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A Theoretical Study of Rectangular Tetrasulfur in a Gas Phase and in the Tetranuclear $[\{Rh_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CH_2)_2\}_2(\mu\text{-}S_4)]^{2+}$ Complex

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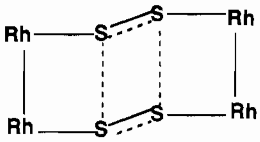
Comparison of the optimized D_{2h} structures for the free S_4, S_4^-, and S_4^{2-} with the experimentally observed structure in the $[\{Rh_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CH_2)_2\}_2(\mu\text{-}S_4)]^{2+}$ complex shows that the S_4 unit in the complex is close to the free S_4^- anion-radical. Calculations for $[\{Rh_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CH_2)_2\}_2(\mu\text{-}S_4)]^{2+}$ followed by population analysis give the total charge on the S_4 unit as about −0.7 e. The bonding character of S_4 with metal atoms in the complex has been described as σ-back-donation from Rh atoms to the S_4 unit accompanied by π-donation onto Rh atoms. For the free S_4^- anion-radical the trans C_{2h} isomer is the most favorable structure, and the rectangular D_{2h} isomer is only 1.3 kcal/mol higher. For the free S_4^{2-} dianion, the nonplanar gauche C_2 structure is calculated to be the most stable form, while the D_{2h} structure lies 16.3 kcal/mol higher.

Introduction

Recently, a novel tetranuclear $[\{Rh_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CH_2)_2\}_2(\mu\text{-}S_4)]^{2+}$, **1**, cationic complex has been synthesized.[1] X-ray structural analysis has demonstrated that the bridging S_4 unit resembles the cyclobutadiene framework.



This is the first example of the rectangular S_4 unit having D_{2h} symmetry. Comparison of **1** with the similar diamagnetic tetranuclear complex $[\{Rh_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CH_2)_2\}_2(\mu\text{-}CN)_2](PF_6)_2$[2] may be used to estimate the formal charge on the S_4 unit in **1**. The latter has two CN^{-1} ligands bridging two $Rh_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CH_2)_2$ moieties which are the same moieties as in **1** and leaves a charge of +2 on $[\{Rh_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CH_2)_2\}_2(\mu\text{-}CN)_2]$, similar to **1**. Hence, the S_4 unit would be expected to have the formal charge −2. However, direct experimental observation of the charge on S_4 as well as the bonding character of this ligand with four Rh atoms in the complex is not possible, and the present theoretical consideration has the objective to clarify these questions.

S_4 species is of interest for both experimental and theoretical chemistry for a long time. While sulfur vapor is a complicated mixture and all S_n in the range $2 \le n \le 10$ have been detected, quite little is known about several of the smaller S_n molecules including S_4, because they can not be prepared in a "pure" state and direct experimental study of their structure is impossible. Despite much efforts over recent years, which have included experimental spectroscopic measurements[3−10] and several theoretical studies,[11−15] there is still no consensus as to the electronic or geometrical structure of S_4. Although the S_4 structure may somewhat change in coordination sphere of a transition metal as compared with the free state, comparison of the experimental structure with the geometry calculated for a free molecule in a gas phase would be interesting.

Results and Discussion

Ab Initio Calculations of $[\{Rh_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CH_2)_2\}_2(\mu\text{-}S_4)]^{2+}$. In order to estimate the charge on the S_4 ligand imbedded in the rhodium cluster, we performed ab initio molecular orbital (MO) calculations on $[\{Rh_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CH_2)_2\}_2(\mu\text{-}S_4)]^{2+}$, which differs from the experimental **1** only by replacement of Me by H in the $\eta^5\text{-}C_5Me_5$ groups. For comparison we also carried out calculations on the $[\{Rh_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CH_2)_2\}_2(\mu\text{-}CN)_2]^{2+}$ complex.[2] Single point HF calculations at experimental geometries have been performed with the following basis: [3s3p3d]/(5s5p3d) for Rh atoms together with the Hay−Wadt effective core potential[16] taking explicitly into account 17 electrons in 4s4p4d5s5p shells, the 6-31G basis set for S_4 and CN units, and the minimal STO-2G basis set for other C and H atoms.[17] All calculations have been carried out

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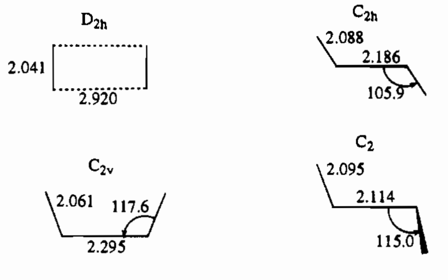
Table 1. Population Analysis Data for $\{(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}CH_2)_2\}_2S_4^{2+}$ and $\{(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}CH_2)_2\}_2(CN)_2^{2+}$

	$\{(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}CH_2)_2\}_2S_4^{2+}$					$\{(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}CH_2)_2\}(CN)_2^{2+}$					
				S–S							
	S	Rh	Rh–S	shorter	longer	(CN)	Rh		Rh–C	Rh–N	C–N
Z_{Mul}[a]	−0.17	−0.69				−0.91	−0.48,	−0.34[e]			
Z_{Nat}[b]	−0.22	−0.09				−0.77	+0.01,	−0.12[e]			
Q[c]			0.27	0.69	0.16				0.26	0.18	1.70
WBI[d]			0.31	1.20	0.25				0.45	0.28	2.66

[a] Mulliken charge. [b] Natural charge. [c] Natural overlap population. [d] Wiberg bond index. [e] The first value corresponds to the Rh atom connected with N; the second value corresponds to Rh connected with C.



a) S_4^{2-}

b) S_4^-

Figure 1. MP2/6-31G(d) optimized geometries of different structures of S_4^{2-} and S_4^-.

using the GAUSSIAN92 program.[18] Mulliken and natural population analyses[19] have been carried out, and their data are collected in Table 1.

According to the data of population analyses, sulfur atoms in the tetrarhodium complex acquire a negative charge. The total charge on the S_4 unit is −0.68 e (Mulliken) or −0.88 e (natural). Thus S_4 in **1** is closer to the S_4^- anion-radical than to the neutral S_4 or the S_4^{2-} dianion. On the other hand, in the μ-cyanide complex the charge on the $(\mu\text{-}CN)_2$ is close to −2, and the total negative charge on four Rh atoms is noticeably smaller than that for the complex with S_4. The concept of formal charge does work therefore for the cyanide complex, but it does not work for the tetrasulfur complex. As a result, the formal charge comparison, which is widely used in coordination chemistry, for these two related compounds appears to be not warranted.

In accord with experiment, the $[\{Rh_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CH_2)_2\}_2(\mu\text{-}S_4)]^{2+}$ complex has a closed shell ground state. The UHF triplet lies about 29 kcal/mol higher than the RHF closed shell singlet at the experimental geometry; the electron correlation usually lowers the closed-shell singlet more than the triplet, and higher levels of calculations are not likely to change the conclusion.

Geometry of S_4^{2-} and S_4^-. In order to compare geometry of the S_4 unit in **1** with free S_4 bearing various charges, we performed an ab initio MO study of different geometrical isomers of S_4^{2-} and S_4^-. Earlier, structures of S_4^{2-} were calculated by the HF/4-31G method[20] and a planar trans configuration of C_{2h} symmetry was found to be a global minimum for the dianion. We have refined the theoretical consideration employing the higher level approach. Optimization of geometric structures of different isomers and analytical frequency analysis have been carried out at the MP2/6-31G(d) level and single point energy calculations have been performed at the QCISD(T)/6-31+G(2d) level.[17] Optimized geometries of various isomers of S_4^{2-} and S_4^- are shown in Figure 1 and their energies are summarized in Table 2.

As seen in Table 1, the nonplanar gauche C_2 structure is the most stable form of S_4^{2-}. Interestingly, the C_2 isomer of the dianion has a geometry similar to that of the S_4 fragment in the most stable structure of H_2S_4 sulfane.[12] Deprotonation of the sulfane leads to a small elongation of SS bonds (from 2.06 to 2.10−2.11 Å) and opening of the SSS angle (from 106 to 115°). The rectangular D_{2h} structure is also a local minimum according to the frequency analysis and lies 16.3 kcal/mol higher than C_2 at our best QCISD(T)/6-31+G(2d)//MP2/6-31G(d) level with or without zero-point energy correction (ZPE). The planar rectangular geometry is thus very unstable relative to the most favorable C_2 structure, and the interaction with a transition metal is not likely to upset the preference. Moreover, the MP2/6-31G(d) optimized interatomic distances in S_4^{2-} (D_{2h}), 2.04 and 2.92 Å, are quite different from those found in the S_4 unit of the rhodium complex, 1.98 and 2.70 Å.[1] These results confirm that S_4^{2-} is not a likely candidate for the S_4 unit in complex **1**.

For S_4^-, MP2 optimization of geometry within C_2 symmetry converges to the trans C_{2h} structure of the ^2B_g electronic state. Optimization under C_{2v} symmetry leads to the rectangular D_{2h} geometry with ^2A_u electronic state. Both C_{2h} and D_{2h} structures are real minima on the potential energy surface (no imaginary frequencies at the MP2/6-31G(d) level). At the MP2 level, the D_{2h} structure is more stable than C_{2h} by 10.8 kcal/mol; however, at the QCISD(T)/6-31+G(2D) level, the order is reversed: the C_{2h} geometry is 1.3 kcal/mol more favorable than D_{2h}. Anyway, the rectangular isomer of S_4^- is stable enough and can be imbedded into the tetrarhodium cluster. The MP2/6-31G(d) calculated SS distances in the D_{2h} structure of the monoanion, 1.98 and 2.75 Å, are quite close to the values measured experimentally in **1**.

Comparison of Rectangular Isomers of S_4, S_4^-, and S_4^{2-}. The rectangular structure is one of the most stable isomers of neutral S_4 Raghavachari et al.[13] calculated it to lie 1.7 kcal/mol lower than another planar C_{2v} isomer in the QCISD(T)/6-31G-(d)//HF/3-21G(d) approximation and to be a real minimum with zero imaginary frequency at the MP2/6-31G(d) level. According to Quelch and co-workers,[14] the D_{2h} structure is not the

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Table 2. Relative Energies (kcal/mol), Zero-Point Energy Corrections (ZPE, kcal/mol) and Number of Imaginary Frequencies (NIMAG, in Parentheses) for Different Structures of S_4^{2-} and S_4^-

	S_4^{2-}				S_4^-		
	SCF/4-31G[a]	MP2/6-31G(d)		QCISD(T)/6-31+G(2d)	MP2/6-31G(d)		QCISD(T)/6-31+G(2d)
symmetry	E_{rel}	E_{rel}	ZPE[b]	E_{rel}	E_{rel}	ZPE[b]	E_{rel}
D_{2h}	39.6	10.7	2.7 (0)	16.3	0.0[d]	3.0 (0)	1.3
C_{2h}	−1.6	2.0	2.6 (0)	2.1	10.8	2.9 (0)	0.0[e]
C_{2v}	6.6	10.5	2.3 (1)	11.4			
C_2	0.0	0.0[c]	2.7 (0)	0.0[c]			
D_{4h}							
singlet	95.9						
triplet-UHF	82.2						
triplet-RHF	84.8						

[a] Data from ref 20. [b] ZPE are scaled by 0.95 as recommended in ref 17. [c] The total energy in hartrees is −1590.45266 at the MP2/6-31G(d) level and −1590.66062 at the QCISD(T)/6-31+G(2d) level. [d] The total energy in hartrees is −1590.57557. [e] The total energy in hartrees is −1590.73875.

Table 3. S−S Bond Distances (Å) in Rectangular (D_{2h}) S_4, S_4^-, and S_4^{2-} at Different Levels of Theory

	S_4		S_4^-		S_4^{2-}	
method	shorter	longer	shorter	longer	shorter	longer
HF/3-21G(d)[a]	1.861	2.543				
HF/4-31G[b]					2.150	2.917
MP2/6-31G(d)	1.945	2.848	1.982	2.747	2.041	2.920
MP2/MC-311(2d)	1.959	2.659	2.001	2.673	2.067	2.844
QCISD(T)/MC-311G(2d)[c]	1.93	2.61	2.00	2.70	2.07	2.96

[a] Data from ref 13. [b] Data from ref 16. [c] The geometry optimization has been performed by the point-by-point method assuming the parabolic dependence of the energy on the S−S bond distances.

Table 4. Scaled Normal Frequencies[a] (cm^{-1}) and Intensities (kM/mol) for S_4 (D_{2h}), S_4^- (D_{2h}), and S_4^{2-} (D_{2h}) at the MP2/6-31G(d) Level

S_4			S_4^-			S_4^{2-}		
sym	freq	intens	sym	freq	intens	sym	freq	intens
A_g	109	0.0	A_u	160	0.0	A_u	102	0.0
A_u	175	0.0	A_g	200	0.0	A_g	159	0.0
B_{3g}	242	0.0	B_{3g}	245	0.0	B_{2u}	178	6.6
B_{2u}	281	0.2	B_{2u}	323	17	B_{3g}	205	0.0
A_g	605	0.0	A_g	581	0.0	A_g	528	0.0
B_{1u}	659	32.0	B_{1u}	615	2.0	B_{1u}	536	32.2

[a] Calculated normal frequency values are scaled by 0.95, as recommended in ref 17, to estimate the fundamental frequencies.

global minimum at the two-reference CISD+Q/TZP level, but it is only 0.3 kcal/mol higher than the most favorable C_{2v} isomer. Hence, neutral S_4 species most probably exist in the planar rectangular form. MP2/6-31G(d) optimized S−S distances for S_4 (D_{2h}) are 1.95 and 2.85 Å.[13] However, the long S−S distance is very sensitive to the theoretical method used,[13,14] and the MP2/6-31G(d) approximation is not good enough to reproduce the bond length correctly. Therefore we have recalculated the geometry of D_{2h} structures for S_4, S_4^-, and S_4^{2-} at higher levels, MP2 and QCISD(T), with a better basis function, MC-311G-(2d), i.e. with the valence triple-ζ Mclean-Chandler[21] basis set including double-ζ polarization d-functions. The results are shown in Table 3. At the best QCISD(T)/MC-311G(2d) level the shorter S−S distance in the neutral S_4 is 1.93 Å, the long S−S bond length is 2.61 Å, and deviation from the experimental geometry, 1.98 and 2.70 Å, measured by X-ray diffraction for **1** is substantial. QCISD(T)/MC-311G(2d) optimized geometry of the dianion is still very different from the structure of S_4 found in **1**. On the other hand, the optimized S−S bond lengths in the monoanion, 2.00 and 2.70 Å, are very close to the experimental values. Thus the S_4 unit in the complex resembles the S_4^- anion-radical.

It is worthwhile mentioning that our QCISD(T)/MC-311G-(2d) calculations for the neutral S_4 confirm superiority of the C_{2v} isomer over the rectangular D_{2h} structure. At the QCISD-(T)/MC-311G(2d)//CISD(SCF)/DZP level (geometries are taken from the Quelch and Schaefer results),[14] the former is 0.8 kcal/mol more stable than the latter. When we use for energy calculations the best geometries available, CISD(TCSCF)/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.

Vibrational Spectra. MP2/6-31G(d) normal frequencies and intensities for S_4 (D_{2h}), S_4^- (D_{2h}), and S_4^{2-} (D_{2h}) are calculated and frequencies are scaled by 0.95[17] for anharmonicity correction to be compared directly with experiment, as shown in Table 4. The most intensive vibration for S_4 and S_4^{2-} corresponds to antisymmetric stretch of the short S−S bonds (B_{1u}) and has scaled wave numbers of 659 and 536 cm^{-1}, respectively. For the monoanion the B_{1u} frequency is 615 cm^{-1}. Also, as seen in Table 4, there should be another observable vibration for the monoanion and for the dianion, at 323 and 178 cm^{-1}, respectively, corresponding to the antisymmetric stretch of the longer S−S distances (B_{2u}). In the neutral species the intensity of this mode is close to zero, while in S_4^- this mode is even more intensive than B_{1u}.

There is only one characteristic experimental frequency for the S_4 unit in **1**, 579 cm^{-1}, assigned to the stretch of the shorter S−S bond. It is between the calculated values for S_4^- and S_4^{2-}, closer to the former. However, the MP2/6-31G(d) approximation may not be accurate enough for frequency analysis of these species, having extremely flat potential energy surfaces. For instance, in neutral S_4 and S_4^- the longer S−S distance shortens by 0.24 and 0.05 Å, respectively, in going from MP2/6-31G to the QCISD(T)/MC-311G(2d) level of theory. This can lead to a significant change of the corresponding B_{2u} wave number. The shorter S−S distance is less sensitive to the approximation used, however, even a small change in this bond length by 0.02−0.03 Å may result in a noticeable shift of the B_{1u} frequency. Hence, comparison of the calculated vibrational spectra with the experimental one has only qualitative character. Also, imbedding the S_4 unit into the tetrarhodium complex can change intensities of vibrations, which may be a reason for the absence of the B_{2u} band in experiment.

Bonding Character in the Tetrarhodium Cluster. The correlation diagram for the complex, drawn in Figure 2, clarifies the bonding character between metal atoms and the rectangular S_4 unit. There are two MO's in the complex responsible for the bonding. The deeper one (−0.495 hartree) is σ-bonding and made from the lowest unoccupied molecular orbital (LUMO) of neutral S_4 or the singly occupied a_u MO of S_4^- and occupied MO's of $\{Rh_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CH_2)_2\}_2$ consisting

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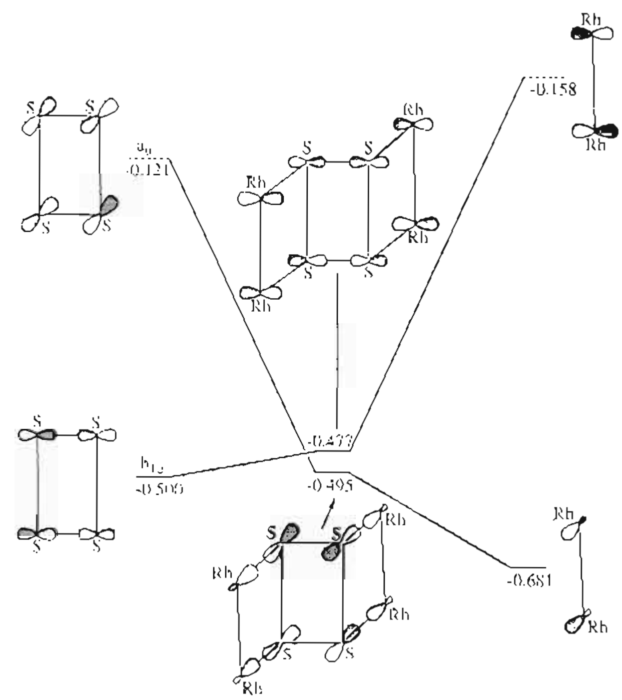

Figure 2. Important orbital correlation for $[(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CH_2)_2Rh_2]^0$ + $[(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CH_2)_2Rh_2]^{2-}$ + $S_4 \rightarrow \{[\eta^5\text{-}C_5H_5)_2(\mu\text{-}CH_2)_2Rh_2]_2S_4\}^{2+}$. Calculated orbital energies are given in hartrees.

mostly of sp-hybrid atomic orbitals of Rh atoms. The a_u MO represents the antibonding π-orbital system perpendicular to the rectangle plane. If one considers bonding of Rh atoms with the neutral S_4 unit, particular filling of this orbital by back-donation from metal leads to a weakening of both shorter and longer S−S bonds and formation of the S_4^- anion-radical ligand. The other bonding orbital (−0.477 hartree) is formed by the occupied b_{1u} MO of S_4 and an unoccupied MO of the Rh_2 moieties containing mostly p-AO of Rh's. This orbital is π-bonding between Rh and S. Hence, the bonding character of S_4 with the metal atoms can be described as π-donation onto Rh atoms and σ-back-donation. Overall, starting from the neutral S_4, σ-back-donation is by about 0.7 e larger than π donation, as evidenced by the charges in the population analysis.

The rectangular isomer of S_4 is stabilized in the complex 1 by the appropriate arrangement of the Rh atoms. For instance, the length of the Rh−Rh bond in the complex, 2.66 Å, is close to the lengths of the long sides in the neutral S_4 and S_4^- rectangles. In complexes with another geometry alternative isomers of S_4 may be stabilized. For example, in the $Rh(C_5H_4\text{-}CO_2Me)(PPh_3)S_4$ and $(Cp^*RhS_4)_2(\mu\text{-}CO)$ complexes,[22] S_4 unit has a structure resembling the geometry of the C_{2v} cis isomer of the neutral S_4 and orients toward a single Rh atom by the long nonbonding S−S side.

Concluding Remarks

Comparison of the calculated D_{2h} structures for the free S_4, S_4^-, and S_4^{2-} with the structure, experimentally observed in 1 shows that the S_4 unit in the complex is close to S_4^-. The similar conclusion can be done from the population analysis of $[\{Rh_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CH_2)_2\}_2(\mu\text{-}S_4)]^{2+}$ which gives the total charge on the S_4 unit about −0.7 e. Therefore, the formal charge concept, widely used in coordination chemistry and applicable for the related $[\{Rh_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CH_2)_2\}_2(\mu\text{-}CN)_2]^{2+}$ species, cannot be applied for the complex 1. Interaction of the S_4 ligand with Rh atoms has been described as σ-back-donation from the metal atoms to fill, in particular, the a_u LUMO of S_4, accompanied by π-donation onto Rh atoms.

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