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Preliminary Communication

On the molecular structure of $[Fe_3(CO)_{12}]$ in the solid state

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Abstract

The determination of precise, low-temperature crystal structures of $[Fe_3(CO)_{12}]$ has shown that, on decreasing the temperature, the bridging ligands become progressively more symmetric, the bridged Fe–Fe bond shortens and the atomic displacement parameters show a congruent behaviour with temperature.

$[Fe_3(CO)_{12}]$ is one of the most studied binary carbonyls [1]. As clearly illustrated first by Wei and Dahl [2] and then by Cotton and Troup [3] the molecule shows orientational disorder in the solid state. At room temperature the molecule possesses ten terminal ligands and two asymmetric bridging carbonyls along the shortest edge of the iron triangle [2.558(1) *vs.* 2.677(2) and 2.683(1) Å]. The molecule has formal C_2 symmetry with a pseudo two-fold axis passing through the middle of the bridged Fe–Fe bond and the opposite Fe atom. The disorder is possible because of 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 inverse. The interest in the structure of this prototypical binary carbonyl has been revitalized by the discovery that $[Fe_3(CO_{12}]$ undergoes a dynamic process in the solid state [4].

The CPMAS spectral features at temperatures below 178 K are consistent with the presence of two bridging and ten terminal carbonyls, while at 297 K there are three pairs of resonances of similar integrated intensities which cannot be explained on the basis of the observed crystal structure [4c]. These features have been interpreted in (at least) three different ways: (i) in-plane 60° jumps of the Fe_3-triangle within the ligand envelope [4c,d]; (ii) shifts of the bridging CO's along the triangle edges without full scale ligand migration [5] accompanied by changes in Fe–Fe and Fe–C bond lengths; and (iii) librational motion of the triangle about the molecular pseudo two-fold axis in order to bring about partial isomerizations between the limiting C_2 (with two symmetric bridging CO's) and D_3 (all terminal) molecular conformations [6]. This latter model is in agreement with the preferential orientation of the atomic displacement parameters (ADP) obtained for the Fe atoms by Cotton and Troup [3].

Beside providing precise dimensions for this molecule, our objective was to establish the exact nature of the disorder (whether static or dynamic) both in terms of motion about equilibrium positions (*i.e.* ADP) and of motion far from equilibrium (reorientation, libration) [7]. Furthermore, the possibility of a phase transition of the kind observed for organometallic molecules such as ferrocene [7], or $[(C_4H_4S)Cr(CO)_3$ [9] or inorganic molecules such as monoclinic S_8 [10], could not be ruled out on the basis of all previous experiments.

In order to carry out a detailed analysis of the crystal structure of $[Fe_3(CO)_{12}]$ diffraction data have been collected at 250 K and at 160 K. In this preliminary communication we wish to report that temperature greatly affects the molecular structure of $[Fe_3(CO)_{12}]$. As the temperature is decreased: (i) the crystal retains the disordered centrosymmetric monoclinic structure in $P2_1/n$ down to 160 K with no trace of a phase-transition to the non-centrosymmetric space-group $P2_1$ hence (ii) the relative population of the two images refine successfully to 50%, *i.e.* the "average" centre of symmetry of the disorder is preserved; (iii) the bridging ligands become progressively more symmetric [see caption to Fig. 1]; (iv) the bridged Fe–Fe bond shortens [2.551(2), 2.545(2) Å at 250 K and 160 K, respectively] while the other two bonds do not change with respect to the room temperature struc-

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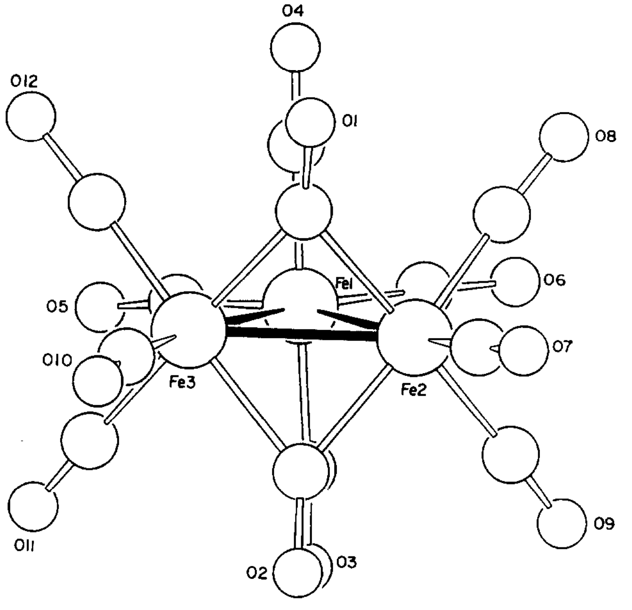

Fig. 1. The molecular structure at 160 K showing the labelling scheme. Selected bond distances at 250 K and 160 K are compared with those from ref. 3 (RT). Fe(2)–Fe(3), Fe(1)–Fe(2), Fe(1)–Fe(3): 2.558(1), 2.677(2), 2.683(1); 2.551(2), 2.677(2), 2.682(2); 2.545(2) 2.674(2), 2.684(2) Å; Fe(2)–C(1), Fe(3)–C(1): 2.11(4), 1.96(4); 2.10(1), 1.97(2); 2.02(3), 1.96(3) Å; Fe(2)–C(2), Fe(3)–C(2) 1.93(4), 2.21(4); 1.99(1), 2.11(1); 2.02(3), 2.08(3) Å, for RT, 250 K and 160 K, respectively.

ture [2.677(2), 2.682(2) *vs.* 2.674(2), 2.684(2) Å]. A second aspect of relevance is the behaviour with temperature of the ADP for the Fe atoms: as shown in Fig. 2 the Fe atom ADP show a congruent decrease with the temperature. The pattern observed at room temperature is essentially retained showing preferential oscillation about the molecular two-fold axis rather than around the triangle three-fold axis [6]. This is relevant because we compare data derived from three different crystal specimens and collected in different laboratories (and thus affected by different kinds of systematic errors). This consideration strenghtens the idea that ADP (when measured with sufficient accuracy) contain relevant dynamic information. However, the presence of a component of static disorder cannot be confidently ruled out at the present stage of our analysis.

The observed *intramolecular* effect on the bridging CO's has, very likely, an *intermolecular* origin: as the temperature decreases the "intermolecular compression" increases causing shortening of intermolecular C···O and C···C contacts [shortest O···O: 2.791, 2.821 at 250 K; 2.657, 2.757 at 160 K *vs.* 2.879, 3.052 Å at RT]. This is also accompanied, however, by a shortening of some *intramolecular* C···O and C···C interactions. The partial "loss" of intramolecular energy (as the molecule approaches C_s-symmetry) is very likely compensated by the gain in crystal cohesion as the temperature is decreased. We believe that the dynamic behaviour of $Fe_3(CO)_{12}$ in the solid state should be examined in the light of these findings.

The temperature dependence of the molecular structure of $[Fe_3(CO)_{12}]$ demonstrates that when the molecular structure is flexible (*i.e.* easily deformable as it is the case of fluxional organometallic complexes) the optimization of the intermolecular assemblage (*viz.* of the crystal structure) * can have far from negligible effects on the molecular structure.

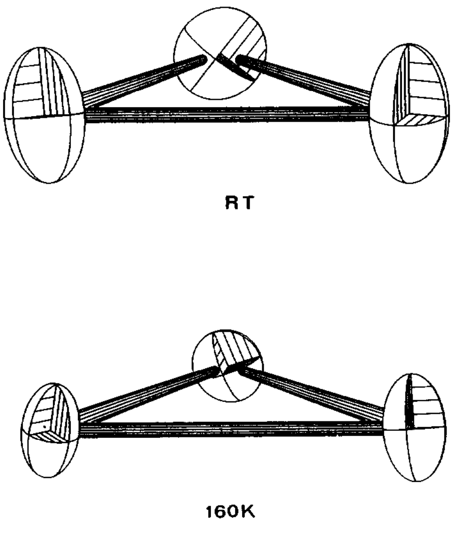

Fig. 2. Comparison of the Fe-atom ADP (50% probability) at room temperature (from refs. 3 and 6) and 160 K.

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* Diffraction intensities were collected on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator (Mo-Kα radiation, $\lambda = 0.71069$ Å) and an Enraf-Nonius low-temperature device at 250(2) K and 160(2) K on two different crystal specimens (dark green parallelepipeds, crystal size $0.25 \times 0.30 \times 0.20$, $0.20 \times 0.20 \times 0.30$ mm for the two crystals, respectively). Decay correction was applied to both data sets (correction range 0.98–1.00 and 0.96–1.00 for data at 250 K and 160 K, respectively). Data were corrected for absorption by azimutal scanning of high-χ reflections. All atoms were allowed to vibrate anisotropically. SHELX92 [11] was used for data treatment and refinement based on F^2. Coordinates from ref. 3 were used as input. At 250 K: 2366 independent reflections collected, $R_W(F^2) = 0.183$, R_F [for $F > 4\sigma(F)$] = 0.068, $S(F^2) = 1.042$; at 160 K: 2730 independent reflections collected, $R_W(F^2) = 0.142$, R_F [for $F > 4\sigma(F)$] = 0.058, $S(F^2) = 1.196$ for 244 parameters. Full lists of atomic coordinates, bond lengths and angles, and temperature factors have been deposited with the Cambridge Crystallographic Data Centre.

Acknowledgements

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