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Highlight Review

Chemistry of Tetrasulfur Including Mysterious Rectangular S_4 Metal Complexes

Kiyoshi Isobe

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Abstract

Of eleven possible isomers for neutral S_4, rectangular S_4 has been proposed theoretically as one of the most stable forms. There has, however, been no consensus as to the S_4 ground-state geometric structure despite much effort over recent years, because of the lack of direct structural information from experimental work due to lack of preparation in a pure state. The principal question is whether the ground-state geometry is rectangular D_{2h} or open planar C_{2v}. Our group found first rectangular S_4 in coordination compounds of Rh and Ir tetranuclear complexes as a ligand and disclosed mysterious rectangular S_4 by X-ray analysis and theoretical studies. Here, the newly developed chemistry of rectangular S_4 complexes together with the related tetrasulfur species is introduced both from experimental and theoretical view points. In addition, more accurate argument of the principal question mentioned above is also described using results obtained from recent high-level theoretical calculations.

◆ Introduction

Sulfur vapor, liquid sulfur, and the atmosphere of Jupiter's Galilean moon Io contain the neutral S_4 molecule.[1,2] It has been only detected in mixtures with other sulfur molecules by Raman, infrared, and UV–vis spectroscopy as well as mass spectrometry.[1] In sulfur vapor and in matrix isolated condensates of sulfur vapor, S_4 exists as two isomers but the structures of these isomers have not been established yet.[1,3]

Despite a number of theoretical investigations, S_4 has puzzling problems in geometric and electronic structures which are found to be extremely sensitive to the sophistication of the theoretical methods employed. As a result, to date several different isomers have been proposed as the global energy minimum of the neutral S_4.[4] Recent development of high levels of electron correlation and multireference treatment is expected to find the most stable ground-state isomer among candidates with small energy differences, in particular, as seen between planar C_{2v} and rectangular D_{2h} (point groups and the corresponding structures of S_4 isomers are shown in Figure 1).[5]

In 1994 and 2004, we had chances to find two kinds of rectangular S_4 shapes in metal complexes of $[\{Cp^*M(\mu\text{-}CH_2)\}_2(\mu\text{-}S_4)]X_2$ (Cp^*: $\eta^5\text{-}C_5Me_5$, M = Rh and Ir, X = halides and other counter anions) which were characterized by X-ray analysis.[6,7] Stimulated by our findings the Mealli and Hoffmann group has done theoretical studies of the two complexes and clarified that both S_4 units are stable forms and two disulfide units form an unusual S_4^{2-} rectangle through a two-electron oxidation of two disulfide S_2^{2-}.[8,9]

Oxidation of elemental sulfur by certain powerful oxidants in solvents of low basicity produces the square-planar colorless cation S_4^{2+} which is isolated in crystalline salts with various anions and characterized, inter alia, by X-ray crystallography and theoretical calculation.[10] On the other hand, reduction of elemental sulfur by alkali metals gives the pale yellow tetrasulfide anion S_4^{2-} which is also isolated in various compounds of main group and transition elements and structurally characterized by X-ray diffraction on single crystals.[11,12] This anion is of nearly C_2 symmetry.

There have been a limited number of studies of S_4^+ and S_4^- compared with other S_4 species. The former was found in anodic or chlorine-oxidation of elemental sulfur[13] and the latter in a DMF solution of Li_2S_n ($n > 6$) at 303 K or in aqueous solution of S_4^{2-} with $Fe^{2+/3+}$.[14] The theoretical work of these charged species precedes the experimental and has proposed cis planar C_{2v} for the most stable S_4^-.[15] For S_4^+ there has been still no agreement as to its most stable geometric structure, for which at least three different structures of C_{2v}, D_{4h}, and C_{2h} have been calculated.[4,16] A recent theoretical work has suggested that a rectangular D_{2h} isomer is also a candidate for the stable ground state.[17] In this review, these charged species also will be described briefly.

◆ Neutral S_4 Molecule

The paper entitled by "Resolution of a Long-Standing Problem in Elemental Sulfur Chemistry: A Theoretical Study of Tetrasulfur" was reported by Quelch et al. in 1990.[18] However, many theoretical investigations of the neutral S_4 species are still in progress. Quelch et al. tried to solve the principal question mentioned in ***Abstract***, using ab initio electronic structure theory at the two-reference CISP[19] + TZP[19] level (the reference number 19 presents the glossaries of all abbreviations for theories and calculation methods described in this paper, and hereafter these abbreviations are shown without the reference number 19). They concluded that the D_{2h} structure is not the global minimum, but it is only 0.3 kcal mol^{-1} higher than the most favorable C_{2v} isomer among the eleven possible isomers (Figure 1).

Kiyoshi Isobe[1,2]
[1]*Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency (JST), Kawaguchi Center Building, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012*
[2]*Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, 744 Moto-oka, Nishi-ku, Fukuoka 819-0395*
E-mail: isobetcm@mail.cstm.kyushu-u.ac.jp

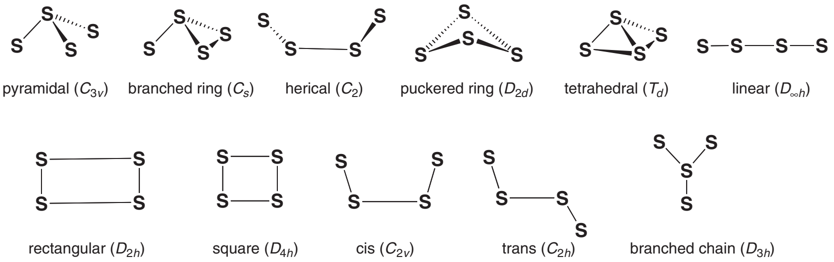
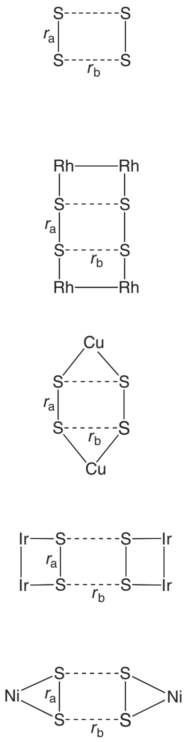


Figure 1. Structures of S_4 isomers.



r_a (Å)	r_b (Å)	
1.95	2.85	K. Raghavachari et al.[20]
1.93	2.61	R. O. Jones et al.[23]
1.904	2.514	M. W. Wong et al.[5]
1.91	2.57	A. Ramírez-Solís et al.[28]
1.979(1)	2.702(1)	in complex **1**[6]
1.950(1)	2.740(1)	in complex **4**[30b]
2.049(3)	2.895(3)	in complex **2**[7]
1.944(2)	2.777(2)	in complex **6**[31]

Figure 2. Theoretical and experimental data for the bond distances of S_4 (D_{2h}).

While, in the same year Raghavachari et al.[20] reoptimized the D_{2h} structure at the MP2/6-31G* level and predicted the bond lengths as shown in Figure 2. They mentioned also that due to "the shallow nature of the bending potential energy surface," further work is necessary to predict conclusively which of two related structures (D_{2h} or C_{2v}) is lower in energy.

Morokuma et al. have recalculated the neutral S_4 at higher levels.[21] Their QCISD(T)/MC-311G(2d) calculations have confirmed the superiority of the C_{2v} isomer over the rectangular D_{2h} structure. At the QCISD(T)/MC-311G(2d)//CISD(SCF/DZP) level, the former is 0.8 kcal mol^{-1} more stable than the latter. When they used for energy calculation the best geometries available, CISD(TSCF/DZP) for the C_{2v} structure and QCISD(T)/MC-311G(2d) for D_{2h}, C_{2v} is still lower by 0.7 kcal mol^{-1}. Moreover, Millefiori et al. have considered D_{2d}, D_{2h}, C_{2v}, and C_{2h} symmetry of the neutral S_4 by using DFT within the B3LYP approximation.[22] Their results suggest that C_{2v}, D_{2d}, and C_{2h} are minima at B3LYP/cc-pVDZ potential energy surface but that the rectangular D_{2h} is a transition state and the planar C_{2v} form to be the ground state. The D_{2h} is higher in energy by 2.11 kcal mol^{-1}. On the other hand, in 2003, Jones et al. have claimed again that the most stable form is a $(S_2)_2$ "dimer" with D_{2h} symmetry, using all-electron DFT calculation with an extended one-electron basis of contracted Gaussian-type orbitals.[23]

At the same time, Wong and Steudel have presented a noteworthy paper in *Chem. Phys. Lett.*[5] They have mentioned that most high-level ab initio MO calculations favor the planar C_{2v} structure. MP2, MP4, and certain DFT calculations seem to yield a rectangular structure as the global minimum. Therefore, they have used a significantly higher level of theory than those reported previously, employing three different methods of G3 X (MP2), CCSD(T)/aug-cc-pVTZ, and complete active space CASSCF. The G3 X (MP2) theory represents a modification of the G3(MP2) theory with three important changes as shown in ref 19. They have established definitively the C_{2v} form as the ground state of S_4: at both the B3LYP/6-31G(2df) and CCSD(T)/aug-cc-pVTZ levels; the D_{2h} structure is calculated to be a transition state for the interconversion of two equivalent C_{2v} forms. Geometric optimization has been done using the CCSD(T)/aug-cc-pVTZ level, which has shown the D_{2h} structure is 1.2 kcal mol^{-1} less stable than the C_{2v} forms. In addition, they have obtained another important result from the calculation of electronic absorption spectra [CIS/6-311+G(3df)] and vibrational spectra B3LYP/6-31G(2df) which allow a convincing assignment of the observed green (520–530 nm) absorbing species and the red (625 nm) one in sulfur vapor to the cis planar (C_{2v}) and the trans planar (C_{2h}), respectively. This assignment is in distinct contrast to the previous assignments and is consistent with experimental data.[24]

McCarthy et al. have confirmed experimentally that S_4 with the C_{2v} ground state automerizes through a transition state with D_{2h} symmetry (Figure 3a), using Fourier transform microwave and long-path millimeter-wave absorption spectroscopy.[25] The structure of the C_{2v} ground state has been proposed as shown in Figure 3b. The transition state lies about 1.4 kcal mol^{-1} above the two C_{2v} equivalent minima on the potential energy surface. These structural and electronic predictions have been reinforced theoretically by Harkless et al. using singles and doubles coupled-clusters including CCSD(T) and MRCI levels.[26] VMC and DMC calculations also have led to analogous results.[27] The latest theoretical simulations on the D_{2h} and C_{2v} isomers have been performed using AIMD simulations.[28] After a careful calibration of the electronic strucure, calculations have been done using BPW91/aug-cc-pVTZ, and it was concluded that the

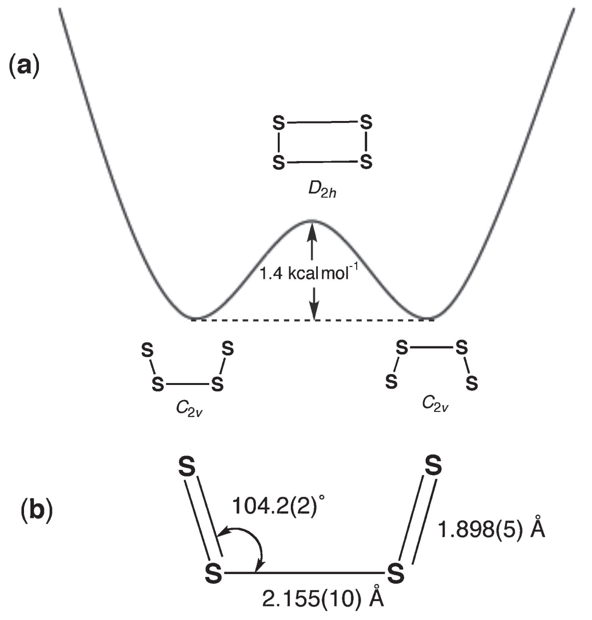


Figure 3. The double-minimum potential of S_4, showing the C_{2v} structure and the D_{2h} transition state (a) and equilibrium structure (minimum on the potential-energy surface) derived from the rotational specrtoscopic data and coupled-cluster theory calculation (b).

D_{2h} structure is a transition state linking two equivalent (mirror images) C_{2v} isomers. The trajectories show that the C_{2v} isomers interconvert when passing through the D_{2h} transition state.

Thus, after Wong and Steudel's precise work,[5] the theoretical argument of the structure and electronic state of the neutral S_4 is coming to a settlement as described above, and the theoretical results obtained well explain the experimental data.

♦ Rectangular S_4 Species in Metal Complexes

In 1994, our group found that in the presence of excess H_2S, air oxidation of the hydrogen sulfide complex $[\{Cp^*Rh(\mu\text{-}CH_2)\}_2(\mu\text{-}SH)]BF_4$ proceeds to form an intriguing rectangular S_4 complex $[\{Cp^*Rh(\mu\text{-}CH_2)\}_4(\mu\text{-}S_4)](BF_4)_2$ (**1**) by a unique intermolecular oxidative coupling (Figure 4a).[6]

The X-ray analysis revealed the structure of **1**, which is shown without the counter anions in Figure 5a. The rectangular planar S_4 unit bridges two $Rh_2(\mu\text{-}CH_2)_2$ groups to form a Rh_4S_4 eight-membered ring with a centrosymmetric chair-like core. Two of the four S–S distances (S1–S2* and S1*–S2 1.979(1) Å) are short and correspond to a double bond. The other two distances (S1–S2 and S1*–S2* 2.702(1) Å) are quite long. It seems to be less than a single bond. Intriguingly, the geometry is similar to those of the neutral free S_4 molecule with D_{2h} symmetry calculated by Raghavachari,[20] Jones,[23] and many other groups[5,28] (Figure 2).

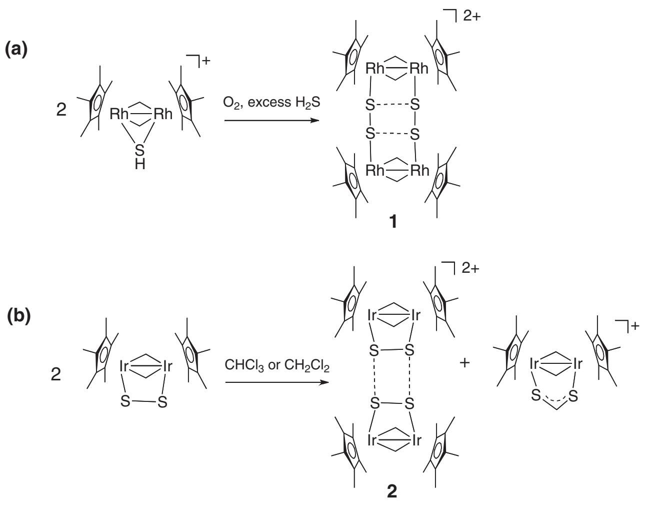


Figure 4. Formation of complexes **1** (a) and **2** (b).

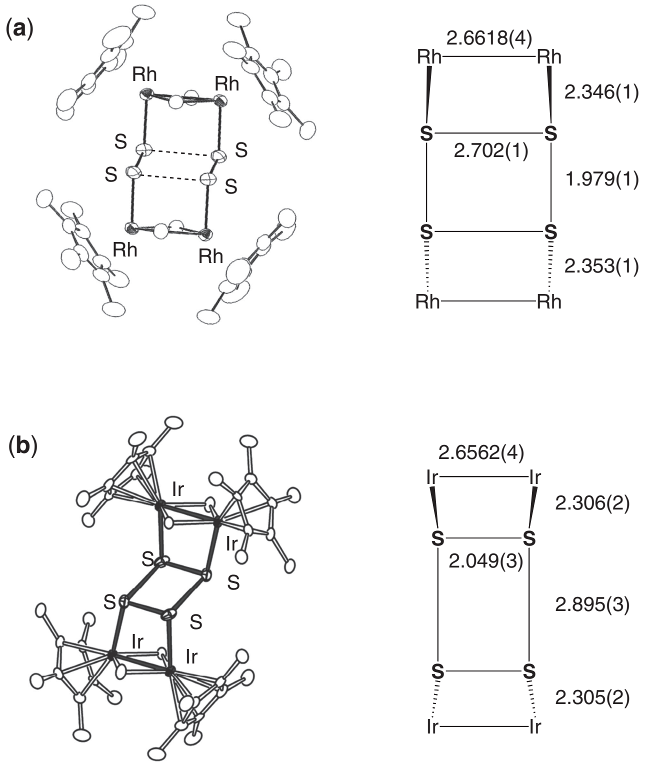
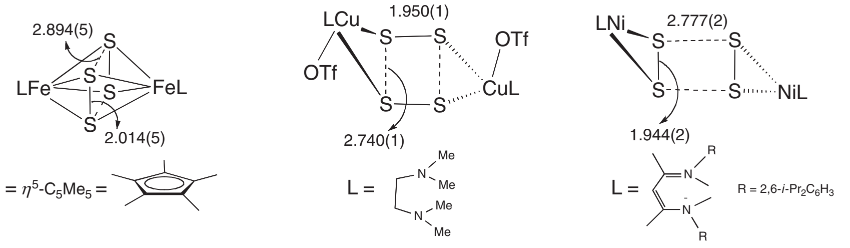


Figure 5. ORTEP drawings of complexes **1** (a) and **2** (b) without the counter anions, and their core structures (S–S and M–M bond distances: Å).

Morokuma and co-workers have compared the optimized D_{2h} structures for the free S_4, S_4^-, S_4^{2-} with the S_4 unit in complex **1** and shown that the S_4 unit in **1** is close to the free S_4^- anion radical by QCISD(T)/MC-311G(2d).[21] The optimized S–S bond lengths in the monoanion, 2.00 and 2.70 Å, are very similar to the experimental values. Calculations for the model complex of **1** with Cp (η^5-C_5H_5) instead of Cp* followed by population analysis give the total charge on the S_4 unit as about -0.7 e.

In 2004, our group again has encountered another type of rectangular S_4 complex.[7] The disulfide complex $[\{Cp^*Ir(\mu\text{-}CH_2)\}_2(\mu\text{-}S_2)]$ reacts with $CHCl_3$ or CH_2Cl_2 to form $[\{Cp^*Ir(\mu\text{-}CH_2)\}_4(\mu\text{-}S_4)]Cl_2$ (**2**) (Figure 4b) and $[\{Cp^*Ir(\mu\text{-}CH_2)\}_2(\mu\text{-}S_2CH)]Cl$. Like the Rh analog, complex **2** has a chair-like

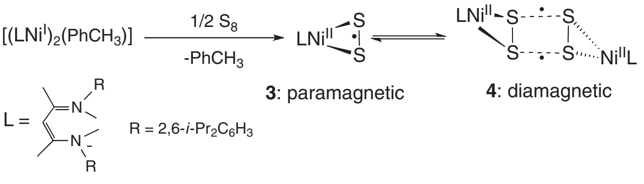


3 **4** **6**

Figure 6. Schematic structures of complexes **3**, **4**, and **6** (S–S bond distances: Å).

structure with the S_4 unit bound to two iridium dinuclear moieties (Figure 5b). The S_4 unit has two short S–S bonds (2.049(3) Å) with double bond character and two long S–S bonds (2.895(3) Å) with less than single bond character. The shorter S–S bonds lie parallel to the Ir–Ir bonds, and the longer ones lie perpendicular to the Ir dinuclear backbone. This arrangement of the short and long S–S bonds in the complex is just opposite to the corresponding Rh complex, which rotates by 90°. Thus, the two S atoms in the short S–S bond bridge the two Ir atoms of one $[Cp^*Ir(\mu\text{-}CH_2)]_4$ unit. It is worthwhile to note that although the Rh and Ir complexes have the two weak S–S bonds, there is no equilibrium with dissociation in solution.

Hoffmann et al. have received an impetus to carry out theoretical studies from two kinds of S_4 with D_{2h} structures in our Rh and Ir complexes shown in Figure 5.[8] Their DFT calculation suggests that, while experiments give the rectangle coordinated with its long edge parallel to Rh–Rh bonds and perpendicular to the Ir–Ir bonds, either orientation is feasible for both metals. The most stable structure for both Rh and Ir is that with the long S–S bond parallel to the M–M axis; however, the differences are less than 4 kcal mol^{-1} in each case. They do not wish to attribute much significance to this preference; it may change with the level of the calculation. They have also attempted to find the path of interconversion between two S_4 rectangles by using single-point DFT calculations; although rotation of the S_4 rectangle is likely a multistep process, a calculated barrier of 46 kcal mol^{-1} for a simple interconversion pathway going through a trapezoidal, not a square, transition state was indicated. An argument is presented, based on molecular orbital calculations, that the long S–S contacts (2.70 Å for Rh and 2.90 Å for Ir) in the rectangle are in fact two-center-three-electron bonds (or "half bonds"). Moreover, the −2 charge on the S_4 rectangle is related to a Jahn–Teller distortion from a square to a rectangle. The Mealli and Hoffmann group has continued to study theoretically how to form the S_4 rectangle in **1** and **2**.[9] The S_4 formation is related to the oxidation of parallel S_2^{2-} molecules. The removal of two electrons can occur either externally or by an internal metal–ligand redox process. In the resulting M_4S_4 framework through both processes, in particular, the latter, depopulation of the high-lying S_4 σ^* MO and population of a lower metal level may occur. This situation accelerates an interaction described as metal back-donation. They have found that the formation of an S_4^{2-} unit is favored by metals which cannot stabilize high oxidation state (e.g., Fe(IV) or Cu(III)), whereas the two S_2^{2-} units remain substantially uncoupled with early transition metal in high oxidation states (e.g., Ti(IV)).



Scheme 1.

The chemical, structural, and computational evidence for the rare rectangular S_4^{2-} ring in **1** and **2** has prompted the Mealli and Hoffmann group to inquire whether such a unit may exist in other chemical compounds.[9] They have found in the Cambridge Structural Database at least two other candidates that could contain a S_4^{2-} ring. These are $[Cp^*Fe(\mu\text{-}S_2)_2FeCp^*](X_2)$ (**3**, X = PF$_6$,[29a] I[29b]), and $[(tmeda)Cu(\mu\text{-}S_2)_2Cu(tmeda)](OTf)_2$ (**4**, tmeda: $Me_2NCH_2CH_2NMe_2$, OTf: trifluoromethanesulfonate) (Figure 6).[30] In complex **3**, four S atoms bind to four Fe atoms to make a triple-decker frame. Its rectangular S_4 unit has similarly two short S–S bonds (2.014(5) Å) and two long S–S bonds (2.894(5) Å). Complex **4** has a new type of the chair-like frame in which two S atoms in the long S–S bond (2.740(1) Å) chelate one Cu atom. In the short S–S bond (1.950(1) Å) sides there is no bonding interaction with Cu atoms.

The theoretical study by the Mealli and Hoffmann group of the formation of the rectangular S_4 unit has received experimental support, recently. Yao et al. have synthesized a paramagnetic supersulfide nickel complex $[LNi(S_2)]$ (**5**, $L^- = CH\{(CMe)(2,6\text{-}i\text{-}Pr_2C_6H_3N)\}_2^-$), which crystallizes in the form of a diamagnetic dimer $[\{LNi(S_2)\}_2]$ (**6**) (Scheme 1).[31] The dimer **6** has also a chair-like frame similar to **4** (the short S–S bonds: 1.944(2) Å, the long S–S bonds: 2.777(2) Å). However, the two S atoms in the short S–S bond bind one Ni atom in chelate. This arrangement of the short and long S–S bonds in **6** is just opposite to **4**, which rotates by 90°. This situation is analogous to that between **1** and **2** as mentioned before. The two S atoms in the short S–S bond and the long S–S bond either are able to participate in the chelation of metal ions. Namely, we can see that the prediction of "either orientation is feasible" by the Mealli and Hoffmann group is also valid for the chelating S_4 of **4** and **6**. In Figure 2, the S–S bond distances of **1**, **2**, **4**, and **6** are presented, and there seems to be only a little difference in their rectangular sizes between the chelating and bridging S_4 ligands, but the Ir atom enlarges the size.

Interestingly, the dimer **6** dissociates in benzene at ambient temperature to the paramagnetic **5**, though **1** and **2** do not. It might come from a difference in the coordination mode.

Furthermore, Solomon et al. have also noticed a bonding interaction between the two S_2 units in **4**[30a] which might have passed unrecognized.[30b]

◆ Charged S_4 Species Including S_4^{2+}, S_4^{2-}, S_4^{+}, and S_4^{-}

S_4^{2+}: This species was first detected in solution of sulfur in 30% fuming sulfuric acid and identified by magnetic circular dichroism.[16,32] A pure yellow solid compound of $S_4(SO_3F)_2$ containing the S_4^{2+} dication was obtained from a mixture of powdered sulfur and $S_2O_6F_2$ in liquid SO_2. A colorless crystal of $S_4(AsF_6)_2 \cdot AsF_3$ was analyzed by X-ray crystallography.[33] The diamagnetic S_4^{2+} possesses a square-planar structure (S–S bond (Å): 1.999(4), 1.946(4), 1.924(4), and 1.986(4), S–S–S bond angle (deg): 91.7(2), 91.5(2), 87.9(2), and 88.9(2)), with a quasi-aromatic 6π four-membered ring. In the early stage of theoretical study of S_4^{2+}, Fukui et al. performed calculation of its electronic state using semiemprical INDO method for valence electrons and assigned the weak absorption band at 280 nm to the $2e_u \rightarrow 3e_u$ transition which is forbidden by symmetry.[34] The several ab initio studies including a full-dress treatment by Janssen have addressed the geometric and electronic structure of S_4^{2+}.[35,36] The electronic structure of S_4^{2+} was understood as seemingly simple chemical systems; overall the four atomic $3p_z$ orbitals are assembled into one π-bonding, two nonbonding, and one empty π^*-antibonding, and in total one π bond is delocalized over all four S atoms. It, however, has turned out to be rather complex and has, therefore, been the focus of many theoretical discussions. Sountamo et al. have proposed that S_4^{2+} has less diradical character than the corresponding Se_4^{2+} and Te_4^{2+}, using both the symmetry-broken Hartree–Fock formalism and multiconfigurational CAS method.[37] While, Klapötke et al. have performed valence-bond calculation with D95 basis set and used the Mulliken, Löwdin, and Hiberty structural weights to show that S_4^{2+} involves the two singlet diradical structure (I and II) with structural weights of 0.23 each, which are by far the most important individual Lewis structures having the S–S single bond (Figure 7).[38]

Geerlings et al. have disclosed a unique aromaticity of S_4^{2+} by the calculation of current-density maps using the ipsocentric CTOCD-DZ/6-311G** approach. The calculated map finds that S_4^{2+} is supported by diatropic π current suggesting an aromaticity of S_4^{2+}.[39a] The π current is weakened by σ circulation. The electron localization function shows that the S–S bonds in S_4^{2+} are single bonds and that the aromaticity arising from lone pair electrons on the S atoms differs from that of the classic hydrocarbons. Thus, the term "lone pair aromaticity" has been proposed.[39b]

S_4^{2-}: This species was prepared according to eq 1 or 2 from elemental sulfur in liquid ammonia or in solid-state reaction at high temperature.

$$2M + 1/2S_8 \rightarrow M_2S_4 \quad M = Na \text{ or } Li \tag{1}$$

$$M_2S + 3/8S_8 \rightarrow M_2S_4 \tag{2}$$

The tetrasulfide ion S_4^{2-} in Na_2S_4 has helical (C_2) symmetry. The S–S bond distances are 2.074(1) (terminal) and 2.061(1) Å (middle).[40] Cederbaum et al. have investigated the electronic stability of S_4^{2-} using the standard SCF RHF and ROHF techniques with their DZ basis set.[41] A population analysis has revealed that the excess charges are essentially localized at the terminal S atoms such that the inner atoms carry only small amounts of negative charge.[16] However, in actual occurrence of solid Na_2S_4 the charge localization is compensated by the close contacts with Na^+ ions (the number of the contacts, terminal S: four and middle S: two).

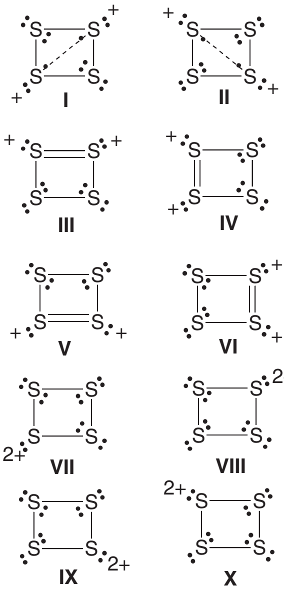


Figure 7. Singlet diradical structures **I** and **II**, Kekulé structures **III–VI**, and "co-ionic" structures **VII–X** for S_4^{2+}.

The S_4^{2-} ion coordinates to various main group and transition elements as a chelate ligand.[12] Many coordination compounds have been structurally characterized by X-ray diffraction on single crystals. The coordination of the S_4^{2-} ion perturbs its native symmetry, S–S bonds and S–S–S angles under the influence of metal ions and peripheral ligands because of the very accommodating character of the S element; symmetry change between helical C_2 and planar C_{2v} has been observed in the Cambridge Structural Database. The S_4^{2-} transition-metal complex is a typical polysulfido complex. It plays an important role for catalysts and intermediates in enzymatic processes and in industrial reaction such as the desulfurization of oil and coal.[12]

S_4^{+}: Mass spectrometric investigations of sulfur vapor involving both electron impact ionization and photoionization clearly showed the formation of radical S_4^+ which reacts readily with NO_2 to give oxidation products of S_4O^+ and S_2NO^+.[42] It reacts also with NH_3 to produce $S_2NH_3^+$.[43] To date, however, pure S_4^+ has not been synthesized and isolated yet. The successive oxidation of sulfur by $S_2O_6F_2$ and oleum with AsF_5 was monitored with several experimental techniques such as magnetic circular dichroism, magnetic measurements, UV–vis, and ESR spectroscopy.[36] These methods did not give distinct evidence for the existence of the singly charged cation S_4^+, but it was pointed out that the cation exists in equilibrium between the diamagnetic cations such as S_8^{2+} and S_{19}^{2+}.[36] While, anodic oxidation or the oxidation of elemental sulfur with chlorine in NaCl–$AlCl_3$ likely produces S_4^+ together with several sulfur cationic species.[13] Recently, Krossing et al. have suggested that S_4^+ may be present and detectable in sulfur dioxide solutions given on oxidation of sulfur by AsF_5 in the presence of a facilitating agent.[44]

There are a limited number of theoretical investigation of S_4^+. Again, as in the case of neutral S_4, the cis C_{2v}, trans C_{2h}, and D_{2h} rectangular isomers are included as the lower-lying S_4^+ isomers. Au et al. have acquired these isomers by means of B3LYP DFT and predicted that the C_{2v} isomer is the most stable similarly to the neutral counter part, according to the total energy.[16a] While, Zakrzewski et al. have predicted that the $^2B_{1u}$ state of the square D_{4h} ring isomer is the lowest using the HF/6-31+G* theory.[16b] Recently, Krossing and Rosmus groups have optimized the geometry of S_4^+, and both have found that the square D_{4h} ring isomer is the global minimum using B3PW91/6-311+G* level of theory and CASSCF method together with cc-pVTZ basis set, respectively.[17,44]

These results of geometry optimization depend on the level of the theory, and more experimental studies would be needed on the S_4^+ system.

S_4^-: This radical species is also produced as a mixture of other anionic sulfur species in gas phase by the electron impact ionization of sulfur vapor,[43] direct laser vaporization of sulfur,[45] and pulsed arc cluster ion source.[15,46]

In wet chemistry, the sulfur species in the red solution prepared from sulfur and Na_2S_4 in DMF, HMP (hexamethylphosphoric triamide) or acetone was thought to be the red S_4^- anion. However, no convincing proof for it has been obtained from spectroscopic studies.[14] In 1997, Levillain et al. have identified the S_4^- anion with $g = 2.031$ by ESR spectroscopy of a solution of Li_2S_n ($n > 6$) in DMF at 303 K.[47] Steudel has proposed the reasonable formation of the S_4^- anion as below (eq 3).[14]

$$S_7^{2-} \rightleftarrows S_3^- + S_4^- \qquad (3)$$

Zakrzewski[16b] and Ganteför[15,46] groups have optimized the geometry of the S_4^- anion using the HF/6-31+G* and a combination of density functional calculation with molecular dynamics (MD/DF), respectively: both the groups have suggested that a planar C_{2v} species is the most stable isomer. However, Morokuma et al. have mentioned that the free S_4^- anion has the C_{2h} isomer as the most favorable structure using QCISD(T)/MC-311G(2d).[21] More recently, Au[45] and Rosmus[17] groups have supported the results of Morokuma et al. and reported that the trans planar structure of C_{2h} symmetry is the energetically most stable form using B3LYP DFT and CASSCF together with cc-pVTZ basis set, respectively.

◆ Conclusions and Outlook

Sulfur is the element with the largest number of solid allotropes. More than 30 crystalline allotropes have been prepared and characterized by X-ray diffraction, most of which are composed of homocyclic rings.[48] In the small allotropes, the structures of $S_2(D_{\infty h})$,[48] S_3(open C_{2v}),[48] and S_5(ring C_s)[20,49] are known, but that of S_4 has been not identified for many years. Recent theoretical study, however, is leading to clarification of the structure: S_4 has planar C_{2v} structure in the ground state and rectangular D_{2h} structure is in a low lying transition state as mentioned before.[5] Intriguingly, the rectangular structure of S_4 has been found as a charged species in transition-metal complexes. Hoffmann et al. have simply suggested that the ligand S_4 in $[\{Cp^*Rh(\mu\text{-}CH_2)\}_4(\mu\text{-}S_4)]^{2+}$ has −2 formal charge from the analogy of $[\{Cp^*Rh(\mu\text{-}CH_2)\}_4(\mu\text{-}CN)_2]^{2+}$,[8] though Morokuma et al. have calculated the model complex of **1** with Cp instead of Cp* and performed population analysis to obtain the total charge on the S_4 unit as about −0.7 e as mentioned before. The S_4 with −2 formal charge has opened a new sulfur reaction with two-electron transfer from disulfide species through the interaction of transition-metal atoms. Here, it is worth quoting the suggestion made by Mealli, Hoffmann, et al.: "we also begin to see how the nature of the main-group element and of the metal influence 2 S^{2-}/S_2^{2-} and 2 S_2^{2-}/S_4^{2-} systems which are probably relevant and regulate important biological processes based on the inner electron-transfer process."[8,9]

Chemistry of both double-charged S_4 species, S_4^{2+} and S_4^{2-}, has made steady progress based on experiments and theoretical calculations. As concerns the former species, the new concept of "lone pair aromaticity" arising from its D_{4h} square geometry deserves special mention.[39b] The latter species has been employed mainly as a chelate ligand of nearly C_2 symmetry in many transition-metal complexes which are important polysulfido complexes. They have attracted interest as catalysts and intermediates in enzymatic processes and in industrial reactions as mentioned above.[12]

For both single-charged S_4 species, S_4^+ and S_4^-, their chemistry is still infant and needs more experimental data, in particular, convincing structural information for progress.

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19 Glossary of abbreviation for theories and calculation methods described in this paper. For basis set nomenclature, consult the Gaussian 09 User's Reference (Gaussian 09 Help Table of Contents-Preparing Input Files-Basis Sets).

Naming convention, for example, **RHF/6-31+G(d,p)//RHF/6-31G(d)**, which means that the energy calculation was performed using Hartree–Fock theory and the 6-31+G(d,p) basis set on a structure optimized with Hartree–Fock theory and the 6-31+G(d) basis set.

AIMD: ab initio molecular dynamics, **B3LYP**: hybrid functional Becke and HF exchanges and Lee–Yang–Parr correlation function, **B3PW91**: adiabatic connection method using Becke exchange and PW91 functionals, **CAS**: complete active space, **CASSCF**: complete active space self-consistent-field, **CCSD(T)**: coupled-cluster theory in singles and doubles approximation with perturbative triple excitation corrections, **CIS**: configuration interaction including only single electronic excitations, **CISD**: configuration interaction with single and double excitations, **CISD(TCSCF/DZP)**: CISD(two-configuration SCF and the DZP basis set), **CISP**: single and double excitation configuration interaction, **CTOCD-DZ**: continuous transformation of origin of current density-diamagnetic zero, **DFT**: density functional theory, **DMC**: fixed-node diffusion Monte Carlo, **G3(MP2)**: A variation of Gaussian 3 theory is presented in which the basis set extensions are obtained at the second-order Møller–Plesset perturbation level. **G3X(MP2)**: A modification of G3 theory incorporating three changes is presented. The three new features include: (1) B3LYP/6-31G(2df,p) geometry; (2) B3LYP/6-31G(2df,p) zero-point energy; and (3) addition of a g polarization function to the G3Large basis set for second-row atoms at the Hartree–Fock level, **HF**: Hartree–Fock, **INDO**: intermediate neglect of differential overlap, **MD/DF**: a combination of density functional calculation with molecular dynamics, **MP2**: Møller–Plesset perturbation (second order), **MP4**: Møller–Plesset perturbation (fourth order), **MRCI**: multireference configuration interaction, **QCISD(T)**: theory of quadratic configuration interaction with single and double excitations and triple excitations added perturbatively, **RHF**: restricted Hartree–Fock, **ROHF**: restricted open-shell Hartree–Fock, **SCF**: self-consistent field, **VMC**: variational Monte Carlo.

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