

Dynamic Disorder in $[\text{Fe}_2\text{Os}(\text{CO})_{12}]$. Structural Evidence of the Metal Triangle Rotation

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Clear-cut crystallographic evidence of dynamic disorder arising from a reorientational jumping motion of the metal triangle is provided by variable-temperature diffraction experiments on the molecular and crystal structure of $[\text{Fe}_2\text{Os}(\text{CO})_{12}]$.

Dynamic processes in organometallic crystals have been detected by means of spectroscopic techniques,¹ mainly ¹³C CPMAS NMR spectroscopy and ¹H spin–lattice relaxation time measurements.² Although dynamic behaviour has also been ascertained in crystals of some transition metal clusters,³ to the best of our knowledge no direct crystallographic evidence has ever been attained. We now report the first example of a reorientational jumping motion of a metal cluster in the solid state, detected by variable-temperature X-ray diffraction experiments.

$[\text{Fe}_2\text{Os}(\text{CO})_{12}]$ **1** is isostructural and isoelectronic with $[\text{Fe}_3(\text{CO})_{12}]$ **2** and their crystals are closely related.^{4,5} While **2** has been extensively investigated by experimental and theoretical approaches, this is not so for **1**. The interpretation of the solid state dynamic behaviour of **2** has not been without controversy and still offers matters of intense debate.⁶ Three different models have been put forward to rationalize the dynamic process: (a) in-plane 60° jumps of the Fe_3 triangle within the ligand envelope;^{6b,c} (b) shifts of the bridging COs along the triangle edges without full scale ligand migration;^{6d} and librational motion of the triangle about the molecular pseudo-twofold axis between the structure with two symmetric bridging COs and that possessing only terminal CO ligands.^{6e} However, no experimental approach, whether spectroscopic or diffraction, has provided conclusive evidence in favour of one of the three hypotheses.

Here we report that the variable-temperature X-ray diffraction study of crystalline $[\text{Fe}_2\text{Os}(\text{CO})_{12}]$ affords unequivocal evidence for the occurrence of a dynamic process in the solid state. As previously shown by Churchill and Fettinger,⁴ at room temperature the two independent molecules of **1** in the asymmetric unit show a disorder of the metal atoms which is similar to that observed in $[\text{Fe}_3(\text{CO})_{12}]$, viz. a 'Star of David' with the metal triangle in two opposite, but almost coplanar, orientations. The average occupancy ratio for **1** (12:1), however, differs markedly from the crystallographically imposed 1:1 ratio in the centrosymmetric $[\text{Fe}_3(\text{CO})_{12}]$. On decreasing the temperature, the minor component in $[\text{Fe}_2\text{Os}(\text{CO})_{12}]$ disappears in both the independent molecules. There is no trace of disorder at 220 K, as well as at the lowest temperature of our experiment, 120 K.[†] On the other hand, on increasing the temperature to 323 K, the relative population of the two orientations changes from 12:1 to 2:1. On increasing the temperature further (373 K) the crystal appears to undergo a phase transition, probably owing to the onset of a full reorientational motion of the metal triangle. The *b* axis of unit cell at 373 K is half of the unit cell observed below 323 K, hence the cell becomes comparable to that observed for $[\text{Fe}_3(\text{CO})_{12}]$ in the space group $P2_1/n$. Disorder of the CO ligands is not appreciable at room temperature, whereas double images, of the type resolved by Cotton and Troup in $[\text{Fe}_3(\text{CO})_{12}]$,^{5b} are present in the high temperature crystal. The dependence on the temperature of the relative populations of the two disorder images is shown in Fig. 1. The increase of the population of the two 'minor' images as the temperature increases is a clear manifestation of a temperature-dependent dynamic process.

A correlation between site occupancy and temperature has never been observed in cluster systems, nor it is very common in organic or inorganic systems.⁷ A situation similar to the one discussed here has been observed with monoclinic sulfur,

whose crystal contains two independent S_8 molecules at room temperature, one of which is 50% disordered over two centrosymmetric sites. As the temperature is decreased the low energy site is increasingly populated, to a maximum of 98% at 113 K.⁸

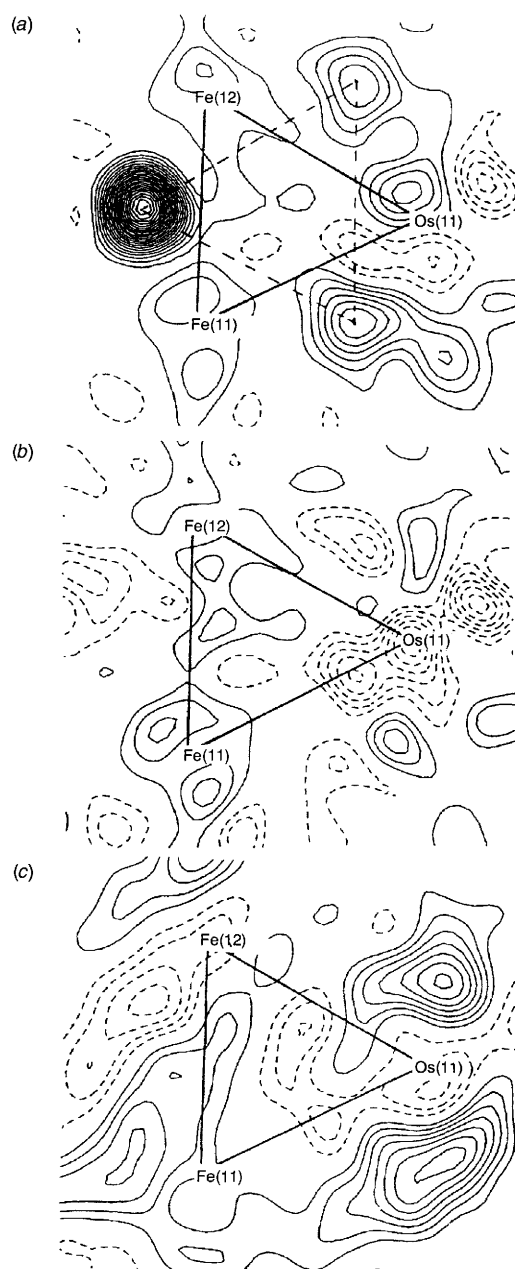


Fig. 1 Difference Fourier sections through the triangle Os(11)–Fe(11)–Fe(12) from structural analysis at 292 (a, b) and 120 K (c). Contours are drawn at the levels 0.5 (a) and 0.3 (b, c) e Å⁻³. The minor component is not included in the Fourier calculation in (a), while it is in (b), indicating the satisfactory modelling of the experimentally electron density. No trace of the secondary Os position is discernible in (c).

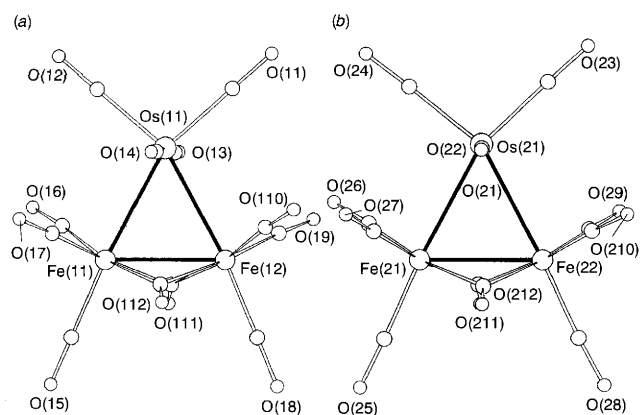


Fig. 2 Comparative view, perpendicular to the Fe_2Os triangle, of the structures of the two independent molecules (*a* and *b*) of $[\text{Fe}_2\text{Os}(\text{CO})_{12}]$ at 120 K. Relevant bond distances (\AA) are: (*a*) $\text{Os}(11)\text{--Fe}(11)$ 2.739(2), $\text{Os}(11)\text{--Fe}(12)$ 2.744(2), $\text{Fe}(11)\text{--Fe}(12)$ 2.566(3), $\text{Fe}(11)\text{--C}(111)$ 2.09(1), $\text{Fe}(11)\text{--C}(112)$ 1.93(1), $\text{Fe}(12)\text{--C}(111)$ 1.94(1), $\text{Fe}(12)\text{--C}(112)$ 2.07(1); (*b*) $\text{Os}(21)\text{--Fe}(21)$ 2.744(2), $\text{Os}(21)\text{--Fe}(22)$ 2.739(2), $\text{Fe}(21)\text{--Fe}(22)$ 2.575(3), $\text{Fe}(21)\text{--C}(211)$ 2.04(1), $\text{Fe}(21)\text{--C}(212)$ 1.97(1), $\text{Fe}(22)\text{--C}(211)$ 2.00(1), $\text{Fe}(22)\text{--C}(212)$ 2.05(1).

The dynamic behaviour of **1** was also examined in solution. At room temperature a ^{13}C -enriched sample of **1** showed a sharp singlet at δ 200.1 arising from the averaged environment of all the carbonyls. On cooling, this singlet broadened and finally disappeared into the baseline at 193 K. Although no mechanistic information can be obtained from this, it is clear that the dynamic processes in **1** leading to complete carbonyl scrambling are of higher energy than those for **2**, since in the latter molecule a single sharp resonance is observed down to -150°C .⁹

As well as providing an unprecedented example of dynamic disorder in the solid state, this study also affords insight into the molecular structure of $[\text{Fe}_2\text{Os}(\text{CO})_{12}]$. At all temperatures, the two independent molecules are not identical, differing both in the torsion of the $\text{Os}(\text{CO})_4$ unit and in the degree of asymmetry of the bridging CO ligands as shown in Fig. 2.

These findings shed new light on the $[\text{Fe}_3(\text{CO})_{12}]$ system, strongly supporting the model of the Fe_3 triangle jumping motion to explain the dynamic behaviour in the solid state; this main motion is very likely accompanied by a librational component about the molecular twofold axis. We now plan to reexamine the behaviour of crystalline $[\text{Fe}_3(\text{CO})_{12}]$ at very low temperatures.

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† Data were collected on CAD4 diffractometers, equipped with a Nonius liquid nitrogen device (Bologna) or an Oxford Cryosystems Cryostream

unit (Glasgow) at 120 (Glasgow), 223 (Bologna), 288 (Bologna), 292 (Glasgow), 323 K (Bologna). The unit cell at 373 K was also determined (Bologna). The three data collections at Bologna were carried out on the same crystal, two crystals were used at Glasgow. Details of all data collections are given in the deposited material. Good quality data collected at 120 and 223 K were corrected for absorption by azimuthal scanning of high- λ reflections (or by the method of Walker and Stuart^{10a} at 120 K). All atoms were allowed to vibrate anisotropically. SHELXL93^{10b} was used for data treatment and refinement based on F^2 . At 120 K (223 K in parentheses): 4965 (3085) independent reflections collected, $R_w(F^2) = 0.0980$ (0.0916), R_F [for $F > 4\sigma(F)$] = 0.0274 (0.0321), $S(F^2) = 1.245$ (1.086), 487 (489) parameters. The high percentage of disorder present at 323 K, in addition to the low quantity and quality of the data (owing to the high temperature) made a satisfactory refinement of the CO ligand positions and of the minor image of the metal triangles difficult [2908 independent reflections collected, $R_w(F^2) = 0.3427$, R_F [for $F > 4\sigma(F)$] = 0.0929, $S(F^2) = 1.017$, 334 parameters]. A further detailed examination of the data and, perhaps, a new data collection at high temperature are thus required. Cell parameters at 120 K: $a = 8.219(9)$, $b = 22.289(3)$, $c = 9.843(1)$ \AA , $\beta = 96.23(1)^\circ$; at 223 K: $a = 8.265(3)$, $b = 22.434(7)$, $c = 8.894(3)$ \AA , $\beta = 96.24(3)^\circ$; at 288 K: $a = 8.337(6)$, $b = 22.609(7)$, $c = 8.924(5)$ \AA , $\beta = 96.48(5)^\circ$; at 292 K: $a = 8.3573(7)$, $b = 22.651(3)$, $c = 8.932(2)$ \AA , $\beta = 96.55(1)^\circ$; at 323 K: $a = 8.378(4)$, $b = 22.767(8)$, $c = 8.941(3)$ \AA , $\beta = 96.65(3)^\circ$; at 373 K: $a = 8.47(1)$, $b = 11.46(2)$, $c = 8.949(8)$ \AA , $\beta = 96.59(9)^\circ$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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