An EXAFS Study of the Structure of $Fe_3(CO)_{12}$ in Solution

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Analysis of the Fe *K*-edge extended *X*-ray absorption fine structure (EXAFS) with multiple scattering calculations indicates that $Fe_3(CO)_{12}$ adopts primarily an all-terminal carbonyl co-ordination in light petroleum solution (mean Fe–Fe distance 2.65 Å), but that there is substantial population of bridging sites in a frozen CH_2Cl_2 solution (mean Fe–Fe distance 2.59 Å).

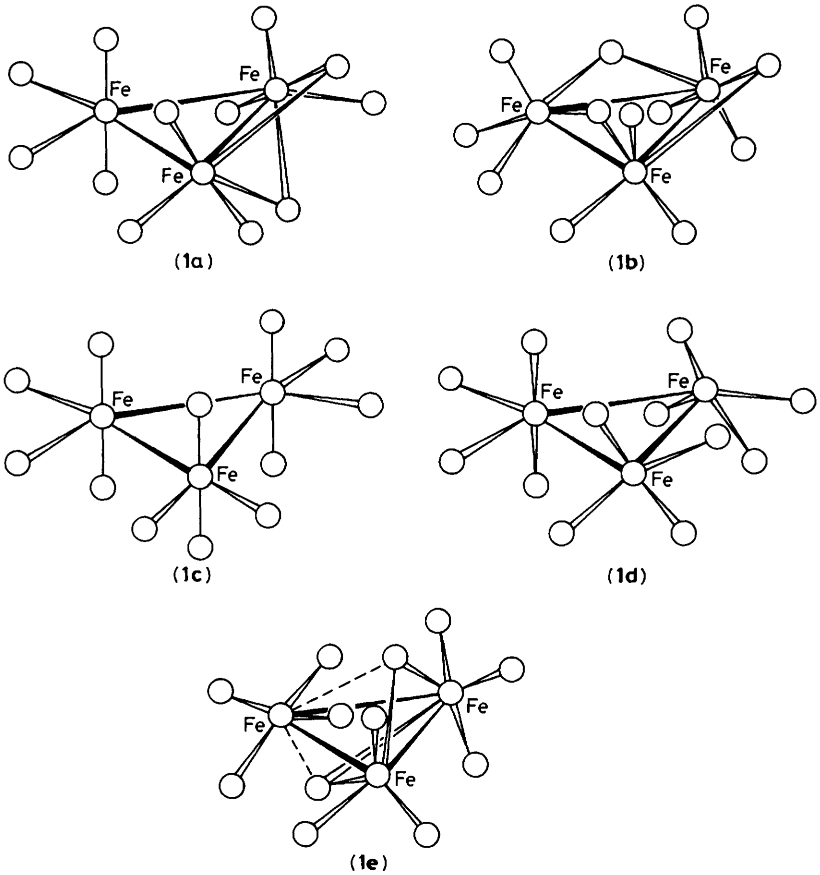
Although the molecular structure of $Fe_3(CO)_{12}$ in the crystal is well established,[1,2] there is still considerable doubt over the interpretation of spectroscopic studies of its solutions.

I.r. spectra in the ν(CO) region of the cluster in solution are not in accord with that expected for a C_{2v} structure,[3,4] the idealised symmetry of the molecular structure [(**1a**) in Figure 1] observed in both the crystal and an argon matrix (at 20 K).[5] Early proposals to account for the solvent-dependent i.r. spectra include a C_{3v} geometry with three bridging CO groups (**1b**),[1,3] and a D_{3h} structure (**1c**) based on an anticubo-octahedral CO cage as observed for the ruthenium and osmium analogues.[4] Later, alternatives maintaining the icosahedral arrangement of the carbonyl ligands in (**1a**) have been proposed,[6] *viz.* a D_3 all-terminal isomer (**1d**) and an alternative with two semi μ_3-CO groups (**1e**). Indeed, Cotton and Hunter have proposed that the potential energy surface between these isomers is relatively flat and that there is a range of species with varying degrees of bridging occupation.[4] The recent development of an algorithm for analysis of EXAFS data by spherical wave procedures with multiple scattering contributions[7] has allowed us to establish that consideration of scattering to third order will account for the observed EXAFS in metal complexes.[8] This effect is strongly dependent upon the M–C–O bond angle and may be used to estimate the mean bond angle in a cluster complex. Indeed the precision is far greater than would be obtained if the angle were derived from three independent pair-correlation functions, and this underlines the correlated nature of multiple scattering. We report the application of these procedures to the structure of $Fe_3(CO)_{12}$ in solution.

Fe *K*-edge *X*-ray absorption spectra of polycrystalline samples of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ (Station 7.4) and a frozen solution of the latter in CH_2Cl_2 (Station 7.1) were recorded at the Synchrotron Radiation Source at the Daresbury Laboratory. The larger flux provided by the Wiggler Station 9.2 was necessary to obtain satisfactory data for a solution of

Table 1. Fe *K*-edge EXAFS-derived parameters for $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ (standard deviations in parentheses).

		Shell radius (Å)		Mean Fe–C–O bond angle (°)				
Sample	Shell	EXAFS	XRD	EXAFS	XRD	Debye–Waller ($Å^2$)	*R* Factor (%)	Energy range (eV)
$Fe_2(CO)_9$	Fe–C	1.84(1)	1.93			0.015(1)		
(solid)	Fe–Fe	2.50(1)	2.52			0.014(1)		
	Fe···O	2.95(1)	3.01	160(1)	159	0.010(1)	24	15—662
$Fe_3(CO)_{12}$	Fe–C	1.81(1)	1.89			0.009(1)		
(solid)	Fe–Fe	2.62(1)	2.64			0.020(1)		
	Fe···O	2.93(1)	2.96	161(1)	164	0.007(1)	14	17—624
$Fe_3(CO)_{12}$	Fe–C	1.80(1)				0.007(1)		
(petroleum	Fe–Fe	2.65(2)				0.033(5)		
solution)	Fe···O	2.91(1)		180(5)		0.010(1)	14	17—622
$Fe_3(CO)_{12}$	Fe–C	1.82(1)				0.016(1)		
(CH_2Cl_2, frozen	Fe–Fe	2.59(1)				0.015(1)		
solution, 77 K)	Fe···O	2.96(1)		152(1)		−0.004(1)	21	17—515



(**1a**) (**1b**) (**1c**) (**1d**) (**1e**)

Figure 1. Proposed structures for $Fe_3(CO)_{12}$.

$Fe_3(CO)_{12}$ in light petroleum solution (b.p. 40—60 °C). The Fourier-filtered (*ca.* 0.8—3.5 Å) EXAFS data for the two polycrystalline samples were analysed by various approaches to assess the information content of the spectra. In neither case could bridging and terminal Fe–C and Fe···O distances be resolved, because of the high degree of correlation between parameters for closely spaced shells. The results of the best fits are presented in Table 1. They indicate the following guidelines for analysis of the solution data: (i) the Fe–C distance is strongly weighted towards the shorter distances;†

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† We attribute this primarily to the difficulty in obtaining a satisfactory background subtraction. Similar difficulties have been encountered with other studies of metal carbonyls. This may be due to problems in deconvoluting these low-frequency contributions from the oscillatory part of the atomic scattering background.

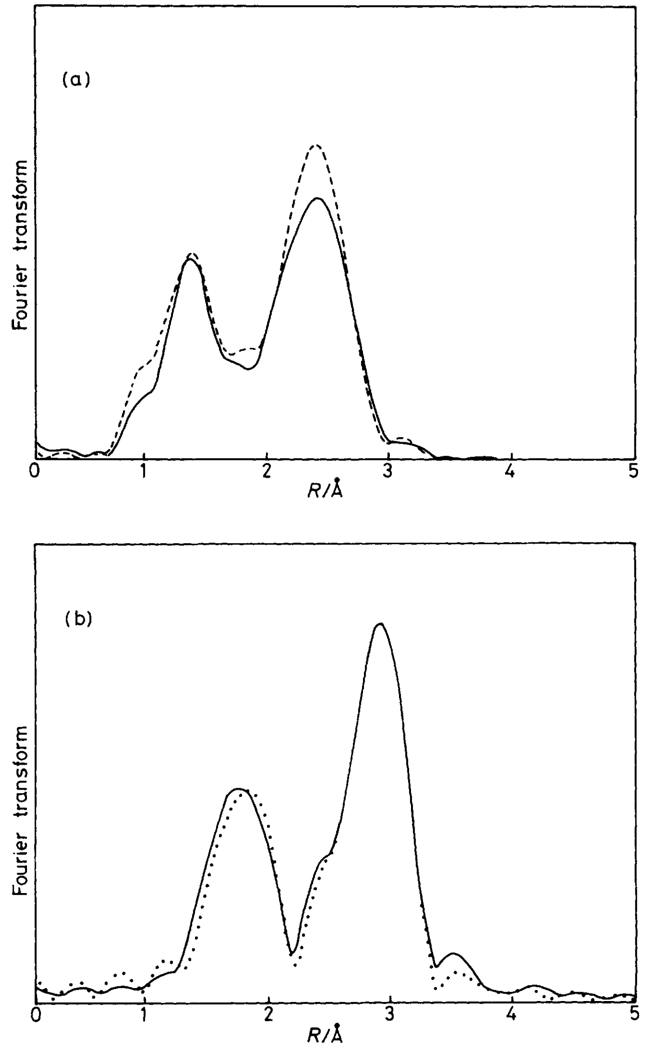

Figure 2. (a) Fourier transform of the Fe *K*-edge EXAFS data of $Fe_3(CO)_{12}$ as a polycrystalline sample (——) and in light petroleum solution (---). (b) Phase-corrected (for carbon) Fourier transforms of the Fe *K*-edge EXAFS of $Fe_3(CO)_{12}$ in a frozen CH_2Cl_2 solution at 77K: experimental (——) and calculated (...).

(ii) the Fe–Fe and Fe···O distances can be determined to a precision of *ca.* 1%; and (iii) the mean Fe–C–O bond angle replicates that determined by *X*-ray diffraction to an accuracy of a few degrees.

An incidental result is the confirmation that the structure determination for $Fe_2(CO)_9$, obtained using a crystal of anomalous habit,[9] is representative of the molecular structure in a polycrystalline sample. Indeed we have added further support for this with powder *X*-ray diffraction (XRF) measurements; the reflections computed from the single-crystal determined atomic positions agree satisfactorily with those observed for the powdered sample.

The spectra for the samples of $Fe_3(CO)_{12}$ in light petroleum and frozen CH_2Cl_2 solutions were noisier than those obtained from the solid samples. Fourier-filtered (*ca.* 0.8—3.3 Å) EXAFS was again analysed (we have demonstrated that little distortion is caused by this technique[8]), but the data range for the latter sample had to be truncated. Both sets of data were analysed initially according to the co-ordination numbers of the C_{2v} structure (**1a**), but it was clear that a better model in the hydrocarbon solvent was an all-terminal structure, and so the CO co-ordination numbers were modified to 4.0 for this system. The most significant difference between the EXAFS in light petroleum solution and that of the solid sample is the increase in intensity of the Fe···O shell [Figure 2(a)]. This can be attributed to the increase in the mean Fe–C–O bond angle giving increased multiple scattering contributions. This angle refined to 180°, and the standard deviation was estimated as 5° from a contour map of the fitting index values for the two most strongly correlated parameters, θ(Fe–C–O) and the associated Debye–Waller factor. The Fe–Fe shell parameters show smaller divergences on dissolution. The mean Fe–Fe bond length and, more particularly, the associated Debye–Waller factor increased. Indeed, it was possible to split the Fe shell into a major component at 2.67(1) Å and a minor one at 2.51(1) Å. Although the spectrum obtained for the frozen CH_2Cl_2 solution was less satisfactory, there was evidence of both a smaller Fe–Fe distance and a smaller Fe–C–O angle than in the less polar solvent. Indeed the Fourier transform clearly shows a shoulder on the short distance side of the composite peak involving Fe–Fe and Fe···O (and multiple scattering contributions) for the frozen CH_2Cl_2 solution sample [Figure 2(b)].

EXAFS provides information relating to the structure on a 10^{-15} s timescale[10] and so gives a population-weighted mean. It is clear that the majority of molecules in light petroleum solution contain only terminal Fe–C–O groups, as has been suggested from the weak bridging ν(CO) i.r. bands in hydrocarbon solvents.[4] The Fe–Fe distance in such structures appears to be *ca.* 2.65—2.67 Å. This is rather longer than that proposed for the D_3 structure (**1d**) in an icosahedral CO cage,[6] but it matches the value predicted for that model (2.60 Å) more closely than that for the alternative D_{3h} structure (*ca.* 2.80 Å). There may also be a minor coexisting structure with a smaller mean Fe–Fe distance (*ca.* 2.51 Å). In the more polar medium of a frozen CH_2Cl_2 solution, it appears that the proportion of bridging groups is higher than in the crystal and accompanies a reduction in the observed Fe–Fe distance, probably due to the μ-CO-supported Fe–Fe bonds. This could be either the C_{3v} structure (**1b**) or the C_2 alterative (**1e**).

These results favour the major species in the two solvent systems as being different, and each being distinct from the molecular structure in the crystal. A remaining question is the Cotton and Hunter proposal of a continuum of structures.[4] The static and vibrational disorder related to this flat potential energy surface would be expected to cause an increase in the Debye–Waller factors of those shells affected by the disorder. There is no clear evidence for this in these results; rather the variations appear to be dominated by the expected relative static disorder for the relevant structures. If we consider the dominant isomer in light petroleum solution to be the D_3 form (**1d**) as proposed by Johnson, the Fe–C shell would be relatively ordered; indeed this displays the smallest Debye-Waller factor of the Fe–C shells in Table 1. The large Debye-Waller factor for the Fe–Fe shell may be due to the coexistence of a minor isomer with a short Fe–Fe bond, possibly that in frozen CH_2Cl_2 solution. The predominant isomer in that medium appears to have a high bridging-to-terminal CO ratio (giving a low Fe–C–O angle and large Fe–C Debye–Waller factor), and a relatively short and ordered Fe–Fe shell. This suggests a structure like (**1b**) in which the bridging-to-terminal co-ordination ratio at iron is 2 : 3 and all Fe bonds are equivalent.

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