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Carbon-13 Magic-angle Spinning NMR Investigation of 'Site Effects' in Crystalline $Os_3(CO)_{12}$

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Many metal carbonyls are fluxional in the solid state. Molecular motion of this type can dramatically shorten longitudinal relaxation times from hours to minutes [1]. $Os_3(CO)_{12}$ shows no such fluxionality, as is evident by inequivalence of carbonyls, but does have a short relaxation time. The advantage of NMR characterization of static metal carbonyls is detection of 'site effects', not easily investigated by other techniques.

Kettle and Stanghellini [2] have shown in Raman studies that site effects in mixed crystals of $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ produce frequency changes as the ratio of these metal carbonyls is varied. They interpreted these results as originating from minor changes in molecular size and shape to adapt to sites in the crystal structure.

Solid-state ^{13}C magic-angle spinning (MAS) NMR spectroscopy detects differences in the electronic environments of the carbonyls. Dorn *et al.* [3] observed that *cis*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$, which has a site symmetry of C_1 and a molecular symmetry of C_{2v}, gave rise to more resonances in the solid spectrum than in solution because of the lower site symmetry.

We observe a similar phenomenon in the ^{13}C MAS NMR spectra of $Os_3(CO)_{12}$. By comparison with solution NMR spectra, we infer that site effects slightly alter chemical shielding. X-ray diffraction measurements of $Os_3(CO)_{12}$ support this explanation.

Experimental

$Os_3(CO)_{12}$ was obtained from Strem Chemicals, and was isotopically and uniformally enriched to approximately 35% by refluxing in toluene for four days under an atmosphere of 90% ^{13}CO. The ^{13}C MAS NMR spectrum was obtained using a Chemagnetics m100-S instrument, operating at 25.013 MHz. The spinning rate was 2700 Hz. A single 90° pulse, with a width of 6.6 μs, was used for data acquisition.

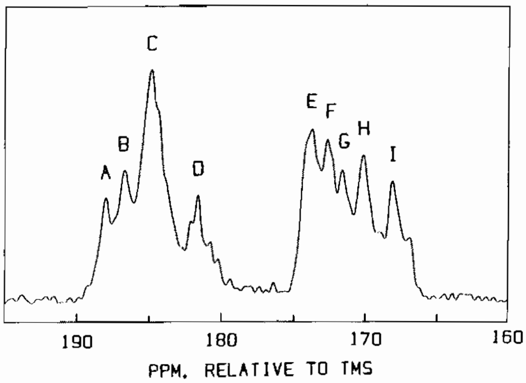

Fig. 1. Carbon-13 MAS NMR spectrum of $Os_3(CO)_{12}$ (35% ^{13}C enriched) at room temperature.

Accumulations of 164 transients were taken with a repetition time of 2 min for the enriched sample. It was necessary to collect 3400 transients with the same repetition rate to observe a similar spectrum for an unenriched sample. A static ^{13}C spectrum of the enriched sample was taken on a home-built spectrometer operating at 14.18 MHz frequency. A Hahn spin echo sequence [4] with a 4-μs 90° pulse and two-minute delay was used to remove baseline artifacts, and 1400 transients were collected.

Results and Discussion

Figure 1 shows a ^{13}C MAS NMR spectrum of $Os_3(CO)_{12}$ at room temperature. This spectrum has at least nine resolved resonances plus many small shoulders. From this, we infer that the carbonyls are magnetically inequivalent and that the carbonyls are not fluxional on the NMR time scale at room temperature. Two carbonyl regions of equal intensity are well-defined in this spectrum, with average chemical shifts of 185.0 and 171.4 ppm relative to TMS. These are assigned to axial and equatorial carbonyls, respectively. The values compare closely with the positions of resonance observed for $Os_3(CO)_{12}$ in solution at room temperature, namely, 182.3 and 170.4 ppm [5, 6]. The fine structure of these two regions in the solid-state spectrum is not present in the solution spectrum, even at low temperatures, at which carbonyl exchange in solution is slow [5, 6].

The unit cell packing of $Os_3(CO)_{12}$ is given in Fig. 2, as determined by X-ray diffraction measurements [7, 8]. The D_{3h} symmetry of this molecule demands that the six axial carbonyls be equivalent and that the six equatorial carbonyls be equivalent in solution. However, in the solid state, the crystal packing must be considered. It has been determined by X-ray diffraction that the monoclinic unit cell

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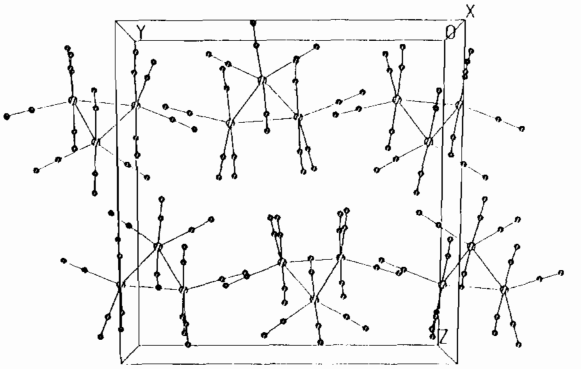

Fig. 2. Unit cell packing diagram for $Os_3(CO)_{12}$, as constructed from published atomic coordinates [8].

($P2_1/n$) contains four molecules of $Os_3(CO)_{12}$ without crystallographic symmetry [7, 8]. In a crystalline sample, the molecule is slightly distorted from D_{3h} symmetry due to packing effects. This distortion is evident from the differences in Os–Os, Os–C, and C–O bond lengths observed with X-ray diffraction. Churchill *et al.* [8, 9] determined that one of the Os–Os bonds is slightly longer than the other two, a difference of only 0.0080 ± 0.0006 Å. Although this difference is probably of little energetic significance, it is also observed for $Ru_3(CO)_{12}$, and is presumed to result from crystal forces. Churchill and DeBoer [8] calculated the average Os–C(axial) bond length to be 1.946 Å, which is 0.034 ± 0.009 Å longer than the average Os–C(equatorial) bond length of 1.912 Å. However, the variation in Os–C bond lengths has a range of 0.044 Å for axial carbonyls and 0.054 Å for equatorial carbonyls. This variation in metal–carbon bond lengths implies a similar variation in electronic environments of the carbonyls, which may be detected by ^{13}C NMR. Thus, the differences in magnetic resonance frequencies of the carbonyls are most likely due to the effects of crystal packing on the $Os_3(CO)_{12}$ molecular symmetry.

Although C–O bond lengths also vary in the solid state, the difference between axial and equatorial carbonyls is much less significant, only 0.011 Å. The closest intermolecular distance occurs between carbonyl oxygens and is calculated to be 2.979 Å from published atomic coordinates [8], which is sufficiently large to preclude direct intermolecular interactions as a source of carbonyl inequivalence.

Since ^{13}C MAS NMR spectroscopy detects differences in the electronic environments of the carbonyls, it would seem that assigning the resonances according to X-ray diffraction values of Os–C bond lengths would be reasonable. However, one is limited by the diffraction technique, with estimated standard deviations of bond lengths ranging from 0.010 to 0.012 Å. Thus, we can only conclude that the molecule is distorted in the crystalline state and that the dispersion of intramolecular Os–C bond lengths accounts for the magnetic inequivalence of the carbonyls.

TABLE I. Chemical Shifts and Relative Intensities of $Os_3(CO)_{12}$

	Chemical shift[a]	Relative intensity[b]
Axial carbonyls	188.1 (A)	1.0
	186.8 (B)	1.0
	185.0 (C)	3.0
	181.7 (D)	1.0
Equatorial carbonyls	173.9 (E)	1.6
	172.8 (F)	1.0
	171.7 (G)	0.8
	170.2 (H)	1.4
	168.2 (I)	1.1

[a] Chemical shifts are reported in ppm relative to TMS, with positive shifts at lower shielding, and the digital resolution is 0.1 ppm. [b] The relative intensities were approximated graphically, with an estimated error of ±0.1.

The chemical shifts and approximate relative intensities of the resonances are given in Table I. The axial carbonyls show an intensity ratio of 1:1:3:1. The upfield side of peak C appears to have two shoulders, suggesting that there are actually three unresolved carbonyl resonances. The relative intensities of the equatorial carbonyls are more difficult to assign since the resonances tend to be broader than those of the axial carbonyls. This is most noticeable as a small secondary peak upfield of peak I in the spectra of both the enriched and unenriched materials, and is most likely due to $^{13}C-^{189}Os$ dipolar coupling. Assuming the resonance is split, the coupling constant is estimated to be 61 ± 3 Hz.

A static ^{13}C spectrum of $Os_3(CO)_{12}$ obtained at ambient temperature shows an asymmetric powder pattern with an average chemical shift anisotropy (CSA) of −330 ± 5 ppm. This spectrum is a superposition of many powder patterns, each due to a magnetically inequivalent carbonyl. The CSA value differs from that reported by Gleeson and Vaughan [10] (−347 ppm), but, in that case, the edges of the pattern were not observed.

Conclusion

Site effects, first observed with Raman spectroscopy, can explain the complex splitting in ^{13}C NMR spectra of crystalline $Os_3(CO)_{12}$. It is inferred that the D_{3h} symmetry of the molecule is slightly distorted when it is packed in the crystal lattice, as confirmed by X-ray diffraction [8, 9]. In addition, $^{13}C-^{189}Os$ dipolar coupling constants of 61 ± 3 Hz are observed. Finally, a chemical shift anisotropy (averaged over all sites) of −330 ± 5 ppm is found from the nonspinning spectrum.

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