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The S_3^{2+} Dication: The First 16-Valence-Electron Triatomic with an Equilateral Triangle Triplet Ground State?

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Abstract: Six isomers of the S_3^{2+} dication have been studied by theoretical methods. SCF, CISD, CISD+Q, QCISD, and QCISD(T) techniques have been used, in conjunction with DZP, TZ2P, and TZ2Pf basis sets. Structural parameters have been optimized and harmonic vibrational frequencies evaluated. An equilateral triangle triplet state ($^3A_1'$, D_{3h} symmetry) is the global minimum at all levels of theory. Its bond length is 2.03 Å. Our best estimate is that it lies about 45 kJ mol^{-1} lower than the most stable singlet state, which has C_{2v} symmetry and a bond angle near 72°. A second C_{2v} singlet state whose bond angle is about 52° is a true minimum at the SCF level of theory, but a transition state once correlation effects are considered. A linear singlet state is a true minimum at both SCF and correlated levels of theory, but it lies about 70 kJ mol^{-1} above the triangular triplet. We believe that S_3^{2+} is the first 16-valence-electron triatomic species which unquestionably has a triplet ground state.

Introduction

In a landmark series of papers, Walsh developed a theoretical framework which allowed predictions to be made concerning the shapes of simple molecules.[1] By considering the variations in orbital energy with bond angle, he was able to show that triatomic molecules with 12–16 valence electrons are expected to be linear, whereas those with 17–21 valence electrons should be bent.[1] As these rules were remarkably successful for the molecules characterized at that time, it was generally believed that the problem of molecular shape had essentially been solved. Even though the non-hydride examples discussed by Walsh all contained atoms from the first row of the Periodic Table (Li–Ne), there was no reason to suppose that his rules might not be universally applicable.

However, as structural chemists turned their attention to detailed analyses of compounds containing heavier elements, it became clear that rather than being wholly typical in their structural patterns, the first-row elements might in fact be special cases. Four independent theoretical studies of Si_3 (12 valence electrons), which were published almost simultaneously,[2-5] showed this system to be acutely bent with a bond angle close to 80°, and thus very different from C_3 which is linear (or perhaps quasilinear).[6] In a slightly later survey which contrasted the structures of first- and second-row triatomic molecules, Burdett and Marsden (BM) predicted[7] that two phosphorus-containing ions, both unknown at that time, would also differ structurally from their first-row analogues. P_3^+ (14 valence electrons) was predicted to have a triangular singlet ground state, unlike N_3^+ which is a linear triplet with both π_g nonbonding orbitals singly occupied. A rather rich structural chemistry was revealed for P_3^- (16 valence electrons); an acutely bent singlet state was found to be only about 15 kJ mol^{-1} above the linear singlet state which would be expected from Walsh's rules[1] (recall that the azide anion, N_3^-, is rigidly linear like CO_2[8]), though the barrier separating the linear and bent singlets for P_3^- was shown to be of the order of 100 kJ mol^{-1}. It further appeared that the lowest-energy structure for P_3^- is possibly neither of these singlet states, but in fact a triangular triplet, though the calculations in that survey were not sufficiently rigorous for that point to be definitively established. More detailed computational studies of P_3^- by Hamilton and Schaefer (HS) soon confirmed[9] that the triangular triplet and linear singlet states are within a few kJ mol^{-1} of each other, with the triplet probably being the global minimum. It is interesting to note that while nothing was known from experiment concerning Si_3, P_3^+, or P_3^- when the theoretical studies were first performed, suggestive, though not yet conclusive, spectroscopic evidence has now been obtained for both phosphorus-containing ions[7,9] (and for SiC_2 as well,[10] though we are not aware of any direct experimental data for Si_3). These comments illustrate nicely the potential for cooperative interplay between theory and experiment in the advancement of contemporary chemistry.

In their qualitative discussion of structural trends in triatomic molecules, BM suggested[7] that the net negative charge in P_3^-, which is concentrated on the terminal atoms, would tend to destabilize the acutely bent singlet state as compared to the linear species. It therefore appeared that 16-electron systems which bear a net positive charge might favor a bent rather than linear geometry, and recent work on PS_2^+[11,12] supports this contention. However, nothing was said in that work concerning any influence of net charges on the energy of the triangular triplet state relative to the linear singlet. We decided that a theoretical study of the 16-valence-electron species S_3^{2+} would be of great interest; although this ion has not yet been reported, it is a plausible synthetic target, as several other polyatomic sulfur cations have been structurally characterized, including S_4^{2+},[13] S_5^+,[14] S_8^{2+},[15] and S_{19}^{2+}.[16] We are not aware of any other detailed theoretical study of S_3^{2+}, though a few results have been reported recently by Pyykkö;[17] as discussed below, our results do not agree well with his.

Computational Methods

Three different Gaussian basis sets were used in this work. The smallest is the double-ζ plus polarization (DZP) set due to Dunning and Hay,[18] for which a d exponent 0.532 was adopted. A triple-ζ plus double polarization (TZ2P) set was derived from the 12s9p primitives of Huz-

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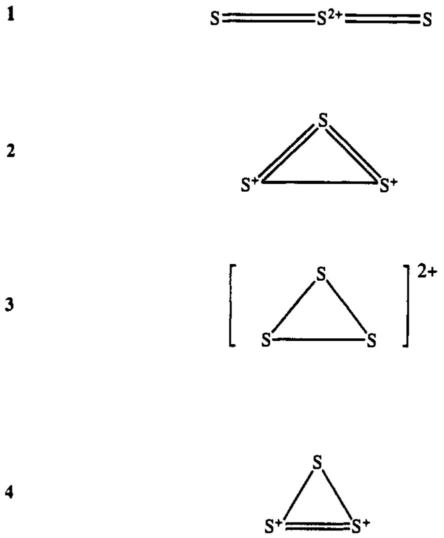

Figure 1. Sketches of the four most important structural isomers of S_3^{2+}.

inaga,[19] flexibly contracted to 9s6p, with d exponents of 0.4 and 1.5, while the largest set, denoted TZ2Pf, was obtained from the TZ2P basis by the addition of a set of f functions, whose exponent was 0.6. Six Cartesian d-type functions were used with the DZP and TZ2P basis sets, but spherical harmonic polarization functions (i.e. five d, seven f) were used for the TZ2Pf calculations.

The major portion of the calculations described in this work was performed in Georgia, using the PSI suite of programs.[20] Geometries were optimized from analytical first derivatives for both self-consistent-field (SCF)[21] and configuration interaction wave functions (limited to single and double excitations (CISD)[22]). Harmonic vibrational frequencies were evaluated either from analytical SCF second derivatives[23] or by numerical differentiation of CISD gradients. The fifteen lowest-energy MO's were frozen for the CISD calculations, but excitations into all virtual orbitals were permitted. Some preliminary SCF calculations were performed in Melbourne, using the Gaussian programs,[24,25] where the "quadratic configuration interaction" results[26] (QCISD and QCISD(T), depending on whether only single and double or single, double, and triple excitations were considered) were also obtained. It should be noted that despite its name, QCISD theory is probably best thought of as more closely related to the coupled-cluster (CC) approach.[27] Geometries were optimized at the DZP/QCISD level of theory by interpolation of individual energy points, since gradient optimization, which would have required all electrons and all MO's to be correlated, was not feasible for a system the size of S_3^{2+} (46 electrons and 72 MO's). Optimized structural parameters obtained in this way are believed to be precise to better than 0.002 Å or 0.2°. The fifteen lowest- and highest-energy MO's were frozen for all QCI calculations. DZP/QCISD(T), TZ2P/QCISD, and TZ2P/QCISD(T) energies were obtained at optimized DZP/QCISD geometries.

Results and Discussion

We begin with some important qualitative aspects concerning the electronic structures of the various different states of S_3^{2+} which have been considered in this work, which are shown in Figure 1; then we present our results for optimized geometries and energies for these states. Vibrational frequencies are described subsequently, and we close with some more general comments, including an analysis of relationships between the states of S_3^{2+} and those of the isoelectronic system P_3^-.

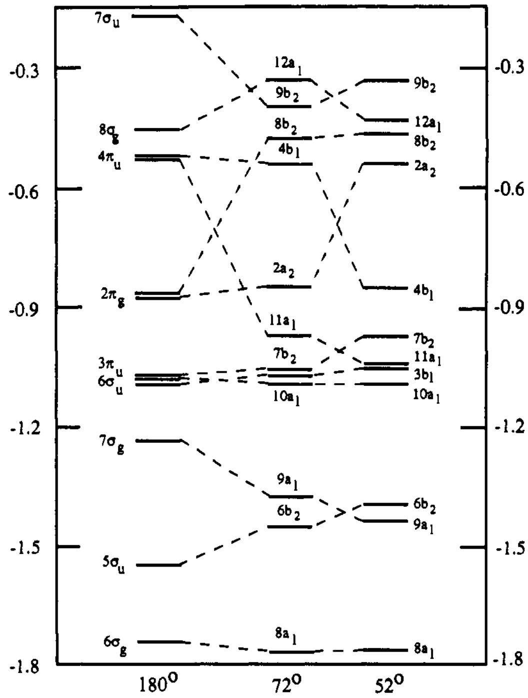

Figure 2. Orbital energies (in au) obtained for singlet S_3^{2+} at the DZP/SCF level, as a function of S–S–S bond angle.

Structure **1** is the classic linear ${}^1\Sigma_g^+$ state which would be expected for a 16-valence-electron species on the basis of Walsh's rules[1] (the analogous state appears[28] to be the global minimum for O_3^{2+}, for example). Its valence-electron configuration is $(6\sigma_g)^2(5\sigma_u)^2(7\sigma_g)^2(6\sigma_u)^2(3\pi_u)^4(2\pi_g)^4$. The primary valence-bond description of **1** contains two double bonds; the formal charges are localized on the central atom, which can therefore be regarded as hypervalent (oxidation state +6).

Structure **2** is an acutely bent ${}^1A_1$ state of C_{2v} symmetry, whose optimum bond angle is found to be slightly greater than 70°. It is not derived from the same configuration as **1**. As discussed in detail by BM,[7] the a_1 component of the $4\pi_u$ orbital of linear second-row triatomics (empty for 16-electrons S_3^{2+}) is strongly stabilized when that molecule bends, in a second-order Jahn–Teller interaction with $8\sigma_g$ (or $12a_1$), while the b_2 component of $2\pi_g$ is destabilized due to unfavorable overlap effects. An orbital crossing therefore occurs on bending and occurs much more readily than for first-row systems, due to the weaker π-bonding and relatively slight s–p mixing which differentiates second (and presumably subsequent) row species from their first-row analogues. This crossing is shown in Figure 2, which displays the SCF orbital energies obtained with the DZP basis. The valence-electron configuration for **2** is therefore $(8a_1)^2(6b_2)^2(9a_1)^2(10a_1)^2(3b_1)^2(11a_1)^2(2a_2)^2$. Its simplest valence-bond structure possesses two double bonds and one single bond; the formal charges are located at the singly-bonded (terminal) atoms, while the central (apical) atom has a formal oxidation state of +4.

Figure 2 shows that there are sets of (a_1 + b_2) orbitals which are quite close in energy for **2** with its bond angle of about 72°. If the bond angle is reduced to 60° (D_{3h} symmetry), then a_1 and b_2 orbitals coalesce to form an e′ pair, while a_2 and b_1 join to give an e″ set. A triangular triplet state **3** (${}^3A_2'$) with the valence-electron configuration $(4a_1')^2(5e')^4(5a_1')^2(2a_2'')^2(6e')^4(2e'')^2$ is therefore possible. Its valence-bond structure contains three single bonds, and the positive charges are of course delocalized.

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Table I. Geometries[a] and Energies[b] Predicted for S$_3^{2+}$ Structural Isomers

isomer		basis and method							
		DZP			TZ2P			TZ2Pf	
		SCF	CISD	QCISD	SCF	CISD	QCISD[e]	SCF	CISD[f]
1, $^1\Sigma_g^+$	r	1.784	1.820	1.850	1.770	1.806		1.763	
	E	−1.52998	−1.92031	−1.98126	−1.65466	−2.06584	−2.12416	−1.67111	−2.12107
			−1.98277[c]	−2.01582[d]		−2.12267[c]	−2.16339[d]		−2.19321[c]
	ΔE	220.4	140.2	99.6	224.2	154.4	114.0	206.0	147.9
			109.6[c]	61.8[d]		127.4[c]	75.0[d]		125.5[c]
2, $^1A_1$	r	1.923	1.949	1.982	1.915	1.943		1.903	
	θ	71.4	72.8	73.8	71.8	73.0		72.0	
	E	−1.54856	−1.93151	−1.99183	−1.67760	−2.07484	−2.14077	−1.68926	−2.13677
			−1.99250[c]	−2.02253[d]		−2.14000[c]	−2.17647[d]		−2.20880[c]
	ΔE	171.6	110.8	71.3	164.0	107.2	70.3	158.4	106.7
			84.1[c]	44.2[d]		81.9[c]	40.7[d]		84.5[c]
3, $^3A_1'$	r	2.028	2.055	2.077	2.026	2.054		2.013	
	E	−1.61392	−1.97372	−2.01919	−1.74006	−2.11566	−2.16756	−1.74958	−2.17740
			−2.02452[c]	−2.03937[d]		−2.17119[c]	−2.19196[d]		−2.24099[c]
	ΔE	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
			0.0[c]	0.0[d]		0.0[c]	0.0[d]		0.0[c]
4, $^1A_1$	r	2.143	2.162	2.198	2.138	2.160		2.124	
	θ	51.2	52.0	52.2	51.2	51.9		51.3	
	E	−1.55209	−1.92585	−1.98009	−1.67975	−2.06865	−2.12913	−1.69081	−2.13068
			−1.98346[c]	−2.00520[d]		−2.13076[c]	−2.15909[d]		−2.20007[c]
	ΔE	162.3	125.7	102.7	158.3	123.4	100.9	154.3	122.7
			107.8[c]	89.7[d]		106.2[c]	86.3[d]		107.4[c]

[a] Bond lengths (r) in Å, angles (θ) in deg. [b] Absolute energies (E) in au below −1190.0, relative energies (ΔE) in kJ mol^{-1}. [c] Value includes the "Davidson correction". [d] QCISD(T) energy obtained at QCISD geometry. [e] Energies obtained at DZP/QCISD geometries. [f] Energies obtained at TZ2Pf/SCF geometries.

If the bending process which transformed the orbitals of **2** into **3** is continued, to give an apex angle of less than 60°, then the HOMO and LUMO of **2** are interchanged, as shown in Figure 2. Other energy changes occur concurrently, with a_1 orbitals stabilized but both a_2 and b_1 destabilized. The resulting stationary point **4** has a very acute apex angle of about 52°, and it could perhaps best be described as T-shaped. Its primary valence-bond structure contains one double and two single bonds. The net positive charges are on the doubly bonded atoms, and no atom has a formal oxidation state greater than +2.

Two further open-shell states of S$_3^{2+}$ were investigated briefly, more for the sake of completeness than with any serious expectation that they would turn out to be contenders for the global minimum. Structure **5** is a bent triplet ($^3B_2$) with the configuration ...$(2a_2)^2(11a_1)^1(8b_2)^1$, which may be regarded as derived from a linear triplet involving partial occupation of the $4\pi_u$ orbital. Although $4\pi_u$ is antibonding, Figure 2 shows that one component thereof is strongly stabilized if the molecule bends, so this state is worthy of some attention. We have noted above that degenerate pairs of orbitals are found if the bond angle is exactly 60°. If two electrons are placed in 2e″, $^1E'$ and $^1A_1'$ states are possible in addition to the $^3A_2'$ state **3** already considered. The $^1E'$ state suffers a Jahn-Teller distortion to give $^1B_2$ and $^1A_1$ components in C_{2v} symmetry. This $^1B_2$ state **6** is an open-shell singlet, the counterpart of the triplet state **3**, while the $^1A_1$ component has alread been considered as either **2** or **4**.

Optimized geometries and energies for **1**–**4** are reported in Table I. Energies of the various states relative to **3**, which is found to be the ground state of S$_3^{2+}$, are also presented. As we have results at SCF, CISD+Q (where +Q signifies the "Davidson correction" designed to approximate the effects of unlinked quadruple excitations[29]), QCISD, and QCISD(T) levels of theory, and results obtained with DZP, TZ2P, and TZ2Pf basis sets, we are well placed to study the effects on the properties predicted for the various electronic states of improving both the one-particle basis and the description of electron correlation. We can also extrapolate with some confidence to results which would have been obtained with the TZ2Pf basis and the QCISD(T) method.

At the SCF level, the ordering of relative energies for the four electronic states is **3** < **4** < **2** < **1** with all three basis sets, and the separations between the states vary only slightly with the size of the basis. The triplet **3** is the lowest by a substantial margin of about 150 kJ mol^{-1}, whereas **4** and **2** are very close in energy; the gap between them decreases progressively from 9.3 through 5.7 to 4.1 kJ mol^{-1}, as the basis is enlarged from DZP through TZ2P to TZ2Pf. The linear isomer **1** is some 50–60 kJ mol^{-1} above **2**, becoming gradually closer to **2** as the basis is enlarged.

Electron correlation effects naturally favor the singlet states over **3**. Structure **2** is lowered compared to **4**, while **1** is stabilized relative to both of these, but these changes among the singlet states are not substantial at the CISD level, where the energy ordering is **3** < **2** < **4** < **1** with all three basis sets used here. Structure **2** is now about 100 kJ mol^{-1} above **3**, **4** some 15 kJ mol^{-1} above **2**, and **1** another 40 kJ mol^{-1} higher. These energy separations are not sensitive to the size of the basis.

When the effects of higher excitations are approximately included by the Davidson correction[29] (CISD+Q), all three singlet states are further stabilized compared to the triplet **3**. Structures **1** and **2** are again favored relative to **4**. The energy ordering is still **3** < **2** < **4** < **1**, with all three basis sets, as was found with CISD energies, but the **3**–**2** separation has decreased to about 85 kJ mol^{-1}. The margin between **2** and **4** has increased slightly to about 23 kJ mol^{-1}, a value which is remarkably insensitive to basis size, but the gap between **4** and **1** increases from only 1.8 kJ mol^{-1} with the DZP basis to 18.1 kJ mol^{-1} with the TZ2Pf set.

The QCISD method treats higher excitations more completely[26] than does the CISD+Q approach, and it leads to a further reduction in the stability of the triangular triplet **3** relative to the singlets. With the DZP basis we find **3** < **2** < **1** < **4**, with **1** and **4** separated by only 3.1 kJ mol^{-1}, but the TZ2P basis produces the energy ordering **3** < **2** < **4** < **1**, i.e. the same as the CISD+Q result. Structure **2** is now about 70 kJ mol^{-1} above **3**, and **4** some 30 kJ mol^{-1} above **2**, with both DZP and TZ2P basis sets. It should be noted here that the QCISD (and QCISD(T)) treatments for the triplet **3** used UHF orbitals. However, spin contamination appears negligible for this system, with the value of $\langle S^2 \rangle$ never exceeding 2.03, so we believe that the QCISD results for **3** may fairly be compared with other data for **3** and for the singlet states **1**, **2**, and **4**.

It is generally believed that QCISD(T) energies include most of the non-dynamical electron correlation effects,[30,31] so they should

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Table II. Vibrational Wavenumbers (ω) and Intensities (I)[a] Predicted for S_3^{2+} Structural Isomers

			basis and method							
isomer			DZP			TZ2P			TZ2Pf	
			SCF	I	CISD	SCF	I	CISD	SCF	I
1, $^1\Sigma_g^+$	ω_1	σ_g	630	0	581	638	0	582	651	0
	ω_2	π_u	156	2	138	185	3	155	189	3
	ω_3	σ_u	1025	139	989	1060	130	1003	1078	130
2, $^1A_1$	ω_1	a_1	745	0	745	798	2	747	806	2
	ω_2	a_1	423	3	369	428	5	386	430	5
	ω_3	b_2	499i	226	727	385i	200	649	333i	195
3, $^3A_2'$	ω_1	a_1	751	0	751	749	0	694	750	0
	ω_2	e'	509	34	509	507	34	501	513	31
4, $^1A_1$	ω_1	a_1	851	2	769	854	1	769	865	1
	ω_2	a_1	541	12	510	550	8	517	553	7
	ω_3	b_2	181	12	270i	130	8	289i	104	10

[a] Units for IR intensities, obtained only at the SCF level, as km mol^{-1}.

be good approximations to MR-CISD (MR indicates multireference) results. To check that this expectation is reasonable for the S_3^{2+} dication, we obtained some QCISD and QCISD(T) results for the isoelectronic ion P_3^-, for which MR-CISD data are already available.[9] We find the DZP energy separation between the triangular triplet and linear singlet states of P_3^- to be 35.3 and 15.2 kJ mol^{-1} at QCISD and QCISD(T) levels (at the CISD geometries), whereas HS found 56.1, 38.5, 22.2, and 9.6 kJ mol^{-1}, at the CISD, CISD+Q, MR-CISD, and MR-CISD+Q levels of theory, respectively (also at the CISD geometries).[9]

Triple excitations preferentially stabilize all three singlet states compared to the triplet **3**, but they do not change dramatically the relative energies of the various singlets. With both DZP and TZ2P basis sets the energy ordering is **3** < **2** < **1** < **4**. The bent singlet **2** is some 40–45 kJ mol^{-1} above **3**. While the QCISD(T) **2**–**3** separation is slightly smaller with the TZ2P basis than the DZP, we note that the addition of f functions to the basis increases this gap at the CISD+Q level, so we feel confident that **3** will be the lowest energy form of S_3^{2+} at the TZ2Pf/QCISD(T) level, by about 45 kJ mol^{-1}. As the basis is enlarged from DZP to TZ2P, the **2**–**1** separation increases from 17.6 to 34.3 kJ mol^{-1}, but the margin between **2** and **4** of about 45 kJ mol^{-1} is scarcely affected.

Results for **5** and **6** were obtained with UHF methods, since the ROHF procedure incorporated in the Gaussian programs could not be persuaded to converge. Spin contamination was minor for **5**, but considerable for the open-shell singlet **6**, with $\langle S^2 \rangle$ values of 2.11 and 1.06, respectively. Structure **5** was found to be 90 kJ mol^{-1} above **3** and to have a bond length of 1.948 Å and a bond angle of 114.4°. Since we did not anticipate that the correlation energy of **5** would exceed that of **3** by any substantial margin, further calculations were not felt to be worthwhile for that state. A very acute bond angle of 56.1° was found for **6**, and a bond length of 2.09 Å, but since it lies 60 kJ mol^{-1} above **3** at the UHF level, we felt once again that correlated studies were not warranted. These results for **5** and **6** are very similar to those already reported for the analogous states of P_3^-,[7,9] for both structures and relative energies.

We may summarize these findings for the relative energies of **1**–**4** as follows. The triangular triplet state **3** is the global minimum form of S_3^{2+} for all theoretical methods and basis sets used in this work. Even though its margin of stability over the lowest singlet state is progressively decreased as the treatment of electron correlation is improved, from over 150 kJ mol^{-1} at the SCF level to about 45 kJ mol^{-1} with QCISD(T) energies, we are confident that this margin substantially exceeds the uncertainities due to the residual limitations in our calculations. The acutely bent isomer **2** is the most stable singlet state, followed by T-shaped **4** and then linear **1**. Increasing the size of the basis beyond DZP makes only rather minor changes to the energy separations between the various states; in particular, f functions have almost no differential effect.

No discussion of the energetics of highly unusual species, in terms of high charge in the case of S_3^{2+}, is complete without a discussion of the relative thermodynamic stability of these species with respect to expected stable products. In this case formation of S_2^+ and S^+ (doublet or quartet states) would seem most likely. Evaluation of the relative energies of $S_2^+ + S^+$ (relative to isomer **3**) at the QCISD(T) level at the optimized QCISD geometry with a TZ2P basis set gives values of −94.1 kJ mol^{-1} (S^+ doublet) and −321.1 kJ mol^{-1} (S^+ quartet). Such large energy differences are to be expected for highly charged species. However, each minimum (as given in Table II) has appreciable vibrational frequencies indicating a deep well for each. A study of kinetic stability of each isomer would require the evaluation of a transition state to products. Such searches, particularly for highly charged species, can be difficult.[32] In addition, since the global minimum has a triplet electronic ground state, location of a transition state will be especially difficult due to the large spin recoupling that would be involved.

Six different geometrical predictions are presented in Table I for each of the important states of S_3^{2+}, and one may reasonably ask which of the combinations of basis and theoretical method is to be preferred. We believe that the DZP/SCF results are probably as reliable as any, judged by the accuracy achieved for S_2 (predicted 1.881 Å, experimental r_e = 1.889 Å[33]) and H_2S_2 (predicted r_e(S–S) = 2.072 Å, experimental r_z = 2.061 Å[34]). Fortunately, the structural parameters of the different states change only slightly as the theoretical method is varied. CISD bond lengths are greater than SCF values by 0.02–0.04 Å, and similar small extensions are found at the QCISD level, while basis enlargement from DZP to TZ2P then to TZ2Pf reduces bond lengths by 0.01–0.02 Å. There are minor increases in the apex angle of the singlet states **2** and **4** in the series SCF–CISD–QCISD.

The bond length in linear **1** of about 1.79 Å is substantially shorter than the presumably standard S=S double bond in S_2 (1.889 Å). However, it should be remembered that the bonds in CO_2 (valence-isoelectronic with S_3^{2+}) are shorter than typical C=O bonds in ketones by some 0.05 Å;[35] since there is also a tendency for bonds in cations to be shorter than those in related neutral molecules, the present results for **1** do not appear anomalous.

Structure **2** contains two distances of about 1.93 Å which slightly exceed the standard S=S double bond length. The increase in bong length from **1** to **2** may be easily understood in orbital terms: the $11a_1$ orbital which becomes occupied in **2** has substantial lone pair character on the central S but is also antibonding between the central and terminal atoms, while the $8b_2$ orbital which is occupied in **1** but vacant in **2** is nonbonding for linear S_3^{2+}. The distance between the terminal atoms in **2** is 2.24 Å; this is much longer than a standard single bond, but we believe there is an attractive interaction between these atoms, as judged by the positive Mulliken overlap population[36] of 0.072 and the

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unusually large force constant for the acute bond angle of 5.09 mdyn Å rad^{-2} (both at the DZP/SCF level).

The bond distance in **3** of 2.03 Å is slightly shorter than the standard S–S single bond length; as already noted, this behavior would be expected for a cation. Geometrical differences between **2** and **4** follow straightforwardly from the changes in orbital occupations. The $2a_2$ orbital, which is occupied in **2** but empty in **4**, is central atom–terminal atom nonbonding but antibonding between the terminal atoms, whereas $4b_1$, which is occupied in **4** but not in **2**, is antibonding between central and terminal atoms but bonding between the two terminal atoms. Excitation of an electron pair from $2a_2$ to $4b_1$ therefore leads to significant reduction of the distance between the terminal atoms, to only 1.86 Å, somewhat shorter than a typical double bond, and simultaneous lengthening of the central–terminal distance to 2.14 Å, rather longer than a normal S–S single bond.

Vibrational frequencies for the various states of S_3^{2+} are presented in Table II. IR intensities obtained at the SCF level are also reported. These data serve two important functions. First, since S_3^{2+} has not yet been prepared, they should be useful aids for the detection of this species in future experiments designed to synthesize it. Most crucial, however, is the information they convey concerning the nature of the different stationary points located by our optimization procedures, since some of this information turns out to be rather unexpected. We note that zero-point vibrational energies have almost no influence on the relative energies of the different states of S_3^{2+}. Our best values (TZ2P/CISD), in kJ mol^{-1}, are 10.1 for **3**, 10.7 for **2**, and 11.3 for **1**. The nature of **4** is discussed below.

Both the triangular triplet **3** and the linear singlet **1** are true minima at all levels of theory used in this work. Their frequencies vary little with the size of the basis. The antisymmetric stretching frequency (ω_2, e′) of **3** is particularly insensitive to the level of theory; we extrapolate its true harmonic frequency to be 505 ± 15 cm^{-1}. Its IR intensity is modest, but probably detectable, if S_3^{2+} can be formed. The symmetric stretching frequency (ω_1, a_1') of **3** varies somewhat irregularly with theoretical method, so it is more difficult to extrapolate with confidence; 680 ± 40 cm^{-1} is our best estimate. It will be useful to consider the vibrational frequencies for **3** with special care, since this isomer is the global minimum for S_3^{2+}. The antisymmetric stretching frequency (ω_2, e′) is particularly insensitive to the level of theory. We obtain our best estimate as follows. At the SCF level it increases by just 2 cm^{-1} as the basis is enlarged from DZP to TZ2P and then increases by 6 cm^{-1} when f functions are added, suggesting that the SCF limiting value would be 515 ± 7 cm^{-1}. Correlation effects are unusually small for this mode; single and double excitations, as incorporated by the CISD method, change the frequency by less than 1 cm^{-1} with the DZP basis and decrease it by only 6 cm^{-1} with the larger TZ2P set. Allowing a few cm^{-1} for any possible influence of higher excitations and larger basis sets, we estimate the total correlation effect to be −10 ± 7 cm^{-1}. When these considerations are combined, we obtain a final value for ω_2 of 505 ± 10 cm^{-1}. The symmetric stretching mode (ω_1, a′) varies more irregularly with the level of theory, so the uncertainty in our final estimate is larger. It changes so little with basis set size at the SCF level (DZP, 751; TZ2P, 749; TZ2Pf, 750 cm^{-1}) that the SCF limiting value may be estimated as 750 ± 4 cm^{-1}. Correlation effects at the CISD level change from less than 1 cm^{-1} with the DZP basis to a reduction of 55 cm^{-1} (or 7.3%) with the TZ2P basis. It seems prudent to suppose that a larger basis set and a more complete account of correlation would both reduce the frequency further; our best estimate for the harmonic frequency is 680 ± 40 cm^{-1}. This mode is IR-inactive, but its Raman intensity is predicted to be substantial (60 Å^4 amu^{-1} at the DZP/SCF level).

Structure **2** is seen to be a transition state at the SCF level of theory. Its single imaginary frequency is the antisymmetric stretching motion (b_2 symmetry), which might be expected to lead to dissociation of **2** into (S_2 + S) fragments. In fact, however, this mode leads directly to **4**, as was verified by geometry optimization in C_s symmetry. Structure **4** is a true minimum at the SCF level. Structure **2** can thus be regarded as a transition state for pseudorotation on the SCF $^1E'$ surface of S_3^{2+}; the $^1E'$ state with valence electron configuration $(4a_1')^2(5e')^4(5a_1')^2(2a_2'')^2(6e')^4(2e'')^2$ is of course Jahn–Teller distorted away from D_{3h} symmetry, giving $^1A_1$ and $^1B_2$ states in C_{2v} symmetry. Even though the magnitude of its imaginary vibrational frequency decreases markedly as the basis is enlarged, from 499i (DZP) through 385i (TZ2P) to 333i cm^{-1} (TZ2Pf), we do not doubt that **2** will still be a transition state at the Hartree–Fock limit. This reduction in the magnitude of ω_3 naturally parallels the reduction in energy separation between **2** and **4** at the SCF level, which has already been noted above.

We have shown how **4** becomes less stable than **2** once electron correlation is included. This change in relative energies is reflected in the vibrational nature of the two states. Structure **4** becomes a transition state at the CISD level of theory, whereas **2** becomes a true minimum. The change in character for **2** is remarkably abrupt; ω_3 passes from 499i to 727 (real) cm^{-1} with the DZP basis. The changes for **4** in the reverse direction are not so dramatic, as ω_3 passes from 181 (real, SCF) to 270i (CISD) cm^{-1}. Since the energy separation between **2** and **4** is progressively enlarged as the theoretical method used becomes more complete (from about 15 (CISD) to about 45 (QCISD(T)) kJ mol^{-1}), we believe that **2** will continue to be a true minimum, and **4** a transition state, at higher levels of theory then CISD. For P_3^-, the state equivalent to **2** is a true minimum at the SCF level, while that analogous to **4** is a transition state. Although vibrational frequencies have not been calculated for the various states of P_3^- at correlated levels of theory, we expect that the characteristics of **2**-like and **4**-like states will not be changed by correlation, since **2** is consistently more stable than **4** for P_3^-.[9]

As far as we are aware, S_3^{2+} is the first 16-valence-electron species which has been shown beyond doubt to have a triangular triplet ground state. For P_3^-, the states equivalent to **3** and **1** are separated by a small margin of only some 10 kJ mol^{-1}, to which HS added uncertainities of +8, −17 kJ mol^{-1}.[9] Comparing the energy differences between the various electronic states of S_3^{2+} with P_3^-, the feature which differentiates S_3^{2+} is not so much the special stability of the triangular triplet **3**, since the corresponding triplet at 56.5 kJ mol^{-1} (TZ2P/CISD+Q) below the bent singlet **2** for P_3^-,[9] compared to 81.9 kJ mol^{-1} for S_3^{2+}. It is rather the linear singlet **1** which appears particularly unstable for S_3^{2+}, being 127.4 kJ mol^{-1} above **3** (TZ2P(CISD)+Q), whereas the analogous energy gap for P_3^- is only 33.5 kJ mol^{-1}.[9] Detailed analysis of the SCF orbitals and eigenvalues for the different states of S_3^{2+} does not seem worthwhile, as the relative energies of these states and also their vibrational character change substantially with the level of theory, as we have shown.

Two qualitative points are, however, worth making. First, we note that the central atom in **1** may be regarded as being in the oxidation state +6, a state which is particularly unstable for S unless several highly electronegative atoms or groups are attached. Thus while SO_3 contains S formally in the +6 state, the corresponding branched isomer of S_4 is 77 kJ mol^{-1} (TZ2P/CISD+Q) above the global minimum, which has a planar *cis* structure[37] and in which no S atom is in an oxidation state higher than +2. For S_2O_2, however, the SO_3-like isomer appears to be the ground state, some 70 kJ mol^{-1} (TZ(2)P/CCD) below the planar *cis* state.[38] Second, we may perhaps rationalize the greater correlation energy of **2** than of **4** as a consequence of the greater number of double bonds **2** contains, as correlation effects are generally more important for multiple bonds than single, due to their greater "concentration" of electrons.

In an analysis of many 16-valence-electron ABC species, Pyykkö has recently presented results obtained at the 6-31G*/SCF level of theory for isomer **1**.[17] Interestingly, he found that it bends

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spontaneously (bending force constant for the linear species is −0.0231 mdyn Å rad^{-2}), to give a slightly bent true minimum whose bond angle is 173.9° and bending frequency is 69 cm^{-1}. These results are inconsistent with those obtained here at the DZP/SCF level, for which the linear species is a true minimum, whose bending force constant of 0.240 mdyn Å rad^{-2} produces a bending frequency of 156 cm^{-1}. Our DZP results are similar to those obtained with larger basis sets (TZ2P and TZ2Pf bending frequencies are 185 and 189 cm^{-1}, respectively), so it seems clear that the DZP basis performs much more satisfactorily than does the 6-31G*. We doubt that the discrepancy is due to the choice of polarization exponent, as the 6-31G* value of 0.65 is not greatly different from that of 0.532 which we used in this work, but suggest that the constraint of equal s and p exponents made in the interest of computational efficiency may be responsible for the poor performance of the 6-31G* basis in this case. It is notable that the optimum s and p Slater exponents are indeed almost equal for first-row atoms such as oxygen (2.246 for 2s and 2.227 for 2p[39]) but rather different for sulfur (2.122 for 3s and 1.827 for 3p). The contracted nature of the 3s orbitals relative to 3p for second-row atoms has been highlighted by Kutzelnigg[40] and by BM.[7] It seems possible that this undesirable feature of the 6-31G* basis contributes to the discrepancies apparent in two recent theoretical studies of the structural isomerism of S_4; the 6-31G* basis was used in one case,[41] whereas DZP and TZ2P basis sets similar to those employed here were adopted in the other.[37]

A point of structural interest concerns the possible dimerization of two S_3^{2+} units to form S_6^{4+}, since Te_6^{4+} has been isolated and shown to adopt a trigonal prismatic structure (D_{3h} symmetry),[42] while Te_3^{2+} is as yet unknown. We believe that this possibility is most unlikely in the sulfur case, at least for S_3^{2+} as an isolated species. The geometry of S_6^{4+} (assumed to be a singlet, since the ready observation of an ordinary Te NMR spectrum[42] for Te_6^{4+} strongly suggests that it is a singlet) was optimized at the DZP/SCF level, under the constraint of D_{3h} symmetry. Within the triangular faces the distance is 2.037 Å, typical of an S–S single bond and almost identical with that found for **3**, but the distance between the trigonal faces of 2.775 Å indicates a weak interaction between them. No vibrational analysis was performed for S_6^{4+}, but its SCF energy is no less than 1317 kJ mol^{-1} higher than 2 mol of **2** (the lowest singlet state of S_3^{2+}), and at the MP3 level the energy separation is still 1278 kJ mol^{-1}. It is, however, conceivable that S_6^{4+} might be stabilized in the solid state by the high lattice energy which its 4+ charge would produce or that interactions with a highly polar solvent might be strong enough to favor S_6^{4+} over two S_3^{2+} molecules. The binding between the trigonal faces is evidently much stronger in Te_6^{4+} than in S_6^{4+}, since the distance in the Te compound between the triangular faces of 3.133 Å exceeds that within the faces by only 0.458 Å,[42] or 17%, a substantially smaller margin than the 0.738 Å (36%) found here for S_6^{4+} at the DZP/SCF level. "Secondary bonding", or association of small units into larger polymeric ones, is characteristic of atoms as heavy as Te.[43]

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Polymorphism in the Heavier Analogues of the Ethyl Cation

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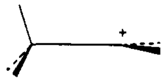
Abstract: Exploration of the potential energy surfaces for $X_2H_5^+$ throughout group 14 is carried out through ab initio calculations. Besides to two forms well-documented for the ethyl cation, the classical form $H_3C{-}CH_2^+$, **1**, and the C_{2v} bridged nonclassical form, **2**, there exist two other possible isomers, corresponding to the adduct $XH_4 + XH^+$. One is singly bridged, $H_3X{-}H{-}XH^+$, **4**, and the other one is doubly bridged $H_2X{<}^{H}_{H}{>}XH^+$, **3**. These forms, close in energy and separated by small barriers, are found to be true minima in all surfaces except for $C_2H_5^+$. The doubly bridged form **3** happens to be the preferred isomer for $Sn_2H_5^+$ and $Pb_2H_5^+$. The nonclassical form **2** is only a saddle point for $Ge_2H_5^+$, $Sn_2H_5^+$, and $Pb_2H_5^+$. The existences and relative stabilities of the various forms can finally be estimated as follows: $C_2H_5^+$, **2**; $Si_2H_5^+$, $\mathbf{1} \approx \mathbf{2} < \mathbf{3} < \mathbf{4}$; $Ge_2H_5^+$, $\mathbf{1} < \mathbf{3} < \mathbf{4}$; $Sn_2H_5^+$ and $Pb_2H_5^+$, $\mathbf{3} < \mathbf{4} < \mathbf{1}$. The minimum energy barriers for **1**–**3** intramolecular conversions are calculated at around 20 kcal/mol, which should support the coexistence of both isomers. The relative stabilities of **1** and **3** can be roughly predicted from the balance between the X–X σ bond energies and the almost constant energy increments required in the dissociation of the double bridges into two fragments. Such simple modelling should apply to any competition between and X–X σ bond and X–H–X bridges.

The gas-phase structure of the ethyl cation $C_2H_5^+$ is now well-established from theoretical studies. The most refined calculations show that there is only one minimum on the corresponding potential energy surface, namely the nonclassical singly bridged C_{2v} form, **2**.[1-4] The classical form $H_3C{-}CH_2^+$, **1**, which is found to be a real minimum at lowest levels of calculations, actually collapses into the bridged form as soon as correlation effects are properly taken into account. The classical form is thus only a saddle point in an intramolecular hydrogen scrambling



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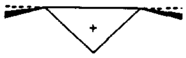

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