Volume 22
Number 22
October 26, 1983

Inorganic Chemistry

Communications

Structure and Energetics of $SiF_4 \cdot NH_3$: Ab Initio Molecular Orbital Calculations

Sir:

The 1:1 adducts of SiF_4 and $(CH_3)_nNH_{3-n}$ (n = 0–3) amines have recently been studied by infrared spectroscopy coupled with matrix isolation.[1,2] The adducts are trigonal bipyramidal, with the amine occupying an *axial* site. This conclusion is remarkable. Of the huge range of five-coordinate derivatives known of P and S, all examples containing only monodentate groups have the axial sites occupied by the most electronegative ligands, with the possible exception of $(CF_3)_nPF_{5-n}$.[3] It would be surprising if this simple rule, supported by empirical evidence,[4] the VSEPR approach,[5] and MO calculations, both semiempirical[6] and ab initio,[7] were to apply to P and S compounds but not to Si derivatives.

The vibrational assignment of $SiF_4 \cdot NR_3$ adducts was incomplete[1,2] and the crucial Si–N stretching mode not detected. In view of the surprising shape deduced for these adducts, and the difficulties associated with experimental studies,[1,2] we have undertaken a series of molecular orbital calculations on these systems. We present here results for $SiF_4 \cdot NH_3$, which support the experimental findings,[1] and offer some clues about the factors determining its shape.

Most calculations used the GAUSSIAN 80 program,[8] employing complete geometry optimization by gradient techniques. Full double-ζ basis sets were chosen: Si (11s7p)/[6s4p],[9] F and N (9s5p)/[4s2p], and H (4s)/[2s].[10] Polarization functions were added on Si and N. Geometries of SiF_4 and NH_3 were reproduced satisfactorily. The calculated Si–F distance, 1.560 Å, compares with r_a = 1.552 (2) Å,[11] while in NH_3 the bond length, 1.005 Å, and H–N–H angle, 107.1°, are close to experimental r_e values of 1.012 Å and 106.7°.[12]

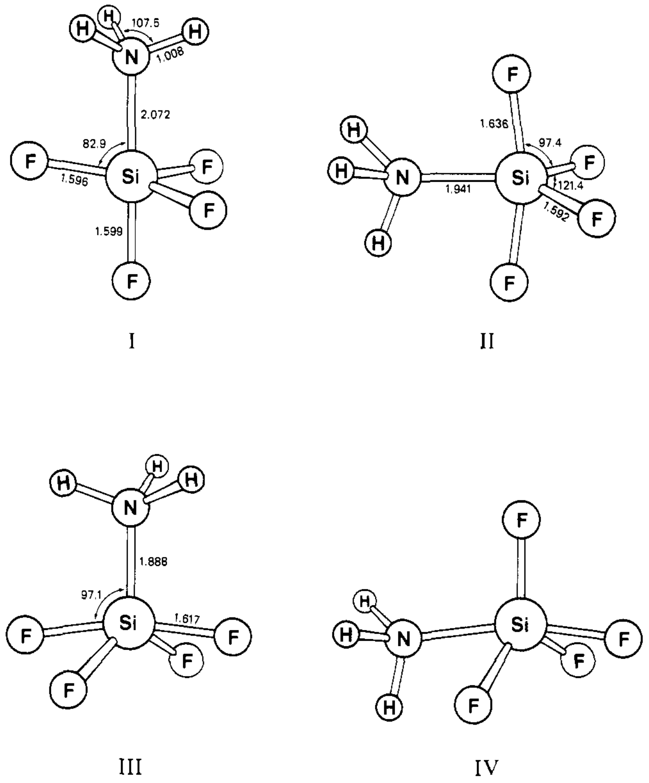

Figure 1. Four different geometries investigated for $SiF_4 \cdot NH_3$. Optimized bond lengths are in angstroms and angles in degrees.

Four different geometries of $SiF_4 \cdot NH_3$, illustrated in Figure 1, were explored. I and II are trigonal bipyramidal, while III and IV are derived from a tetragonal pyramid. NH_3 occupies an axial site in I and III but an equatorial (basal) position in II and IV. Point-group symmetries of the F_4NSi skeleton are as follows: I, C_{3v}; II, C_{2v}; III, C_{4v}; IV, C_s. Optimized geometrical parameters are given in Figure 1.

I is the lowest energy arrangement found for $SiF_4 \cdot NH_3$. Its energy of −743.23144 au indicates an apparent binding energy of 51 kJ mol^{-1}, relative to SiF_4 and NH_3. As the superposition error was found to be 15 kJ mol^{-1}, the true SCF binding energy is 36 kJ mol^{-1}. The Si–N distance in I is substantially greater than typical single-bond lengths of about 1.73 Å.[13] Its stretching force constant of 1.07 mdyn Å^{-1} and the large positive interaction constant linking it to the N–Si–F_{eq} angle

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[1] Ault, B. S. *Inorg. Chem.* **1981**, *20*, 2817.
[2] Lorenz, T. J.; Ault, B. S. *Inorg. Chem.* **1982**, *21*, 1758.
[3] Oberhammer, H.; Grobe, J.; Le Van, D. *Inorg. Chem.* **1982**, *21*, 275.
[4] Muetterties, E. L.; Mahler, W.; Schmutzler, R. *Inorg. Chem.* **1963**, *2*, 613. Muetterties, E. L.; Mahler, W.; Packer, K. J.; Schmutzler, R. *Ibid.* **1964**, *3*, 1298.
[5] Gillespie, R. J.; Nyholm, R. S. *Q. Rev., Chem. Soc.* **1957**, *4*, 389. Gillespie, R. J. "Molecular Geometry"; Van Nostrand-Reinhold: New York, 1972.
[6] Hoffmann, R.; Howell, J. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1972**, *94*, 3027.
[7] Rank, A.; Allen, L. C.; Mislow, K. *J. Am. Chem. Soc.* **1972**, *94*, 3035. Keil, F.; Kutzelnigg, W. *Ibid.* **1975**, *97*, 3623.
[8] Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* **1981**, *13*, 406.
[9] Dunning, T. H.; Hay, P. J. In "Methods of Electronic Structure Theory"; Schaefer III, H. F., Ed.; Plenum Press: New York, 1977; Vol. 4, Chapter 1.
[10] Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823.
[11] Hagen, K.; Hedberg, K. *J. Chem. Phys.* **1973**, *59*, 1549.
[12] Helmenninger, P.; Delucia, F. C.; Gordy, W. *J. Mol. Spectrosc.* **1971**, *39*, 94.
[13] Beagley, B. In "Molecular Structure by Diffraction Methods"; Chemical Society: London, 1973; Vol. 1, p 120.

0020-1669/83/1322-3177$01.50/0

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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(14) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem., Symp.* **1976**, *No. 10*, 1.

(15) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833.

(16) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 88.

(17) Cowley, A. H.; Schweiger, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 4179.

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Received December 8, 1982

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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(1) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.

(2) Chisholm, M. H.; Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 356.

(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 (≥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 Kα radiation, 6° > 2θ > 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.

0020-1669/83/1322-3178$01.50/0