# Iron–Sulphur Clusters with Rigid Chiral Frameworks

By ROBIN T. EDIDIN, LEONARD A. ZYZYCK, and JACK R. NORTON*†
(*Department of Chemistry, Princeton University, Princeton, New Jersey* 08544)

*Summary* The ${}^1H$ n.m.r. spectra of appropriate derivatives show that the iron–sulphur frameworks of $(C_5H_4R)_4Fe_4S_6$ and $[Fe_2(CO)_6SR]_2S$ are chiral in solution.

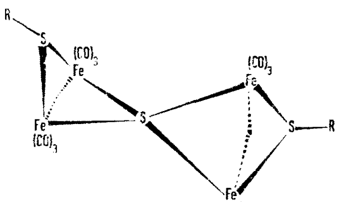
WHAT few data there are suggest that metal–metal-bonded frameworks in polynuclear complexes rearrange readily.[1] We have found that the metal–metal bonds in $[(C_5H_5)M'(CO)_2PAr_2]_2M^+BF_4^-$ ($M' = Fe, Ru; M = Rh, Ir$) are readily

---

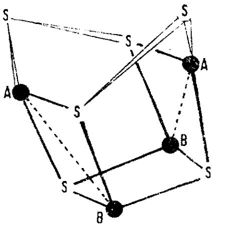
† *Present address:* Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523.

distorted, with consequent racemization.[2] Heaton, Chini, and their co-workers[3] have found that the platinum clusters $[Pt_3(CO)_6]_n^{2-}$ ($n$ = 1—5), which exhibit chiral helical structures in the solid state, show pronounced skeletal mobility in solution: the $Pt_3(CO)_6$ triangles undergo rapid intramolecular rotation and intermolecular exchange. These results are not surprising; M–M bond energies are less than M–CO bond energies,[4] and the latter are easily broken and reformed in rearrangements of polynuclear complexes.[1]

In contrast, Vahrenkamp and Richter have recently reported the n.m.r. observation of a rigid chiral framework in the $\mu_3$-S bridged cluster $(C_5H_5)MoFeCo(CO)_8S$.[5] We suggest that the stability of this framework is due to its bridging sulphur and that this result is general for frameworks containing such heteroatoms. We here report conclusive evidence for rigid chiral frameworks in two other clusters with sulphur bridges, $[Fe_2(CO)_6SR]_2S$ (**1**) and $(C_5H_4R)_4Fe_4S_6$ (**2**). Both are drawn with the idealized $C_2$ symmetry they display in the solid state (**1a**,[6] **2a**[7]).



(**1**) a; R = Me
b; R = Bu$^t$
c; R = Pr$^i$



● = $(C_5H_4R)Fe$
(**2**)
a; R = H
b; R = Me

Replacement of a carbonyl ligand on (**1b**) by dimethylphenylphosphine gives a monosubstituted cluster with diastereotopic methyl groups. However, the chirality could arise only as a result of phosphine substitution, a situation analogous to that noted by Vahrenkamp and Richter for $Co_2Fe(CO)_9S$.[5] That the entire molecule is indeed dissymmetric in solution is shown by the observation of diastereotopic methyl groups in the isopropyl derivative (**1c**) [prepared from Pr$^i$SH and $Fe_3(CO)_{12}$]. There are two signals at $\delta$ 2·585 and 2·549 (60 MHz) in $C_2D_2Cl_4$, each split by the methine proton ($J_{HH}$ 6·6 Hz). No change was observed in the spectrum up to 135 °C. As the coalescence temperature is at least 150 °C, racemization of (**1**) (if it occurs at all) is opposed by a barrier of at least 23 kcal mol$^{-1}$.

The chiral cluster (**2**) contains two inequivalent pairs (A and B) of cyclopentadienyl ligands, the two in each pair being related by the $C_2$ axis. As the ring $^1H$ n.m.r. spectrum of the methylcyclopentadienyl ligand is known to be an effective chirality probe, we prepared {from $[(C_5H_4Me)Fe(CO)_2]_2$ and $S_8$} the methylcyclopentadienyl analogue (**2b**) of the known[7] $(C_5H_5)_4Fe_4S_6$ (**2a**). Two methyl signals, at $\delta$ 1·90 and 2·20, corresponding to sites A and B, were observed. Although the ring $^1H$ n.m.r. resonances could not be fully resolved, the complexity of their pattern indicated a chiral environment and suggested that the dissymmetric framework of (**2**) was rigid at room temperature.

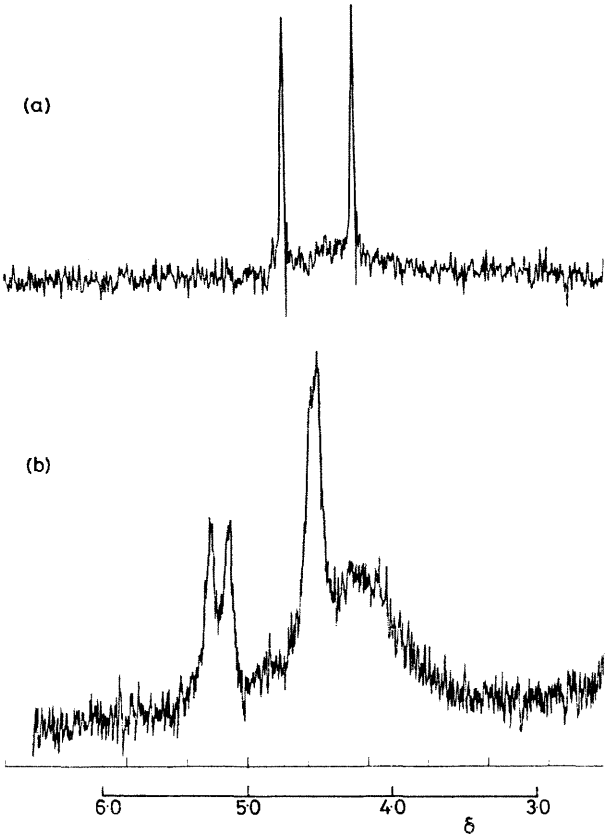


FIGURE. $^1H$ N.m.r. spectra of $(C_5H_5)_4Fe_4S_6$ (**2a**) in $CDCl_3$: (a) before and (b) after addition of Eu-optishift.

This has been confirmed by the use of the chiral shift reagent tris[3-(heptafluoropropylhydroxymethylene)-(—)-camphorato]europium(III) (Eu-optishift) with (**2a**). Before its addition two cyclopentadienyl peaks, corresponding to sites A and B, are observed [see spectrum (a) in the Figure]. The chiral shift reagent [spectrum (b) in the Figure] moves both cyclopentadienyl peaks downfield, and also splits one of them into two peaks of equal area. One pair (either A or B) of cyclopentadienyl ligands is thus shifted differently in each of the enantiomers of (**2**). The broadening of the other cyclopentadienyl signal suggests that a similar, but smaller, inequivalence is being introduced into the other pair of cyclopentadienyl ligands. The chiral framework of (**2**) thus retains its rigidity in solution.

We thank the National Science Foundation for support of this work, the Alfred P. Sloan and Dreyfus Foundations for fellowships (to J.R.N.), and P. J. Vergamini and G. J. Kubas for helpful discussions of unpublished results.

(*Received, 4th April* 1979; *Com.* 357.)

---

[1] E. Band and E. L. Muetterties, *Chem. Rev.*, 1978, **78**, 639.

[2] A. Agapiou, S. E. Pedersen, L. A. Zyzyck, and J. R. Norton, *J. C. S. Chem. Comm.*, 1977, **393**; A. Agapiou, R. F. Jordan, L. A. Zyzyck, and J. R. Norton, *J. Organometallic Chem.*, 1977, **141**, C35.

[3] C. Brown, B. T. Heaton, P. Chini, A. Fumagalli, and G. Longoni, *J. C. S. Chem. Comm.*, 1977, **309**.

[4] J. A. Connor, *Topics Current Chem.*, 1977, **71**, 71.

[5] F. Richter and H. Vahrenkamp, *Angew. Chem. Internat. Edn.*, 1977, **17**, 864.

[6] J. M. Coleman, A. Wojcicki, P. J. Pollock, and L. F. Dahl, *Inorg. Chem.*, 1967, **6**, 1236.

[7] P. J. Vergamini and G. J. Kubas, *Progr. Inorg. Chem.*, 1976, **21**, 261.