Possibly, the experimental binding energies are increasing not as a consequence of an electronic distribution in the ground state but because of some other phenomenon—possibly relaxation, which may well be expected to predominate in the hydrides.[7,12] However, *all* charge calculations will predict the polarity of the Ge–H and Si–H bonds to be M(δ−)–H(δ+), contrary to dipole moment measurements[9] on alkylsilanes. Alternatively, we could assume that the binding energies are indeed changing as a reflection of electronic redistributions and reevaluate our charge calculations. To maintain the validity of our base plots (Figure 1) we cannot alter any χ values except that of χ_H. We therefore recalculate binding energies using the value $\chi_H = 8.7 + 12.85\delta_H$ (the value of $a = 8.7$ gives a good fit for GeH_4 and SiH_4 and fits the concept of a "weakly electronegative" halogen). The resulting comparisons between calculated and observed binding energies are given in part b of Tables II–VII. Allowing for the simplicity of the model, the total neglect of relaxation effects, and the arbitrary value of *a*, the agreement between calculated and experimental binding energies for *all* levels is remarkably good. As in our earlier paper,[1] the largest discrepancy is in the values of the Si 2p levels in the fluorosilanes. Thus, the EESOP calculations, which are ignoring pπ–dπ bonding, estimate too high a positive partial charge on silicon and too high a negative charge on fluorine resulting in an estimated binding energy that is considerably higher than experimental for silicon (Table V, part b) and lower for fluorine (Table VII, part b). Of course, pπ–dπ bonding, if present, would have the effect of reducing the positive charge on silicon and correspondingly decreasing the negative charge on fluorine. The same discrepancy is not seen for the Ge 3d levels in the fluorogermanes.

Acknowledgment. We thank the National Research Council of Canada for financial support.

Registry No. Me_4Ge, 865-52-1; Me_3GeH, 1449-63-4; Me_2GeH_2, 1449-64-5; $MeGeH_3$, 1449-65-6; GeH_4, 7782-65-2; Me_2HGeF, 34117-35-6; MeH_2GeF, 30123-02-5; $MeHGeF_2$, 30123-03-6; Me_2HGeCl, 21961-73-9; MeH_2GeCl, 29914-10-1; Me_4Si, 75-76-3; Me_3SiH, 993-07-7; Me_2SiH_2, 1111-74-6; $MeSiH_3$, 992-94-9; SiH_4, 7803-62-5; Me_2HSiF, 865-46-3; MeH_2SiF, 753-44-6; $MeHSiF_2$, 420-34-8; Me_2HSiCl, 1066-35-9; MeH_2SiCl, 993-00-0; $MeGeHCl_2$, 1111-82-6; Me_2GeHBr, 53445-65-1; $MeGeH_2Br$, 30123-09-2; $MeGeHBr_2$, 30123-10-5; Me_2GeHI, 33129-32-7; $MeGeH_2I$, 30123-01-4; $MeGeHI_2$, 30123-05-8; $MeSiHCl_2$, 75-54-7; Me_2SiHBr, 2441-22-7; $MeSiH_2Br$, 1631-88-5; $MeSiHBr_2$, 2441-24-9; Me_2SiHI, 2441-21-6; $MeSiH_2I$, 18089-64-0; $MeSiHI_2$, 16642-68-5.

Supplementary Material Available: Figure 1 showing core-level binding energies for the halo(methyl)germanes and -silanes as a function of δ (1 page). Ordering information is given on any current masthead page.

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Crystal Structure of Tetrasulfur Tetranitride (S_4N_4) at 120 K

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Received January 17, 1978

Tetrasulfur tetranitride (S_4N_4) is the starting material for the synthesis of $(SN)_x$, the first superconducting polymeric material. It is an unusual cage compound (Figure 1), the room-temperature structure of which was established by Clark[1] and Sharma and Donohue.[2] The molecule in the crystal conforms closely to D_{2d} symmetry and may be considered as an eight-membered ring, folded back on itself so as to form two "across-the-ring" S–S distances of 2.576 (8) and 2.586 (8) Å at room temperature.[2] Though these distances are more than 1 Å shorter than the sum of the van der Waals radii, they are still considerably longer than a single S–S bond, which was listed by Hordvik as 2.10 Å,[3] or the S–S bond in *cyclo*-octasulfur which is 2.057 (1) Å.[4] The nature of the bonding in S_4N_4 has therefore been the subject of several publications. Bonding schemes by Mingos[5] and Gleiter[6] assign bonding character to the S–S interaction, while Banister[7] invokes d orbitals in a bonding scheme that also involves bonding between S atoms separated by two S–N bonds, such as S(1) and S(2). Theoretical calculations by the CNDO/BW,[8] SCF Xα,[9] and EHMO[10] methods also predict bonding mainly of p character in the "across-the-ring" S---S interaction.

The low-temperature crystallographic study was undertaken (a) to provide more accurate bond lengths, (b) to measure the temperature dependence of the S---S distances which should be small if the bond is of significant strength, (c) to obtain net atomic charges through a valence-shell population refinement, and (d) to obtain the detailed three-dimensional electron distribution for a more detailed analysis of the electronic structure of this compound.

We report here on the results of (a) and (b) and give a preliminary description of the charge density distribution. The detailed electron distribution and its comparison with results from theoretical calculations near the Hartree-Fock level by Rys and King will be discussed in a later publication.

Experimental Section

Tetrasulfur tetranitride was prepared as described by Jolly.[11] Crystals formed upon slow evaporation of a chloroform solution. X-ray data were collected at 120 K on an automated Picker diffractometer controlled by the Vanderbilt operating system.[12] Cooling was achieved with the self-regulating CT-38 cryostat.[13] Cell dimensions obtained by least-squares refinement of the orientation of 24 reflections are compared with neutron values[14] and room-temperature cell dimensions in Table I, which also lists other experimental information. A total

Table I. Physical and Crystallographic Data

molecular mass: 184.284 daltons
space group: $P2_1/n$
temp of data collection: 120 K
technique: θ–2θ step scan
wavelength: Mo Kα 0.7107 Å
$\rho_{\text{X-ray}}$: 2.297 g/cm^3

cell dimension	X-ray 120 K	neutron 125 K[a]	X-ray room temp[b]
a, Å	8.752 (2)	8.729	8.75
b, Å	7.084 (7)	7.100	7.16
c, Å	8.629 (2)	8.640	8.65
β, deg	93.68 (5)	93.20	92.5
Z	4	4	4

[a] Reference 14. [b] Reference 2.

Table II. Positional Parameters (As Fractions of the Unit Cell Edge) and Thermal Parameters ($\times 10^4$)[a]

	x	y	z	$U(11)$	$U(22)$	$U(33)$	$U(12)$	$U(13)$	$U(23)$
S(1)	0.00514 (5)	0.92167 (7)	0.30433 (5)	184 (2)	256 (2)	198 (2)	0 (1)	11 (1)	−95 (1)
S(2)	0.15149 (4)	0.70853 (6)	0.09900 (4)	121 (1)	197 (2)	168 (1)	23 (1)	10 (1)	−13 (1)
S(3)	−0.14966 (4)	0.79887 (6)	0.05795 (5)	124 (1)	201 (2)	184 (2)	23 (1)	−09 (1)	−4 (1)
S(4)	−0.04076 (5)	0.54600 (7)	0.27272 (5)	206 (2)	237 (2)	175 (2)	−12 (1)	15 (1)	39 (1)
N(1)	0.0100 (2)	0.7641 (2)	−0.0245 (1)	173 (2)	207 (7)	135 (5)	34 (4)	9 (4)	1 (4)
N(2)	−0.0272 (2)	0.7230 (3)	0.3915 (3)	243 (6)	355 (9)	140 (5)	11 (6)	25 (4)	−25 (5)
N(3)	−0.1818 (2)	0.6035 (3)	0.1481 (2)	141 (4)	231 (7)	221 (7)	−33 (5)	1 (4)	7 (5)
N(4)	0.1641 (2)	0.8843 (2)	0.2193 (2)	145 (5)	229 (7)	238 (6)	−25 (5)	−2 (4)	−56 (5)

[a] $U(ij)$ is defined by $T = \exp[-2\pi^2(a^{*2}h^2U(11) + b^{*2}k^2U(22) + c^{*2}l^2U(33) + 2hka^*b^*U(12) + 2hla^*c^*U(13) + 2klb^*c^*U(23)]$.

of 7234 reflections with $(\sin\theta)/\lambda < 0.98$ Å^{-1} were averaged after application of absorption and Lorentz-polarization corrections to give 2762 unique data for the least-squares refinement. Scattering factors were as listed in ref 15a, while the anomalous dispersion correction for sulfur was taken from ref 15b. Final agreement factors defined as $R(F) = \sum(F_o - |kF_c|)/\sum F_o$ and $R(wF) = [\sum w(F_o - |kF_c|)^2/\sum wF_o^2]^{1/2}$ are 0.039 and 0.049, respectively. Positional and thermal parameters are listed in Table II, while intra- and intermolecular distances and angles are compared with room-temperature values in Table III.

Discussion

The results show that even though S_4N_4 is thermochromic and loses its orange color on cooling,[16] no structural transition occurs between room temperature and 120 K. While intermolecular distances contract 1–2% in this temperature range, the S---S intramolecular distance is remarkably constant, the low-temperature values being 2.601 and 2.597 Å after correction for apparent shortening due to thermal motion as given by a rigid-body analysis (2.595 (1) and 2.590 (1) Å before correction). This is longer than the room-temperature distances of Sharma and Donohue, 2.576 (8) and 2.586 (8) Å, which, however, were not corrected for thermal shortening.[2] From a comparison of low- and room-temperature thermal parameters we estimate the thermal correction to the room-temperature S---S distances to be about 0.014 Å. The resulting values of 2.590 and 2.600 Å are within experimental error equal to the distances at low temperature, indicating that the S---S distance does not contract on cooling and suggesting a relatively strong interaction with a well-defined minimum in the potential energy vs. distance curve.

Refinements of the occupancy of a spherical valence shell with a variable radial function for each type of atom[17] consistently show a charge transfer of 0.2–0.3 electron from sulfur to nitrogen, in qualitative agreement with theoretical results[8–10] and with the relative electronegativities of sulfur and nitrogen.

We note that the electropositivity of the sulfur atom allows formation of a third bond. A trivalent sulfur atom would have a formal positive charge, in analogy with the quadrivalent nitrogen in NH_4^+. In the cage compound P_4S_4, in which sulfur may be expected to be the negative atom, bonding occurs between the phosphorus atoms.[18]

Bonding between the sulfur atoms is also supported by the results of the electron density study. The deformation density, defined as the difference between the observed density and a superposition of spherical atoms, shows a peak of about 0.15 e Å^{-3} in the region between the sulfur atoms.[19] This peak is elongated along the bond and its height is comparable to the peak heights in the S–N bonds of S_4N_4. In addition, an electron density peak of about 0.20 e Å^{-3} is observed in the center of the molecule between the two perpendicular S–S bonds.

We note that these two bonds are at a distance of only 2 Å from each other. The peak in the center of the molecule connects through two saddle points with each of the S–S bond peaks. Its occurrence may be interpreted as evidence for four-center bonding involving all four sulfur atoms. Support for this interpretation is found in the SCF Xα study by Salahub and Messmer in which one molecular bonding orbital

Table III. Bond Lengths and Bond Angles for S_4N_4

Bond Lengths (Å)

	a	b	c
Intramolecular			
S(1)–N(4)	1.632 (2)	1.636	1.631 (13)
S(2)–N(4)	1.621 (2)	1.625	1.605 (19)
S(2)–N(1)	1.627 (1)	1.630	1.621 (14)
S(3)–N(1)	1.623 (1)	1.627	1.616 (17)
S(3)–N(3)	1.621 (2)	1.625	1.596 (14)
S(4)–N(3)	1.633 (2)	1.637	1.617 (22)
S(4)–N(2)	1.619 (2)	1.623	1.610 (14)
S(1)–N(2)	1.629 (2)	1.634	1.634 (18)
S(1)–S(3)	2.595 (1)	2.601	2.586 (8)
S(2)–S(4)	2.590 (1)	2.597	2.576 (8)
S(1)–S(2)	2.709 (1)	2.716	2.693 (8)
S(1)–S(4)	2.703 (3)	2.709	2.702 (10)
S(3)–S(4)	2.706 (2)	2.712	2.689 (8)
S(2)–S(3)	2.706 (1)	2.711	2.688 (6)
Intermolecular[d] (<3.25 Å at 120 K)			
S(1)---N(3) [A]	3.152		3.235
S(2)---N(4) [B]	3.162		3.260
S(2)---N(3) [C]	3.094		3.170
S(4)---N(1) [C]	3.092		3.157
N(1)---N(3) [C]	3.220		3.255

Bond Angles (deg)

	a	c
N(2)–S(1)–N(4)	104.20 (9)	103.3 (1.6)
N(3)–S(3)–N(1)	105.09 (8)	104.9 (1.6)
N(1)–S(2)–N(4)	104.56 (8)	105.1 (1.5)
N(2)–S(4)–N(3)	104.18 (8)	104.6 (1.3)
S(2)–N(1)–S(3)	112.72 (8)	112.3 (6)
S(4)–N(2)–S(1)	112.60 (10)	112.8 (7)
S(3)–N(3)–S(4)	112.50 (9)	113.6 (7)
S(1)–N(4)–S(2)	112.82 (8)	112.6 (7)
N(4)–S(1)–S(3)	89.43 (6)	
N(2)–S(1)–S(3)	89.56 (7)	
N(3)–S(3)–S(1)	89.43 (7)	
N(1)–S(2)–S(4)	89.66 (6)	
N(4)–S(2)–S(4)	89.47 (7)	
N(2)–S(4)–S(2)	89.92 (7)	
N(3)–S(4)–S(2)	89.81 (6)	

[a] This work. [b] This work, corrected for thermal shortening. [c] Reference 2. [d] Distance from molecule at x, y, z to molecule: [A] $-{}^1/_2 - x, y + {}^1/_2, {}^1/_2 - z$; [B] ${}^1/_2 - x, y - {}^1/_2, {}^1/_2 - z$; [C] $-x, 1 - y, {}^1/_2 - z$.

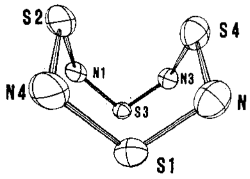

Figure 1. ORTEP drawing of 50% probability ellipsoids.

has an appreciable amplitude near the center of the molecule.[9] Because of the importance of this conclusion, further experiments are being considered and a comparison with an extended basis set H–F calculation is to be made.

Acknowledgment. The authors thank Dr. E. D. Stevens and Mr. J. Rys for assistance with data collection and computations. Support of this work by the Petroleum Research Fund, administered by the American Chemical Society, and by the National Foundation (Grant CHE 7613342 AO1) is gratefully acknowledged.

Registry No. S_4N_4, 28950-34-7.

Supplementary Material Available: A table listing observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

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The Molybdenum-to-Molybdenum Triple Bond. 5. Preparation and Structure of Dimethyltetrakis(dimethylamido)dimolybdenum[1]

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Received March 1, 1978

The existence of an extensive chemistry centering around the triply bonded Mo–Mo and W–W units is now well established and has recently been reviewed.[3,4] A firm structural base for interpreting this chemistry has been provided by more than a score of X-ray crystallographic structure determinations. Among these, however, there have been only a few pairs of molybdenum and tungsten compounds with the same or very similar sets of ligands. The comparisons afforded by such pairs are valuable in developing the comparative chemistry of the M–M multiple bonds in the second and third transition series.

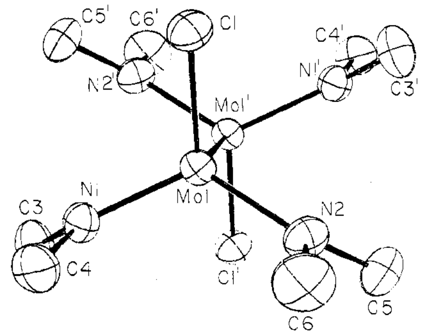

Figure 1. ORTEP view of molecule I using 50% probability ellipsoids and showing the atom labeling scheme.

To further this structural basis we report here the preparation and structural characterization of dimethyltetrakis(dimethylamido)dimolybdenum, $Mo_2Me_2(NMe_2)_4$. The structure may be compared to that of the close ditungsten analogue, $W_2Me_2(NEt_2)_4$, the structure of which has already been reported.[5] The preparation of this new compound was accomplished by taking advantage of our recently published route[6] to substitution products of the readily available $Mo_2(NMe_2)_6$, viz., reaction 1, and then replacing Cl by methyl by means of the methyllithium reagent, reaction 2. At a later

$$Mo_2(NMe_2)_6 + 2Me_3SiCl \rightarrow Mo_2Cl_2(NMe_2)_4 + 2Me_3SiNMe_2 \quad (1)$$

$$Mo_2Cl_2(NMe_2)_4 + 2MeLi \rightarrow Mo_2Me_2(NMe_2)_4 + 2\ LiCl \quad (2)$$

time we shall report further studies of reactions of type 2 which have also allowed the isolation of alkyls, such as $M_2Et_2(NMe_2)_4$, for which β-H elimination is not impossible.

Results and Discussion

Synthesis. The compounds $M_2Cl_2(NMe_2)_4$, where M = Mo and W, react with ether and tetrahydrofuran: reaction 2 was carried out in toluene. $Mo_2Me_2(NMe_2)_4$ was isolated from (2) as a yellow, crystalline, diamagnetic, air-sensitive compound in greater than 70% yield. It is thermally stable and may be sublimed at 100 °C (10^{-2} Torr). In the mass spectrometer a molecular ion $Mo_2Me_2(NMe_2)_4^+$ together with many other Mo_2-containing ions were observed. IR, NMR, and analytical data are recorded in the Experimental Section.

Structural Results. $Mo_2(NMe_2)_4Me_2$ is isostructural with $M_2(NMe_2)_4Cl_2$. The asymmetric unit consists of half of each of two independent dinuclear molecules, each molecule having crystallographically imposed C_i symmetry but deviating only slightly from C_{2h}. Atomic thermal and positional parameters are given in Table I. An ORTEP drawing of molecule I is shown in Figure 1. Bond distances and angles are given in Table II. The atom labeling scheme used for molecule II parallels that used for molecule I with Mo(2), N(3)–N(4), and C(7)–C(12) replacing Mo(1), N(1)–N(2), and C(1)–C(6), respectively.

Discussion of Structure. The crystal structure of $Mo_2(NMe_2)_4Me_2$ is closely similar to those[6] of $Mo_2(NMe_2)_4Cl_2$ and $W_2(NMe_2)_4Cl_2$. In all of these, the presence of four molecules in a unit cell belonging to the space group $P2_1/c$ does not correspond, as is usually the case, to the molecule being the asymmetric unit, with the four molecules then being related by the two types of crystallographic inversion center at 0, 0, 0 and $^1/_2$, 0, $^1/_2$. In these structures the asymmetric unit is composed of halves of two different molecules. This means that there are two crystallographically independent, centrosymmetric molecules, each type located on a crystallographic center of inversion. However, as Table II shows, the differences between the two molecules of $Mo_2(NMe_2)_4Me_2$ are completely insignificant, not only chemically but in terms of the statistical validity of the differences.

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