mean that the vibrational motion best described as the Si–N stretch is expected near 200 cm^{-1}, with a low infrared intensity resulting from the slight change in dipole moment.

II is 47 kJ mol^{-1} higher than I, or unbound once the superposition error is considered, while III is 10 kJ mol^{-1} above II. IV is not a local minimum on the potential energy surface but relaxes, with progressive energy lowering, toward I.

These calculations have shown I to be the most stable arrangement of $SiF_4{\cdot}NH_3$ at the SCF level. However, such support for the experimental result[1] must be qualified until that level has been passed. Although a realistic calculation of the adduct's correlation energy far exceeds our computing resources, we believe we can show it to differ so little for I and II that the conclusions reached at the SCF level remain valid. Reasoning that the essence of the *difference* in correlation energies for I and II would be present in a suitable model system, we studied $SiH_4{\cdot}NH_3$ at geometries I′ and II′ analogous to I and II for $SiF_4{\cdot}NH_3$. Correlation energies obtained by second-order Möller–Plesset perturbation theory[14] were 0.30731 au for I′ and 0.30730 au for II′, a trivial difference of 0.03 kJ mol^{-1} in favor of I′. An appreciable post-SCF contribution to the binding of $SiF_4{\cdot}NH_3$ is indicated, since the correlation energy of I′ exceeds those of SiH_4 and NH_3 added together by 23 kJ mol^{-1}.

NH_3 transfers 0.13 electron to SiF_4 on adduct formation, according to the population analysis.[15] Those orbitals mainly localized on NH_3 are stabilized but those on SiF_4 raised in energy. Net atomic charges are as follows: N, 1.15–; H, 0.43+; Si, 1.81+; F, 0.49– (axial) and 0.48– (equatorial). In a comparison of these with the charges on N and H in NH_3, 1.01– and 0.34+, with the same basis, it appears that the electron density transferred from NH_3 to SiF_4 in I originated on the H atoms and that N in I is more negatively charged than *either* N in NH_3 *or* F in $SiF_4{\cdot}NH_3$.

It is tempting to correlate electronegativity, "the power of an atom in a molecule to attract electrons to itself",[16] with Mulliken net atomic charges.[15] One could thereby rationalize the axial position adopted by NH_3 in $SiF_4{\cdot}NH_3$, in conformity with the well-known rule,[4] as N would appear to be more electronegative than F, as judged by its net charge. Furthermore, since N has gained its excess charge chiefly from the H atoms in $SiF_4{\cdot}NH_3$, N in PF_4NH_2 would have a reduced capacity to become so "electronegative", as it could drain electron density from only two N–H bonds, rather than three as in $SiF_4{\cdot}NH_3$. The equatorial position adopted by N in PF_4NH_2[17] would thereby fit comfortably with its axial site in $SiF_4{\cdot}NH_3$. Unfortunately, the electron density is partitioned in an arbitrary if plausible manner during the population analysis with numerical results sensitive to minor basis set details, so it would be prudent to regard these arguments as not more than suggestive.

Other calculations have shown that H_2O forms an adduct with SiF_4, of lower stability than $SiF_4{\cdot}NH_3$, but that neither SiH_4 nor CF_4 forms an adduct with NH_3.

Acknowledgment. I thank Dr. P. R. Taylor for performing the counterpoise calculation to determine the basis set superposition error in $SiF_4{\cdot}NH_3$.

Registry No. $SiF_4{\cdot}NH_3$, 71562-57-7.

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Conversion of $L_3Mo{\equiv}MoL_3$ to $L_3Mo(\mu\text{-}L)_3MoL_3$ Type Compounds and Mechanistic Implications

Sir:

The chemistry of dimetal compounds containing d^3–d^3 metal electron configurations (with the potential of forming metal–metal triple bonds) is characterized by a rich variety of geometries.[1-3] We report here the first observation of the conversion of a "Chisholm type" compound (Mo_2L_6 staggered ethane-like and typified by alkoxide and amido ligands with consistently strong metal–metal triple bonds) to a face-shared bioctahedral geometry (Mo_2L_9 characterized previously by halide complexes and a variable metal–metal distance and bond strength).

During our studies of early-transition-metal aryloxide chemistry we have investigated the, at first sight, trivial difference between aryloxide and alkoxide ligands on the chemistry of dimetal centers.[4] Use of the sterically quite demanding ligand 2,6-dimethylphenoxide leads to substitution chemistry quite analogous to that of alkoxides with slight differences due to steric influences. Hence, addition of the parent phenol to $Mo_2(NMe_2)_6$ yields (via an intermediate) the hexaaryloxide $Mo_2(OAr')_6$ (OAr′ = 2,6-dimethylphenoxide) in good yield.[5] However, use of the less sterically demanding 4-methylphenol (HOAr) gives different products. Addition of HOAr to $Mo_2(NMe_2)_6$ in hexane results in the formation of a dark solution from which a compound of formula $[(H_2NMe_2)]^+$-$[(Mo_2(OAr)_7(HNMe_2)_2]^-$ (**1**) crystallizes.[6] This formulation was confirmed by a single-crystal X-ray diffraction study.[7]

Figure 1 shows an ORTEP view of the anion along with some pertinent bond distances and angles. The overall geometry can be seen to be a confacial bioctahedron with the dimethylamine ligands being terminal and arranged so as to generate C_2 symmetry. The Mo–Mo distance of 2.60 Å is only slightly shorter than that found in Mo_2Cl_9.[3-8] Not unexpectedly, the compound is slightly paramagnetic at room temperature ($\mu_{eff} < 0.3\ \mu_B$ by Evans' method). The ^1H NMR

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[3] For molybdenum and tungsten, three basic configurations exist: (a) metal–metal triple bonds with no bridging atom bonded to both metals (this does not rule out bridging groups where a different atom is bonded to each metal), typified by molecules such as $Mo_2(OR)_6$, $W_2(NMe_2)_4Cl_2$, and $W_2(O_2CNMe_2)_6$; (b) two metal centers bridged by two atom centers in an edge-shared bioctahedral structure typified by $W_2Cl_3(py)_4$; (c) two metal atoms bridged by three atom centers in a confacial-bioctahedral environment typified by $M_2Cl_9{}^{3-}$ (M = Cr, Mo, W).
[4] Coffindaffer, T. C.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.*, in press.
[5] Addition of 2,6-dimethylphenol (excess) to $Mo_2(NMe_2)_6$ in hexane gave on standing an almost quantitative yield of orange crystals of $Mo_2(NMe_2)_2(OAr')_4$. Anal. Calcd for $Mo_2C_{36}H_{48}N_2O_4$: C, 56.53; H, 6.33; N, 3.66. Found: C, 56.44; H, 6.49; N, 3.64. ^1H NMR (30 °C, C_6D_6): δ 6.6–7.1 (m, OC_6H_3), 2.21 (s, Me), 4.43, 1.70 (s, NMe_2). This compound reacts further with the excess phenol at 80 °C to give $Mo_2(OAr')_6$ as a red solid in excellent yield. Anal. Calcd for $Mo_2C_{48}H_{54}O_6$: C, 62.75; H, 5.92. Found: C, 62.20; H, 6.01. ^1H NMR (30 °C, C_6D_6): δ 6.6–7.1 (m, OC_6H_3), 2.09 (s, Me).
[6] Addition of 4-methylphenol ($\geq$7 equiv) to $Mo_2(NMe_2)_6$ in hexane gave a dark solution from which dark crystals of $[H_2NMe_2][Mo_2(OAr)_7(HNMe_2)_2]$ (*n*-hexane) separated in good yield. Use of only 6 equiv of 4-methylphenol resulted in formation of the salt, but in reduced yields. Analysis of the parent solution showed the presence of a mixture of as yet unidentified aryloxide–amido compounds. Anal. Calcd for $Mo_2C_{61}H_{79}N_3O_7$: C, 63.08; H, 7.21; N, 3.62. Found: C, 62.50; H, 7.31; N, 3.62.
[7] Crystal data for $Mo_2C_{48}H_{54}O_6$ at –163 °C: space group $P\bar{1}$, $a = 14.677$ (6) Å, $b = 16.627$ (7) Å, $c = 14.402$ (6) Å, $\alpha = 115.78$ (2)°, $\beta = 107.67$ (2)°, $\gamma = 77.82$ (2)°, $Z = 2$, $d_{calcd} = 1.281$ g cm^{-3}. Of the 6714 unique reflections collected with Mo $K\alpha$ radiation, $6° > 2\theta > 45°$, the 5560 with $F > 2.33\ \sigma(F)$ were used in the full-matrix refinement. Final residuals are $R(F) = 0.0730$ and $R_x(F) = 0.0668$.
[8] Cotton, F. A.; Ucko, D. A. *Inorg. Chim. Acta* **1972**, *6*, 161.

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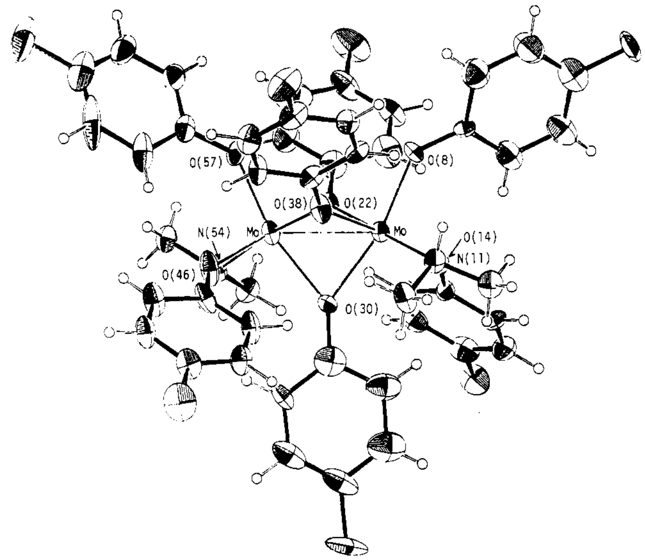

Figure 1. ORTEP view of the anion in the parent compound. Some pertinent bond distances (Å) and angles (deg) are as follows: Mo–Mo = 2.601 (2), Mo–O(terminal) = 2.040 (av), Mo–O(bridge) = 2.113 (av), Mo–N = 2.245 (av); Mo–O–Mo = 76.2 (av).

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]

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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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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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