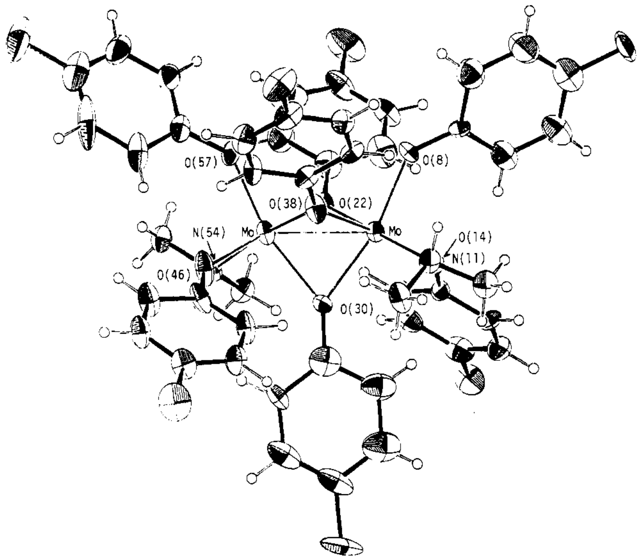

Figure 1. ORTEP view of the anion in the parent compound. Some pertinent bond distances (Å) and angles (deg) are as follows: Mo–Mo = 2.601 (2), Mo–O(terminal) = 2.040 (av), Mo–O(bridge) = 2.113 (av), Mo–N = 2.245 (av); Mo–O–Mo = 76.2 (av).

spectrum at 30 °C shows, besides a series of broad resonances, a set of four sharp peaks between δ 5.0 and 6.0 in the ratio of 2:2:2:1.[9] These we assign to the *p*-methyl resonances of the four types of aryloxide ligands in the anion, concluding that the molecule is nonfluxional on the NMR time scale at this temperature. The chemical shift of these signals is 4 ppm downfield of their normal position, and hence they are contact shifted. When the system is cooled from +35 to −70 °C (90 MHz, toluene-d_8) the signals shift upfield toward their expected diamagnetic value. This magnetic behavior is similar to, although of slightly smaller magnitude than, that observed for $Mo_2Cl_9^{3-}$.[10]

The question arises as to how the molecule is formed. The elegant reaction schemes worked out by Chisholm and coworkers for $Mo_2(OR)_6$ compounds show that addition of neutral donor ligands (such as $HNMe_2$) results in the formation of species $Mo_2(OR)_6(L)_2$. Structural studies show these compounds to contain four-coordinate metal centers separated by an unbridged metal–metal triple bond.[11] It is the formal addition of OAr^- to a species of this type that generates the anion in **1**. However, a more reasonable pathway for formation of the ion is coordination of free phenol to give $[Mo_2(OAr)_6(HOAr)]$, which is then deprotonated by amine.

Two interesting points are raised by these observations. The first is that they demonstrate, at least for aryloxide ligands, that a confacial bioctahedral geometry is a possible low-energy intermediate for anion substitution chemistry at M_2L_6 ($M\equiv M$) centers as long as the metal substituents are sufficiently small. Furthermore, this illustrates the possibility that the reported isomerization on substitution of $Mo_2Br_2(CH_2SiMe_3)_4$ by anions in which alkyl migration across the metal–metal bond occurs need not involve deprotonation as initially proposed.[12] The possibility of a general synthetic route to aryloxide compounds of formula $Mo_2(OAr)_6(X)_2(L)_2$ by addition of anions, X^-, to hexaaryloxide compounds in the presence of added ligand molecules is being investigated.[13]

Acknowledgment. We thank the National Science Foundation (Grant CHE-8219206 to I.P.R.), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Research Corp. for support.

Registry No. 1, 87145-60-6; $Mo_2(NMe_2)_2(OAr')_4$, 87145-58-2; $Mo_2(OAr')_6$, 87145-58-2; $Mo_2(NMe_2)_6$, 51956-20-8.

Supplementary Material Available: Listings of atomic coordinates and anisotropic temperature factors (5 pages). Ordering information is given on any current masthead page.

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(9) ^{1}H NMR (30 °C, $C_6D_5CD_3$): a set of four well-resolved lines at δ 5.75, 5.57, 5.40, and 5.10 in the ratio of 2:2:1:2. All other resonances were broad and unassignable.

(10) (a) Theoretical treatments of the bonding in M_2L_9 type compounds have been published. In the case of M = Mo, the overlap of metal orbitals is poor and can therefore result in easily accessible paramagnetic excited states that can be thermally populated. See: Summerville, H. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3821. Trogler, W. C. *Inorg. Chem.* **1980**, *18*, 697. (b) Grey, I. E.; Smith, P. W. *Aust. J. Chem.* **1971**, *24*, 73.

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(12) Addition of $LiNMe_2$ to 1,2-$Mo_2Br_2(CH_2SiMe_3)_4$ generates 1,1-$Mo_2(NMe_2)_2(CH_2SiMe_3)_4$. This present work raises the question whether addition of an anion Y^- to an Mo_2X_6 molecule gives an unbridged $(X)_3(Y)MM(X)_3$ or bridged $(X)_2M(\mu\text{-}X)_2(\mu\text{-}Y)M(X)_2$ structure. Such an intermediate would explain the observed alkyl migration without invoking the deporotonation pathway previously proposed; see: Chisholm, M. H.; Folting, K.; Huffman, J. C.; Rothwell, I. P. *Organometallics* **1982**, *1*, 252.

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Tetrakis(ethane-1,2-dithiolato)divanadate(III): A Binuclear Complex with a Quadruple Bridge, a Metal–Metal Bond, and Nonoctahedral Stereochemistry

Sir:

In the course of the development of the synthesis and stereochemistry of complexes of thiolates RS^-, a fundamental ligand type, certain regularities have emerged. With the divalent transition-metal ions M = Mn(II), Fe(II), Co(II), Zn(II), and Cd(II) the reactant mole ratios RS^-:M(II) = >4:1, 3:1, and 2.5:1 afford, under appropriate conditions,[1-3] complexes of the general types $[M(SR)_4]^{2-}$ (**1**), $[M_2(\mu\text{-}SR)_2(SR)_4]^{2-}$ (**2**), and $[M_4(\mu\text{-}SR)_6(SR)_4]^{2-}$ (**3**), respectively. Each type contains tetrahedral $M^{II}S_4$ coordination units,[1-6] with **2**[1,3,5]

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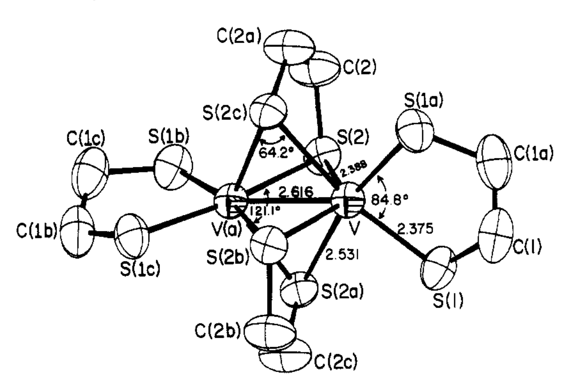
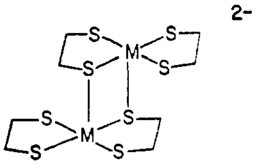


Figure 1. Structure of $[V_2(edt)_4]^{2-}$ with selected bond distances and angles. Atoms labeled with letters are related to those in the asymmetric set V–S(1,2)–C(1,2) under D_2 symmetry.

involving edge-shared tetrahedra and **3**[1,2,6] containing an adamantane-like $M_4(\mu\text{-SR})_6$ cage. Use of the bidentate ligand 1,2-$C_2H_4S_2^{2-}$ (edt), which tends to enforce bite angles nearer 90° than 109.5°, results in the formation of tetrahedral $[M(edt)_2]^{2-}$ with ions (Mn(II),[2] Co(II)[7]) having high tetrahedral stereochemical preference. Substantially less information is available for M(III)–thiolate complexes. Stable tetrahedral $[Fe(SR)_4]^-$ species are formed with monodentate[8] and flexible bidentate[4a] ligands. However, the binuclear species $[M_2(edt)_4]^{2-}$ (**4**), having distorted-trigonal-bipyramidal coordination of Fe(III)[9] and Mn(III),[2,10] are stabilized with the more constraining ligand. Lateral doubly bridged dimers, especially with sulfur ligands, are unexceptional for the preceding M(II) set.[2,11] The generality of structure **4** with M(III) ions of the early transition series has been further examined.



4

An anaerobic reaction mixture consisting of 6.5 mmol of VCl_3 and 13 mmol of Na_2edt in 160 mL of methanol was stirred for 6 h. Et_4NCl (13 mmol) in 20 mL of methanol was added, and the solvent was removed in vacuo. The filtrate from extraction of the residue with 100 mL of acetonitrile was reduced in volume by ~25% and cooled to -20 °C. Large, red-brown, block-shaped crystals were collected, washed with ether, and dried in vacuo, affording 1.25 g (53%) of $(Et_4N)_2[V_2(edt)_4]$.[12] Crystals so obtained were suitable for X-ray structural analysis. The compound crystallizes in orthorhombic space group *Ccca* with a = 17.840 (6) Å, b = 13.769 (4) Å, c = 14.600 (5) Å, and Z = 4. The crystal structure was solved and refined by standard procedures.[13,14]

Table I. Selected Interatomic Distances (Å) and Angles (deg)

V–V(a)	2.616 (2)	S(1)–V–S(1a)	84.8 (1)
V–S(1)	2.375 (2)	S(1)–V–S(2a)	82.4 (1)
V–S(2)	2.388 (1)	S(2a)–V–S(2c)	110.5 (1)
V–S(2a)	2.531 (2)	S(1)–V–S(2)	109.7 (1)
C(1)–S(1)	1.825 (6)	S(1)–V–S(2b)	112.9 (1)
C(2)–S(2)	1.813 (6)	S(1)–V–S(2c)	167.1 (1)
S(1)···S(1a)	3.202 (3)	S(2)–V–S(2a)	71.7 (1)
S(1)···S(2a)	3.233 (3)	S(2)–V–S(2b)	121.1 (1)
S(1)···S(2b)	3.969 (3)	S(2)–V–S(2c)	75.7 (1)
S(2)···S(2a)	2.883 (3)	S(1)–V–V(a)	137.6 (1)
S(2)···S(2c)	3.021 (3)	V–S(2)–V(a)	64.2 (1)
C(1)–C(1a)	1.501 (13)	V–V(a)–S(2)	55.2 (1)
C(2)–C(2a)	1.451 (10)	V–V(a)–S(2a)	60.6 (1)

It consists of well-separated cations and binuclear anions. The anion structure is shown in Figure 1; interatomic distances and angles are collected in Table I.

The structure of $[V_2(edt)_4]^{2-}$ does not conform to type **4**, found first for $[Fe_2(edt)_4]^{2-}$ [9] and subsequently for $[Mn_2(edt)_4]^{2-}$.[2,10] Instead, there are two terminal chelate rings and two bridging edt ligands whose sulfur aoms S(2,2a–c) are bonded to the two V(III) atoms forming the quadruple $V(\mu\text{-S})_4V$ bridge unit. The chiral anion has imposed D_2 symmetry, with the atom set V, S(1,2), C(1,2) constituting the crystallographic asymmetric unit. All other atom positions are generated by the three C_2 axes. One of these ($C_2(z)$) contains the V–V vector and bisects the C–C bonds of the terminal rings. The other two are perpendicular to the V–V vector and bisect the C–C bonds of the bridging ligands and the nonbonding S···S distances (2.883 (3) Å) of the bridge. The orthogonal $V_2(\mu\text{-S})_2$ bridge planes are perfect. However, the bridge unit departs from fourfold symmetry by virtue of pairs of appreciably inequivalent V–S distances (2.388 (1), 2.531 (2) Å) and S–V–S angles (71.7 (1), 75.7 (1)°). Consequently, the $(\mu\text{-S})_4$ group is puckered with nearest-neighbor atoms displaced 0.135 Å above and below the least-squares plane. The V atom is located 1.308 Å above this plane, which forms a 90° dihedral angle with the chelate plane V–S(1)–S(1a). The dihedral angle between the latter and the bridge plane V–S(2a)–S(2c)–V(a) is 179.8°, placing the pairs S(1)–S(2a) and S(1a)–S(2c) in eclipsed positions with respect to the $C_2(z)$ axis. The VS_6 coordination unit has C_{2v} symmetry and is of unusual nonoctahedral stereochemistry. The coordination geometry may be idealized as a cube minus two atoms at the ends of a face diagonal or, equivalently, as a twisted trigonal prism having one edge rotated by 45° from the D_{3h} arrangement.

$[V_2(edt)_4]^{2-}$ is the first vanadium–thiolate complex to have been prepared. Its structure contains several noteworthy features. While pseudooctahedral quadruple bridges $M(\mu\text{-L})_4M$ are precedented,[15,16] including instances with L = RS^-,[16]

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(13) Crystal dimensions were 0.30 × 0.20 × 0.20 mm; d_{calcd} (d_{obsd}) = 1.35 (1.37) g/cm^3. Diffraction data were collected at ~25 °C on a Nicolet R3m diffractometer: $\lambda(\text{Mo K}\bar{\alpha})$ = 0.710 69 Å; absorption coefficient μ = 10.1 cm^{-1}; minimum and maximum transmission factors, 0.509 and 0.580; data collected, $+h,+k,+l$ ($\theta/2\theta$ mode). Atomic scattering factors were taken from a standard source (Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England 1974) and were corrected for $\Delta f'$ and $i\Delta f''$ terms. The structure was solved by a combination of direct methods and difference Fourier techniques employing SHELXTL programs (Nicolet XRD Corp., Fremont, CA). All non-hydrogen atoms were refined with anisotropic temperature factors; fixed contributions of hydrogen atoms were included in the latter stages of least-squares refinement. With use of 725 ($(F_o^2) > 3\sigma(F_o^2)$, $4.0° \le 2\theta \le 45.0°$) of 1189 unique data the structure was refined to R (R_w) = 3.7 (3.9)%.

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

that encountered here is the initial example in a first-transition-series compound. Indeed, among discrete species it is the first example with M $\neq$ Mo. To our knowledge the coordination geometry of the VS_6 group has been found elsewhere only in C-M_2O_3 crystals,[17] where the MO_6 units are polymeric. The V–V distance of 2.616 (2) Å falls in the range (2.2–2.7 Å) associated with metal–metal bonds in other binuclear vanadium complexes,[18] none of which contains V(III). The presence of a V–V bond is further supported by the solid-state diamagnetism and extended Hückel MO calculations.[19] The latter indicate an orbital, interpreted as a V–V σ bond, which is mainly (V + V(a))$3d_{z^2}$, is ~0.60 eV below the HOMO, and is stabilized with decreasing V–V distance. The HOMO (ϕ_a) and LUMO (ϕ_s), separated by 0.17 eV, consist of antisymmetric and symmetric combinations, respectively, of $3d_{x^2-y^2}$ (δ symmetry) on each metal with appropriate symmetry combinations of bridging S $3p_{x,y}$ orbitals. The energy order $\phi_a < \phi_s$ is related to different overlaps with bridge orbitals disposed in the acute (64°) V–S–V fragments; a related behavior in metal dimers has been encountered.[20] At this stage the molecular diamagnetism is ascribed to the presence of a V–V single bond and antiferromagnetic coupling of the remaining two electrons transmitted through bridging sulfur atoms. The same orbital scheme with $[Mn_2(edt)_4]^{2-}$ would require population of ϕ_s and the next orbital ~1.1 eV less stable. As already observed, this complex and $[Fe_2(edt)_4]^{2-}$ adopt a different structure (**4**) than that of $[V_2(edt)_4]^{2-}$.

In acetonitrile solution $[V_2(edt)_4]^{2-}$ exhibits a well-defined one-electron oxidation with $E_{1/2} = -0.62$ V (vs. SCE, ΔE_p = 90 mV, $i_{p,a}/i_{p,c} \simeq 1$). The properties of this apparent mixed-valence species together with a more detailed analysis of the bonding in the $[M_2(edt)_4]^{2-}$ set of complexes and the magnetic properties of $[Mn_2(edt)_4]^{2-}$ [2] will be presented subsequently.

Acknowledgment. Ths research was supported by NIH Grant GM 28856. X-ray diffraction equipment used in this research was obtained by NSF Grant CHE 80-00670.

Registry No. $(Et_4N)_2[V_2(edt)_4]$, 87145-62-8; V, 7440-62-2.

Supplementary Material Available: X-ray structural data for $(Et_4N)_2[V_2(edt)_4]$: listings of positional and thermal parameters and calculated hydrogen atom positions and tables of $10|F_o|$ and $10|F_c|$ (6 pages). Ordering information is given on any current masthead page.

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