mirror appeared to be relatively independent of the maximum temperature of the sublimator over the range 123–212 °C and a pressure range 0.01–3.8 torr.

It is interesting to note that, of the literally hundreds of metal β-diketone chelates studied for their volatility in this laboratory, only the palladium MDA complex vaporized and then formed a deposit of the free metal under these moderate temperature and pressure conditions. These observations of the behavior of the palladium MDA complex suggested that a sublimation technique could be used to produce palladium (front-surface) mirrors and possibly palladium catalysts by depositing the metal on a catalyst support. Porous plugs 1 cm long of charcoal (activated carbon) and Chromosorb P and W were placed in the fractional sublimator in the temperature range where palladium metal was deposited. Palladium was readily deposited on the carbon and Chromosorb support.

The sublimation-produced palladium was tested for catalytic activity by comparing its activity with a commercial hydrogenation catalyst with 5% palladium on activated carbon. Cyclohexene, benzophenone, p-nitrotoluene, and maleic acid were each hydrogenated with the commercial catalyst and the catalyst produced in the sublimation apparatus. Comparable results were obtained with the different catalysts. The hydrogenation of maleic acid was studied in more detail. The average of three runs with each catalyst showed virtually no difference in the yields, which ranged from 92 to 96%. The primary difference noted was that the half-hydrogenation times with the commercial catalysts were significantly less than for the sublimation-produced palladium. The slower catalytic activity of the sublimation-produced catalysts on carbon and Chromosorb P and W is believed due to its lower palladium content, ~2.5% Pd, compared to that of the commercial catalyst, which was 5% Pd.

Registry No. $Pd(MDA)_2$, 74577-84-7; $Cr(MDA)_3$, 15636-02-9; tetramethoxypropane, 102-52-3; palladium, 7440-05-3; maleic acid, 110-16-7.

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Enthalpy of Formation and Magnetic Susceptibility of Curium Sesquioxide, Cm_2O_3

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Monoclinic Cm_2O_3 has been prepared from the long-lived isotope ^{248}Cm ($t_{1/2} = 3.4 \times 10^5$ y), and its enthalpy of formation has been determined at 298 K to be −1682 ± 12 kJ mol^{-1} from solution calorimetry measurements on four different samples. The magnetic susceptibility of three of these samples has been measured on a Faraday balance between 2 and 298 K. Cm_2O_3 exhibits Curie–Weiss behavior from 100 to 300 K with $\mu_{eff} = 7.89 \pm 0.04\ \mu_B$ and $\Theta = -130 \pm 2$ K. The compound appears to order magnetically as the temperature decreases and has an antiferromagnetic transition at 13 ± 2 K. The results are interpreted by comparison with similar properties of related lanthanide and actinide compounds.

Introduction

Curium sesquioxide was first reported in 1955[1] and has been prepared many times since then. Although many compounds of curium are now known, very few properties other than their crystal structures have been determined because of the high α specific activities of the most common isotopes (^{242}Cm, $t_{1/2}$ = 163 d, specific activity 7.36×10^9 disintegrations min^{-1} μg^{-1}; ^{244}Cm, $t_{1/2}$ = 18.1 y, specific activity 1.80×10^8 disintegrations min^{-1} μg^{-1}).[2] The recent availability of the very long-lived isotope ^{248}Cm ($t_{1/2} = 3.39 \times 10^5$ y, specific activity 9.44×10^3 disintegrations min^{-1} μg^{-1})[2] has made possible many chemical measurements that would be severely hindered by the more radioactive isotopes.

The metal is the only Cm species for which both thermodynamic and magnetic properties have been measured. Because of the importance of Cm_2O_3 as a key Cm(III) compound and as a pivotal member of the actinide sesquioxides (all three common M_2O_3 structure types are easily prepared), we have determined the enthalpy of formation and magnetic susceptibility of monoclinic Cm_2O_3 using ^{248}Cm. These two properties are essential for a complete understanding of Cm^{3+} ($5f^7$ configuration, half-filled 5f subshell).

Table I. Composition of Curium Samples (Atom Percent Referred to Total Cm)

	samples			samples	
	A, B, E	C, D		A, B, E	C, D
Na[a]	0.1	a	^{245}Cm[b]	0.05	0.03
Si[a]	0.3	a	^{246}Cm[b]	2.56	2.76
Cl[a]	0.2	a	^{247}Cm[b]	0.018	0.02
K[a]	0.02	a	^{248}Cm[b]	97.37	97.19
Pm[a]	0.1	a	^{249}Bk[c]	0.01	0.01
^{244}Cm[b]	0.0003	0.0002	^{252}Cf[b]	0.00002	0.000001

[a] By spark-source mass spectrometry on sample A only. Other elements not detected or detected at levels ≤0.01 atom %: Mg, Al, S, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Br, Rb, Sr, Y, Zr, Sb, I, Ba, Sm, Ta, Hg, Pb, U. [b] By mass spectrometry and α-energy spectrum. [c] By β counting.

The body-centered cubic form of Cm_2O_3 exists below 800 °C, the monoclinic form between 800 and 1615 °C, and the hexagonal form above 1615 °C.[3] Two higher temperature polymorphs have also been found.[3] We chose to study monoclinic Cm_2O_3 for several reasons: It can be prepared by H_2 reduction of CmO_{2-x} at 825 °C,[4] it does not oxidize readily,[5] it is stoichiometric,[6] and it does not suffer lattice distortion from α self-irradiation.[4,7,8] There have been no

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calorimetric measurements on Cm_2O_3 or, for that matter, on any compound of curium(III).

Kanellakopulos and Müller have measured the magnetic susceptibility of ^{244}Cm(III) and -(IV) oxides.[9] Their results, and other magnetic measurements on $5f^7$ compounds, will be discussed later in this paper.

Experimental Section

Purification of ^{248}Cm. This nuclide is separated in multimilligram amounts from highly purified ^{252}Cf at Oak Ridge National Laboratory after storage for periods of about 2 years:[10,11]

$$^{252}_{98}Cf \rightarrow ^{248}_{96}Cm + ^{4}_{2}He \quad (t_{1/2} = 2.646\ y) \qquad (1)$$

Two 20-mg batches of ^{248}Cm were used in this research. As received from Oak Ridge, each batch was radiochemically quite pure. Other isotopes of curium contributed more α activity to these samples than did the ^{248}Cm; short-lived ^{249}Bk, present in trace amounts, also contributed substantial β^- activity (Table I, second and third columns). To achieve high chemical purity, each batch was taken through two stages of "cleanup" cation exchange.[12] The final column operations were performed entirely with leached quartz glassware, ultrapure reagents, and leached graded sulfonic acid cation-exchange resin (Aminex Q-150S, Bio-Rad Laboratories, 8% cross-linked, 28 ± 7 μm diameter). The success of the purification operation was confirmed by spark-source mass spectrometry of a sample taken from the first batch (Table I).

Preparation of Cm_2O_3. Each final ion-exchange fraction was collected in a minimal volume (0.5 cm^3), evaporated to dryness, dissolved in a minimal volume of 0.1 mol dm^{-3} nitric acid, and precipitated with an excess of oxalic acid solution prepared from recrystallized oxalic acid. After centrifugation and removal of supernatant solution, the curium(III) oxalate hydrate was air-dried under an infrared lamp and then was calcined to CmO_{2-x} in dry oxygen at 550 °C; this temperature was chosen by thermal cycling of a trial sample in a Mettler Thermoanalyzer 2. Reduction was carried out in dry ultrapure H_2 at 800–825 °C for 1–2 h. The Cm_2O_3 products, pale green or gray-green, were handled exclusively in N_2-filled dryboxes.

Each batch of ^{248}Cm was used to make two or three Cm_2O_3 samples (Table I). A Debye-Scherrer X-ray powder photograph was taken of each sample after preparation and also of sample D after completion of magnetic susceptibility measurements. Sample A was predominantly monoclinic Cm_2O_3 with a few body-centered cubic diffraction lines. Samples B–E were single-phase monoclinic Cm_2O_3. The unit-cell parameters were refined by least squares with use of the Nelson–Riley extrapolation correction for sample thickness:[13] for sample B, a = 14.276 ± 0.003 Å, b = 3.6521 ± 0.0004 Å, c = 8.8983 ± 0.0009 Å, and β = 100.32 ± 0.01°; for sample C, a = 14.278 ± 0.006 Å, b = 3.652 ± 0.002 Å, c = 8.904 ± 0.007 Å, and β = 100.215 ± 0.005° (errors represent standard deviations). These values agree excellently with literature results.[3,4,7]

Magnetic Susceptibility. Very small cylindrical aluminum cups (3.0-mm diameter, 6.4 mm high), machined with snugly fitting caps, were placed inside Plexiglas or aluminum secondary containers fitted with screw-cap covers. Each of these empty assemblies was calibrated at temperatures between 1.5 and 298 K in a Faraday magnetic balance.[14] Samples of Cm_2O_3 were weighed into the cups on a Cahn GRAM electrobalance in a nitrogen-filled drybox. The filled assemblies were transferred quickly to the magnetic balance, which was promptly evacuated and back-filled with helium to protect the Cm_2O_3 against oxidation. Susceptibility measurements were made at several field strengths between 3 and 7 kOe. To ensure that the Cm_2O_3 did not oxidize, sample A was reweighed after the entire magnetic susceptibility measurements had been completed (2 days), and the weight remained constant to ±0.001 mg; an X-ray powder photograph of sample D following magnetic measurements showed only monoclinic Cm_2O_3. The entire susceptibility samples D and E were used for calorimeter experiments (Table II), and the consistency of their enthalpies of solution with the other experiments confirmed the presence of unoxidized Cm_2O_3.

Table II. Enthalpy of Reaction of $^{248}Cm_2O_3$ (Monoclinic) with 6.00 mol dm^{-3} HCl Solution (8.5 cm^3) at 298.15 K

sample	mass/mg	enthalpy/J[a]	ΔH/kJ mol^{-1}
B	1.9445	1.4103	−394.4
B	1.288	0.9496	−399.4
B	1.3315	0.9758	−398.8
C	1.099	0.8238	−407.7
C	0.834	0.6043	−394.2
C	1.227	0.9150	−405.7
C	1.958	1.3039	−397[b]
D	0.650	0.4675	−391.3
E	3.232	2.4188	−407.1
		mean:	−400 ± 5 (95% confidence)

[a] Corrected for ampule breaking and evaporation of solvent into gas in ampule. [b] Corrected for 9% of sample in neck of ampule (undissolved), after assay by neutron counting. This result weighted 50% of others.

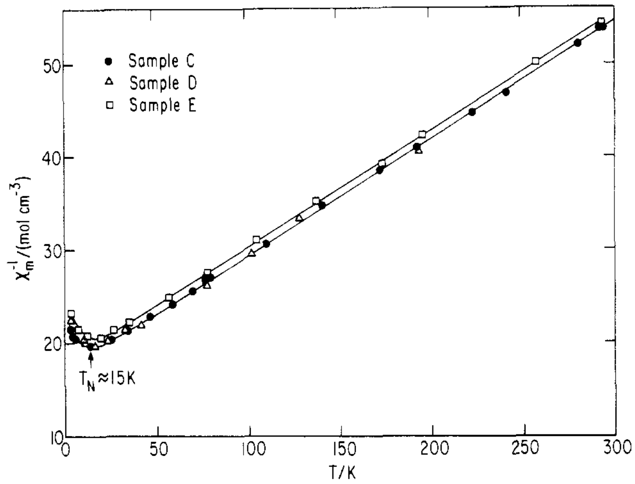

Figure 1. Magnetic susceptibility of $^{248}CmO_{1.5}$.

Calorimetry. Microcalorimeter sample bulbs were loaded, weighed on the Cahn GRAM electrobalance, and sealed in dry nitrogen. Since preliminary dissolution trials with ca. 100-μg samples of Cm_2O_3 showed slow reaction in 1.0 mol dm^{-3} hydrochloric acid but rapid reaction in 6.0 mol dm^{-3} hydrochloric acid, the microcalorimeter[15] was charged with 8.5 cm^3 of the latter acid for each experiment. The results of all experiments are shown in Table II.

Results and Discussion

Magnetic Susceptibility. The reciprocal of the molar susceptibility of $CmO_{1.5}$, χ_M, in units of cm^3 mol^{-1} (unrationalized cgs system), is plotted vs. absolute temperature in Figure 1. These data have been corrected for diamagnetism of Cm^{3+} (-32×10^{-6} cm^3 mol^{-1})[16] and O^{2-} (-7.0×10^{-6} cm^3 mol^{-1})[17] although these corrections are nearly negligible. Data on

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Table III. Magnetic Susceptibilities of Cm(III) and Bk(IV) Compounds

compd	temp range/K	μ_{eff}/ μ_B	Θ/K	ref
$CmF_3{\cdot}xH_2O$		7.7	−5	Marei and Cunningham[a]
CmOCl		7.6	−22	Marei and Cunningham[a]
CmF_3 in LaF_3		7.7	−6	Marei and Cunningham[a]
Cm^{3+} in	7.5–25	7.9	−4	Hendricks et al.[b]
$Cs_2NaLuCl_6$	25–45	7.5	−1	
Cm_2O_3	2–50	6.1	−22.5	Kanellakopulos and Müller[c]
	100–300	7.5	−72	
Cm_2O_3	20–80	8.20	−149	this research
	100–300	7.89	−130	
CmN	140–300	7.02	+109	Kanellakopulos et al.[d]
CmAs	100–300	6.58	+88	
BkO_2	10–95	7.7	−12	Karraker[e]
	95–220	5.8	+34	
BkF_4		7.80	+8	Nave et al.[f]
BkO_2		7.96	−250	Nave et al.[f]

[a] Averaged values of data reported by: Marei, S. A.; Cunningham B. B. *J. Inorg. Nucl. Chem.* **1972**, *34*, 1203. [b] Reference 18. [c] Reference 9; μ_{eff} calculated from eq 2. [d] Kanellakopulos, B.; Charvillat, J. P.; Maino, F.; Müller, W. In "Transplutonium Elements"; Müller, W., Lindner, R., Eds.; North-Holland Publishing Co.: Amsterdam, 1976; pp 181-190. [e] Karraker, D. G. *J. Chem. Phys.* **1975**, *62*, 1444. [f] Nave, S. E.; Haire, R. G.; Huray, P. G. *Lawrence Berkeley Lab.*, [*Rep.*] *LBL* 1981, *LBL-12441*, 144-146.

samples C and D agreed at all temperatures within 2%; the susceptibility of sample E showed a slightly more negative Weiss constant (Figure 1). The susceptibility follows the Curie–Weiss law (see eq 2) from 100 to 300 K, with μ_{eff} =

$$\mu_{eff} = \left(\frac{3k\chi_M(T-\Theta)}{N\beta^2}\right)^{1/2} = 2.828(\chi_M(T-\Theta))^{1/2}\mu_B \quad (2)$$

7.89 ± 0.04 μ_B and $\Theta_1 = -130 \pm 2$ K. Below 100 K, the susceptibility increases more slowly with decreasing temperature, presumably due to magnetic ordering; in the region 20–80 K, the susceptibility is represented by $\mu_{eff} = 8.20 \pm 0.08$ μ_B and $\Theta_2 = -149 \pm 2$ K. There is an antiferromagnetic transition at 13 ± 2 K. (The susceptibility of sample A showed noticeable field-strength dependence, presumably due to a ferromagnetic impurity; data from this simple were disregarded.)

The magnetic susceptibilities of a number of Cm(III) compounds have been measured (Table III). Also included in Table III are susceptibilities of isoelectronic Bk(IV) compounds. All have the $5f^7$ electron configuration with the $^8S_{7/2}$ ground state and free-ion magnetic moment 7.94 μ_B, although Hendricks et al.[18] calculated that intermediate coupling should yield a Cm^{3+} free-ion moment of only 7.64 μ_B at all but lowest temperatures.

We note that both cubic and hexagonal Pu_2O_3 parallel Cm_2O_3 with antiferromagnetic transitions at 16 and ~19 K, respectively, and that the susceptibility of Pu_2O_3 is also less than that calculated from the free-ion Pu^{3+} moment.[19,20]

We believe that the susceptibility data of Kanellakopulos and Müller[9] on $^{244}CmO_{1.5}$ differ from our results because of the α radiolysis due to ^{244}Cm; they noted a substantial increase in the susceptibility of $^{244}CmO_{2-x}$ with time. A detailed comparison between their results and ours is not meaningful because the crystal structure, stoichiometry, and purity of their samples were not reported.

Table IV. Reaction Scheme for $\Delta H_f°(Cm_2O_3, c)$

Cm_2O_3(c, monocl) + 6HCl (6 mol dm^{-3}) = $2CmCl_3$ (in 6 mol cm^{-3} HCl) + $3H_2O$ (in 6 mol dm^{-3} HCl)	$\Delta H_3 = -400 \pm 5$ kJ[a]
2Cm(c) + 6HCl (6 mol dm^{-3}) = $2CmCl_3$ (in 6 mol dm^{-3} HCl)	$\Delta H_4 = -2(611 \pm 5)$ kJ[b]
$H_2(g) + O_2(g) = H_2O$ (in 6 mol dm^{-3} HCl)	$\Delta H_5 = -286.6 \pm 0.4$ kJ[c]

$$\Delta H_f°(Cm_2O_3, c, monocl) = -\Delta H_3 + \Delta H_4 + 3\Delta H_5 = -1682 \pm 12 \text{ kJ mol}^{-1}$$

[a] This research. [b] Estimated from: Fuger, J.; Oetting, F. L. "The Chemical Thermodynamics of Actinide Elements and Compounds"; IAEA: Vienna, 1976; Part 2. [c] Parker, V. B.; Wagman, D. D.; Garvin. D. *Natl. Bur. Stand.*, [*Tech. Rep.*] *NBSIR* (*U.S.*) 1976, *NBSIR-75-968*.

Table V. Thermochemical and Structural Data for Monoclinic Sesquioxides

M	$\Delta H_f°(M^{3+}, aq)$/ kJ	$\Delta H_f°(M_2O_3, c)$/ kJ	$\Delta H°(soln, M_2O_3)^e$/kJ	molec vol/Å^3 [d,f]
Sm	−691.1 ± 1.7[a]	−1823.6 ± 1.8[b,c]	−416 ± 4	74.8
Eu	−605.6 ± 2.3[a]	−1651.4 ± 3.4[b,c]	−418 ± 6	73.1
Gd	−687.0 ± 2.1[a]	−1815.6 ± 3.6[b,d]	−416 ± 6	72.1
Cm	−615.0 ± 5.0[g]	−1682 ± 12[h]	−406 ± 16	76.1

[a] Morss, L. R. *Chem. Rev.* 1976, *76*, 827. [b] Gschneidner, K. A., Jr.; Kippenhan, N.; McMasters, O. D. Report IS-RIC-6; Institute for Atomic Research; Iowa State University: Ames, IA, 1973. [c] Schumm, R. H.; Wagman, D. D.; Bailey, S.; Evans, W. H.; Parker, V. B. *NBS Tech. Note* (*U.S.*) 1973, *No. 270-7*. [d] "Gmelins Handbuch der Anorganische Chemie", Springer-Verlag: Berlin, 1974; Seltenerdelemente, Teil C1, pp 118-122, 131-133. [e] For the reaction $M_2O_3(c) + 6H^+(aq) \rightarrow 2M^{3+}(aq) + 3H_2O(l)$, $\Delta H°(soln) = 2\Delta H_f°(M^{3+}, aq) + 3\Delta H_f°(H_2O, l) - \Delta H_f°(M_2O_3, c)$. [f] Eyring, L. In "Handbook on the Physics and Chemistry of Rare Earths"; Gschneidner, K. A., Jr.; Eyring, L., Eds., North-Holland Publishing Co.: Amsterdam, 1979. [g] Fuger, J.; Oetting, F. L. "The Chemical Thermodynamics of Actinide Elements and Compounds"; IAEA: Vienna, 1976; Part 2. [h] This research.

Thermochemistry. The calorimetry data of Table II are combined with literature enthalpies in the reaction scheme shown in Table IV to yield $\Delta H_f°(Cm_2O_3$, c, 298.15 K) = −1682 ± 12 kJ mol^{-1}. Error limits represent estimated 95% confidence intervals.

We have previously shown[21] that there is a nearly linear correlation between the enthalpies of solution of the lanthanide and actinide dioxides and their unit-cell lengths. This correlation represents the slow and smooth change in the difference between the hydration enthalpies of the M^{4+} ions and the lattice energies of these isostructural compounds. Similar behavior is to be expected for any set of aqueous ions and isostructural compounds of the same oxidation state. All of these sets of data show that, as the size of the cations increases, both hydration and lattice energy decrease in magnitude but lattice energy decreases faster since the enthalpy of solution becomes more negative.

Selected thermochemical and structural values for the monoclinic lanthanide and actinide sesquioxides have been collected in Table V. All of these compounds have nearly the same molecular volumes, and as expected from the above reasoning, the $\Delta H°(soln, Cm_2O_3)$ is consistent with that for the monoclinic lanthanide sesquioxides. Similar data for the hexagonal sesquioxides, including Pu_2O_3, show that $\Delta H°(soln, Pu_2O_3)$ is ca. 80 kJ mol^{-1} more positive than $\Delta H°$(soln) of the isostructural hexagonal lanthanide sesquioxides.[22] Instead of using either of these data points (Cm_2O_3 or Pu_2O_3) to predict the thermochemical properties of the other actinide

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sesquioxides, we are focusing our attention on measurement of enthalpies of formation of Am_2O_3 and Cf_2O_3 in order to establish the thermochemical regularities of this important set of compounds in relation to the aqueous ions.

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Registry No. Cm_2O_3, 12371-27-6.

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Structure of Tetrasulfur Dinitride

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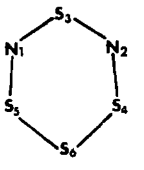
The structure of the six-membered ring S_4N_2, which was predicted to be planar by a CNDO/2 calculation, has been investigated by use of extended Hückel calculations. Our results show that the molecule should have the half-chair conformation, which is in good agreement with an X-ray crystallographic analysis. The results have been rationalized within an MO framework. The structures of related six-membered rings $S_4N_2^{2+}$, $S_4N_2^{2-}$, $S_3N_3^-$, $S_3N_3^+$, S_6, and S_6^{2+} are discussed briefly.

Introduction

The structures of a large number of compounds containing rings or chains of alternating sulfur and nitrogen only have been reported.[1,2] This class of compounds has frustrated chemists for a long time because various structure determinations have often shown that structures which had been predicted for these compounds were wrong.[3] One of the examples is tetrasulfur dinitride.

The structure of the molecule S_4N_2 has been the subject of several studies.[3-5] Nelson and Heal[4] reduced the number of structural alternatives to structure **1** by use of mass, vibrational, and ^{14}N NMR spectroscopy and dipole moment measurements. But they could not make a firm assignment regarding the conformation. Jolly[3] suggested a half-chair conformation in which the sulfur atom S_6 in structure **1** was tilted out of the plane of the other five atoms. However, in 1978, Adkins and Turner predicted a planar conformation on the basis of CNDO/2 calculations. Recently a low-temperature X-ray crystallographic analysis by Chivers[6] showed that the six-membered ring S_4N_2 has the half-chair conformation illustrated in Figure 1. Small, Banister, and Hauptman[7] report a similar result from their X-ray structure determination.



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In this paper we have carried out extended Hückel calculations[8] for S_4N_2 in an attempt to understand conformational preferences of six-membered rings. Although the method can be expected to be quantitatively poor, it seems to be qualitatively correct[9] and it captures the essence of energy changes that accompany variations of bond angles.[10] Surprisingly, our results for S_4N_2 are quantitatively in good agreement with the X-ray experiments.[6,7] A comparison with CNDO/2 calculations[5] has been made, and the results have been rationalized within an MO framework. Extended Hückel calculations on $S_3N_3^-$ and S_6 were also performed, and the structures of related six-membered rings $S_4N_2^{2+}$, $S_4N_2^{2-}$, $S_3N_3^-$, $S_3N_3^+$, S_6, and S_6^{2+} are discussed briefly. This work is part of a larger study of the electronic structures of inorganic rings.[2]

Details of the Calculations

In all of the calculations presented here, we used the computer program ICON8.[11] The following set of Coulomb integrals and orbital exponents is built into the program: $H_{ii}(2s) = -26.0$ eV, $H_{ii}(2p) = -13.4$ eV, $\zeta(2s) = \zeta(2p) = 1.95$ for nitrogen; $H_{ii}(3s) = -20.0$ eV, $H_{ii}(3p) = -13.3$ eV, $\zeta(3s) = \zeta(3p) = 1.817$ for sulfur. We also used the charge iteration feature of the program with the following iteration parameters: $B = 13.7$, $C(2s) = 26.4$, $C(2p) = 13.4$ for nitrogen; $B = 9.70$, $C(3s) = 22.50$, $C(3p) = 11.94$ for sulfur. We did not include a 3d basis function for sulfur because to do so would have greatly increased the computer requirements, and the work of others[10,12] indicates that sulfur 3d AO's can be safely neglected in work on similar problems.

The geometric parameters of S_4N_2 were taken from the X-ray results (see Figure 1). For the geometry of $S_3N_3^-$ we assumed a hexagon with the S–N bond length of 1.60 Å and the bond angles $\angle S = 117°$, $\angle N = 123°$; the structure was based on X-ray experimental data.[13] The structure of S_6 has been determined by two different groups,[14,15] and we used the bond length 2.068 Å from the more recent work.[15]

Results and Discussions

S_4N_2. According to Jolly's suggestion[3] and Nelson and Heal's experiments,[4] the possible conformations of S_4N_2 are planar, boat, chair, and half-chair. We define the angle be-

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