Kinetic Study of the Skeletal Inversion in a Tetrairon-Sulfur Cluster $\{\eta^5\text{-}C_5H_4(SiMe_3)\}_4Fe_4S_6$

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A chiral cluster $Cp^{S1}{}_4Fe_4S_6$ ($Cp^{S1} = \eta^5$-$C_5H_4(SiMe_3)$) was found to be fluxional due to the skeletal inversion. The line shape analysis for variable temperature ^1H NMR spectra (400 MHz, toluene-d_8) yielded activation parameters: $\Delta H^{\ddagger} = 63.7 \pm 16.0$ kJ mol^{-1} and $\Delta S^{\ddagger} = -20.8 \pm 16.0$ J mol^{-1} K^{-1}. A plausible mechanism for the dynamic behavior is proposed.

X-ray structure analysis of $Cp_4Fe_4S_6$ revealed that the molecule has a chiral Fe_4S_6 core with two iron-iron single bonds in the solid state.[1-3] On the basis of ^1H NMR spectral measurements, Norton et al. reported that $(C_5H_4R)_4Fe_4S_6$ (R = H, Me) retains the rigid Fe-S framework in solution at room temperature.[4] However, low resolution of the NMR pattern prevented definite signal assignment.

Recently we prepared a closely related, chiral cluster $Cp^{S1}{}_4Fe_4S_6$.[5,6] X-ray structure analysis revealed that the structure of the Fe_4S_6 core was almost identical with that of $Cp_4Fe_4S_6$. The ^1H NMR spectrum of the cluster at room temperature (Figure 1) was consistent with the structure

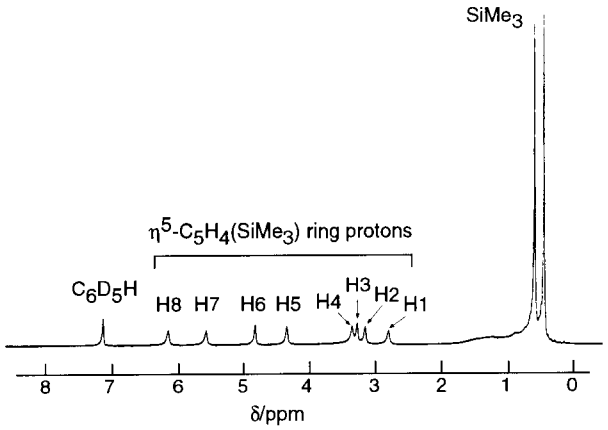


Figure 1. ^1H NMR spectrum (200 MHz) of $Cp^{S1}{}_4Fe_4S_6$ in C_6D_6 at room temperature.

determined by the X-ray analysis:[5] The spectrum showed two singlets assignable to the $SiMe_3$ groups which indicates the presence of two kinds of Cp^{S1} ligands with chemically different environments. The ring protons on Cp^{S1} ligands gave eight signals with equal intensity, apparently due to the diastereotopic relationship between each pair of α protons and β protons with respect to the $SiMe_3$ group in the Cp^{S1} ligands. These are numbered from H1 at the highest field to H8 at the lowest field. Interestingly, the cluster became fluxional upon warming due to the skeletal inversion of the Fe_4S_6 core.

In this work, the skeletal inversion of the cluster is investigated by variable temperature ^1H NMR (VT ^1H NMR) technique. This paper presents the results of the complete line shape analysis of VT NMR spectra for the iron-sulfur cluster.

The cluster $Cp^{S1}{}_4Fe_4S_6$ was prepared as reported previously.[5] Toluene-d_8 and benzene-d_6 were dried over a potassium mirror and transferred into NMR tubes under vacuum before use.

NMR spectra were recorded on JEOL FX-90Q, Varian XL-200, and JEOL GX-400 spectrometers. A Pyrex NMR tube (5 mm ϕ) was charged with the cluster and connected to a vacuum line. Dry toluene-d_8 (about 0.4 ml) was transferred to the sample tube by conventional trap-to-trap distillation. The NMR tube was then flame-sealed under vacuum. ^1H NMR spectra (400 MHz) for line shape analysis were recorded in 20 K increments from 193 K to 373 K. The line shape analysis was carried out using the DNMR3 program.[7] Computer simulated spectra were fitted to the observed spectra to evaluate the rate constants for the dynamic process at the different temperatures.

In order to assign each signal to the ring protons shown in Figure 1, H-H COSY spectrum was measured at room temperature (Figure 2). From the inspection of the signals, it can

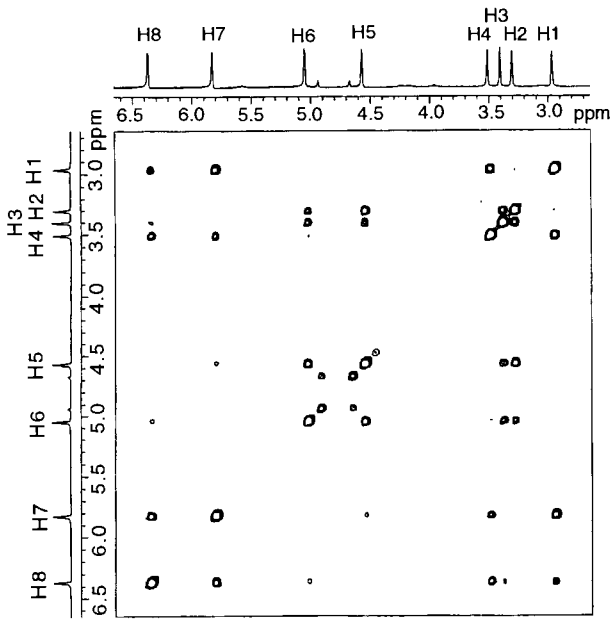


Figure 2. H-H COSY spectrum (400 MHz) of $Cp^{S1}{}_4Fe_4S_6$ in toluene-d_8 at room temperature.

be concluded that H1, H4, H7, and H8 exist on two chemically equivalent Cp^{S1} rings and H2, H3, H5, and H6 on the other two Cp^{S1} rings. Each of signals H1, H2, H5, and H7 show fine splitting into six lines due to two large couplings and one small coupling (J values are 2.4, 2.4, and 1.4 Hz), while each of signals H3, H4, H6, and H8 splits into five lines with a broad central line due to one large coupling and two small couplings (J values are

2.4, 1.4, and 1.4 Hz). From these coupling patterns, the former and the latter signals can be assigned to the β and α protons, respectively, with respect to the $SiMe_3$ group in Cp^{S1} ligands. In a Cp^{S1} ring, H3 and H6 protons occupy the α positions with respect to the $SiMe_3$ group, while H2 and H5 protons, the β positions. Similarly, H4 and H8 protons occupy α positions and H1 and H7 protons, β positions in another Cp^{S1} ring which is chemically different from the former ring. Therefore, diastereotopic pairs are H3 and H6, H2 and H5, H4 and H8, and H1 and H7.

Figure 3 shows the VT ^1H NMR spectra of $Cp^{S1}{}_4Fe_4S_6$

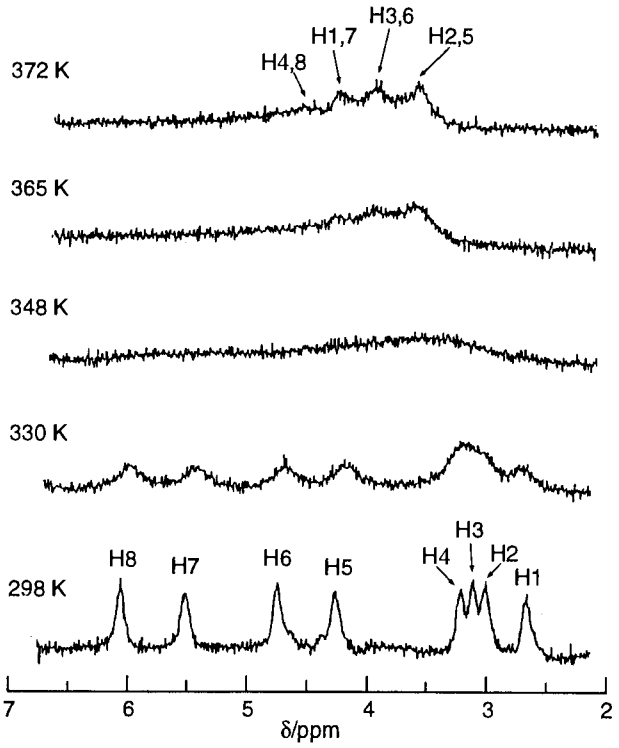
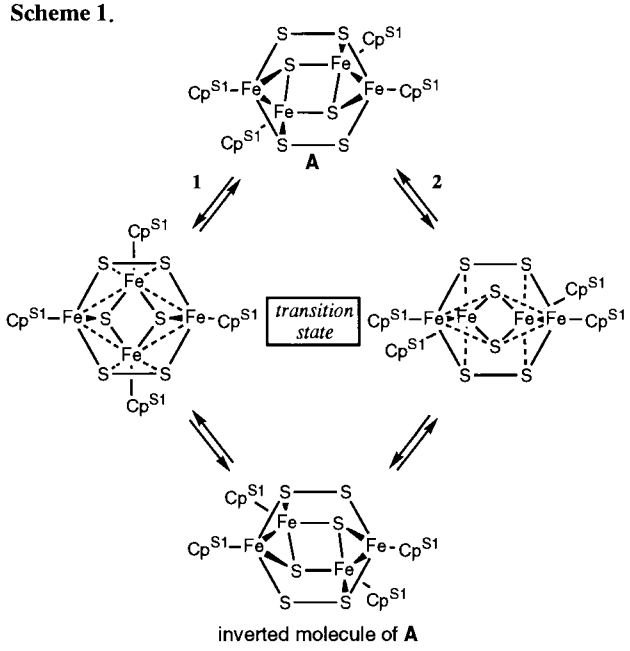


Figure 3. VT ^1H NMR spectra of $Cp^{S1}{}_4Fe_4S_6$ (toluene-d_8, 90 MHz).

measured in toluene-d_8 with a 90 MHz NMR spectrometer. The eight signals observed at room temperature coalesced at elevated temperature and finally four signals appeared. The coalescence occurred exactly as expected from the assignment of signals just mentioned above. This clearly shows that the fluxionality is caused by the inversion of the cluster core. Rauchfuss et al. recently reported a similar coalescence of the ring protons of methylcyclopentadienyl ligands in a chiral cluster $[(MeC_5H_4)_4Ru_4S_4](PF_6)_2$.[8,9] In this case, however, eight signals observed at low temperature coalesce on warming to give two equally intense signals, owing to the fluxional process of the Ru_4 core which equalizes all the methyl cyclopentadienyl ligands.

In order to determine the rate constants at different temperatures, computer-simulated spectra were fitted to the experimentally observed spectra. The activation parameters thus evaluated are $\Delta H^{\ddagger} = 63.7 \pm 5.3$ kJ mol^{-1} and $\Delta S^{\ddagger} = -20.8 \pm 16.0$ J mol^{-1} K^{-1}. The enthalpy of activation is relatively small and the entropy of activation, negative but small. These suggest that the skeletal rearrangement occurs through a concerted process. Possible mechanisms of the skeletal inversion which are consistent with the findings mentioned above are shown in Scheme 1. The cluster structure is depicted as viewed from

Scheme 1.



$(FeS_2)_2$ six-membered ring side along with a pseudo-two fold axis. When the $(FeS)_2$ four-membered ring located in the bottom of cluster **A** rotates anti-clockwise (route 1), the cleavage and recombination of two iron-iron bonds and two iron-sulfur bonds occur with a concerted manner to give the inverted molecule of **A**. As an alternative mechanism, it is also possible that the four membered ring rotates clockwise (route 2). However, this may be an unlikely process, because the iron-iron bonds which are usually the weakest are not cleaved, but the cleavage and recombination of four iron-sulfur bonds occur. Furthermore, in this route, the four bulky Cp^{S1} ligands must come into the same plane in the transition state. As a result, route 1 is the mechanism proposed for the skeletal inversion.

References and Notes

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