(22) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N.Y., 1967.
(23) T. Takano, O. B. Kallai, R. Swanson, and R. E. Dickerson, *J. Biol. Chem.*, **248**, 5234 (1973).
(24) E. Margoliash, S. Ferguson-Miller, J. Tulloss, C. H. Kang, B. A. Feinberg, D. L. Brautigan, and M. Morrison, *Proc. Nat. Acad. Sci. U.S.*, **70**, 3245 (1973).
(25) L. Smith, H. C. Davies, M. Reichlin, and E. Margoliash, *J. Biol. Chem.*, **248**, 237 (1973).
(26) T. Takano, R. Swanson, O. B. Kallai, and R. E. Dickerson, *Cold Springs Harbor Symp. Mol. Biol.*, **36**, 397 (1971).
(27) R. E. Dickerson, *Sci. Amer.* **226**, 58 (1972).
(28) Pseudo-first-order kinetics were observed in ref 25. Making an approximation that the cytochrome oxidase concentration is at least 20-fold in excess of the ferrocytochrome *c* concentration, an estimated upper limit to the second-order rate constant is calculated as given.
(29) K. Minnaert, *Biochim. Biophys. Acta*, **50**, 23 (1961).
(30) L. E. Andréasson, B. G. Malmstrom, C. Stromberg, and T. Vanngard, *FEBS* (*Fed. Eur. Biochem. Soc.*) *Lett.*, **28**, 297 (1972).
(31) E. Antonini, M. Brunori, C. Greenwood, and B. G. Malstron, *Nature* (*London*), **228**, 936 (1970).
(32) C. L. Hamilton and H. M. McConnell in "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman, San Francisco, Calif., 1968, pp 115–149.

The Hypervalent Molecules Sulfurane (SH_4) and Persulfurane (SH_6)

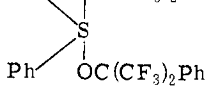
Gretchen M. Schwenzer and Henry F. Schaefer III*

Department of Chemistry and Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720. *Received October 15, 1974*

Abstract: The electronic structures of SH_2, SH_4, and SH_6 have been investigated by ab initio theoretical methods. The geometry of each species has been predicted using self-consistent-field wave functions employing a S(12s 9p/7s 5p), H(5s/3s) basis set of contracted Gaussian functions. Using these geometries, the effects of hydrogen scale factor, d functions on sulfur, and p functions on hydrogen have been explored. It is concluded that SH_4 lies energetically above $SH_2 + H_2$, and that SH_6 lies at least 36 kcal/mol above $SH_2 + 2H_2$. Thus SH_4 and SH_6 at best represent local minima on their respective potential energy surfaces. The structure predicted for SH_4 is quite reminiscent of the known geometry of SF_4. The bonding in these two model systems is discussed making use of population analyses. A number of molecular properties are predicted.

The well characterized SF_4 and SF_6 molecules are the simplest known hypervalent[1] sulfur compounds, i.e., the simplest S(IV) and S(VI) compounds. SF_6 is of course octahedral, with S-F bond distance[2] 1.56$_4$ Å. The more interesting structure of the SF_4 molecule[3] is seen in Figure 1 and might be considered "nearly octahedral." That is, its geometry is roughly approximated by the removal of two adjacent F atoms from the SF_6 structure. However, there are significant deviations from the octahedral model. In particular the axial S-F bond lengths are 0.101 Å longer than the equatorial ones. In addition the F-S-F bond angles are somewhat distorted from their idealized values of 180 and 90°. Finally, we note in Figure 1 that all four fluorine atoms lie in the right hemisphere of the molecule.

Polyfluoro compounds of the types RSF_3 and RSF_5 have been known for some time. Perhaps the earliest research in this area was the preparation of CF_3SF_3 and CF_3SF_5 by Tyczkowski and Bigelow[4] via the fluorination of carbon disulfide. One of the most important *recent* developments in organosulfur research has been the preparation, particularly by Denney[5] and by Martin,[6] of a series of more general hypervalent sulfuranes and persulfuranes. Among the most interesting compounds discovered to date is



(1)

which Martin and coworkers have found to be very useful as a reagent in the dyhydration of alcohols, and to react with amides and amines in a unique manner.[6] These recent developments certainly suggest that hypervalent sulfur compounds have a rich chemistry, only the surface of which has been touched to date.

Concurrent with these experimental developments, Musher[1,7,8] has developed a qualitative theory of the electronic structure of hypervalent sulfur molecules. In addition to providing a framework for the understanding of the known properties of sulfuranes and persulfuranes, Musher has made several intriguing predictions concerning their chemistry.[1,7] In his most recent paper Musher (with Koutecky)[9] has reported semiempirical CNDO/2 calculations of the electronic structures of SF_2, SF_4, SF_6, SH_2, and the two hypothetical molecules SH_4 and SH_6. Since SH_4 and SH_6 are the very simplest hypervalent sulfur molecules, these species serve as models for the many more complicated S(IV) and S(VI) compounds. For this reason, Musher has given the simple name sulfurane to SH_4 and called SH_6 persulfurane.

The present ab initio theoretical study may be viewed as the logical extension of Koutecky and Musher's semiempirical studies of SH_2, SH_4, and SH_6. However, this paper is also a sequel to two semiempirical[10,11] studies and one ab initio treatment[12] of the model hypervalent phosphorous compound PH_5. We note that Rauk, Allen, and Mislow predicted PH_5 to lie ~50 kcal/mol above $PH_3 + H_2$. In this regard it should be noted that the bonds in, e.g., SH_6 must be much stronger than those in SF_6 in order for SH_6 to exist. This is because the bond in the F_2 molecule is rather weak (~39 kcal/mol[13]), so that stability with respect to $S + 3F_2$ requires that each S-F bond energy be only ~20 kcal/mol. On the other hand, the stronger H_2 bond (109 kcal/mol[14]) requires an S-H bond strength of 55 kcal/mol in order that SH_6 lie energetically below $S + 3H_2$.

The goal of the present study, then, is first to predict the geometries of SH_4 and SH_6 and whether either molecule is a thermodynamically stable entity. Second, we seek to elucidate the electronic structures of these two prototype molecules, in particular the nature of the occupied molecular orbitals. In addition we will attempt to determine the importance of d functions on sulfur and p functions on hydrogen.

Initial Basis Sets. Although the H_2S molecule has been

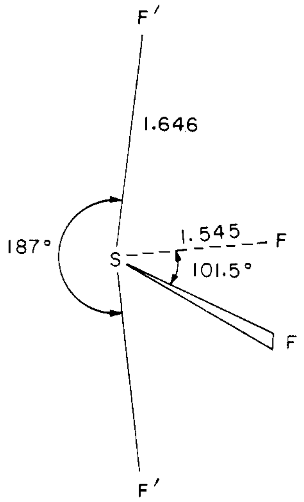


Figure 1. Experimental equilibrium geometry[3] of the SF_4 molecule.

studied previously by several theoretical groups, we have nevertheless included it here to allow a direct comparison with SH_4 and SH_6. We note that the most accurate previous ab initio calculation on H_2S appears to be that of Rothenberg et al.[15] who used a S(12s 9p 1d/6s 4p 1d), H(5s 1p/2s 1p) basis set of contracted Gaussian functions. Good agreement with experiment was found for a number of molecular properties, and a total self-consistent-field (SCF) energy of −398.6862 hartrees was obtained.

In the present calculations on all three molecules, the same sulfur primitive Gaussian basis set of Veillard[16] was used. However, a more flexible contraction, S(12s 9p/7s 5p), than that of Rothenberg et al.[15] was employed. The s contraction can be described as 6111111 and the p contraction as 51111. That is, the primitive Gaussians with the smallest exponents α were given maximum flexibility. The s basis set used for hydrogen was Dunning's (5s/3s) contraction[17] of Huzinaga's primitive Gaussian basis.[18] As will be seen, the overall scale factor of the hydrogen s set was varied in several calculations.

Geometry Optimizations. The basis sets described above were used for the SCF predictions of the geometries of SH_2, SH_4, and SH_6. There is now a fair body of information[19,20] that implies that if one does not intend to go beyond the Hartree-Fock approximation, this type of basis is roughly optimal. Although the addition of polarization functions to the basis will significantly lower the total SCF energy, this can sometimes yield bond distances significantly shorter than experiment. The effect of electron correlation is then to lengthen the bond distances, ultimately bringing them into close agreement with experiment.

For H_2S, the hydrogen scale factor was optimized to yield $\zeta = 1.19$ at the experimental geometry. Using this scale factor, the total SCF energy was then minimized with respect to the bond distances and bond angle. As seen in Table I, the ab initio geometry is in surprisingly poor agreement with experiment. The bond distance is too long by 0.029 Å and the bond angle too large by 4.0°. In fact it seems likely (in retrospect) that a geometry optimization employing a basis set including polarization functions would yield significantly better agreement with experiment.

Note that in Table I there are two SH_4 entries. In the first, an octahedral structure was assumed, with all four SH bond distances equal. The hydrogen scale factor of 1.19 from H_2S was assumed. The second entry describes our complete SH_4 study, in which the energy was minimized with respect to both angles, both bond distances, and the hydrogen scale factor. Although a serious effort was made to simultaneously optimize all five parameters, we cannot unequivocally guarantee that the absolute minimum in the five-dimensional space has been reached.

There is a rather large energy difference, 0.0445 hartree = 28 kcal/mol, between the octahedral and "unrestricted C_{2v}" geometries of SH_4. Perhaps even more significant is the fact that the distortions (relative to the octahedral model) are quite analogous to those observed experimentally[3] for SF_4. While the difference between axial and equatorial bond distances is 0.10 Å in SF_4, the same difference for SH_4 is 0.35 Å. As comparison with Figure 1 shows, the axial F'SF' angle of 187° becomes 192° in SH_4. Finally the FSF equatorial angle of 101.5° in SF_4 becomes 105.6° in SH_4. Thus theory predicts the structure of SH_4 to be quite analogous to that of the known molecule SF_4.

The predicted bond distance in SH_6 is 0.104 Å longer than that of SH_2. This difference can be compared with that between SF_6 (1.564 Å) and SF_2 (1.589 Å[21]), namely −0.025 Å. In this regard it is clear SH_6 is not to SH_2 what SF_6 is to SF_2.

Finally, it should be mentioned that the hydrogen scale factors in SH_4 and SH_6 are significantly less than for SH_2. Since $\zeta = 1.0$ is optimum for an isolated H atom, it would seem that the H atoms in SH_4 and SH_6 are less "positively charged," in a naive picture, than those in SH_2. We will return to this point later.

Polarization Functions and Relative Energies. With the geometries optimized as described above, polarization functions were added to the basis sets of each atom. Specifically, a set of six d-like functions ($x^2e^{-\alpha r^2}$, $xye^{-\alpha r^2}$, $xze^{-\alpha r^2}$, $y^2e^{-\alpha r^2}$, $yze^{-\alpha r^2}$, and $z^2e^{-\alpha r^2}$ except for a normalization factor) were added to sulfur, and a set of p functions (p_x, p_y, p_z) to each hydrogen. Then, for each molecule, the SCF total energy was minimized with respect to the two orbital exponents. The results are summarized in Table II.

The total energy obtained for SH_2 is the lowest reported to date, lying 0.0064 hartree below the SCF calculation of Rothenberg et al.[15] Based on much more exhaustive calculations[22,23] on the related H_2O molecule, we estimate our final H_2S energy to lie ~0.03 hartree above the true Hartree-Fock energy. Although equally reliable estimates of the Hartree-Fock energies of SH_4 and SH_6 cannot be made at present, we can at least suggest that our final SH_6 energy is unlikely to lie more than 0.1 hartree above the true Hartree-Fock limit.

Table II shows that the optimized polarization function orbital exponents are quite similar for the two molecules. The sulfur d function values of α are all somewhat larger than the value of 0.6 used by Rothenberg.[15] Also the hydrogen p exponent is significantly less than "standard" values,[19] which usually fall in the range 0.7–1.0. The energy lowering due to polarization functions is of course greatest for SH_6, which has the most atoms. However, while the number of SH bonds may be correlated with the relative energy lowerings in SH_2 and SH_4, this progression is not valid for SH_6. That is, polarization functions are significantly more important per bond for SH_6 than for SH_2 and SH_4. Similarly, Rauk, Allen, and Mislow[12] have shown that d functions lead to a greater energy lowering per bond for PH_5 than for PH_3.

The next question to be asked is "Does SH_4 lie below $SH_2 + H_2$?" To answer this question, a comparable calculation was carried out on H_2 at its experimental bond distance,[24] 0.741 Å. The optimum scale factor ($\zeta = 1.04$) and p exponent ($\alpha = 0.99$) were determined and a total energy of −1.1327 hartrees was obtained. With this result and the energies in Table II, one is able to predict that SH_4 lies 0.1560 hartree or 98 kcal/mol above $SH_2 + H_2$. Since both reactants and products for the process $SH_2 + H_2 \rightarrow SH_4$

Table I. Predicted Geometries of SH_2, SH_4, and SH_6[a]

	SH_2	SH_4	SH_4	SH_6
r(S–H)	1.357 (1.328)	1.489	1.70	1.461
r(S–H')		1.489	1.35	1.461
θ(HSH), deg	96.2 (92.2)	90	105.6	90
θ(H'SH'), deg		180	191.8	180
Hydrogen scale factor	1.19	1.19[c]	1.00	1.02
Energy, hartrees	−398.6469	−399.5308	−399.5753	−400.5351

[a] Bond distances (Å) and bond angles are specified in a manner analogous to Figure 1. The experimental H_2S geometry[b] is given in parentheses. [b] Geometry recalculated by L. E. Sutton and D. H. Whiffen, *Chem. Soc., Spec. Publ.*, No. 18 (1965), using monents of inertia from H. C. Allen and E. K. Plyer, *J. Chem. Phys.*, 25, 1132 (1956). [c] Not optimized.

Table II. Effect of Polarization Functions on the Monosulfur Hydrides[a]

	SH_2	SH_4	SH_6
Sulfur d exponent α	0.846	0.771	0.883
Hydrogen p exponent α	0.595	0.483	0.560
E(without polarization)	−398.6469	−399.5753	−400.5351
E(with polarization)	−398.6926	−399.6693	−400.7305
ΔE	0.0457	0.0940	0.1954

[a] The geometries used were those seen in Table I. Energies are in hartrees.

are closed shell species, one has reason to hope that the correlation energies will cancel.[25] Perhaps more realistically, SH_4 has one more bond than $SH_2 + H_2$, and could have as much as 0.05 hartree more correlation energy. However, even this increment would not allow SH_4 to be bound, and we conclude that it is not thermodynamically stable.

The energy of $SH_2 + 2H_2$ is −400.9580 hartrees in our calculations, or 0.2275 hartrees = 143 kcal/mol lower than SH_6. If we assume that our basis set is deficient by 0.10 hartree for SH_6 but only 0.03 hartree for $SH_2 + 2H_2$, the energy difference is reduced to 0.1575 hartree = 99 kcal/mol. If in addition we assume that SH_6 has 0.10 hartree more correlation energy than $SH_2 + H_2$, it is possible to conclude that SH_6 lies 0.0575 hartree = 36 kcal/mol above $SH_2 + 2H_2$. Our feeling is that this 36 kcal/mol represents a *lower limit* to the magnitude of the energy difference between SH_6 and $SH_2 + 2H_2$. In any case SH_6 is not thermodynamically stable with respect to $SH_2 + 2H_2$. However, this does not necessarily mean that SH_6 cannot be made. If octahedral SH_6 corresponds to a deep enough relative minimum on the SH_6 potential energy surface, then it might be isolated by some appropriate means. In this regard we note that adjacent H atoms are separated by 2.07 Å, which is so much greater than the equilibrium H_2 distance (0.741 Å) that one anticipates a substantial barrier or activation energy for $SH_6(O_h) \rightarrow SH_2 + 2H_2$. Although we have not pursued this point further, it would fall within the realm of possibly using the "force method" of Pulay.[26]

Electronic Structure. The orbital energies of SH_2, SH_4, and SH_6 are shown in Table *III*, which gives results with and without polarization functions. Perhaps the first point to be made is that the ordering of the orbital energies is produced correctly without S d functions or H p functions. Thus we agree with several recent papers[9,11,12] which emphasize that the qualitative features of the electronic structure of hypervalent molecules such as PH_5 and SH_6 are not affected by d functions. Koutecky and Musher[9] tabulate orbital energies for SH_2 and their ordering of the valence orbitals is identical to ours. However, our results do differ qualitatively from those of Koutecky and Musher[9] with regard to the position of the sulfur atom 3p orbital energy relative to the highest occupied molecular orbitals (HOMOs) of the three molecules. In each case we find the HOMO to lie *above* the S 3p orbital. A related observation is that there is a correlation between predicted stability ($SH_2 >$ $SH_6 > SH_4$) and the value of the HOMO orbital energy.

If it were possible to isolate SH_4 and SH_6, Table III suggests that their photoelectron spectroscopy might be quite interesting. If we use the S 1s orbital energy in H_2S as a reference, then the corresponding ionization potential of SH_4 is 3.1 eV greater, and that of SH_6 is 4.5 eV greater. Chemical shifts of this nature are certainly observable.[27] If we analyze the S 2s ionization potentials in the same way, the relative values are 0.0, 2.8, and 3.6 eV.

One of the most direct, if necessarily arbitrary, way of looking at electronic structure is via Mulliken population analyses.[28] Accordingly we display in Table IV such populations for the valence molecular orbitals of SH_2, SH_4, and SH_6. Looking first at the SH_2 populations, one sees first the surprising result that the sulfur d function there is one additional orbital of H_2S, the $2a_1$ (~S 2s), which has significant d function population, + 0.024. In any case, the known existence of negative Mulliken populations is one of the established drawbacks to this type of analysis. Our conclusion is that these d populations are of limited value, but that the magnitude of the contributions to the different orbitals may be of some qualitative worth. Thus it is clear that d functions are more important for SH_6 than for either SH_2 or SH_4. However, the orbital d populations are in no case large enough to suggest that a qualitatively correct picture of the bonding could not be obtained without d functions. It is also noteworthy that p functions on hydrogen are significantly

Table III. Orbital Energies in Hartree Atomic Units[a]

S		H		SH_2			SH_4			SH_6		
1s	−92.003	1s	−0.500	$1a_1$	−91.978	−91.969	$1a_1$	−92.111	−92.084	$1a_{1g}$	−92.198	−92.137
2s	−9.003			$2a_1$	−8.977	−8.965	$2a_1$	−9.102	−9.067	$2a_{1g}$	−9.174	−9.097
2p	−6.681			$1b_1$	−6.664	−6.652	$1b_2$	−6.788	−6.754	$1t_{1u}$	−6.864	−6.788
3s	−0.879			$3a_1$	−6.663	−6.651	$3a_1$	−6.785	−6.753			
3p	−0.437			$1b_2$	−6.660	−6.650	$1b_1$	−6.785	−6.753			
				$4a_1$	−0.995	−0.977	$4a_1$	−1.090	−1.051	$3a_{1g}$	−1.132	−1.068
				$2b_1$	−0.595	−0.594	$2b_2$	−0.684	−0.667	$2t_{1u}$	−0.695	−0.653
				$5a_1$	−0.486	−0.492	$2b_1$	−0.583	−0.568			
				$2b_2$	−0.390	−0.384	$5a_1$	−0.554	−0.541			
							$6a_1$	−0.264	−0.283	$1e_g$	−0.315	−0.348

[a] For SH_2, SH_4, and SH_6 the second entry is from the calculation including polarization functions. Note that the t_{1u} orbitals of SH_6 are triply degenerate, while the e_g orbital is doubly degenerate.

Table IV. Valence Shell Population Analyses for SH_2, SH_4, and SH_6[a]

	S			H	
	s	p	d	s	p
			SH_2		
$4a_1$	1.588	0.029	−0.085	0.217	0.018
$2b_1$	0.000	0.868	0.028	0.536	0.016
$5a_1$	0.292	1.262	−0.009	0.221	0.006
$2b_2$	0.000	1.973	0.000	0.000	0.013
Totals	1.880	4.132	−0.066	0.974	0.053
			SH_4		
$4a_1$	1.489	0.015	−0.044	0.200 (0.039)	0.025 (0.006)
$2b_2$	0.000	0.908	0.031	0.510 (0.000)	0.019 (0.001)
$2b_1$	0.000	1.108	0.001	0.000 (0.422)	0.009 (0.014)
$5a_1$	0.199	1.327	−0.002	0.207 (0.021)	0.007 (0.003)
$6a_1$	0.033	0.138	0.062	0.007 (0.879)	0.001 (−0.004)
Totals	1.721	3.496	0.048	0.924 (1.361)	0.061 (0.020)
			SH_6		
$3a_{1g}$	1.524	0.000	−0.131	0.546	0.062
$2t_{1u}$	0.000	3.180	0.000	2.689	0.131
$1e_g$	0.000	0.000	0.244	3.756	0.000
Totals	1.524	3.180	0.113	6.991	0.193

[a] For SH_4, the equatorial H populations are followed in parentheses by the axial hydrogen populations.

Table V. Molecular Properties of the Three Monosulfur Hydrides[a]

	SH_2	SH_4	SH_6
Moments (with Respect to the Center of Mass) of the Electronic Charge Distribution			
$\langle x \rangle = \langle y \rangle$	0.368	0.245	
$\langle xx \rangle = \langle yy \rangle$	−16.13	−17.61	−29.45
$\langle zz \rangle$	−12.42	−39.53	−29.45
$\langle xy \rangle$	0.14	0.70	
$\langle xxx \rangle = \langle yyy \rangle$	−11.63	−10.92	
$\langle xxy \rangle = \langle xyy \rangle$	1.60	1.86	
$\langle xzz \rangle = \langle yzz \rangle$	0.47	−3.48	
Multipole Moments			
μ	0.521	0.346	
$\theta_{xx} = \theta_{yy}$	1.37	4.04	
θ_{zz}	−2.75	−8.08	
θ_{xy}	−0.33	−0.50	
$\Omega_{xxx} = \Omega_{yyy}$	1.58	5.34	
$\Omega_{xxy} = \Omega_{xyy}$	−1.20	−1.36	
$\Omega_{xzz} = \Omega_{yzz}$	−0.38	−3.98	
Electric Field Gradient			
$q_{xx}(S) = q_{yy}(S)$	−1.45	0.67	
$q_{zz}(S)$	2.89	−1.34	
$q_{xy}(S)$	1.02	1.29	
$q_{xx}(H)$	−0.24	−0.23 (0.03)	−0.15
$q_{yy}(H)$	0.10	0.10 (0.03)	0.07
$q_{zz}(H)$	0.14	0.12 (−0.07)	0.07
$q_{xy}(H)$	0.02	0.05 (0.00$_5$)	
$q_{xz}(H) = q_{yz}(H)$		(−0.00$_5$)	
Potential			
$\phi(S)$	−59.21	−59.10	−59.03
$\phi(H)$	−1.01	−0.97 (−1.14)	−1.11

[a] Atomic units[b] are utilized throughout. The SCF wave functions used were obtained using our largest basis set S(12s 9p 1d/7s 5p 1d), H(5s 1p/3s 1p). For SH_4, properties of the equatorial H atoms are followed (in parentheses) by the axial H atom properties. [b] S. Rothenberg and H. F. Schaefer, *J. Chem. Phys.*, 53, 3014 (1970).

more important for SH_6 than for SH_2 or SH_4. Thus we conclude that while polarization functions are important for a quantitative description of the electronic structure of SH_4 and SH_6, d orbitals do not play a major role in the bonding.

The total atomic populations on sulfur in SH_2, SH_4, and SH_6 are 15.95, 15.27, and 14.82, and show the same trend as those of Koutecky and Musher,[9] 16.08, 15.47, and 15.07. Both sets of populations imply the same qualitative result, that the added hydrogen ligands in the hypervalent molecules SH_4 and SH_6 act as electron-withdrawing groups. The other particularly noteworthy result concerns the equatorial and axial hydrogen populations in SH_4: 0.99 and 1.38. These may be compared with the analogous semiempirical results of Koutecky and Musher, 0.93 and 1.34. The agreement is excellent and suggests a very uneven electron distribution for SH_4. For comparison the *ab initio* hydrogen populations in SH_2 and SH_6 are 1.03 and 1.20.

Since all three molecules have one occupied molecular orbital with a significantly higher orbital energy than the others, the nature of these HOMO's is an important consideration in any future discussions of the reactivities and electronic spectra of SH_2, SH_4, and SH_6. For H_2S, Table IV shows that the $2b_2$ orbital ($\epsilon = -0.0384$ hartree) is almost entirely sulfur 3p. On the contrary, the $6a_1$ orbital ($\epsilon = -0.283$ hartree) of SH_4 is primarily the symmetric combination of axial hydrogen 1s orbitals. For SH_6, the highest occupied MO is the doubly degenerate $1e_g$ ($\epsilon = -0.348$). Inspection of Table IV indicates that this $1e_g$ orbital is predominantly H 1s in character, with a noticeable sulfur 3d population. In conclusion, the HOMO's of the two hypervalent molecules are qualitatively linear combinations of hydrogen 1s orbitals, while for H_2S the H 1s orbitals become a part of the lower lying MO's.

Molecular Properties. As a final comparison of the three molecules, a number of one-electron properties have been calculated for SH_2, SH_4, and SH_6. These are summarized in Table V. Of these, the only quantity which may be compared directly with experiment is the H_2S dipole moment. The calculated dipole moment is 1.32 D, compared to experiment,[29] 1.02 D. Note that symmetry requires most of the properties to be identically zero for SH_6. The dipole moment of SH_4 is predicted to be 0.88 D, somewhat smaller than that of SH_2, but larger than the SF_4 dipole moment,[3] 0.63 D.

To interpret some of the properties, it is necessary to have a clear picture of the coordinate system used and the positions of the atoms. For SH_6 there is no ambiguity, since the S atom is placed at the origin and the six H atoms along the coordinate axes. For SH_2 and SH_4, the atoms have been placed in the coordinate systems to maintain as close an analogy with SH_6 as possible. For example, for SH_2 the two H atoms lie close to the positive x and y axes. Specifically they are at (2.556, −0.1384, 0) and (−0.1384, 2.556, 0). In Table V, when a property is reported relative to hydrogen, it is the former H atom in particular. Similarly, for SH_4, the equatorial H atom (with respect to which the actual computations were performed) lies at (2.5264, −0.3461, 0) and the axial H atom at (0.2333, 0.2333, 3.193).

One particularly telling indicator of the differences between SH_2, SH_4, and SH_6 is the expectation value $\langle z^2 \rangle$. For SH_2, of course, the magnitude of $\langle z^2 \rangle$ is small, since all three atoms lie in the xy plane. For SH_4, with its elongated axial SH bonds, the absolute value of $\langle z^2 \rangle$ is greatest. In this context SH_6 plays an intermediate role.

Also noteworthy is the magnitude of the elements of the quadrupole moment tensor for SH_4. The elements θ_{xx} and θ_{zz} are roughly three times greater than those predicted for SH_2. This is of particular interest since the quadrupole moments of SF_4 are also unusually large[30]

$$\theta_{aa} = -8.0 \pm 2.1 \text{ au}$$

$$\theta_{bb} = 0.4 \pm 2.3 \text{ au}$$

$$\theta_{cc} = 7.5 \pm 3.3 \text{ au}$$

given in the principal axis system. For direct comparison, our calculated principal axis results for SH_4 are

$$\theta_{aa} = -8.08 \text{ au}$$
$$\theta_{bb} = 3.54 \text{ au}$$
$$\theta_{cc} = 4.54 \text{ au}$$

The electric field gradients at S are of interest since they are so different for SH_2 and SH_4. Actually the difference in $q_{zz}(S)$ values is not surprising since the two axial atoms (lying close to the positive and negative z axes) are not present in SH_2. However, the SH_2 group in SH_4 is similar structurally to that in SH_2 and hence one might expect the $q_{xx}(S) = q_{yy}(S)$ values to be nearly equal.

Finally, the calculated potentials at sulfur reflect the fact, also indicated by the population analyses and S 1s orbital energies, that the S atom is most positively "charged" in SH_6.

Acknowledgment. This research was supported in part by the National Science Foundation, Grants GP-31974, 39317, and 41509X. We thank Professor Jerry Musher for helpful discussions. The calculations were for the most part carried out on our Datacraft 6024/4 minicomputer. The LBL CDC 7600 was used for a few test computations.

References and Notes

(1) J. I. Musher, *Angew. Chem., Int. Ed. Engl.*, **8**, 54 (1969).
(2) V. C. Ewing and M. Polanyi, *Trans. Faraday Soc.*, **59**, 1241 (1963).
(3) W. M. Tolles and W. D. Gwinn, *J. Chem. Phys.*, **36**, 1119 (1962).
(4) E. A. Tyczkowski and L. A. Bigelow, *J. Am. Chem. Soc.*, **75**, 3523 (1953).
(5) D. B. Denney, D. Z. Denney, and Y. F. Hsu, *J. Am. Chem. Soc.*, **95**, 4064, 8192 (1973).
(6) E. F. Perozzi, J. C. Martin, and I. C. Paul, *J. Am. Chem. Soc.*, **96**, 580 (1974); J. C. Martin and E. F. Perozzi, *ibid.*, **96**, 3155 (1974); J. C. Martin and M. M. Chau, *ibid.*, **96**, 3319 (1974); J. C. Martin, J. A. Franz, and R. J. Arhart, *ibid.*, **96**, 4604 (1974).
(7) J. I. Musher, *Advan. Chem.*, **110**, 44 (1972).
(8) J. I. Musher, *J. Am. Chem. Soc.*, **94**, 1370 (1972).
(9) V. B. Koutecky and J. I. Musher, *Theor. Chim. Acta*, **33**, 227 (1974).
(10) J. B. Florey and L. C. Cusachs, *J. Am. Chem. Soc.*, **94**, 3040 (1972).
(11) R. Hoffmann, J. M. Howell, and E. L. Muetterties, *J. Am. Chem. Soc.*, **94**, 3047 (1972).
(12) A. Rauk, L. C. Allen, and K. Mislow, *J. Am. Chem. Soc.*, **94**, 3035 (1972).
(13) J. J. De Corpo, R. P. Steiger, J. L. Franklin, and J. L. Margrave, *J. Chem. Phys.*, **53**, 936 (1970).
(14) A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, London, 1968.
(15) S. Rothenberg, R. H. Young, and H. F. Schaefer, *J. Am. Chem. Soc.*, **92**, 3243 (1970).
(16) A. Veillard, *Theor. Chim. Acta*, **12**, 405 (1968).
(17) T. H. Dunning, *J. Chem. Phys.*, **55**, 716 (1971).
(18) S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965).
(19) H. F. Schaefer, "The Electronic Structure of Atoms and Molecules: A Survey of Rigorous Quantum Mechanical Results", Addison-Wesley, Reading, Mass., 1972.
(20) H. F. Schaefer, "Critical Evaluation of Chemical and Physical Structural Information," D. R. Lide and M. A. Paul, Ed., National Academy of Sciences, Washington, D.C. 1974.
(21) D. R. Johnson and F. X. Powell, *Science*, **164**, 950 (1969).
(22) E. Clementi and H. Popkie, *J. Chem. Phys.*, **57**, 4870 (1972).
(23) T. H. Dunning, R. M. Pitzer, and S. Aung, *J. Chem. Phys.*, **57**, 5044 (1972).
(24) B. Rosen, "Spectroscopic Data Relative to Diatomic Molecules", Pergamon Press, Oxford, 1970.
(25) L. C. Snyder, "Thermochemistry and the Electronic Structure of Molecules", Bulletin No. 29, The Robert A. Welch Foundation, Houston, Texas.
(26) W. Meyer and P. Pulay, *Theor. Chim. Acta*, **32**, 253 (1974).
(27) K. Siegbahn, "ESCA Applied to Free Molecules", North-Holland Publishing Co., Amsterdam, 1969.
(28) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841 (1955).
(29) R. E. Hillger and M. W. P. Strandberg, *Phys. Rev.*, **83**, 575 (1951).
(30) R. G. Stone, H. L. Tigelaar, and W. H. Flygare, *J. Chem. Phys.*, **53**, 3947 (1970).

Nitrogen-Bound and Carbon-Bound Xanthine Complexes of Ruthenium Ammines

Michael J. Clarke and Henry Taube*

Contribution from the Department of Chemistry, Stanford University, Stanford California 94305. *Received July 29, 1974*

Abstract: Complexes of a series of alkylated xanthine derivatives in which ruthenium(II and III) is bound to the N_7 or C_8 sites of the purine are described. The N-bound ruthenium(III) complexes exhibit two ligand-to-metal charge transfer bands, which provide information about the energies of molecular orbitals on the xanthine ligand. The ruthenium(II) complexes exhibit metal-to-ligand charge transfer transitions in the ultraviolet. Reduction potentials for the neutral and deprotonated ligand complexes are reported. Measurements of pK_a values for both N- and C-bound Ru(II and III) complexes are presented. Evidence for a trans labilization effect in the series of C_8-xanthinylideneruthenium(III) complexes is described.

The effect of metal ions on purine bases is of considerable interest for several reasons. Metal ions participate in the biological functions of nucleic acids.[1-3] Heavy-metal adducts of nucleic acids have proved useful in an X-ray structure determination of a tRNA[4] and have been investigated in attempts to sequence nucleic acids by electron microscope techniques.[5] Several platinum compounds have shown antitumor activity believed to be due to their ability to form complexes with nucleic acids.[6]

Xanthines have been studied as models for nucleosides[7] and are attractive as ligands because various methylated derivatives are available. Alkylation of the xanthine ring limits the number of possible metal binding sites and increases the solubility of the ligand. The aquopentaammineruthenium(II) ion exhibits a high degree of selectivity for binding to unsaturated nitrogens.[8] This behavior coupled with the use of methylated xanthines has led to the synthesis of a number of pentaammineruthenium(II and III) xanthine complexes with the metal bound at N_7. These ruthenium complexes are substitution inert in both the 2+ and 3+ oxidation states, a feature which facilitates their isolation and systematic study.

Purine ligands can also bind to the metal ion through the carbon adjacent to the nitrogens on the imidazole ring in a manner analogous to the series of ruthenium-imidazolylidene compounds synthesized in this laboratory by Sundberg.[9] An X-ray structure determination of one of the compounds, whose synthesis is reported here, shows that the ruthenium is indeed bonded to the C_8 site.[10] These compounds can be considered to be complexes of a purine ylide