

be cleanly effected with a stoichiometric amount of  $\text{Et}_3\text{N}$ .) Further treatment of **2a** or **2b** with 2 equiv of acid affords low yields of  $[(\eta^5\text{-C}_5\text{H}_4\text{Me})_3\text{Mn}_3(\text{NO})_3(\text{NH})\text{Y}]$  ( $\text{Y} = \text{BF}_4$ , **3a**;  $\text{Y} = \text{PF}_6$ , **3b**), which may be more conveniently obtained from the reactions of **1** with an excess of the appropriate acid in  $\text{CH}_2\text{Cl}_2$ .<sup>8</sup> The product complexes **2** and **3** are relatively air-stable, black crystalline solids.

Single-crystal X-ray crystallographic analyses of **2a** and **3b**<sup>9</sup> confirmed the identities of the hydroxyimido- and imido-containing cations, respectively, and revealed their molecular structures (Figures 1 and 2). To the best of our knowledge, **2a** and **3b** represent the first structurally characterized examples of  $\text{M}_3$ - $(\mu_3\text{-NOH})$  and  $\text{M}_3$ - $(\mu_3\text{-NH})$  linkages.<sup>10</sup> In both complexes, the central  $\text{Mn}_3(\text{NO})_3$  core is essentially the same as that found for  $(\eta^5\text{-C}_5\text{H}_5)_3\text{Mn}_3(\text{NO})_4$  (**1'**),<sup>12</sup> the cyclopentadienyl analogue of **1**; selected intramolecular dimensions are presented in the captions to Figures 1 and 2. The most chemically interesting features of both structures involve the unique apical ligands. Both ligands are attached closer to the equilateral  $\text{Mn}_3$  triangle than the triply bridging nitrosyl ligand in **1'** (i.e.,  $\text{Mn-N}(4)$  (av) = 1.872 (3) or 1.873 (3) Å vs. 1.929 (11) Å). Also, the N-O bond length of the NOH ligand in **2a** (i.e., 1.393 (4) Å) is considerably longer than that of the  $\mu_3\text{-NO}$  ligand in **1'** (i.e., 1.247 (5) Å). These two structural features are indicative of the relatively greater electron-accepting abilities of the  $\mu_3\text{-NOH}$  and  $\mu_3\text{-NH}$  groups. Both the hydroxyimido and the imido ligands in **2a** and **3b**, respectively, are also linked by hydrogen bonds to the counteranions. This hydrogen bonding in **2a** ( $\text{H}\cdots\text{F} = 1.91$  (6) Å) produces a pronounced distortion of the  $\text{BF}_4^-$  anion to local  $\text{C}_{3v}$  symmetry, but in **3b** ( $\text{H}\cdots\text{F} = 2.24$  (4) Å) it is not sufficiently strong to result in a unique P-F bond length in the  $\text{PF}_6^-$  anion.

The spectroscopic properties of the trimetallic cationic complexes can be readily understood in terms of their solid-state molecular structures, thus confirming that the basic structural units also persist in solutions. The IR absorptions attributable to the  $\mu_2\text{-NO}$  groups in both **2** and **3** occur some 40  $\text{cm}^{-1}$  higher in energy than those in **1**, thereby indicating the diminished electron density of the  $\text{Mn}_3(\mu_2\text{-NO})_3$  framework in the former species. The distortion of the  $\text{BF}_4^-$  anion in **2a** is also detectable by IR spectroscopy both in the solid state (Nujol) and in weakly coordinating solvents such as  $\text{CH}_2\text{Cl}_2$ . Analogous effects of hydrogen bonding are not observable in the IR spectra of the other cations. The  $^1\text{H}$  NMR spectra of **3a** and **3b** in  $\text{CD}_2\text{Cl}_2$  verify that the imido hydrogen atom remains bonded to the  $\mu_3\text{-N}$  atom (e.g., for **3a**,  $\delta$  21.95 (1 H, t,  $J_{\text{H-N}} = 61$  Hz)). However, similar spectra of **2a** and **2b** in  $(\text{CD}_3)_2\text{CO}$  do not display detectable signals due to  $\mu_3\text{-NOH}$  in the range  $\delta$  +30 to -35, a probable consequence of H bonding (vide supra).

The proton-induced transformations **1**  $\rightarrow$  **2**  $\rightarrow$  **3** represent two steps of a possible process for the reduction of NO to  $\text{NH}_3$ . (The two electrons required in the second step are most likely provided intermolecularly by the manganese atoms of the cluster.) In this sense, the process is analogous to that described by Shriver and co-workers for the conversion of bound CO to  $\text{CH}_4$  by strong protonic acids.<sup>13</sup> Unlike the related carbonyl clusters, however, the cations **3** are unaffected by  $\text{HBF}_4\cdot\text{OMe}_2$  or  $\text{HPF}_6(\text{aq})$ . Investigations concerning other aspects of the characteristic chemistry of complexes **1-3** are currently in progress.

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**Registry No.** **1**, 66795-25-3; **2a**, 85649-56-5; **2b**, 85661-38-7; **3a**, 85649-58-7; **3b**, 85649-59-8.

**Supplementary Material Available:** Listings of all spectroscopic and X-ray diffraction data and tables of fractional coordinates and isotropic and anisotropic thermal parameters for **2a** and **3b** (8 pages). Ordering information is given on any current masthead page.

## Atomic Fits to Electron Densities in Polyatomic Molecules. Correlation of Atom Size and Charge

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The size and shape of a molecule may be defined by a surface of constant electron density. Size comparisons among different molecules may be made either by defining a single value of the electron density function,  $\psi^2$ , as the surface value for all systems or by allowing this value to vary from one molecule to another as to enclose a fixed (high) percentage of the total electron density.<sup>2</sup> Representation of molecular size and shape is also the function of space-filling (CPK) models.<sup>3</sup> While these provide highly portable representations, i.e., molecules are built up from atoms, they cannot be expected to yield as accurate a picture of three-dimensional size and shape as do total electron density distributions.

In order to combine the accuracy and detail available from total electron densities with the convenience and portability of space-filling models, we have examined fitting total electron density surfaces, calculated from a uniform level of nonempirical molecular orbital theory, to spheres centered on the individual atomic positions. In this initial report we describe briefly the numerical procedures involved in the fitting and, by way of example, illustrate expected correlations between atom sizes in molecules and atomic charges.

The left-hand side of Figure 1 shows the calculated total electron density surface of dimethyl sulfide, obtained by using the 3-21G(\*) supplemented split-valence basis set,<sup>4,5</sup> based on a surface contour level of 0.002<sup>6</sup> (corresponding to enclosure of approximately 98% of the total electron density), and produced by using the PHOTOMO computer program.<sup>7</sup> Detailed numerical procedures involved in the construction and display of images such as these are described

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(2) This second approach suffers in that a surface incorporating a fixed percentage of the total density of a molecule containing a large number of electrons is not directly comparable to the surface of equal percentage enclosure for a molecule with a small number of electrons.

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(6) This contour level leads to average "sizes" of atoms in molecules that are comparable to van der Waals radii. For a discussion, see: M. M. Francl, R. F. Hout, Jr., and W. J. Hehre, submitted for publication in *J. Am. Chem. Soc.*

(7) R. F. Hout, Jr., W. J. Pietro, and W. J. Hehre, to be submitted for publication in *QCPE*.

(7) Yields: **2a**, 66%; **2b**, 43%. Anal. Calcd for  $\text{C}_{18}\text{H}_{22}\text{Mn}_3\text{N}_4\text{O}_4\text{PF}_6$  (**2b**): C, 32.35; H, 3.32; N, 8.39. Found: C, 32.38; H, 3.36; N, 8.24.

(8) Yields: **3a**, 13%; **3b**, 14%. Anal. Calcd for  $\text{C}_{18}\text{H}_{22}\text{Mn}_3\text{N}_4\text{O}_3\text{BF}_4$  (**3a**): C, 36.39; H, 3.73; N, 9.43. Found: C, 36.19; H, 3.74; N, 9.18.

(9) Supplementary material.

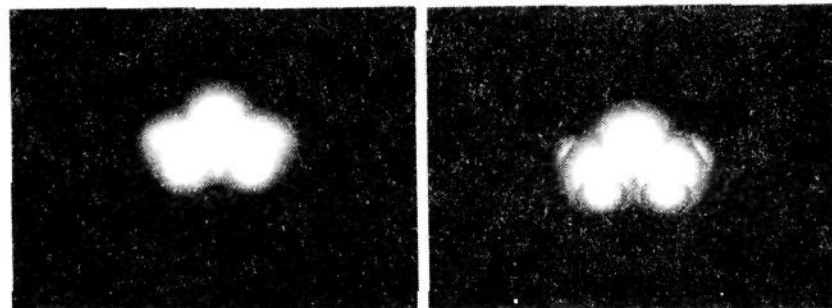
(10)  $\text{Ru}_3(\text{CO})_{10}(\mu_3\text{-NOH})^2$  and  $\text{Fe}_3(\text{CO})_{10}(\mu_3\text{-NH})^{11}$  have been characterized spectroscopically.

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**Figure 1.** Left: total electron density of  $\text{CH}_3\text{SCH}_3$ . HF/3-21G(\*)//HF/3-21G(\*). Right: best fit by nuclear-centered spheres of total electron density.

in the original paper.<sup>8</sup> The image on the right-hand side of Figure 1 represents the least-squares fit to the total electron density surface by a set of spheres centered at the individual atomic positions. Visual inspection reveals that, aside from the "seams" in the sphere-fit-model, the two images are nearly identical. This is also the case for the remainder of the systems examined in this paper. Best atomic radii,  $r$ , are established by the following iterative procedure, starting from an arbitrary initial guess and continuing until self-consistent. For each atom in a molecule: (a) select from a set of 194 points spaced (approximately) uniformly on the surface of a sphere of radius  $r^0$  those points that *do not* fall inside spheres associated with other atoms; (b) for each such point, calculate the gradient of the total electron density and move along the gradient direction until contacting the actual density surface of the molecule, i.e.,  $\psi^2 = 0.002$ ; (c) obtain a new radius as the average distance from the center of the sphere to each of the contact points.

Calculated sizes for sulfur in a variety of its simple compounds are given in Table I. Size data for the free atom in its  $^3\text{P}$  ground state, as well as for  $\text{S}^+$  ( $^4\text{S}$ ) and  $\text{S}^-$  ( $^2\text{P}$ ), are also provided and correlate linearly with atomic charge. Calculated sizes for sulfur in molecules, brought onto the same scale, lead then to specification of formal charge in these systems. These are also given in Table I and are compared to atomic charges obtained from a standard Mulliken population analysis.<sup>10,11</sup> The following points are worthy of comments:

1. Calculated atom sizes in the inorganic sulfur compounds (except  $\text{SCl}_2$ ) closely parallel formal oxidation numbers.<sup>12</sup> For example, the sulfur atom in  $\text{SO}_3$  (formally  $\text{S}^{\text{VI}}$ ) is 0.08 and 0.09 Å smaller than those in  $\text{SF}_4$  and  $\text{SO}_2$ , respectively (both formally  $\text{S}^{\text{IV}}$ ). The sulfurs in these two molecules are 0.07 and 0.06 Å smaller than that in  $\text{SF}_2$  ( $\text{S}^{\text{II}}$ ), which, in turn, is 0.07 Å smaller than the value for the free atom ( $\text{S}^0$ ). The calculated size of sulfur in sulfur dichloride is similar to that in the free atom, suggesting assignment of oxidation state as  $\text{S}^0$  rather than as  $\text{S}^{\text{II}}$  (as in  $\text{SF}_2$ ). Formal oxidation states for sulfur bonded to carbon are more difficult to assign (the two elements have about the same electronegativity), and correlations here are less meaningful.

2. Atomic charges based on atom sizes only roughly parallel those obtained from a Mulliken population analysis. According to both schemes, sulfur is positively charged in hypervalent compounds and (nearly) neutral or negatively charged in normal-valent systems. Mulliken charges for all compounds are more positive than those obtained by size correlations. In addition some specific and significant differences do exist between the two sets of "charges". For example, Mulliken charges for what appear to be

**Table I.** Calculated Sizes and Atomic Charges for Sulfur in Molecules<sup>a</sup>

molecule	calcd radius, Å	charge on S ( $\times 10^{-2}$ electrons)	
		from fit to total electron density	from Mulliken population analysis
$\text{SO}_3$	1.76	134	145
$\text{S}^+$	1.81	100	100
$\text{SF}_4$	1.84	82	163
$\text{SO}_2$	1.85	70	100
$\text{SF}_2$	1.91	40	77
S	1.96	0	0
$\text{CS}_2$	1.98	-10	10
$\text{SCl}_2$	1.99	-16	26
SCO	2.00	-27	2
$\text{CH}_2\text{CH}_2\text{S}$	2.00	-28	7
$\text{H}_2\text{S}$	2.01	-33	-27
$\text{H}_2\text{S}_2$	2.02	-36	-14
$\text{S}(\text{CH}_3)_2$	2.03	-45	17
$\text{CH}_3\text{CH}_2\text{SH}$	2.03	-45	-5
$\text{S}^-$	2.11	-100	-100

<sup>a</sup> HF/3-21G(\*)//HF/3-21G(\*) level. Optimum structures from ref 3, except the following:  $\text{SF}_2$ ,  $C_{2v}$ ,  $r(\text{SF}) = 1.592$ ,  $\angle\text{FSF} = 98.3$ ;  $\text{CS}_2$ ,  $D_{\infty h}$ ,  $r(\text{CS}) = 1.542$ ;  $\text{SCl}_2$ ,  $C_{2v}$ ,  $r(\text{SCl}) = 2.019$ ,  $\angle\text{ClSCl} =$

102.5; SCO,  $C_{\infty v}$ ,  $r(\text{CS}) = 1.565$ ,  $r(\text{CO}) = 1.147$ ;  $\text{CH}_2\text{CH}_2\text{S}$ ,  $C_{2v}$ ,  $r(\text{CC}) = 1.490$ ,  $r(\text{CS}) = 1.817$ ,  $r(\text{CH}) = 1.071$ ,  $\angle\text{HH}'\text{CC} = 150.8$ ,  $\angle\text{HCH} = 115.3$ ,  $\text{S}(\text{CH}_3)_2$ ,  $C_{2v}$ ,  $r(\text{CS}) = 1.813$ ,  $r(\text{CH}_t) = 1.082$ ,  $r(\text{CH}_g) = 1.082$ ,  $\angle\text{CSC} = 99.4$ ,  $\angle\text{H}_t\text{CS} = 107.7$ ,  $\angle\text{H}_{gg}'\text{CS} = 128.2$ ,  $\angle\text{H}_g\text{CH}_g' = 109.6$ ;  $\text{CH}_3\text{CH}_2\text{SH}$ ,  $C_s$ ,  $r(\text{CC}) = 1.541$ ,  $r(\text{CS}) = 1.829$ ,  $r(\text{C}_1\text{H}_t) = 1.084$ ,  $r(\text{C}_1\text{H}_g) = 1.083$ ,  $r(\text{C}_2\text{H}_g) = 1.081$ ,  $r(\text{SH}) = 1.327$ ,  $\angle\text{CCS} = 109.1$ ,  $\angle\text{H}_g\text{C}_1\text{C}_2 = 109.9$ ,  $\angle\text{H}_{gg}'\text{C}_1\text{C}_2 = 127.2$ ,  $\angle\text{H}_g\text{C}_1\text{H}_g' = 108.6$ ,  $\angle\text{H}_{gg}'\text{C}_2\text{C}_1 = 126.1$ ,  $\angle\text{H}_g\text{C}_2\text{H}_g' = 108.9$ ,  $\angle\text{CSH} = 97.9$ .

two closely related molecules,  $\text{CH}_3\text{CH}_2\text{SH}$  and  $\text{CH}_3\text{SCH}_3$ , differ greatly, while those based on size are identical, i.e., the calculated size of the sulfur in each of these compounds is the same.

Further efforts are underway to establish the sizes of atoms (and common groups of atoms) in a variety of molecular environments and to explore additional correlations between atom size in molecules and observable properties.

### Direct Observation of Radical-Pair Interaction and Decay in Anionic Micelles. A Time-Resolved Electron-Spin-Echo Study<sup>†</sup>

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Photochemical reactions in micelles currently receive considerable attention.<sup>1-5</sup> They provide models for reactions in biological

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