined to discrepancy indices $R_1 = 0.0632$ and $R_2 = 0.107$. Both compounds exhibit one-electron oxidations with potentials very close to that of the ferrocene-ferrocenium couple itself. Attempts to further oxidize either of the compounds led to their destruction.

Introduction

A common thread running through the chemistry of the middle transition elements is the facility with which these elements form dimeric complexes containing four bridging carboxylate groups and possessing strong metal–metal bonds [1]. Such species are known for Cr [2], Mo [3], W [4], Tc [5], Re [6], Ru [7], Os [8] and Rh [9]. Prototypal of these species is of course $Mo_2(O_2CCH_3)_4$, first reported by Stephenson, Bannister and Wilkinson [10], structurally characterized first by Lawton and Mason [11] and subsequently with greater accuracy by Cotton, Mester and Webb [12]. Over the years this compound has become the starting material of choice for the synthesis of other carboxylates and of a myriad of other multiply-bonded dimers of molybdenum [13].

The mechanism by which the aforementioned ligand exchanges occur has not yet been extensively examined, although a few studies of this process [14–16] have been reported. There has been no report of the isolation and characterization of any intermediates of stoichiometry $M_2(O_2CCH_3)_{4-n}(O_2CR)_n$ from the pure carboxylate exchange process, although ring-opening processes in which the $M_2O_2C_2$ fragment of the skeleton of the complex is disrupted by the addition of small phosphines have been documented by the structural characterization of the adducts resulting from these processes [17,18].

In the course of our studies of the use of the anion of ferrocenemonocarboxylic acid (hereafter designated FCA) as a ligand we prepared the title compounds. The tetrakis compound constitutes the first dimetal carboxylate in which a second, different metal (Fe in this case) is contained in the pendant group of a carboxylate ligand. We report single-crystal X-ray studies and electrochemical studies of the title compounds herein.

Experimental

All operations were carried out under an atmosphere of prepurified argon using standard Schlenk techniques. $Mo_2(O_2CCH_3)_4$ was prepared according to previously-reported [19] methods. Pyridine was stored over KOH for 48 h and was subsequently distilled from BaO under argon. Dimethylsulfoxide was stirred over 3Å molecular sieves and purged with argon prior to use. Acetonitrile was distilled from P_2O_5 under argon. All reagents were commercially obtained and were of reagent grade or better. Electrochemical studies were carried out in DMF on a BAS-100 electrochemical apparatus with platinum electrodes and 0.1 *M* tetrabutylammonium perchlorate as a supporting electrolyte.

Trans-$Mo_2(O_2CCH_3)_2(FCA)_2(C_5H_5N)_2$

FCAH (1.63 g, 1.87 mmol) was dissolved in 25 ml pyridine with stirring. $Mo_2(O_2CCH_3)_4$ (0.20 g, 0.469 mmol) was added and stirring was maintained for an additional 3 h. The initially bright orange solution turns crimson after ca. 10 min. Schlenk filtration followed by washing with hexane and removal of excess solvent in vacuo yielded 0.36 g of the dimer, 96% yield based on the acetate. Crystals suitable for X-ray diffraction were grown by placing a layer of hexane over a dilute solution of the complex in pyridine and allowing slow interdiffusion of solvents to take place. Crystals in the form of large red hexagonal plates resulted within 3 d at room temperature.

$[Mo_2(FCA)_4(ax\text{-}CH_3CN)(ax\text{-}DMSO)](DMSO)_2$

$Mo_2(O_2CCH_3)_4$ (0.20 g, 0.469 mmol) was added to a solution of FCAH (1.07 g, 4.7 mmol) in THF (30 ml). The initially orange homogeneous solution rapidly goes to a dark orange suspension. After stirring for 2 h the reaction mixture was filtered through a medium porosity frit to yield an orange-red solid. The solid was dried in vacuo and washed with hexane. The solid was redissolved in a 1 : 1 mixture of dimethylsulfoxide/acetonitrile and the resulting solution was covered with a layer of hexane in a Schlenk tube under argon. After 3 d of interdiffusion of solvents large red crystals of $[Mo_2(FCA)_4(ax\text{-}CH_3CN)(ax\text{-}DMSO)](DMSO)_2$ (0.406 g, 83% yield based on the acetate) had formed and were used for the structural analysis.

X-Ray crystallography, structural solution and refinement

(a) trans-$Mo_2(O_2CCH_3)_2(FCA)_2(C_5H_5N)_2$. A hexagonal plate of dimensions

TABLE 1

CRYSTALLOGRAPHIC PARAMETERS FOR *trans*-$Mo_2(FCA)_2(O_2CCH_3)_2(C_5H_5N)_2$ AND $[Mo_2(FCA)_4(ax\text{-}CH_3CN)(ax\text{-}DMSO)](DMSO)_2$

Formula	$Mo_2Fe_2O_8N_2C_{36}H_{36}$	$Mo_2Fe_4S_3O_{11}NC_{52}H_{57}$
Formula weight	928.3	1383.5
Space group	*Pbca*	$P\bar{1}$
Systematic absences	$0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h = 2n + 1$	none
a (Å)	8.063(1)	11.877(7)
b (Å)	20.653(2)	13.491(11)
c (Å)	21.095(1)	9.922(12)
α (°)		105.57(2)
β (°)		105.62(2)
γ (°)		101.86(2)
V (Å^3)	3513(3)	1407(6)
Z	4	1
d_{calc} (g cm^{-3})	1.755	1.632
Crystal size (mm)	0.30 × 0.30 × 0.10	0.70 × 0.40 × 0.30
μ(Mo-K_α) (cm^{-1})	15.450	16.2
Data collection instrument	Syntex $P\bar{1}$	Enraf–Nonius CAD4/F
Radiation (monochromated in incident beam)	Mo-K_α	Mo-K_α
Orientation reflections, number, range (2θ)	15, $27.0 < 2\theta < 43.0$	25, $13.77 < 2\theta < 28.16$
Temperature (°C)	22 ± 1	22 ± 1
Scan method	$\omega-2\theta$	$\theta-2\theta$
Data col. range, 2θ, (°)	$5.0 < 2\theta < 55.0$	$4.0 < 2\theta < 50.0$
No. unique data, total with $F_O^2 > 3\sigma(F_O^2)$	882	4525
Number of parameters refined	196	308
Trans. factors, max., min. (exp.)	0.998, 0.810	0.620, 0.250
R [a]	0.057	0.063
R_w [b]	0.068	0.107 [d]
Quality-of-fit indicator	1.209	1.385
Largest shift/esd, final cycle	0.32	0.34
Largest peak (e Å^{-3})	0.568	1.74

[a] $R = \Sigma||F_O| - |F_c||/\Sigma|F_O|$. [b] $R_w = [\Sigma w(|F_O| - |F_c|)^2/\Sigma w|F_O|2]^{1/2}$; $w = 1/\sigma^2(|F_O|)$. [c] Quality-of-fit $= [\Sigma w(|F_O| - |F_c|^2)/(N_{obs} - N_{param})]^{1/2}$. [d] The weighting scheme used $w = 1/[\sigma^2(|F_O|) + (0.07|F_O|)^2 + 4.0]$.

0.30 × 0.30 × 0.10 mm was mounted in a random orientation within a Lindemann capillary with epoxy cement and was installed on the goniometer of a Syntex P$\bar{1}$ autodiffractometer. Data collection procedures have been fully described elsewhere [20]. Lorentz and polarization corrections were applied to the data, as was an empirical absorption correction. Of the 4032 unique data potentially available, only 882 had $F_0^2 > 3\sigma(F_0^2)$; the weak (and hence neglected) reflections were mostly in the 2θ range 45° to 55°.

The positions of the Mo and Fe atoms were determined by the solution of the three-dimensional Patterson synthesis. Two cycles of isotropic full-matrix least-squares refinement gave discrepancy indices of $R_1 = 0.2443$ and $R_2 = 0.3318$. Subsequent alternation of difference Fourier syntheses and cycles of full-matrix least-squares refinement led to isotropic convergence of the structural model at discrepancy indices $R_1 = 0.079$ and $R_2 = 0.093$. Application of anisotropic thermal parameters to all non-hydrogen atoms save those of the axial pyridine ligand led to anisotropic convergence at discrepancy indices $R_1 = 0.057$ and $R_2 = 0.068$. The estimated standard deviation in an observation of unit weight was 1.209, with a final shift/esd of 0.320. The largest peak in the final difference Fourier map had an intensity of 0.568e/Å^3 and was not structurally significant. Relevant crystallographic data are given in Table 1.

(b) [$Mo_2(FCA)_4(ax\text{-}CH_3CN)(ax\text{-}DMSO)](DMSO)_2$. A rhombic tablet of approximate dimensions 0.50 × 0.50 × 0.40 mm was affixed to the end of a glass fiber with epoxy cement and was installed on an Enraf–Nonius CAD/4F diffractometer. The standard procedures of using the SEARCH routine of the instrument followed by indexing and least-squares gave a triclinic cell. Data collection procedures have been described previously [20]. An empirical absorption correction as well as corrections for Lorentz and polarization effects were applied to all data.

The positions of the heavy atoms were determined via use of the direct methods program package MULTAN80. All non-hydrogen atoms comprising the dimeric unit were located by alternation of cycles of full matrix least-squares refinement and difference Fourier syntheses. Both the axial ligands and the lattice solvent molecules were badly disordered (see Discussion). The final structural model refined to discrepancy indices $R_1 = 0.063$ and $R_2 = 0.107$. Relevant crystallographic data are given in Table 1.

Discussion

The ORTEP diagram of the structure of *trans*-$Mo_2(O_2CCH_3)_2(FCA)_2(Py)_2$ is given in Fig. 1. Positional parameters and selected bond distances and angles are given in Tables 2 and 3. The *trans* disposition of ligands about the metal–metal bond is readily apparent, and of itself deserves further comment. Although this compound is the first of the dimolybdenum(4 +) unit containing two different monocarboxylate ligands, it is not the first example of a structurally-characterized partially-substituted carboxylate. The bridging ligands (4-phenylamino)-2-pentanoide [21], diethylpyrazolylborate [22], acetylacetonate [23] and tetrakisisopropoxyaluminum(1 −) [24] have all been successfully substituted for two of the four acetate bridges in $Mo_2(O_2CCH_3)_4$. Interestingly all of the aforementioned complexes save the last exhibit a *cis* geometry in the solid state.

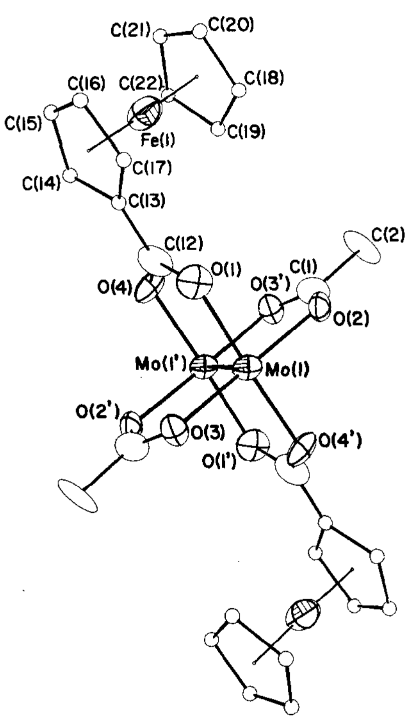

Fig. 1. ORTEP diagram of *trans*-$Mo_2(O_2CCH_3)_2(FCA)_2(C_5H_5N)_2$, indicating the atom numbering scheme. For clarity, the axial pyridine ligands have been omitted, and the carbon atoms of the ferrocenyl groups have been drawn as small circles. All other atoms are represented by their 50% probability ellipsoids.

In light of the fact that a different compound (i.e., $Mo_2(FCA)_4$) results if any of a number of solvents (THF, benzene, DMSO, CH_3CN, toluene, etc.) other than pyridine is employed in the synthesis of these FCA complexes, it may be assumed that the donor strength of pyridine plays a role in the choice of both geometry and stoichiometry of the product obtained. Evidence has been presented that indicates that pyridine assists in the reported opening of the M_2O_2C ring in, e.g., $Mo_2(O_2CCF_3)_4$ [15] and $Mo_2(OSCCH_3)_4$ [16]. If a large excess of a strong donor is present, labilizing acetate groups by attacking the Mo–O bond [15], it is possible that the ability of the FCA anion to replace acetate in such a competition drops to almost nothing after the replacement of two acetate groups. The adoption of a *trans* geometry may be a reflection of electronic factors, but the presence of a large organometallic moiety attached to the $-CO_2$ bridge is presumably of considerable importance. Whether or not the presence of pyridine plays a critical role in the geometrical preference is open to discussion, although the recently-reported [25] $Mo_2(SO_4)_2(Py)_4(ax\text{-}Py)_2$ possesses a *trans* geometry and is preferentially formed in pyridine solution. We are currently attempting to determine whether or not other partially-substituted species can be obtained in this same simple fashion.

The presence of axial ligands is hardly surprising, as adducts of the general formula $M_2(O_2CR)_4L_2$ are quite common [1]. The Mo–N_{ax} distance of 2.645(17) Å is much longer than the analogous distance (2.548(8) Å) in $Mo_2(O_2CCF_3)_4(Py)_2$

TABLE 2

ATOMIC POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS (Å^2) AND THEIR ESTIMATED STANDARD DEVIATIONS FOR *trans*-$Mo_2(O_2CCH_3)_2(FCA)_2(C_5H_5N)_2$

Atom	x	y	z	B (Å^2) ^{a}
Mo(1)	0.0597(2)	0.00713(7)	0.04387(7)	2.38(3)
Fe(1)	0.3535(5)	0.1973(2)	−0.1198(2)	4.32(8)
O(1)	0.143(2)	0.1002(6)	0.0159(5)	3.6(3)
O(2)	0.284(2)	−0.0307(6)	0.0102(5)	2.8(3)
O(3)	−0.158(2)	0.0459(6)	0.0841(5)	2.9(3)
O(4)	0.013(2)	0.0854(5)	−0.0777(5)	3.2(3)
N(1A)	0.306(2)	0.5487(8)	0.1506(8)	3.7(4)*
C(1)	0.283(2)	−0.0491(9)	−0.0492(9)	3.3(5)
C(2)	0.452(3)	−0.073(1)	−0.075(1)	5.0(6)
C(12)	0.098(2)	0.1189(9)	−0.0416(8)	3.0(4)
C(13)	0.153(3)	0.1827(8)	−0.0612(9)	5.0(6)
C(14)	0.105(3)	0.216(1)	−0.120(1)	4.8(6)
C(15)	0.205(3)	0.275(1)	−0.122(1)	5.5(7)
C(16)	0.296(3)	0.281(1)	−0.069(1)	4.8(6)
C(17)	0.262(4)	0.2220(9)	−0.032(1)	6.4(7)
C(18)	0.557(3)	0.139(1)	−0.112(1)	7.2(7)
C(19)	0.433(4)	0.110(1)	−0.149(1)	8.2(8)
C(20)	0.603(3)	0.200(1)	−0.140(1)	7.3(8)
C(21)	0.516(3)	0.206(1)	−0.196(1)	5.8(7)
C(22)	0.404(3)	0.153(1)	−0.203(1)	7.6(8)
C(100)	0.266(3)	0.502(1)	0.1949(9)	3.9(4)*
C(200)	0.198(3)	0.523(1)	0.254(1)	5.5(6)*
C(300)	0.177(3)	0.5888(9)	0.264(1)	4.2(5)*
C(400)	0.214(3)	0.634(1)	0.216(1)	5.3(6)*
C(500)	0.284(3)	0.6087(9)	0.1617(9)	3.3(5)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

[26], although not enormously different from the Mo–O_{ax} distance (2.663(6) Å) in $Mo_2(O_2CPh)_4(diglyme)_2$ [27]. The solid-state structure of $Mo_2(O_2CPh)_4(Py)_2$ has not been determined, but it seems a safe assumption that the Mo–N_{ax} distance would be comparable to that found in the disubstituted FCA compound.

The structure of the tetrakis compound is depicted in the ORTEP diagram given in Fig. 2. Positional parameters and bond distances and angles are given in Tables 4 and 5 respectively. The Mo–Mo distance (2.105(1) Å) is identical within experimental error to that in the disubstituted compound, and is indicative of the presence of a strong quadruple molybdenum–molybdenum bond. The C–C distances (1.419(9) Å, av.), C–C–C angles (108.0(5)°, av.) and Fe–C distances (2.044(5) Å, av.) are all in the normal range for ferrocene and simple substituted ferrocene derivatives [28,29]. The two sets of mutually-*trans* ferrocenyl moieties exhibit both eclipsed and staggered configurations, as has been observed for the analogous dicopper complex [30]. The dicopper and dimolybdenum compounds are the first reported containing purely carbocyclic ferrocenyl moieties in both of the possible limiting conformations.

TABLE 3

SELECTED BOND DISTANCES (Å) AND ANGLES (°) AND THEIR ESTIMATED STANDARD DEVIATIONS FOR *trans*-$Mo_2(O_2CCH_3)_2(FCA)_2(C_5H_5N)_2$

Mo(1′)–Mo(1)	2.107(2)	Mo(1)–O(3)	2.107(12)	Fe(1)–C(ring)	2.047(8) [a]
Mo(1)–O(1)	2.120(13)	Mo(1)–O(4)	2.123(11)	C(ring)–C(ring)	1.42(1) [a]
Mo(1)–O(2)	2.096(12)	Mo(1)–N(1A)	2.64(2)		
Mo(1′)–Mo(1)–O(1)	91.5(3)	O(1)–Mo(1)–O(2)	88.4(5)	O(2)–Mo(1)–O(4)	91.1(5)
Mo(1′)–Mo(1)–O(2)	92.6(3)	O(1)–Mo(1)–O(3)	91.7(5)	O(2)–Mo(1)–N(1A)	93.2(5)
Mo(1′)–Mo(1)–O(3)	91.5(3)	O(1)–Mo(1)–O(4)	176.0(5)	O(3)–Mo(1)–O(4)	88.5(5)
Mo(1′)–Mo(1)–O(4)	92.4(3)	O(1)–Mo(1)–N(1A)	79.2(5)	O(3)–Mo(1)–N(1A)	82.8(5)
Mo(1′)–Mo(1)–N(1A)	168.9(4)	O(2)–Mo(1)–O(3)	175.9(5)	O(4)–Mo(1)–N(1A)	96.9(5)

[a] Indicates average distances.

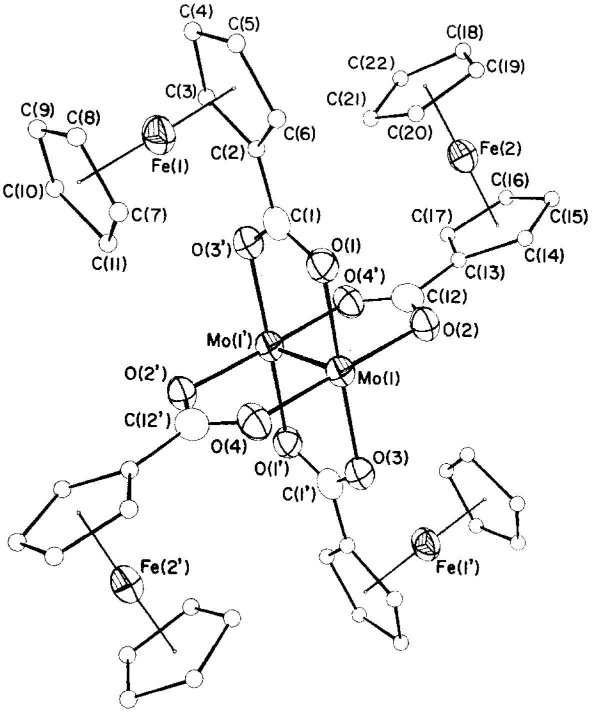

Fig. 2. ORTEP drawing of $Mo_2(FCA)_4(ax\text{-}CH_3CN)(ax\text{-}DMSO)$, indicating the atom numbering scheme. For clarity, the axial ligands have been omitted, and the carbon atoms of the ferrocenyl groups have been drawn as small circles. All other atoms are represented at the 50% probability level.

The structural study of the tetrakis compound presented difficulties due to severe absorption and disorder problems. An initial attempt to refine the structure in the acentric space group $P1$ met with failure in the form of large correlation effects and the resultant impossibility of assigning anisotropic thermal parameters to the non-hydrogen atoms. Conversion of the model into the centric space group $P\bar{1}$ led to a successful refinement. Disordered models for the lattice dimethylsulfoxide molecules were included in the refinement. A process of trial and error was used to determine the identities of the axial ligands, which resulted in the conclusion that an approximately "half and half" model comprising a dimethylsulfoxide and an acetonitrile molecule was the best possible treatment for the disorder. This led to final discrepancy indices of $R_1 = 0.063$ and $R_2 = 0.1062$. The esd's on the important distances and angles, viz., those within the dimer itself, are well within acceptable limits of error and the final structure may be taken as being an accurate representation of the tetrakis compound.

Attempts to cause stepwise oxidations of the ferrocenyl residues in both compounds were carried out electrochemically with limited success. Although an initial reversible oxidation is seen for both of the title compounds near the potential of the ferrocene–ferrocenium couple (to +0.52 V vs. Ag/AgCl, subsequent irreversible processes ensue that result in the destruction of the complexes. The observed

TABLE 4

ATOMIC POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS (Å^2) AND THEIR ESTIMATED STANDARD DEVIATIONS FOR $Mo_2(FCA)_4LL' \cdot 2Me_2SO$

Atom	x	y	z	B (Å^2) [a]
Mo(1)	−0.01547(4)	0.02612(3)	0.10148(4)	2.703(9)
Fe(1)	0.43075(7)	0.32163(6)	0.21607(9)	3.45(2)
Fe(2)	0.25769(7)	−0.25373(6)	0.17893(9)	3.69(2)
O(1)	0.1718(3)	0.1096(3)	0.2202(4)	3.07(8)
O(2)	0.0129(3)	−0.1126(3)	0.1477(4)	3.21(8)
O(3)	−0.2056(3)	−0.0529(3)	−0.0084(4)	3.06(8)
O(4)	−0.0437(3)	0.1679(3)	0.0670(4)	3.27(8)
C(1)	0.2430(5)	0.1073(4)	0.1459(5)	2.8(1)
C(2)	0.3717(5)	0.1702(4)	0.2196(6)	3.2(1)
C(3)	0.4623(5)	0.1757(4)	0.1511(7)	3.6(1)
C(4)	0.5737(5)	0.2574(5)	0.2600(8)	4.6(2)
C(5)	0.5476(6)	0.2997(5)	0.3912(7)	4.3(1)
C(6)	0.4233(6)	0.2476(5)	0.3688(6)	3.9(1)
C(7)	0.3436(8)	0.4378(6)	0.252(1)	7.7(2)
C(8)	0.4622(9)	0.4830(5)	0.267(1)	6.9(2)
C(9)	0.4769(8)	0.4438(6)	0.1377(9)	6.8(2)
C(10)	0.3761(9)	0.3625(6)	0.0287(9)	7.0(2)
C(11)	0.2851(8)	0.3546(6)	0.101(1)	8.6(2)
C(12)	0.0413(5)	−0.1778(4)	0.0551(6)	3.2(1)
C(13)	0.0784(5)	−0.2674(4)	0.0925(7)	4.0(1)
C(14)	0.1035(6)	−0.2772(5)	0.2380(8)	4.9(1)
C(15)	0.1479(7)	−0.3687(5)	0.2290(8)	5.8(2)
C(16)	0.1490(8)	−0.4150(5)	0.085(1)	6.4(2)
C(17)	0.1056(6)	−0.3511(5)	−0.0036(9)	5.3(2)
C(18)	0.4408(6)	−0.2378(6)	0.2607(9)	5.1(2)
C(19)	0.4128(6)	−0.1566(5)	0.3569(8)	4.8(2)
C(20)	0.3607(6)	−0.0971(5)	0.2682(9)	5.3(2)
C(21)	0.3572(7)	−0.1389(6)	0.1255(8)	5.8(2)
C(22)	0.4090(7)	−0.2272(7)	0.1203(9)	6.4(2)
O(5),N	0.0857(5)	0.0498(4)	0.3272(6)	4.7(1)*
S(1)	−0.2053(2)	−0.0361(2)	0.3025(2)	2.49(5)
C(23)	−0.1654(9)	0.0323(8)	0.407(1)	2.9(2)*
C(24)	−0.192(1)	−0.0431(9)	0.477(1)	9.3(3)*
C(25)	−0.314(1)	0.0309(9)	0.284(1)	3.5(2)*
S(2)	0.8288(7)	0.5972(6)	0.4635(8)	20.3(3)
O(6)	0.826(2)	0.485(2)	0.508(2)	26.2(8)*
C(26)	0.969(2)	0.676(1)	0.575(2)	13.7(5)*
C(27)	0.847(2)	0.564(2)	0.287(3)	17.3(7)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

reversible oxidations were shown to be one-electron processes via coulometric studies.

Supplementary Material Available. Tables of observed and calculated structure factors, anisotropic thermal parameters and full tables of bond distances and angles (38 p). Ordering information is given on any current masthead page.

TABLE 5

SELECTED BOND DISTANCES (Å) AND ANGLES (°) AND THEIR ESTIMATED STANDARD DEVIATIONS FOR $Mo_2(FCA)_4LL'\cdot 2Me_2SO$

Mo(1)–Mo(1′)	2.105(1)	O(2)–C(12)	1.260(7)	C(13)–C(14)	1.441(9)
Mo(1)–O(1)	2.109(3)	O(3)–C(1′)	1.265(6)	C(13)–C(17)	1.423(9)
Mo(1)–O(2)	2.112(3)	O(4)–C(12′)	1.261(7)	S(1)–O(5)	1.551(5)
Mo(1)–O(3)	2.118(3)	C(1)–C(2)	1.457(7)	S(1)–C(24)	1.722(13)
Mo(1)–O(4)	2.108(3)	C(2)–C(3)	1.419(8)	S(1)–C(25)	1.721(11)
Mo(1)–O(5),N	2.558(5)	C(2)–C(6)	1.441(8)	C(23)–N	1.414(11)
O(1)–C(1)	1.263(6)	C(12)–C(13)	1.471(7)	C(23)–C(24)	1.402(15)
Mo(1′)–Mo(1)–O(1)	92.5(1)	O(3)–Mo(1)–O(5),N	80.3(1)	O(2)–C(12)–C(13)	119.1(5)
Mo(1′)–Mo(1)–O(2)	91.0(1)	O(4)–Mo(1)–O(5),N	95.5(2)	O(4′)–C(12)–C(13)	117.9(5)
Mo(1′)–Mo(1)–O(3)	90.4(1)	Mo(1)–O(1)–C(1)	116.8(3)	C(12)–C(13)–C(14)	124.2(6)
Mo(1′)–Mo(1)–O(4)	92.0(1)	Mo(1)–O(2)–C(12)	117.3(3)	C(12)–C(13)–C(17)	125.7(6)
Mo(1′)–Mo(1)–O(5),N	167.9(1)	Mo(1)–O(3)–C(1′)	118.3(3)	C(14)–C(13)–C(17)	109.9(5)
O(1)–Mo(1)–O(2)	89.6(1)	Mo(1)–O(4)–C(12′)	116.5(3)	O(5)–S(1)–C(24)	104.6(5)
O(1)–Mo(1)–O(3)	117.0(1)	O(1)–C(1)–O(3′)	121.9(4)	O(5)–S(1)–C(25)	103.8(4)
O(1)–Mo(1)–O(4)	89.8(1)	O(1)–C(1)–C(2)	119.3(4)	C(24)–S(1)–C(25)	99.3(6)
O(1)–Mo(1)–O(5),N	97.1(1)	O(3′)–C(1)–C(2)	118.8(4)	N–C(23)–C(24)	134.0(9)
O(2)–Mo(1)–O(3)	91.3(1)	C(1)–C(2)–C(3)	125.7(5)	Mo(1)–O(5)–S(1)	115.0(3)
O(2)–Mo(1)–O(4)	177.0(1)	C(1)–C(2)–C(6)	124.9(5)	Mo(1)–N–C(23)	157.4(5)
O(2)–Mo(1)–O(5),N	81.6(2)	C(3)–C(2)–C(6)	109.0(5)		
O(3)–Mo(1)–O(4)	89.2(1)	O(2)–C(12)–O(4′)	123.0(5)		

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References

1 F.A. Cotton and R.A. Walton, Multiple Bonds Between Metal Atoms, Wiley-Interscience, New York, 1982.
2 (a) E. Peligot, C.R. Acad. Sci., 19 (1844) 609; (b) F.A. Cotton, M.W. Extine and G.W. Rice, Inorg. Chem., 17 (1978) 176.
3 Reference 1, Chapter 3.
4 (a) A.P. Sattelberger, K.W. McLaughlin and J.C. Huffman, J. Am. Chem. Soc., 103 (1981) 2880; (b) F.A. Cotton and W. Wang, Inorg. Chem., 21 (1982) 3859.
5 F.A. Cotton and L.D. Gage, Nouv. J. Chem., 1 (1977) 441.
6 Reference 1, Chapter 2.
7 (a) M. Mukaida, T. Nomura and T. Ishimori, Bull. Chem. Soc. Japan, 40 (1967) 2462; (b) 45 (1972) 2143.
8 (a) T.A. Stephenson, D.A. Tocher and M. Walkinshaw, J. Organomet. Chem., 332 (1982) C51; (b) T. Behling, G. Wilkinson, T.A. Stephenson, D.A. Tocher and M. Walkinshaw, J. Chem. Soc., Dalton Trans., (1983) 2109.
9 T.R. Felthouse in S.J. Lippard (Ed.), Progress in Inorganic Chemistry, Vol. 29, Wiley-Interscience, New York, 1982, p. 73.
10 T.A. Stephenson, E. Bannister and G. Wilkinson, J. Chem. Soc., (1964) 2538.
11 D. Lawton and R. Mason, J. Am. Chem. Soc., 87 (1965) 921.
12 F.A. Cotton, Z.C. Mester and T.R. Webb, Acta Crystallogr., B30 (1974) 2768.
13 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 4th ed., Wiley-Interscience, New York, 1980, p. 875.
14 K. Teramoto, Y. Sasaki, K. Magita, M. Iwaizumi and K. Saito, Bull. Chem. Soc. Japan, 52 (1979) 446.
15 T.-Y. Dong and T.R. Webb, Inorg. Chem., 21 (1982) 114.
16 A.H. Reid, Jr. and T.R. Webb, Inorg. Chem., submitted for publication.
17 G.S. Girolami, V.V. Mainz, R.A. Andersen, S.H. Vollmer and V.W. Day, J. Am. Chem. Soc., 103 (1981) 3953; G.S. Girolami and R.A. Andersen, J. Organomet. Chem., 182 (1979) C43.
18 F.A. Cotton and D.G. Lay, Inorg. Chem., 20 (1981) 935; D.J. Santure and A.P. Sattelberger, Inorg. Chem., 24 (1985) 3477.
19 A.B. Brignole and F.A. Cotton, Inorg. Synth., 13 (1972) 81.
20 F.A. Cotton, L.R. Falvello and C.A. Murillo, Inorg. Chem., 22 (1983) 382.
21 F.A. Cotton, W.H. Ilsley and W. Kaim, Inorg. Chim. Acta, 37 (1979) 267.
22 D.M. Collins, F.A. Cotton and C.A. Murillo, Inorg. Chem., 15 (1976) 1861.
23 C.D. Garner, S. Parkes, I.B. Walton and W. Clegg, Inorg. Chim. Acta, 31 (1978) L451.
24 (a) L. Hocks, P. Durbut and Ph. Teyssie, J. Mol. Catal., 7 (1980) 75; (b) J. Lamotte, D. Dideburg, L. Dupont and P. Durbut, Cryst. Struct. Comm., 10 (1981) 59.
25 F.A. Cotton and A.H. Reid, Jr., Nouv. J. Chem., (1983) 209.
26 F.A. Cotton and J.G. Norman, Jr., J. Am. Chem. Soc., 94 (1972) 5967.
27 D.M. Collins, F.A. Cotton and C.A. Murillo, Inorg. Chem., 15 (1976) 2950.
28 F.A. Cotton and A.H. Reid, Jr., Acta Crystallogr. C, (1986) in press.
29 F. Takusagawa and T.F. Koetzle, Acta Crystallogr., B35 (1979) 2888.
30 M.R. Churchill, Y.-J. Li, D. Nalewajek, P.M. Shaeber and J. Dorfman, Inorg. Chem., submitted.