

## Triiron Dodecacarbonyl Revisited: Fluxionality in the Solid State

HARRY DORN, BRIAN E. HANSON\*

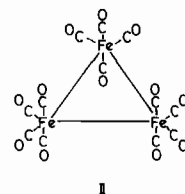
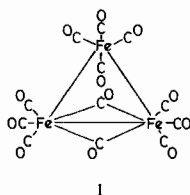
*Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Va. 24061, U.S.A.*

and EDWIN MOTELL

*Department of Chemistry, San Francisco, Calif., U.S.A.*

Received February 24, 1981

Much discussion has centered on the nature of  $\text{Fe}_3(\text{CO})_{12}$  in solution and in the solid state [1]. The solid state structure was conclusively identified by Wei and Dahl [1] to be the dibridged isomer, I, having nearly  $C_{2v}$  symmetry. The molecule was found to be disordered in the solid consisting of a nearly



icosahedral arrangement of CO ligands with two possible orientations of the iron triangle. An inversion center relates the two orientations giving an enantiomeric pair of molecules. Further refinement of this model has confirmed the structure [2].

an icosahedral–cubooctahedral interconversion of COs much in the same manner as postulated by Johnson for  $\text{M}_4(\text{CO})_{12}$  molecules [6].

Also, it has been proposed by Johnson that the triangle of iron atoms may rotate about the  $C_2$  axis independently of the icosahedral array of COs to give a  $D_3$  isomer in which all twelve CO ligands become equivalent [7].

\*Author to whom correspondence should be addressed.

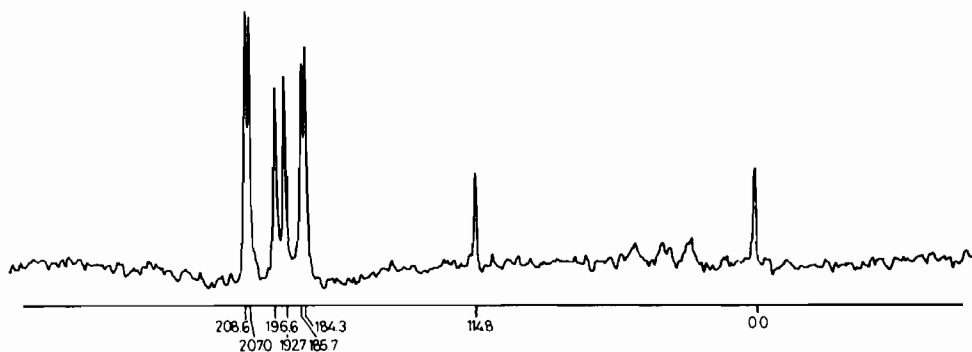


Fig. 1. Solid state carbon-13 NMR spectrum of  $\text{Fe}_3(\text{CO})_{12}$  recorded with magic angle spinning on a JEOL FX60Q spectrometer. Chemical shifts are in ppm relative to the methyl group of hexamethylbenzene present as an internal standard. These may be converted relative to TMS by  $\delta_{\text{TMS}} = \delta_{\text{obs}} + 17.5$ . The average chemical shift of these six resonances is 213.3 ppm relative to TMS. This corresponds very well with the solution value of 212.5 ppm.

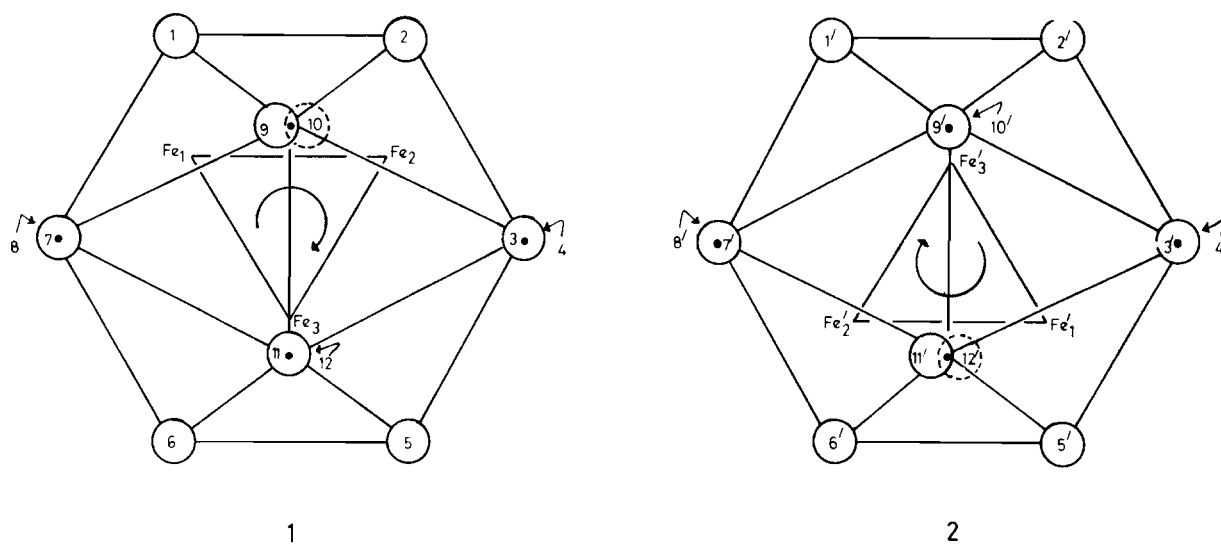


Fig. 2. Schematic representations of the molecular structure as observed in the solid. Vertices of the icosahedra represent CO groups. Molecule 1 is related to molecule 2 by an inversion center. Pairs of equivalent atoms are  $\text{Fe}_1$  and  $\text{Fe}'_1$ ,  $\text{Fe}_2$  and  $\text{Fe}'_2$ ,  $\text{Fe}_3$  and  $\text{Fe}'_3$ , 1 and 5', 2 and 6', 3 and 8', 4 and 7', 5 and 1', 6 and 2', 7 and 4', 8 and 3', 10 and 11', 9 and 12', 11 and 10', and 12 and 9'.

We have recorded the solid state carbon-13 NMR spectrum of  $\text{Fe}_3(\text{CO})_{12}$  and show that it is consistent with the occurrence of a previously unobserved fluxional process. The spectrum\* is shown in Fig. 1.

Clearly the spectrum consists of six resonances in the CO region. The integrated intensities are very nearly equal. Thus to account for all twelve CO ligands the ratio must be 2:2:2:2:2:2. From the crystal structure twelve resonances are possible, one for each of the crystallographically independent COs. Two of the twelve should have chemical shifts characteristic of bridging COs. No resonances assignable to bridging or semibridging COs are observed [8]. This, we feel, rules out the possibility of a static structure with accidentally degenerate resonances.

Idealized representations of the two molecules related by an inversion center are shown in Fig. 2. In representation 1 the bridging CO groups are labeled 9 and 10; these are not identical in the crystal since they are not related by any symmetry operations contained in the space group of the crystal. One molecule, taken by itself, has no crystallographically imposed symmetry other than the identity. The pairs of atoms in the two molecules related by an inversion center are given in the Figure caption. CO groups related by primes, e.g. 1 and 1' do not occupy precisely the same position but are displaced slightly and have thermal ellipsoids that overlap. The

two triangles of iron atoms define parallel planes separated by 0.08 Å [1]. The two molecules may be interconverted simply by rotating the triangle of iron atoms by 60° with a concomitant motion perpendicular to the plane. The iron-iron bonds stretch and contract and the CO ligands must move a distance on the order of magnitude of their normal thermal vibrations to accommodate the rotation.

*On the NMR time scale this rotation of the iron triangle is very rapid.* The motion is schematically represented by arrows in Fig. 2. Using the numbering scheme in representation 1, rotation by 60 or 180° generates six pairs of equivalent COs: 1 and 5, 2 and 6, 3 and 8, 4 and 7, 9 and 12, and 10 and 11. All three iron atoms become equivalent.

The bridging carbonyls, 9 and 10, are averaged with two different terminal COs, 12 and 11 respectively, to give two resonances with chemical shifts midway between typical terminal and typical semibridging COs. These are the peaks at 207.0 and 208.6 ppm relative to hexamethylbenzene.

Other mechanisms may be ruled out in the solid from symmetry considerations. Rapid bridge-terminal exchange along the  $\text{Fe}_1\text{-Fe}_2$  bond would generate a time averaged structure with  $C_{2v}$  symmetry. Carbonyls 3, 4, 7, 8, 9 and 10 would become equivalent directly, while the pairs 1, 2; 5, 6; and 11, 12 would become equivalent by the generation of two mirror planes. Thus a spectrum of four resonances in a ratio of 6:2:2:2 would be anticipated. If the iron triangle could rotate or, perhaps more likely, oscillate about the pseudo-2-fold axis a time averaged structure with no higher symmetry than

\* $\text{Fe}_3(\text{CO})_{12}$ , obtained from Pressure Chemical Company was enriched to ca. 4% in  $^{13}\text{C}$  and recrystallized immediately before the spectrum was recorded.

already contained in the crystal is obtained. Thus no CO ligands would be exchanged\*. Neither of these mechanisms is consistent with the crystal structure.

An upper limit for the activation barrier to rotation of  $50 \text{ kJ mol}^{-1}$  can be estimated from the difference between typical chemical shifts for bridging and terminal CO s and a coalescence temperature of 273 K. This is much larger than the upper limit of the barrier to complete CO exchange in solution (ca.  $20 \text{ kJ mol}^{-1}$ ). The motion that we postulate for solid samples may also occur in solution samples of  $\text{Fe}_3(\text{CO})_{12}$ . However it need not be the pathway of lowest activation energy for exchange nor can it be the only pathway since all twelve CO s are equivalent in solution.

In conclusion the solid state carbon-13 NMR spectrum of  $\text{Fe}_3(\text{CO})_{12}$  is most consistent with the time averaging of the two disordered molecules observed crystallographically. This occurs via rotation of the iron triangle within its plane creating an inversion center on the NMR time scale in the  $\text{Fe}_3(\text{CO})_{12}$  molecule. Therefore on the X-ray crystallography time scale ( $10^{-18}$  sec) the sample is in the slow exchange limit and both enantiomers are observed while on the NMR time scale ( $10^{-1}$ – $10^{-9}$  sec)

---

\*A static structure with perfect  $C_2$  symmetry would give 6 resonances, however in this case one resonance should have a chemical shift characteristic of a semibridging CO. Furthermore  $\text{Fe}_3(\text{CO})_{12}$  occupies a site that does not have two-fold symmetry and hence need not have perfect  $C_2$  symmetry.

a fast exchange spectrum representing an averaged structure is observed.

### Acknowledgements

We would like to thank Professor Herb Kaesz for stimulating discussions at the outset of this work. Also we acknowledge the generous support of the Department of Energy and the State of Virginia for the funds to purchase the JEOL FX60Q NMR Spectrometer.

### References

- 1 C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, **91**, 1351 (1969) and references therein.
- 2 F. A. Cotton and J. Troup, *J. Am. Chem. Soc.*, **96**, 4155 (1974).
- 3 F. A. Cotton and D. L. Hunter, *Inorg. Chim. Acta*, **11**, L9 (1974).
- 4 (a) F. A. Cotton, J. D. Jamerson and B. E. Hanson, *J. Am. Chem. Soc.*, **99**, 6588 (1977).  
(b) R. J. Lawson and J. R. Shapley, *J. Am. Chem. Soc.*, **98**, 7433 (1976).  
(c) G. L. Geoffroy and W. G. Gladfelter, *J. Am. Chem. Soc.*, **99**, 6775 (1977).
- 5 J. R. Wilkinson and L. J. Todd, *J. Organometal. Chem.*, **118**, 199 (1976).
- 6 B. F. G. Johnson and R. E. Benfield, *J. Chem. Soc. Dalton Trans.*, 1554 (1978).
- 7 B. F. G. Johnson, *J. Chem. Soc. Chem. Comm.*, 703 (1976).
- 8 Bridging COs are readily observed in the solid for  $\text{Cp}_2\text{-Fe}_2(\text{CO})_4$  for example. B. E. Hanson and E. Motell, unpublished data.