Synthesis of $Mo_2(NMe_2)_4(C_7H_8N_3C_7H_8)_2$. $Mo_2(NMe_2)_6$ (0.4477 g, 0.98 mmol) and 1,3-di-*p*-tolyltriazine (0.52 g, 1.96 mmol) were placed in a 100-mL round-bottomed flask. Dry toluene (50 mL) was added, yielding a deep red solution which was stirred at room temperature for $^1/_2$ h. Hexane (10 mL) was added, and the flask was placed in the refrigerator at -10 °C. Rust red crystals were obtained. Elemental analyses were erratic and unsatisfactory. IR data obtained from Nujol mull using CsI plates (ν in cm^{-1}): 1596 m, 1380 s, 1340 s, 1293 vs, 1272 vs, 1240 s, 1170 w, 1155 w, 1144 m, 1115 w, 1105 w, 1044 m, 950 s, 935 s, 931 s, 820 s, 759 m, 727 m, 652 m, 624 m, 540 m, 503 m, 366 m. ^1H NMR data obtained from toluene-d_8 at 220 MHz and +16 °C: δ (NMe-proximal) 4.45 (br), 4.28 (sh); δ (NMe-distal) 2.09 (br), 2.53 (sh); δ (tolyl methyls) 2.29 and 2.22; δ (aromatic protons) 7.03, 7.24, 7.42, 7.59 (all doublets with splittings of ca. 7.5 Hz).

X-ray Structural Determination. A crystal of dimensions 0.08 × 0.11 × 0.34 mm was mounted in a nitrogen-filled glovebag and transferred to the liquid-nitrogen boil-off cooling system of the diffractometer.[8] The diffractometer used for data collection was designed and constructed locally. A Picker four-circle goniostat equipped with a Furnas monochromator (HOG crystal) and Picker X-ray generator is interfaced to a TI980 minicomputer, with Slo-Syn stepping motors to drive the angles. Centering is accomplished by using automated top/bottom-left/right slit assemblies. The minicomputer is interfaced by slow-speed data lines to a CYBER 172-CDC 6600 multimain frame system where all computations are performed.

The cell dimensions obtained from 20 reflections at -17 °C with Mo Kα (λ = 0.71069 Å) were a = 27.529 (7) Å, b = 8.728 (2) Å, c = 18.294 (4) Å, β = 58.34 (1)°, V = 3741.58 Å^3, Z = 4, d_{calcd} = 1.45 g cm^{-3}, and space group $C2/c$.

A total of 3730 reflections were collected by using standard moving-detector techniques with the following values: Scan speed = 3° min^{-1}; scan width = 2° + dispersion; single background time at extremes of scan = 5 s; aperture size = 2.5 × 3.5 mm. The limits of data collection were $5° < 2\theta < 50°$. The number of reflections with $F > 2.33\sigma(F)$ was 2853.

For the final refinement, all nonhydrogen atoms were allowed to vary anisotropically. The hydrogen positional parameters were also varied, while their isotropic thermal parameters were kept fixed.

The structure was solved by direct methods and Patterson techniques and refined by full-matrix least-squares techniques to yield final residues: $R_F = 0.039$ and $R_{wF} = 0.040$. The goodness of fit for the last cycle was 1.01, and the maximum Δ/σ was 0.1.

Acknowledgment. We thank the Office of Naval Research, the Marshall H. Wrubel Computing Center, and the taxpayers of the State of Indiana for financial support of this work.

Registry No. $Mo_2(NMe_2)_4(C_7H_8N_3C_7H_8)_2$, 75067-37-7; $Mo_2(NMe_2)_6$, 51956-20-8.

Supplementary Material Available: A table of observed and calculated structure factors (31 pages). Ordering information is given on any current masthead page. The complete structural report, MSC Report 8001, is available upon request in microfiche form only from the Indiana University Chemical Library.

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(8) J. C. Huffman, Ph.D. Thesis, Indiana University, Bloomington, Ind., 1974.

Contribution from the Department of Chemistry, Stanford University,
Stanford, California 94305

Synthesis, Structure, and Properties of the Cluster Complex $[MoFe_4S_4(SC_2H_5)_3(C_6H_4O_2)_3]^{3-}$, Containing a Single Cubane-Type $MoFe_3S_4$ Core

THOMAS E. WOLFF, JEREMY M. BERG, and R. H. HOLM*[1]

Received May 15, 1980

Reaction of the Fe(III)-bridged complex $[Mo_2Fe_7S_8(SEt)_{12}]^{3-}$ with catechol in acetonitrile solution at ambient temperature results in cleavage of this "double-cubane" cluster and formation of a new Mo-Fe-S cluster compound of the formulation $(Et_4N)_3[MoFe_4S_4(SEt)_3(C_6H_4O_2)_3]$. This compound crystallizes in the monoclinic space group $P2_1/c$ with a = 16.844 (4) Å, b = 13.016 (3) Å, c = 29.362 (7) Å, β = 91.57 (2)°, and Z = 4. The anion consists of a single $MoFe_3S_4(SEt)_3$ cluster with a trigonally distorted $MoFe_3S_4$ core. Coordination of the Mo atom is completed by an unprecedented structural feature, viz., attachment via Mo-O-Fe bridges of a $Fe^{III}(C_6H_4O_2)_3$ subunit functioning as a tridentate ligand. This arrangement causes distortions of the unperturbed $[Fe(C_6H_4O_2)_3]^{3-}$ structure which include a shift of the $Fe-O_6$ coordination polyhedron (twist angle ϕ = 35°) toward the trigonal-prismatic limit (ϕ = 45° in the free trianion). Mean dimensions of the cluster are virtually identical with those of individual clusters in the species $[Mo_2Fe_6S_9(SR)_8]^{3-}$, $[Mo_2Fe_6S_8(SR)_9]^{3-}$, and $[Mo_2Fe_7S_8(SR)_{12}]^{3-}$. This result, together with ^{57}Fe isomer and $Fe-SCH_2CH_3$ ^1H NMR isotropic shifts, suggests that the mean oxidation state of core Fe in all clusters thus far prepared with a net 3- charge is the same. Cyclic voltammetry reveals three redox processes. That with $E_{1/2} \simeq -1.31$ V corresponds to cluster electron transfer, while the two others at more and less negative potentials are tentatively ascribed to $Fe(C_6H_4O_2)_3$ subunit metal-centered reduction and ligand-based oxidation, respectively. At present $[MoFe_3S_4(SEt)_3(C_6H_4O_2)_3]^{3-}$ is the only cluster species proven to contain a single $MoFe_3S_4$ cubane-type core, a matter of current interest in view of the possible relevance of this unit as a model for some structural properties of the nitrogenase FeMo cofactor.

Introduction

Recently synthesized molybdenum-iron-sulfur cluster complexes are of substantial interest in view of their possible relevance as models for some structural features of the iron-molybdenum cofactor of nitrogenase. Compositional and physicochemical properties of the latter[2-7] are consistent with a unique type of Mo-Fe-S cluster whose structure is unknown. From the reaction system $FeCl_3/MS_4^{2-}/RS^-$ in methanol or ethanol (M = Mo, W), we have isolated the polynuclear species $[M_2Fe_6S_9(SR)_8]^{3-}$, $[M_2Fe_6S_8(SR)_9]^{3-}$, and $[M_2Fe_7S_8(SR)_{12}]^{3-,4-}$ and have determined their structures and

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(1) To whom correspondence should be addressed at the Department of Chemistry, Harvard University, Cambridge, MA 02138.

(2) V. K. Shah and W. J. Brill, *Proc. Natl. Acad. Sci. USA*, **74**, 3249 (1977); B. K. Burgess, D. B. Jacobs, and E. I. Stiefel, *Biochim. Biophys. Acta*, **614**, 196 (1980).

(3) S. P. Cramer, K. O. Hodgson, W. O. Gillum, and L. E. Mortenson, *J. Am. Chem. Soc.*, **100**, 3398 (1978).

(4) S. P. Cramer, W. O. Gillum, K. O. Hodgson, L. E. Mortenson, E. I. Stiefel, J. R. Chisnell, W. J. Brill, and V. K. Shah, *J. Am. Chem. Soc.*, **100**, 3814 (1978).

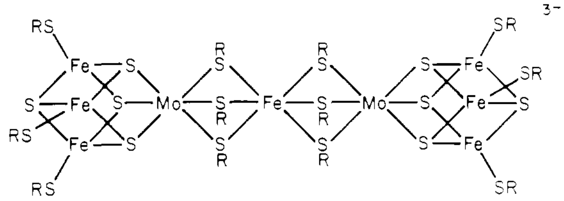
(5) J. Rawlings, V. K. Shah, J. R. Chisnell, W. J. Brill, R. Zimmerman, E. Münck, and W. H. Orme-Johnson, *J. Biol. Chem.*, **253**, 1001 (1978).

(6) B. H. Huynh, E. Münck, and W. H. Orme-Johnson, *Biochim. Biophys. Acta*, **527**, 192 (1979).

(7) B. K. Burgess, E. I. Stiefel, and W. E. Newton, *J. Biol. Chem.*, **255**, 353 (1980).

elucidated certain physicochemical properties.[8-12] Christou, Garner, and co-workers have independently prepared and studied $[M_2Fe_6S_8(SR)_9]^{3-}$ [13-16] and $[M_2Fe_6S_8(SR)_6(OMe)_3]^{3-}$.[16,17] In addition, smaller, bi- and trinuclear M–Fe–S complexes have been synthesized and well characterized.[18,19]

The "double-cubane" species are composed of two $MFe_3S_4(SR)_3$ clusters containing trigonally distorted cubane-type MFe_3S_4 cores which, within and among all of the preceding species, are virtually isodimensional. Individual clusters are triply bridged through M = Mo or W atoms by sulfur or oxygen ligands, except for $[M_2Fe_7S_8(SR)_{12}]^{3-,4-}$ complexes **1** and **2**, which possess the more elaborate $Fe(SR)_6$ bridge unit.[10-12] Structure **1**, containing a bridging Fe(III) atom, has been established for $[Mo_2Fe_7S_8(SEt)_{12}]^{3-}$;[11] the corresponding tetraanions **2** differ only in having Fe(II) in the bridge unit. One aspect of our development of M–Fe–S cluster chemistry involves the preparation of species containing a single MFe_3S_4 core. Such species would allow investigation of electronic and reactivity properties of isolated clusters and may serve as useful precursors for the preparation of other clusters whose metal composition more closely approaches that of the FeMo cofactor (6–8 Fe/Mo[2,6]). Thus far we have not detected any mono cluster species among the products of the aforementioned reaction system. Consequently, attention has been directed to their synthesis by, among other means, removal of bridging iron atoms in $[M_2Fe_7S_8(SR)_{12}]^{3-,4-}$. Here we report the preparation and characterization of one product resulting from the reaction of $[Mo_2Fe_7S_8(SEt)_{12}]^{3-}$ with catechol. This product, $[MoFe_4S_4(SEt)_3(C_6H_4O_2)_3]^{3-}$, does in fact contain a single $MoFe_3S_4$ core, albeit in an unexpectedly substituted form.



1 (3−), **2** (4−)

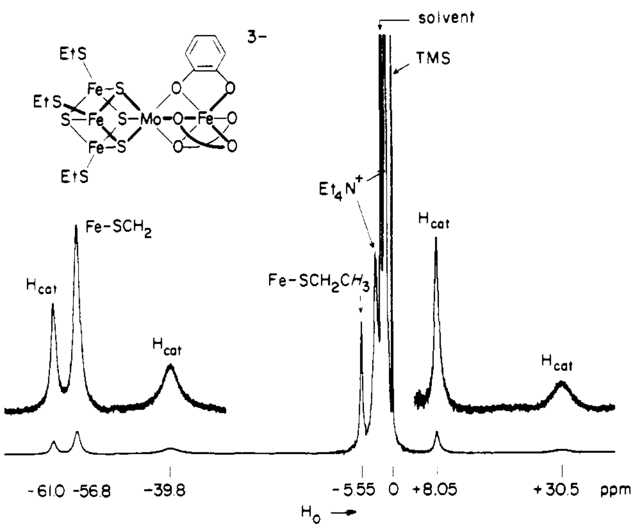


Figure 1. ^1H FT NMR spectrum (360 MHz) of $(Et_4N)_3[MoFe_4S_4(SEt)_3(C_6H_4O_2)_3]$ in CD_3CN solution at ~22 °C. Signal assignments are indicated.

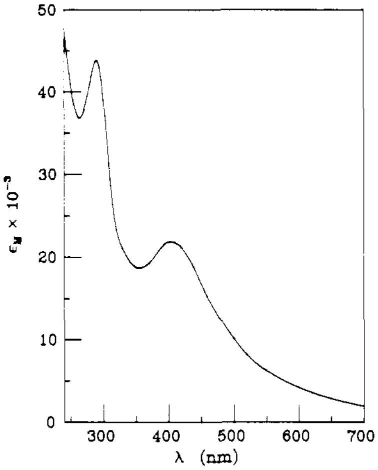


Figure 2. Electronic absorption spectrum of $(Et_4N)_3[MoFe_4S_4(SEt)_3(C_6H_4O_2)_3]$ in acetonitrile solution.

Experimental Section

Preparation of $(Et_4N)_3[MoFe_4S_4(SEt)_3(C_6H_4O)_3]$. All operations were performed under pure dinitrogen atmosphere; solvents were degassed before use. A solution of 2.7 g (25 mmol) of catechol, 5.1 g (51 mmol) of triethylamine, and 5.3 g (25 mmol) of Et_4NBr in 100 mL of acetonitrile was added to 8.3 g (4.2 mmol) of solid $(Et_4N)_3[Mo_2Fe_7S_8(SEt)_{12}]$,[12] which quickly dissolved. Upon stirring of the reaction mixture at room temperature much copper-colored crystalline material appeared within 2 h. The mixture was stirred overnight, cooled to −20 °C for about 1 h, and filtered. The crude product, after washing with ethanol and drying in vacuo, consisted of 7.5 g of brown microcrystalline solid. Recrystallization from 250–300 mL of warm (60 °C) acetonitrile and cooling to −20 °C afforded 4.7 g (41% on the basis of Mo) of black crystals whose ^1H NMR spectrum indicated a nearly pure material; weak impurity resonances were observed 17.7 and 21.7 ppm downfield of Me_4Si. Two additional recrystallizations afforded a product which was shown to be pure by ^1H NMR (Figure 1) and elemental analysis. Anal. Calcd for $C_{48}H_{87}Fe_4MoN_3O_6S_7$: C, 42.83; H, 6.52; Fe, 16.60; Mo, 7.13; N, 3.12; S, 16.67. Found: C, 42.68; H, 6.47; Fe, 16.37; Mo, 7.01; N, 3.21; S, 16.48. Absorption spectrum (acetonitrile, Figure 2): λ_{max} 289 (ϵ_M 43 700), 403 nm (ϵ_M 22 000). A corresponding reaction using 3,5-di-*tert*-butylcatechol gave an apparently similar black crystalline product. This material could not be purified so as to conform exactly to the analogous composition of the compound formed from catechol and will require further investigation.

Collection and Reduction of X-ray Data. A black air-sensitive crystal of $(Et_4N)_3[MoFe_4S_4(SEt)_3(C_6H_4O_2)_3]$ was mounted in a glass capillary under an argon atmosphere. Diffraction studies were carried

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(8) T. E. Wolff, J. M. Berg, C. Warrick, K. O. Hodgson, R. H. Holm, and R. B. Frankel, *J. Am. Chem. Soc.*, **100**, 4630 (1978).

(9) T. E. Wolff, J. M. Berg, K. O. Hodgson, R. B. Frankel, and R. H. Holm, *J. Am. Chem. Soc.*, **101**, 4140 (1979).

(10) T. E. Wolff, J. M. Berg, P. P. Power, K. O. Hodgson, R. H. Holm, and R. B. Frankel, *J. Am. Chem. Soc.*, **101**, 5454 (1979).

(11) T. E. Wolff, J. M. Berg, P. P. Power, K. O. Hodgson, and R. H. Holm, *Inorg. Chem.*, **19**, 430 (1980).

(12) T. E. Wolff, P. P. Power, R. B. Frankel, and R. H. Holm, *J. Am. Chem. Soc.*, **102**, 4694 (1980).

(13) G. Christou, C. D. Garner, F. E. Mabbs, and T. J. King, *J. Chem. Soc., Chem. Commun.*, 740 (1978).

(14) G. Christou, C. D. Garner, F. E. Mabbs, and M. G. B. Drew, *J. Chem. Soc., Chem. Commun.*, 91 (1979).

(15) (a) S. R. Acott, G. Christou, C. D. Garner, T. J. King, F. E. Mabbs, and R. M. Miller, *Inorg. Chim. Acta*, **35**, L337 (1979); (b) G. Christou, C. D. Garner, R. M. Miller, and T. J. King, *J. Inorg. Biochim.*, **11**, 349 (1979).

(16) (a) G. Christou and C. D. Garner, *J. Chem. Soc., Dalton Trans.*, in press; (b) G. Christou, C. D. Garner, R. M. Miller, C. E. Johnson, and J. D. Rush, *ibid.*, in press.

(17) G. Christou, C. D. Garner, T. J. King, C. E. Johnson, and J. D. Rush, *J. Chem. Soc., Chem. Commun.*, 503 (1979).

(18) (a) D. Coucouvanis, E. D. Simhon, D. Swenson, and N. C. Baenziger, *J. Chem. Soc., Chem. Commun.*, 361 (1979); (b) D. Coucouvanis, N. C. Baenziger, E. D. Simhon, P. Stremple, D. Swenson, A. Kostikas, A. Simopoulos, V. Petrouleas, and V. Papaefthymiou, *J. Am. Chem. Soc.*, **102**, 1730 (1980); (c) D. Coucouvanis, N. C. Bazenziger, E. D. Simhon, P. Stremple, D. Swenson, A. Simopoulos, A. Kostikas, V. Petrouleas, and V. Papaefthymiou, *J. Am. Chem. Soc.*, **102**, 1732 (1980).

(19) (a) J. W. McDonald, G. D. Friesen, and W. E. Newton, *Inorg. Chim. Acta*, in press; (b) D. Coucouvanis, E. D. Simhon, and N. C. Baenziger, *J. Am. Chem. Soc.*, **102**, 6644 (1980).

Table I. Summary of Crystal Data, Intensity Collection, and Structure Refinement Parameters for $(Et_4N)_3[MoFe_4S_4(SEt)_3(C_6H_4O_2)_3]$

formula	$C_{48}H_{87}Fe_4MoN_3O_6S_7$
a, Å	16.844 (4)
b, Å	13.016 (3)
c, Å	29.362 (7)
β, deg	91.57 (2)
cryst system	monoclinic
V, Å^3	6435 (5)
Z	4
d_{calcd}, g/cm^3	1.40
d_{obsd}, g/cm^3 [a]	1.39
space group	$P2_1/c$
cryst dimens,[b] nm	0.47 × 0.30 × 0.08
cryst faces	(100), ($\bar{1}$00), (0$\bar{1}$0), ($\bar{1}$2$\bar{1}$), (001), (00$\bar{1}$)
radiatn[c]	Mo ($\lambda_{K\alpha}$ 0.710 69 Å)
abs coeff (μ, cm^{-1})	13.5
transmission factors, %	53.62 (min), 83.60 (max), 73.16 (av)
takeoff angle, deg	3.0
scan speed, deg/min	1.5–29.3 ($\theta/2\theta$ scan)
scan range, deg	0.7 below $K\alpha_1$ to 0.7 above $K\alpha_2$
bkgd/scan time ratio	0.25
data collected	2θ of 3–40°; $+h$, $+k$, $\pm l$
unique data ($F_o^2 > 3\sigma(F_o^2)$)	2484
no. of variables	546
error in observn of unit weight	2.14
R, %	7.9
R_w, %	9.0

[a] Determined by flotation in CCl_4 and cyclohexane. [b] Irregularly shaped crystal. [c] Mosaic graphite monochromator.

out on a Syntex P2$_1$ four-circle diffractometer with a Mo X-ray tube equipped with a graphite monochromator. The machine parameters are summarized in Table I. Fifteen machine-centered reflections whose 2θ values ranged from 15 to 20° were used in the least-squares refinement of the orientation matrix and the lattice parameters of the crystal. Suitable mosaicity for data collection was indicated by several ω scans, all of which showed full width at half-height less than 0.25°. The parameters utilized in intensity collection are listed in Table I. Throughout the data collection no significant variation of intensities of three standard reflections was observed. The diffraction data were processed as described previously.[20] An analytical absorption correction was applied to the data set to account for the irregular crystal shape. The compound belongs to the monoclinic crystal system, and from the systematic absences $0k0$, $k \neq 2n$, and $h0l$, $l \neq 2n$, the space group was uniquely determined as $P2_1/c$. Subsequent solution and refinement of the structure confirmed this assignment.

Solution and Refinement of the Structure. The structure was solved by using the direct methods program MULTAN. With use of 360 normalized structure factors, 32 phase sets were generated. The phase set with the highest absolute figure of merit yielded trial positions for the Mo, three Fe, and four S atoms of the core and the noncore Fe atom. Subsequent difference Fourier maps revealed the location of the remaining nonhydrogen atoms.

The asymmetric unit consists of the entire anion and four cations, two of which have occupancies of 0.5. The anion and cation **1** were well ordered and fully refined anisotropically. Cation **2** is disordered such that several regions of electron density were present near the expected position of one of the four ethyl groups. Refinement of the cation with carbon atoms placed in a tetrahedral arrangement about the nitrogen converged on a nontetrahedral geometry with N(2)–carbon distances of C(1)–N(2) = 1.52 (4), C(3)–N(2) = 1.72 (6), C(5)–N(2) = 1.45 (8), C(7)–N(2) = 1.62 (8), and C(8)–N(2) = 1.99 (6) Å. Susbsequent difference Fourier maps showed no peaks within 1.8 Å of cation **2** that were greater than ~20% the height of a carbon atom. The third cation is equally distributed between two positions (**3** and **4**) which are each on inversion centers. The ethyl groups of cations **3** and **4** were modeled by a total of six atomic positions, four of which were methylene carbon atoms and two of which were pairs of methyl carbon atoms related by the inversion center (cf. footnote *c* of Table VII). Cations **2**–**4** were refined isotropically. All other nonhydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated only for the catecholate rings and cation **1**. Standard geometries were assumed with C–H bond distances and isotropic temperature factors at 0.95 Å and 7 Å^2, respectively. These atoms were included as fixed contributions in the final refinement cycles. The final *R* factors are given in Table I. The highest peak in the final difference Fourier map had ~40% the height of a carbon atom. The more or less random distribution of the residual electron density throughout the map is indicative of reasonably good descriptions of the disorder problems in the final refinement.

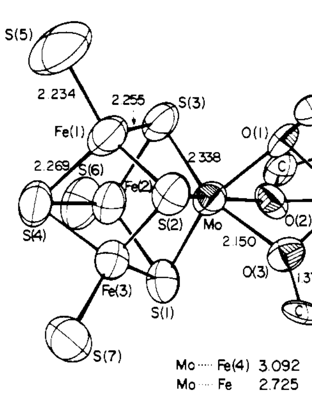

Figure 3. Structure of $[MoFe_4S_4(SEt)_3(C_6H_4O_2)_3]^{3-}$ as its Et_4N^+ salt; shown are 50% probability ellipsoids, the atom labeling scheme, and selected mean interatomic distances. The ethyl groups of the three thiolate ligands and four ring carbon atoms of each of the three catecholate ligands are omitted.

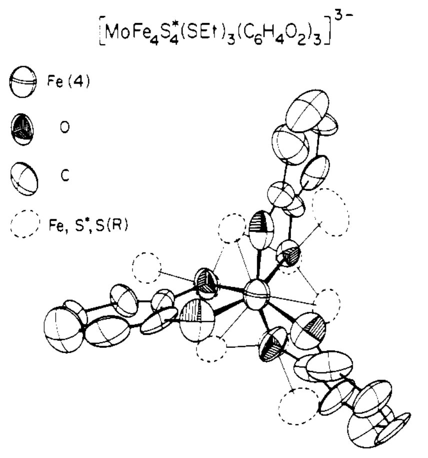

Figure 4. View of $[MoFe_4S_4(SEt)_3(C_6H_4O_2)_3]^{3-}$ down the Fe(4)–Mo–S(4) axis, showing the Fe(4)–O$_6$ coordination unit and the propeller-like tilt of the catecholate ligands.

The following results for $(Et_4N)_3[MoFe_4S_4(SEt)_3(C_6H_4O_2)_3]$ are tabulated: positional and thermal parameters for the anion (Table II); interatomic distances and angles in the anion (Table III); the best weighted least-squares planes for the anion (Table IV); root-mean-square amplitudes of thermal vibration for the anion (Table V); positional and thermal parameters for thiolate and catecholate carbon atoms (Table VI) and for the cations (Table VII); the best least-squares planes for the catecholate rings (Table VIII); dihedral angles in the $Fe(C_6H_4O_2)_3$ subunit (Table IX); values of $10|F_o|$ and $10|F_c|$ (Table X). Tables V–X are available as supplementary material.[21] The structure of the anion is presented in Figures 3 and 4.

Other Physical Measurements. Absorption, ^{1}H NMR, and Mössbauer spectra and cyclic voltammetry were determined under anaerobic conditions by using the equipment and procedures described elsewhere.[10,12,22,23] Redox potentials were measured vs. a saturated

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(20) M. A. Bobrik, K. O. Hodgson, and R. H. Holm, *Inorg. Chem.*, **16**, 1851 (1977). This paper contains a listing of computer programs used in the X-ray diffraction study reported here.

(21) See the paragraph at the end of this article regarding supplementary material.

Table II. Positional and Thermal Parameters[a] for $[MoFe_4S_4(SEt)_3(C_6H_4O_2)_3]^{3-}$

atom	x	y	z	B_{11}[b]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo	0.7474 (1)[c]	0.3322 (2)	0.14713 (8)	5.3 (1)	4.2 (1)	4.5 (1)	0.1 (1)	0.2 (1)	−0.5 (1)
Fe(1)	0.7596 (3)	0.1435 (3)	0.1053 (1)	9.9 (3)	5.1 (2)	5.7 (2)	0.5 (2)	0.2 (2)	−1.1 (2)
Fe(2)	0.8879 (3)	0.2672 (3)	0.1157 (2)	6.7 (2)	6.5 (2)	7.2 (3)	0.8 (2)	1.8 (2)	−0.4 (2)
Fe(3)	0.8240 (2)	0.1730 (3)	0.1892 (1)	6.4 (2)	5.3 (2)	6.0 (2)	0.6 (2)	0.4 (2)	−0.2 (2)
Fe(4)	0.6434 (2)	0.5241 (3)	0.1627 (1)	6.1 (2)	5.0 (2)	4.4 (2)	0.6 (2)	0.4 (2)	−0.3 (2)
S(1)	0.8706 (4)	0.3366 (6)	0.1845 (3)	5.1 (4)	5.9 (4)	7.3 (5)	0.4 (4)	0.9 (4)	0.3 (4)
S(2)	0.6949 (4)	0.1749 (6)	0.1713 (2)	7.5 (4)	4.4 (4)	5.3 (4)	−0.3 (4)	0.6 (4)	1.0 (4)
S(3)	0.7787 (5)	0.2964 (6)	0.0714 (3)	8.2 (5)	5.6 (4)	4.6 (4)	0.9 (4)	1.0 (4)	−0.4 (4)
S(4)	0.8837 (5)	0.0962 (6)	0.1305 (3)	9.7 (5)	5.9 (5)	8.7 (6)	2.5 (4)	1.0 (5)	−0.9 (5)
S(5)	0.7126 (8)	0.0247 (8)	0.0577 (4)	22 (1)	8.3 (6)	12.6 (8)	−1.3 (7)	−6.0 (8)	−2.9 (6)
S(6)	0.9971 (5)	0.3229 (8)	0.0806 (3)	9.3 (5)	10.7 (7)	12.9 (7)	1.0 (6)	4.8 (5)	−1.3 (7)
S(7)	0.8489 (5)	0.0779 (7)	0.2512 (3)	7.5 (5)	8.4 (5)	7.7 (5)	1.0 (5)	−0.8 (4)	1.0 (5)
O(1)	0.6318 (9)	0.383 (1)	0.1274 (5)	6.0 (9)	4.6 (8)	2.8 (8)	−0.3 (8)	1.7 (7)	−1.7 (7)
O(2)	0.7553 (9)	0.496 (1)	0.1359 (5)	7 (1)	6 (1)	5 (1)	1.0 (9)	0.9 (9)	3.2 (9)
O(3)	0.6929 (9)	0.411 (1)	0.2032 (5)	7 (1)	4.7 (9)	3.7 (9)	−0.3 (8)	−0.4 (8)	−1.2 (8)
O(4)	0.5319 (9)	0.506 (1)	0.1657 (5)	8 (1)	5 (1)	3.7 (9)	1.3 (9)	0.0 (8)	−0.4 (8)
O(5)	0.6430 (10)	0.634 (1)	0.1192 (6)	7 (1)	6 (1)	7 (1)	1.0 (9)	1.4 (9)	0 (1)
O(6)	0.6581 (10)	0.607 (1)	0.2170 (6)	9 (1)	5.2 (9)	8 (1)	4.0 (9)	−1 (1)	2.1 (9)

[a] Data for Mo, Fe, S, and O atoms only. [b] The form of the anisotropic temperature factor is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [c] Estimated standard deviations in parentheses in this and succeeding tables.

Table III. Selected Interatomic Distances (Å) and Angles (Deg) in $[MoFe_4S_4(SEt)_3(C_6H_4O_2)_3]^{3-}$

$Fe(C_6H_4O_2)_3Mo$ Unit

Mo···Fe(4)	3.092 (3)
Mo–O(1)	2.122 (14)
Mo–O(2)	2.163 (14)
Mo–O(3)	2.165 (13)
mean	2.150 (24)[a]
Fe(4)–O(1)	2.114 (12)
Fe(4)–O(2)	2.095 (14)
Fe(4)–O(3)	2.058 (14)
mean	2.089 (28)
Fe(4)–O(4)	1.896 (17)
Fe(4)–O(5)	1.918 (15)
Fe(4)–O(6)	1.937 (16)
mean	1.917 (21)
O(1)–Mo–O(2)	73.2 (5)
O(1)–Mo–O(3)	69.8 (5)
O(2)–Mo–O(3)	71.3 (5)
mean	71.4
Mo–O(1)–Fe(4)	93.8 (6)
Mo–O(2)–Fe(4)	93.1 (6)
Mo–O(3)–Fe(4)	94.1 (6)
mean	93.7
O(1)–Fe(4)–O(2)	74.7 (5)
O(1)–Fe(4)–O(3)	72.0 (5)
O(2)–Fe(4)–O(3)	74.8 (6)
mean	73.8
O(1)–Fe(4)–O(4)	80.8 (6)
O(2)–Fe(4)–O(5)	82.4 (6)
O(3)–Fe(4)–O(6)	83.3 (5)
mean	82.2

O(1)–Fe(4)–O(5)	108.9 (5)
O(2)–Fe(4)–O(6)	108.0 (6)
O(3)–Fe(4)–O(4)	105.8 (6)
mean	107.6
O(1)–Fe(4)–O(6)	153.6 (6)
O(2)–Fe(4)–O(4)	154.0 (6)
O(3)–Fe(4)–O(5)	156.1 (6)
mean	154.6
O(4)–Fe(4)–O(5)	97.9 (7)
O(4)–Fe(4)–O(6)	97.7 (7)
O(5)–Fe(4)–O(6)	97.4 (7)
mean	97.7
O(1)···O(2)	2.555 (20)
O(2)···O(3)	2.453 (19)
O(2)···O(3)	2.523 (20)
mean	2.510 (52)
O(1)···O(4)	2.604 (17)
O(2)···O(5)	2.645 (19)
O(3)···O(6)	2.655 (18)
mean	2.635 (27)
O(4)···O(5)	2.875 (22)
O(4)···O(6)	2.886 (23)
O(5)···O(6)	2.896 (22)
mean	2.886 (11)

$MoFe_3S_4$ Unit

Mo–S(1)	2.320 (6)
Mo–S(2)	2.347 (6)
Mo–S(3)	2.347 (6)
mean	2.338 (16)
Mo···S(4)	3.874 (6)
S(1)–Mo–S(2)	102.6 (2)
S(1)–Mo–S(3)	103.4 (2)
S(2)–Mo–S(3)	102.1 (2)
mean	102.7
S(1)–Mo–O(1)	157.4 (4)
S(2)–Mo–O(2)	158.7 (4)
S(3)–Mo–O(3)	157.8 (4)
mean	158.0

Mo–S(1)–Fe(2)	72.6 (2)
Mo–S(1)–Fe(3)	72.6 (2)
Mo–S(2)–Fe(1)	73.0 (2)
Mo–S(2)–Fe(3)	73.0 (2)
Mo–S(3)–Fe(1)	73.6 (2)
Mo–S(3)–Fe(2)	71.7 (2)
mean	72.8
Fe(1)–S(5)	2.216 (9)
Fe(2)–S(6)	2.254 (8)
Fe(3)–S(7)	2.233 (7)
mean	2.234 (19)
S(2)–Fe(1)–S(3)	107.1 (2)
S(1)–Fe(2)–S(3)	109.2 (2)
S(1)–Fe(3)–S(2)	108.2 (2)
mean	108.2

S(1)–Mo–O(2)	89.4 (4)
S(1)–Mo–O(3)	91.3 (4)
S(2)–Mo–O(1)	90.2 (4)
S(2)–Mo–O(3)	90.6 (4)
S(3)–Mo–O(1)	91.8 (3)
S(3)–Mo–O(2)	92.0 (4)
mean	90.9
Mo···Fe(1)	2.756 (4)
Mo···Fe(2)	2.699 (4)
Mo···Fe(3)	2.719 (4)
mean	2.725 (29)
Fe(1)···Fe(2)	2.705 (5)
Fe(1)···Fe(3)	2.691 (5)
Fe(2)···Fe(3)	2.728 (5)
mean	2.709 (19)
Fe(1)–Mo–Fe(2)	59.44 (11)
Fe(1)–Mo–Fe(3)	58.88 (10)
Fe(2)–Mo–Fe(3)	60.46 (10)
mean	59.59
Mo–Fe(1)–Fe(2)	59.23 (10)
Mo–Fe(1)–Fe(3)	59.87 (10)
Mo–Fe(2)–Fe(1)	61.33 (11)
Mo–Fe(2)–Fe(3)	60.13 (10)
Mo–Fe(3)–Fe(1)	61.25 (10)
Mo–Fe(3)–Fe(2)	59.41 (10)
mean	60.20
Fe(2)–Fe(1)–Fe(3)	60.73 (12)
Fe(1)–Fe(2)–Fe(3)	59.39 (12)
Fe(1)–Fe(3)–Fe(2)	59.88 (12)
mean	60.00
Fe(1)–S(2)	2.288 (6)
Fe(1)–S(3)	2.252 (6)
Fe(2)–S(1)	2.237 (7)
Fe(2)–S(3)	2.258 (7)
Fe(3)–S(1)	2.275 (7)
Fe(3)–S(2)	2.222 (6)
mean	2.255 (24)
Fe(1)–S(4)	2.283 (8)
Fe(2)–S(4)	2.269 (7)
Fe(3)–S(4)	2.254 (7)
mean	2.269 (15)
mean of 9	2.260 (21)

S(2)–Fe(1)–S(4)	103.1 (3)
S(3)–Fe(1)–S(4)	104.0 (3)
S(1)–Fe(2)–S(4)	102.6 (3)
S(3)–Fe(2)–S(4)	104.3 (3)
S(1)–Fe(3)–S(4)	101.9 (3)
S(2)–Fe(3)–S(4)	106.2 (3)
mean	103.7
mean of 9	105.2
S(2)–Fe(1)–S(5)	119.3 (4)
S(3)–Fe(1)–S(5)	113.0 (3)
S(1)–Fe(2)–S(6)	114.3 (3)
S(3)–Fe(2)–S(6)	110.1 (3)
S(1)–Fe(3)–S(7)	120.7 (3)
S(2)–Fe(3)–S(7)	111.1 (3)
mean	114.8
S(4)–Fe(1)–S(5)	108.9 (4)
S(4)–Fe(2)–S(6)	115.7 (3)
S(4)–Fe(3)–S(7)	107.5 (3)
mean	110.7
mean of 9	113.4
Fe(1)···S(1)	3.869 (7)
Fe(2)···S(2)	3.868 (6)
Fe(3)···S(3)	3.871 (7)
mean	3.869 (2)
S(1)···S(2)	3.642 (8)
S(1)···S(3)	3.663 (8)
S(2)···S(3)	3.652 (8)
mean	3.652 (11)
S(1)···S(4)	3.517 (8)
S(2)···S(4)	3.580 (8)
S(3)···S(4)	3.573 (8)
mean	3.557 (35)
mean of 6	3.605 (57)
Fe(2)–S(1)–Fe(3)	74.4 (2)
Fe(1)–S(2)–Fe(3)	73.3 (2)
Fe(1)–S(3)–Fe(2)	73.7 (2)
mean	73.8
Fe(1)–S(4)–Fe(2)	72.9 (2)
Fe(1)–S(4)–Fe(3)	72.8 (2)
Fe(2)–S(4)–Fe(3)	74.2 (2)
mean	73.3
mean of 6	73.6

[a] The standard deviation of the mean was estimated from $\sigma \approx s = [\Sigma\chi_i^2 - n\bar{\chi}^2)/(n-1)]^{1/2}$; no value is given for any angular quantity, as the variations exceed those expected from a sample taken from the same population.

Table IV. Best Weighted Least-Squares Planes and Deviations (Å) from Planes for $[MoFe_4S_4(SEt)_3(C_6H_4O_2)_3]^{3-}$

plane	*A*	*B*	*C*	*D*
	$Ax + By + Cz = D$ (orthogonalized coordinates)			
1	−0.9087	0.1351	−0.3950	−12.4290
2	0.2166	0.9455	−0.2431	5.7601
3	0.3494	−0.3344	−0.8753	−0.8921
4	0.3786	−0.3454	−0.8587	1.5878
5	0.1946	0.9534	−0.2303	3.4725
6	−0.9045	0.1505	−0.3990	−14.3680
7	0.4150	0.4392	−0.7968	3.6326
8	−0.3970	−0.1477	−0.9059	−9.4990
9	−0.8111	−0.5730	−0.1175	−13.0934
10	−0.4929	0.7530	−0.4359	−6.1965
11	0.8861	−0.3336	−0.3219	9.6339
12	0.1107	−0.8914	−0.4396	−2.9375

atom	1	2	3	4	5	6
Mo	−0.025 (2)	−0.020 (2)	0.023 (2)			
Fe(1)	−0.089 (5)			−0.074 (4)	0.071 (4)	
Fe(2)		−0.078 (4)		−0.079 (5)		0.093 (4)
Fe(3)			0.075 (4)		0.066 (4)	0.076 (4)
S(1)		0.210 (8)	−0.240 (8)			−0.262 (7)
S(2)	0.239 (7)		−0.230 (7)		−0.209 (7)	
S(3)	0.257 (8)	0.208 (7)		0.225 (8)		
S(4)				0.288 (9)	−0.284 (8)	−0.340 (9)

atom	7	8	9	10	11	12
Mo	0.000 (2)	−0.002 (2)	−0.006 (2)			
Fe(1)	0.000 (4)			−0.008 (4)	0.011 (5)	
Fe(2)		0.008 (5)		0.009 (4)		−0.011 (4)
Fe(3)			0.018 (4)		−0.010 (4)	0.009 (4)
S(1)	0.000 (8)			−0.019 (8)	0.024 (7)	
S(2)		0.015 (7)		0.018 (7)		−0.022 (7)
S(3)			0.046 (8)		−0.024 (8)	0.023 (7)
S(4)	−0.001 (9)	−0.022 (9)	−0.062 (9)			

calomel electrode (SCE) in acetonitrile solution containing 0.05 M n-Bu_4NBF_4 supporting electrolyte.

Results and Discussion

Preparation of $[MoFe_4S_4(SEt)_3(C_6H_4O_2)_3]^{3-}$. The selection of catechol as a reagent to remove bridging iron from $[Mo_2Fe_7S_8(SEt)_{12}]^{3-}$ (**1**) was based on the well-recognized affinity of the catecholate dianion for Fe(III), as manifested by the overall formation constant of $\sim 10^{44}$ for $[Fe(C_6H_4O_2)_3]^{3-}$ in aqueous solution.[24] In an acetonitrile mixture of reactants including a small excess of catechol and a larger excess of Et_4N^+ reaction proceeded smoothly, resulting in the separation of a solid of composition $(Et_4N)_3[MoFe_4S_4(SEt)_3(C_6H_4O_2)_3]$ in a typical yield of ca. 40% on the basis of molybdenum. We have not as yet succeeded in purifying and identifying material isolated from the filtrate of the reaction mixture.

Description of the Structure. $(Et_4N)_3[MoFe_4S_4(SEt)_3(C_6H_4O_2)_3]$ crystallizes in the monoclinic space group $P2_1/c$ and consists of discrete anions and cations. The cations vary in crystal packing characteristics from highly ordered to highly disordered (cf. Experimental Section) but are otherwise unexceptional and are not described. The anion structure is composed of a *single* $MoFe_3S_4(SEt)_3$ cluster with a cubane-type $MoFe_3S_4$ core and, unexpectedly, of a tris chelate $Fe(C_6H_4O_2)_3$ subunit which acts as tridentate ligand to Mo through one oxygen atom of each chelate ring. There is no crystallographically imposed symmetry on the anion. In describing the anion, these two portions are examined in turn, with attention directed to the bond distance and angle data in Table III and the least-squares planes in Table IV. An overall view of the structure, devoid of ethyl substituents and the entirety of phenyl rings, is presented in Figure 3. These parts of the structure are of normal dimensions and are not considered further.

(a) $MoFe_3S_4(SEt)_3$ Cluster. The structure of the $MoFe_3S_4$ core is nearly isodimensional with those present in the nine double-cubane complexes investigated by X-ray diffraction.[9,11,13-15,17] Principal features include interlocking imperfect $MoFe_3$ and S_4 tetrahedra of which the latter is larger, $MoFeS_2$ and Fe_2S_2 core faces which are nonplanar rhombs (planes 1–6), and diagonal planes (7–12) which are nearly perfect. A small rhombic distortion is indicated by variations in certain bond distances. Thus Mo–S(1) (2.320 (6) Å) and S(1)···S(4) (3.517 (8) Å) are shorter and Mo···Fe(1) (2.756 (4) Å) and Fe(2)···Fe(3) (2.728 (5) Å) are longer than other bond distances of the same type. Except for these distortions the core closely approaches local C_{3v} symmetry. The close correspondence of mean values of all distances, including terminal Fe–S distances (2.234 (19) Å), to those in other $MFe_3S_4(SR)_3$ clusters (M = Mo, W) suggests a cluster oxidation level which is nearly or exactly equivalent to those in other compounds (vide infra).

(b) $Fe(C_6H_4O_2)_3Mo$ Unit. A perspective view of the anion structure displaying the stereochemistry of this unit is provided in Figure 4. The following are the principal structural features of this portion of the anion: (1) Roughly octahedral coordination geometry around the Mo atom is very similar to that of the W atom in the methoxide-bridged complex $[W_2Fe_6S_8(SPh)_6(OMe)_3]^{3-}$[17] as shown by comparisons of mean values where Mo–O = 2.150 (24) Å and W–O = 2.123 (9) Å, O–Mo–O = 71.4° and O–W–O = 70.3°, and S–Mo–O = 90.9° and S–W–O = 91.6°. The nearly identical six-coordinate radii of Mo and W in the same oxidation state,[25] manifested by virtually isometric (Mo,W)–Fe–S cluster

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(22) J. G. Reynolds, E. J. Laskowski, and R. H. Holm, *J. Am. Chem. Soc.*, **100**, 5315 (1978).

(23) J. Cambray, R. W. Lane, A. G. Wedd, R. W. Johnson, and R. H. Holm, *Inorg. Chem.*, **16**, 2565 (1977).

(24) A. Avdeef, S. R. Sofen, T. L. Bregante, and K. N. Raymond, *J. Am. Chem. Soc.*, **100**, 5362 (1978).

(25) R. D. Shannon, *Acta Crystallogr., Sect. A*, *A32*, 751 (1976).

Table XI. Comparison of Mean Structural Parameters of Selected $Fe(\widehat{O\ O})_3$ Chelates

parameter	$[MoFe_4S_4(SEt)_3(C_6H_4O_2)_3]^{3-}$	$[Fe(C_6H_4O_2)_3]^{3-}$ [a]	$[Fe(phenSQ)_3]$ [b]	trigonal prism	octahedron
Fe–O(1-3)	2.09 (3)	2.015 (6)	2.027 (4)		
Fe–O(4-6)	1.92 (2)				
chelate O···O' dist,[d] Å	2.64 (3)	2.625 (2)	2.59		
chelate O–Fe–O' angle,[d] deg	82.2	81.3	79.4		
trigonal twist angle ϕ, deg	35.2	44.7	43.6[c]	0	60
polyhedron dihedral angles, deg					
δ at b_1	45.1	57.4[c]	57.0[c]	0	70.5
δ at b_2	89.9	97.4[c]	96.0[c]	120	
polar angles θ, deg					
axis-Fe–O(1-3)	43.9	55.2[c]	59.9[c]	54.7	54.7
axis-Fe–O(4-6)	60.4				

[a] Reference 27. [b] Reference 29. [c] Calculated from cell parameters and atomic coordinates. [d] Primed and unprimed atoms belong to the same chelate ring.

structures,[11,15,26] justifies this comparison. (2) The $Fe(C_6H_4O_2)_3$ subunit is connected to the cluster by Mo–O–Fe bridging involving the oxygen atom (O(1-3)) of each catecholate ligand. This arrangement leads to decidedly unsymmetrical binding of the ligands to Fe(4), with bonds to bridging atoms longer than those to terminal atoms (O(4-6)). These and other features of the subunit are profitably assessed in relation to the structures of $[Fe(C_6H_4O_2)_3]^{3-}$ [27,28] and, to a lesser degree, $Fe(phenSQ)_3$[29] (phenSQ = 9,10-phenanthrenesemiquinone). Comparative mean structural parameters are collected in Table XI. The Fe–O bond distance data reveal the deviations from the unconstrained value of ca. 2.02 Å in the mononuclear tris chelates. Unsymmetrical ligation is further reflected in the difference between the mean $C–O_{bridge}$ distance (1.37 Å) and the mean $C–O_{terminal}$ distance (1.30 Å); in $[Fe(C_6H_4O_2)_3]^{3-}$, the mean C–O distance is 1.338 (10) Å.[27] (3) The $C_6H_4O_2$ groups are nearly planar, but the $C_6H_4O_2Fe$ chelate rings deviate somewhat from planarity, with dihedral angles between the C_6 rings and FeO_2 fragments being 2.0–8.8° (Tables VIII and IX[21]). A similar behavior is found in $[Fe(C_6H_4O_2)_3]^{3-}$ (dihedral angles 4.9–9.2°[27]). (4) The catecholate ligands are disposed in a propeller-like configuration around Fe(4), but the subunit deviates from local C_3 symmetry as revealed by variation in dihedral angles (58–72°) between C_6 rings. (5) The $Fe–O_6$ coordination polyhedron more closely approaches local C_3 symmetry than does the entire subunit. The shape of the polyhedron is intermediate between trigonal prismatic and antiprismatic, as demonstrated by values of certain angular parameters[30-32] in Table XI. The twist angle ϕ is a well-defined parameter because the O(1-3) and O(4-6) planes are virtually parallel (dihedral angle 1.0°). These angles together with other metrical data of the coordination polyhedron are shown in Figure 5. Values of ϕ fall between the angles of the limiting structures while the dihedral angles δ_1 and δ_2 between polyhedral faces[30] span the value for an octahedron. (6) The Mo···Fe(4) separation is 3.092 (3) Å, too long for significant metal-metal bonding.

From the foregoing features the $Fe(C_6H_4O_2)_3$ subunit is observed to be distorted from its presumably unconstrained geometry in $[Fe(C_6H_4O_2)_3]^{3-}$ in the direction of the trigonal-prismatic limit. Bite distances and angles and the mean Fe–O distance are little changed. Unlike the latter complex the twist angle of the subunit cannot be accounted for by a linear relationship between ϕ and normalized bite distance.[27,31,32] The constraint causing this deviation is likely the quite different dimensions of the bridging and terminal O_3 faces (Figure 5), a feature not present in the great majority of complexes from which the linear dependence was deduced. In terms of mean twist angle the subunit ranks with tris(tropolonato)iron(III) (ϕ = 38.5°[31]) and *fac*-tris(benzohydroxamato)iron(III) (ϕ = 35.7°[33]) as the extreme cases of departure of a $Fe(III)–O_6$ coordination unit from the trigonal-antiprismatic configuration. The tendency of catecholate or its semiquinone form to stabilize binuclear Fe[28] and Mo[34] complexes by oxygen bridging is now well established. However, $[MoFe_4S_4(SEt)_3(C_6H_4O_2)_3]^{3-}$ is the first instance of any tris(catecholate) complex acting as a tridentate ligand. This result raises the possibility of $[M(C_6H_4O_2)_3]^{3-}$ species as a generalized ligand, with products such as $[M'\{M(C_6H_4O_2)_3\}_2]^{3-,4-}$ conceivable.

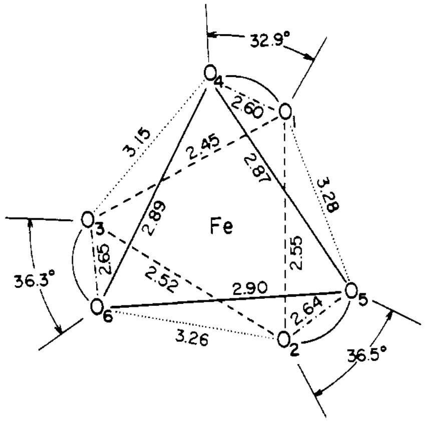

Figure 5. $Fe(4)–O_6$ coordination polyhedron in $[MoFe_4S_4(SEt)_3(C_6H_4O_2)_3]^{3-}$ showing O···O distances (Å) and trigonal twist angles ϕ.

Physicochemical Properties. (a) Mössbauer Spectrum. The ^{57}Fe spectrum of $(Et_4N)_3[MoFe_4S_4(SEt)_3(C_6H_4O_2)_3]$ in zero applied magnetic field at 77 K consists of a single, slightly asymmetric quadrupole doublet with quadrupole splitting ΔE_Q = 0.75 mm/s and isomer shift δ = 0.31 mm/s (vs. Fe metal at the same temperature). These parameters are closely comparable with those for $[M_2Fe_6S_9(SR)_8]^{3-}$, $[M_2Fe_6S_8(SR)_9]^{3-}$, and $[M_2Fe_7S_8(SR)_{12}]^{3-}$ clusters determined in our past investigations.[9,12] As previously, the δ value is taken to

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[26] The structure of $[Mo_2Fe_6S_8(SPh)_6(OMe)_3]^{3-}$ is nearly identical with that of its W analogue: G. Christou, C. D. Garner, and T. J. King, unpublished results; G. Christou, private communication.

[27] K. N. Raymond, S. S. Isied, L. D. Brown, F. R. Fronczek, and J. N. Nibert, *J. Chem. Soc.*, **98**, 1767 (1976).

[28] B. F. Anderson, D. A. Buckingham, G. B. Robertson, and J. Webb, *Nature (London)*, **262**, 722 (1976).

[29] R. M. Buchanan, S. L. Kessel, H. H. Downs, C. G. Pierpont, and D. N. Hendrickson, *J. Am. Chem. Soc.*, **100**, 7894 (1978).

[30] E. L. Muetterties and L. J. Guggenberger, *J. Am. Chem. Soc.*, **96**, 1748 (1974).

[31] A. Avdeef and J. P. Fackler, Jr., *Inorg. Chem.*, **14**, 2002 (1975).

[32] D. L. Kepert, *Prog. Inorg. Chem.*, **23**, 1 (1977).

[33] K. Abu-Dari, J. D. Ekstrand, D. P. Freyberg, and K. N. Raymond, *Inorg. Chem.*, **18**, 108 (1979).

[34] C. G. Pierpont and H. H. Downs, *J. Am. Chem. Soc.*, **97**, 2123 (1975); C. G. Pierpont and R. M. Buchanan, *ibid.*, **97**, 6450 (1975); R. M. Buchanan and C. G. Pierpont, *Inorg. Chem.*, **18**, 1616 (1979).

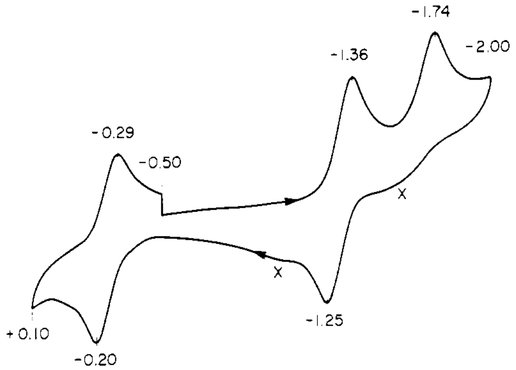

Figure 6. Cyclic voltammogram of $[MoFe_4S_4(SEt)_3(C_6H_4O_2)_3]^{2-}$ in acetonitrile solution at a glassy carbon electrode and a scan rate of 100 mV/s; the feature X is unidentified.

favor the mean +2.67 oxidation state (2Fe(III) + Fe(II)), leading to the core formal electronic description $[Mo^{III}Fe_2{}^{III}Fe^{II}S_4]^{3+}$. This description is also considered reasonable for cores in $[M_2Fe_6S_8(SR)_9]^{3-}$[9] and $[M_2Fe_7S_8(SR)_{12}]^{3-}$,[12] a matter consistent with the virtually identical cluster dimensions noted earlier. A signal corresponding to Fe in the $Fe(C_6H_4O_2)_3$ subunit was not observed and may have been obscured by the core Fe doublet. $K_3[Fe(C_6H_4O_2)_3]$ at 77 K gives a signal broadened by relaxation effects not uncommon to high-spin Fe(III) complexes.

(b) ^{1}H NMR Spectrum. The spectrum at ~22 °C is shown in Figure 1. Assignments of $Fe-SCH_2CH_3$ signals were verified by ligand exchange with benzenethiol, which abolished these signals upon formation of $[MoFe_4S_4(SPh)_3(C_6H_4O_2)_3]^{3-}$.[35] The isotropic shifts of −54.3 ppm (CH_2) and −3.04 (CH_3) are very close to those for terminal ethanethiolate ligands in the double-cubane clusters[12] mentioned above, providing further evidence of corresponding cluster oxidation levels. The catecholate protons are strongly isotropically shifted (−54.2, −33.0, +14.8, and +37.3 ppm), but individual proton assignments and the shift mechanism could not be determined from this one example.

(c) Redox Properties. In acetonitrile solution cyclic voltammetry of $[MoFe_4S_4(SEt)_3(C_6H_4O_2)_3]^{3-}$ reveals three redox processes, displayed in Figure 6. The initial reduction, with $E_{1/2} \simeq -1.31$ v, is essentially chemically reversible ($i_{p,c} \simeq i_{p,a}$) and is attributed to cluster reduction. This feature corresponds closely in potential to the first of two successive reductions (3−/4−, 4−/5−) of $[Mo_2Fe_6S_9(SEt)_8]^{3-}$ ($E_{1/2} = -1.30, -1.49$ V) and $[Mo_2Fe_6S_8(SEt)_9]^{3-}$ ($E_{1/2} = -1.28, -1.47$ V). Assignment of these two processes as reductions of individual clusters within each species is upheld by the absence of a corresponding second step in the voltammogram of $[MoFe_4S_4(SEt)_3(C_6H_4O_2)_3]^{3-}$. The second reduction of the latter complex, an irreversible process with $E_{p,c} = -1.74$ V, is probably due to reduction of Fe(III) in the $Fe(C_6H_4O_2)_3$ subunit. Although this potential is decidedly more negative than the reversible potential (−1.23 V) of the tris(catecholate) complex iron(III) enterobactin in aqueous solution,[36] it is unlikely to correspond to a second cluster reduction. With use of values associated with 5−/6− and 6−/7− couples of several $[Mo_2Fe_6S_8(SR)_9]^{3-}$ species,[16b] it is readily estimated that the potential for the second cluster reduction should be about 0.9–1.1 V more negative than that for the first reduction. The quasireversible oxidation with $E_{1/2} \simeq -0.25$ V cannot be definitely assigned at present. However, noting the absence of comparably well-defined oxidations in other Mo–Fe–S clusters and the multistep electron-transfer series of tris(catecholato)metal(III) complexes initiated at negative potentials (e.g., the Cr(III) system[37]), it is likely that this process involves a one-electron ligand-based oxidation of the $Fe(C_6H_4O_2)_3$ subunit.

The results presented here demonstrate that the Fe(III)-bridged complex $[Mo_2Fe_7S_8(SEt)_{12}]^{3-}$ (**1**) can be cleaved with catechol to afford at least one well-characterized product, $[MoFe_4S_4(SEt)_3(C_6H_4O_2)_3]^{3-}$. At present this is the only Mo–Fe–S cluster proven to contain a single $MoFe_3S_4$ core. Otsuka and Kamata[38] have reported certain properties of a species described as $[(t\text{-}BuS)MoFe_3S_4(SPh)_3]^{2-}$. This (unlikely) formation cannot be accepted until established by X-ray crystallography; the physical properties presented are insufficient for secure deduction of structure. Although the coordination of core Mo by the $Fe(C_6H_4O_2)_3$ subunit is a novel and unanticipated structural feature and thus of interest in its own right, it does not provide a $MoFe_3S_4$ cluster species in a condition spectroscopically and magnetically unadulterated by a proximal paramagnetic fragment. For realization of the desired cluster species current research is directed at cleavage of **1** and **2** with other reagents and removal of Fe from the catecholate subunit of $[MoFe_4S_4(SEt)_3(C_6H_4O_2)_3]^{3-}$ by competitive complexation and reduction reactions.

Acknowledgment. This research was supported by NSF Grant No. CHE 77-04397. We thank Dr. R. B. Frankel for Mössbauer measurements and Dr. G. Christou for communication of results prior to publication.

Registry No. $(Et_4N)_3[MoFe_4S_4(SEt)_3(C_6H_4O_2)_3]$, 75198-30-0; $(Et_4N)_3[Mo_2Fe_7S_8(SEt)_{12}]$, 73589-29-4.

Supplementary Material Available: Root-mean-square amplitudes of thermal vibration for the anion (Table V), positional and thermal parameters for thiolate and catecholate carbon atoms (Table VI) and for nonhydrogen atoms of the cations (Table VII), best least-squares planes for the catecholate rings (Table VIII), dihedral angles in the $Fe(C_6H_4O_2)_3$ subunit (Table IX), and values of $10|F_o|$ and $10|F_c|$ (Table X) (24 pages). Ordering information is given on any current masthead page.

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(35) W. H. Armstrong and R. H. Holm, research in progress.

(36) W. R. Harris, C. J. Carrano, S. R. Cooper, S. R. Sofen, A. E. Avdeef, J. V. McArdle, and K. N. Raymond, *J. Am. Chem. Soc.*, **101**, 6097 (1979).

(37) S. R. Sofen, D. C. Ware, S. R. Cooper, and K. N. Raymond, *Inorg. Chem.*, **18**, 234 (1979).

(38) S. Otsuka and M. Kamata in "Molybdenum Chemistry of Biological Significance", W. E. Newton and S. Otsuka, Eds., Plenum Press, New York, 1980, pp 229–238.