On the Relationship between Crystallographic Disorder and Solid State Dynamic Behaviour in $[Fe_3(CO)_{12}]$ and $[Co_4(CO)_{12}]$

Christopher E. Anson,[a] **Robert E. Benfield,**[b] **Adrian W. Bott,**[a] **Brian F. G. Johnson,**[a] **Dario Braga,**[c] **and Elisabeth A. Marseglia**[d]

[a] *University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.*
[b] *Department of Chemistry, University of Kent, Canterbury CT2 7NH, U.K.*
[c] *Dipartimento di Chimica, 'G. Ciamician,' Università di Bologna, Via F. Selmi, 2, 40126, Bologna, Italy*
[d] *Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, U.K.*

The fluxional behaviour shown by $[Fe_3(CO)_{12}]$ and $[Co_4(CO)_{12}]$ in the solid state can be explained in terms of small librations involving both the encapsulated metal polyhedron and the carbonyl envelope.

Magic-angle spinning (MAS) n.m.r. spectroscopy has been used to study the solid state dynamic behaviour of a number of multinuclear transition metal cluster compounds.[1,2] In the case of the binary metal carbonyl clusters $[Fe_3(CO)_{12}]$ and $[Co_4(CO)_{12}]$, reorientation of the metal atom unit within the carbonyl ligand cage has been invoked to account for both the room temperature and variable temperature solid state ^{13}C n.m.r. spectra.[3,4] Similar processes had been previously postulated to explain the fluxional behavour of these species in solution.[5] Moreover, it was observed that the crystallographic disorder shown by both species is consistent with the proposed motion.[3,4] There are two common types of disorder that occur in crystalline molecular solids: static orientational disorder, which is a result of statistical randomness in site occupancy, and dynamic disorder, which is a result of molecular or sub-molecular motion at the crystal site. These two cases cannot always be distinguished by diffraction data, especially if the data are collected at only one temperature.[6] In the case of $[Fe_3(CO)_{12}]$ and $[Co_4(CO)_{12}]$, however, we believe that the distinction can be made, based on an examination of the crystal structure, the mean square displacement parameters, and the data obtained from solid state MAS n.m.r.

A value of 10^{-18} seconds is often quoted for the time scale associated with *X*-ray diffraction studies. However, it should be stressed that this value is misleading when one is considering the time scale for a diffraction experiment. In fact, a measurement of a single *X*-ray observation (a 'reflection') takes on average $\sim 10^3$ seconds. This is equivalent to about 10^{21} 'snap-shots,' each picture recording the positions of atoms which have been displaced by a different distance from their mean positions. Thus the intensity pattern of the total number of reflections in an *X*-ray experiment represents a time-average of all possible atomic displacements, and thus contains information on all atomic motion (vibrations, rotations, librations, diffusion, *etc.*) that is occurring in the solid. Part of this information can be extracted in the form of mean square displacement (m.s.d.) parameters for individual atoms. Relatively large values for particular m.s.d. parameters indicate a dominance of contributions from low frequency motion along those particular displacement directions.[7,8] This motion can arise, for example, from bond bending vibrational modes, from 'rigid body' motion, or indeed from any motion which involves relatively weak restoring forces. It is not unreasonable, then, to correlate the low activation energy dynamic processes that are observed by MAS n.m.r. spectroscopy with m.s.d. parameters obtained from *X*-ray and neutron diffraction, where such data are of sufficient quality.[11] An example of this correlation has been made recently for the case of fluxional behaviour in $[Rh_6C(CO)_{13}]^{2-}$: the m.s.d. parameters and ^{13}C solution studies both indicate motion of the carbonyl ligands about the unique Rh_4 plane.[12]

X-Ray studies have shown that $[Fe_3(CO)_{12}]$ shows orientational disorder in the solid state.[10] In the molecular structure two carbonyls are in asymmetric bridging positions along one edge of the triangle, which is shorter than the other two. The molecule possesses C_1 symmetry but is very close to C_2 symmetry with a pseudo-two-fold axis passing through the middle of the bridged Fe–Fe vector and the opposite Fe atom. Random occupancy of one or other of two possible molecular orientations in the crystal lattice results in the presence of an

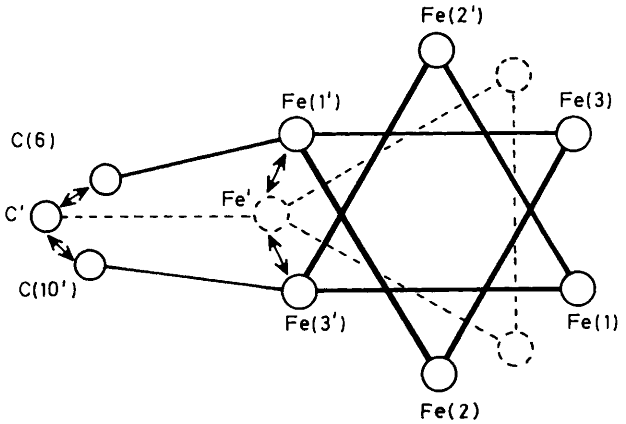

Figure 1. Three-fold rotation of the Fe_3 triangle in solid $[Fe_3(CO)_{12}]$.

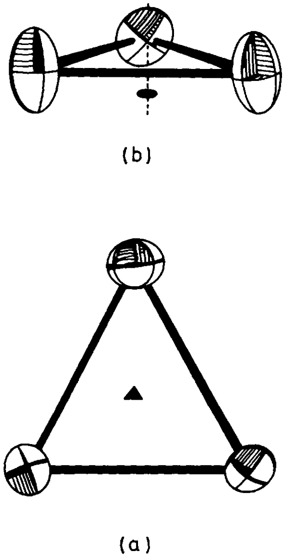

Figure 2. Thermal ellipsoids of Fe atoms in $[Fe_3(CO)_{12}]$. (a) Displacement about pseudo-three-fold axis; (b) displacement about pseudo-two-fold axis.

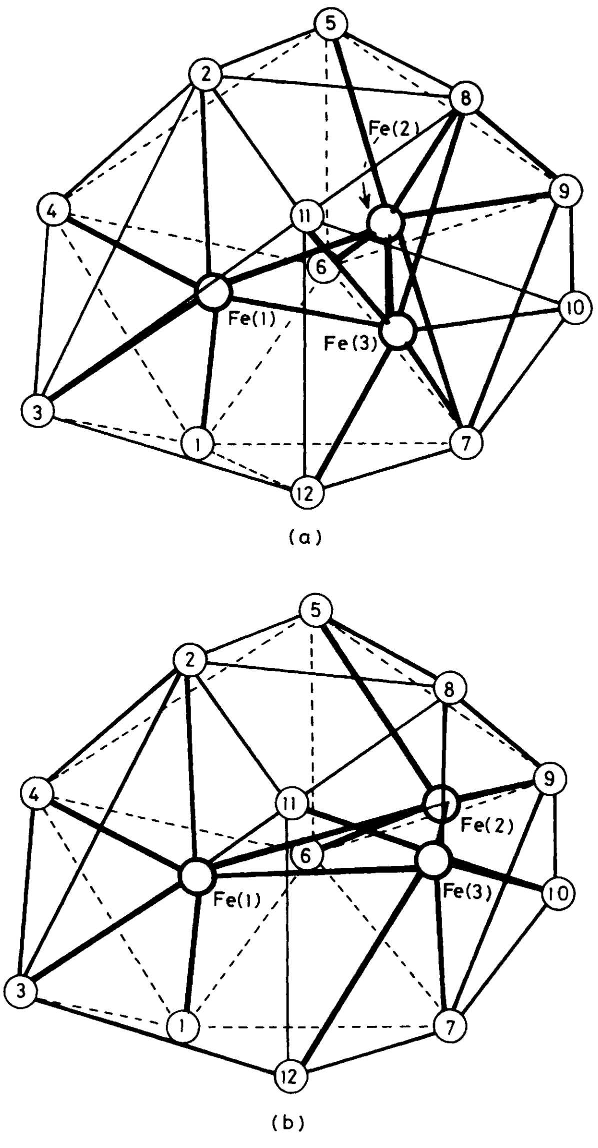

Figure 3. (a) Idealised structure of $[Fe_3(CO)_{12}]$ in the solid (distortions of the carbonyl icosahedron and of the Fe_3 triangle are not shown). Bridging oxygens are labelled 7 and 8. (b) Small rotation of the Fe_3 triangle about pseudo two-fold axis showing resultant change from bridging to terminal positions.

inversion centre within the unit cell statistically relating two crystallographic 'half molecules' in each of the two orientations. In the more recent and more precise of the two independent structural determinations[10b] the almost superposed C and O atom images were distinguished, showing that the O · · · O and C · · · C image pairs are separated, on average, by 0.43 and 0.50 Å, respectively. The disorder has been explained as being due to the high regularity of the outer, almost icosahedral, peripheral polyhedron described by the O atoms, which does not appreciably differ whether the iron triangle is in one orientation or its inverted one.[10a]

Variable temperature MAS ^{13}C n.m.r. solid state measurements on $[Fe_3(CO)_{12}]$ show that at temperatures below −95 °C, the observed spectrum is consistent with the crystal structure, indicating two bridging and ten terminal carbonyls.[3b] At 24 °C, there are three pairs of resonances of similar integrated intensities, and the observed chemical shifts are not consistent with bridging or semi-bridging carbonyls. In order to explain this equivalence of terminal and bridging carbonyls and the temperature dependence of the n.m.r. spectra, it was postulated that the Fe_3 triangle undergoes a fast rotational motion between the two statistical crystallographically determined orientations. Moreover, the 60° jumps between contiguous positions needed to be rapid on the n.m.r. time scale at 24 °C so that the spectrum of an averaged structure could be seen. An activation energy of 50 kJ mol^{-1} for the process was estimated from the coalescence temperature of −55 °C.[3b] Let us examine this motion in more detail. The existence of crystallographically separated images of the nearly superposed carbonyls implies that C and O atoms would have to follow the motion of the Fe_3 triangle. Furthermore, the carbonyl motion would have to be more complicated than a single 'jump' because during the rotation of the triangle some Fe–C interactions would become extremely short [computed separations after a 30° rotation (half-way through) are: Fe(1) · · · C(6), 1.49; Fe(2) · · · C(2), 1.61; Fe(3) · · · C(11), 1.56; Fe(3) · · · C(12), 1.58 Å]. For example, to pass from C(6) to C(10′) [C(6) · · · C(10′), 0.61 Å] a C atom cannot simply switch from one position to the other and maintain a reasonable distance from the Fe atom, which is switching from Fe(1) to Fe(3′), but also has to move outwards and inwards, thus describing an arc (as shown in Figure 1). Therefore, the peripheral carbonyl polyhedron has to expand and contract continuously in order to follow the triangle rotation. Although such a 'breathing' motion may be possible, a higher activation energy would be required in the solid state (compared with a similar process in solution) since the molecules are packed together in three dimensional long range order, and the expansion would have to occur against packing forces dominated by intermolecular O · · · O interactions.

Further evidence that motion about a pseudo-three-fold axis may not be responsible for the n.m.r. results comes from the m.s.d. parameters which have been reported for this molecule.[10b] Analysis of these parameters shows that there is no evidence for preferential motion about the three-fold axis; rather, the thermal ellipsoids for the Fe atoms (shown in Figure 2) indicate a preferred direction for libration of the Fe_3 triangle about the molecular pseudo-two-fold axis. A librational motion of the triangle of a few degrees about this axis is sufficient to change the molecular geometry from C_2 to (pseudo) D_3 symmetry, in which all carbonyls are terminally bound (see Figure 3). (The C_2 symmetry can be achieved by small concerted motions of the carbonyl and iron atoms). Since those carbonyls that adopt a bridging bonding mode in the C_2 conformation will adopt a terminal bond in the (pseudo) D_3 conformation, the room temperature MAS ^{13}C n.m.r. spectrum is consistent with the operation of such a libration.[3a] Furthermore at low temperatures (−95 °C) the amplitude of the libration is greatly reduced, and hence the MAS ^{13}C n.m.r. spectrum observed at this temperature is consistent with the crystal structure. This behaviour is in contrast to that observed for $[Fe_3(CO)_{12}]$ in solution where complete carbonyl equilibration can be achieved by rotation of the Fe_3 triangle about all three of its two-fold axes.[5]

The structure of $[Co_4(CO)_{12}]$ has also been studied independently by different groups and has been shown to be disordered in the solid state.[11] Random occupancy of one or other of two possible molecular orientations in the crystal lattice results in the presence of a two-fold axis within the unit cell which passes through one basal Co atom and the centre of the opposite triangular face. The molecule itself has only C_1 symmetry with three carbonyl groups in edge-bridging positions around a tetrahedral face, the remaining carbonyls being terminally bound. However, the peripheral polyhedron described by the O atoms is again approximately icosahedral, and the molecular symmetry is only slightly distorted from C_{3v}.

MAS ^{13}C n.m.r. spectra for $[Co_4(CO)_{12}]$ have been recorded over a wide temperature range (−62 to +63 °C), showing that above 35 °C only one broad signal can be seen. Below 24 °C four peaks appear and no other changes occur on cooling down to −62 °C. The mean square displacement-parameters reported for $[Co_4(CO)_{12}]$ indicate a preferred librational motion of the Co_4 tetrahedron about its four pseudo-three-fold axes.[4] Such librations again lead to variation in the localised bonding modes of certain carbonyls; in particular, those carbonyls that would be bridging in a C_{3v} structure move between bridging and terminal bonding modes as a result of small amplitude librations about the three three-fold axes that are coincident with pseudo-molecular two-fold axes. The chemical shifts that are observed in the solid state n.m.r. spectra below 24 °C are consistent with such librations. Larger amplitude librations about these axes lead to the total carbonyl equilibration observed at higher temperatures.

We have shown that the observed solid state n.m.r. data can be rationalised in terms of low energy librations, rather than the high energy processes previously postulated. The m.s.d. parameters derived from *X*-ray data provide evidence for such librations; the thermal ellipsoids of the Fe atoms in $[Fe_3(CO)_{12}]$ indicate motion of the iron triangle about its pseudo-two-fold axis, and those of the Co atoms in $[Co_4(CO)_{12}]$ indicate motion about the four three-fold axes of the Co_4 tetrahedron. Other concerted motions of the metal atoms and carbonyl ligands must also be involved in these dynamic processes in order to account for the higher apparent symmetries observed in the solid state n.m.r. experiments; these concerted motions must be consistent with the symmetries of the normal modes of vibration of the system.[13] On the basis of the above arguments, we further propose that the observed crystallographic disorder cannot be due to the motion observed for these molecules by solid state n.m.r.: it arises from the existence of two static orientations of the metal polyhedron within the ligand polyhedron.

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