DALTON
FULL PAPER

The role of molecular shape and axial symmetry in the solid state molecular dynamics of metal carbonyl compounds included in cyclodextrin cavities

Holly C. Canuto,[a] **Stephen J. Heyes,**[a] **Silvio Aime,***[b] **Roberto Gobetto**[b] **and Fabio Napolitano**[b]

[a] *Inorganic Chemistry Laboratory, Department of Chemistry, University of Oxford, South Parks Road, Oxford, UK OX1 3QR. E-mail: holly.canuto@chem.ox.ac.uk*
[b] *Dipartimento di Chimica IFM, Universita' di Torino, Via P. Giuria 7, 10125 Torino, Italy. E-mail: aime@ch.unito.it*

Received 29th June 2000, Accepted 2nd October 2000
First published as an Advance Article on the web 27th October 2000

^{13}C CP/MAS NMR spectra of the metal carbonyl complexes $Cr(CO)_6$, $Fe(CO)_5$ and $Mn_2(CO)_{10}$ included in β- and γ-cyclodextrin (CD) cavities have been studied in the temperature range 133 to 423 K. $Cr(CO)_6$ molecules reorient effectively isotropically within γ-cyclodextrin, $Fe(CO)_5$ molecules in β-cyclodextrin reorient effectively isotropically and show rapid axial–equatorial exchange, but $Mn_2(CO)_{10}$ in the super-cage defined by two γ-cyclodextrin molecules shows MAS sidebands at lower temperatures indicative of a more restricted motion such as molecular gyration. The important role of guest and host molecular shape and symmetry match in the reorientational dynamics of the metal carbonyls is discussed.

Introduction

The concept of including organometallic compounds in molecular cavities such as cyclodextrin (CD) macrocycles and zeolites is not novel,[1,2] but recently the variety of guest dynamics mediated by the host–guest interactions has been explored. Although organometallic dynamics in solution is common,[3] in the solid state mobility is decreased allowing, in most cases, the individual observation of processes having low interatomic potential energy barriers. Observable in the solid state by NMR methods are motions such as arene ring reorientation processes which are typically fast on the chemical shift anisotropy (CSA) timescale (*ca.* 10^4 Hz).[4]

In the case of the cyclodextrin inclusion compound with benzenechromium tricarbonyl we have shown previously[5] that decreased intermolecular interactions facilitate guest mobility; specifically ^{13}C CP/MAS NMR spectra are consistent with rapid axial reorientation of the $M(CO)_3$ unit in the $Cr(C_6H_6)(CO)_3$ inclusion complex even at low temperatures, in contrast to the static nature of the same carbonyl moiety in the non-included material.

The dynamics of organic intercalation products within the cavity or channel of a matrix has been seen to be dependent on the symmetry of the host and guest molecules.[6–8] There have been examples showing that the organic guest molecule will more or less align itself along the principal symmetry axis of its host molecule. In the case of the encapsulation of the C_{60} molecule into *p*-benzylcalixarenes[8] this alignment is considered to be important in determining the further stabilization of the inclusion complex. It could be hypothesized that studies into the dynamics of these complexes may give insight into whether or not this is indeed the case.

The present study reports some novel inclusion compounds of binary metal carbonyls of differing size and shape as guest molecules in cyclodextrin inclusion compounds. It uses ^{13}C Variable Temperature CP/MAS NMR to study the guest molecule dynamics with the specific aim of examining how the interplay of the symmetries and shapes of guest molecules determine the angular extent of the motions.

Results and discussion

$Cr(CO)_6$ in γ-CD

The solid state ^{13}C MAS NMR features of crystalline chromium hexacarbonyl are well documented.[9] There are four principal isotropic resonances, which arise from distortions within the molecule altering its expected O_h symmetry.[10,11] The associated CSA pattern is clearly noted in the spectrum and is consistent with the rigid nature of the complex. The room temperature ^{13}C CP/MAS spectrum [recorded at a spinning speed of 5 kHz of $Cr(CO)_6$ in its γ-CD intercalation compound (Fig. 1)] shows a single carbonyl resonance at δ 215 with a bandwidth at half-height of *ca.* 15–20 ppm, and no sidebands, indicating significantly reduced CSA compared to un-included $Cr(CO)_6$. The ^{13}C CP wideline spectrum of $Cr(CO)_6$/γ-CD shows a narrow peak once again with complete absence of sidebands (Fig. 2). Since octahedral complexes are typically stereochemically rigid[9] the most reasonable explanation is that "fast" effectively isotropic reorientation of the entire molecule occurs inside the γ-CD cavity. This is therefore in contrast to $Cr(C_6H_6)(CO)_3$ in β-CD which reorients only about its principal axis. The higher symmetry of $Cr(CO)_6$ and the larger size of the γ-CD cavity presumably allow the guest molecule to reorient effectively isotropically, little influenced by the axial symmetry of the CD cavity.

$Fe(CO)_5$ in β-CD

There have been a series of studies into the dynamics of solid iron pentacarbonyl.[12] From observation of a coalescence phenomenon at −25 °C in the 90 MHz ^{13}C MAS NMR Hanson and Whitmire[12] proposed axial–equatorial exchange *via* a Berry pseudorotation, before the solid melts.

The ^{13}C CP/MAS spectrum of the ^{13}C enriched $Fe(CO)_5$/β-CD inclusion complex at a MAS rate of 5 kHz (Fig. 3) shows a single isotropic peak for the carbonyl groups at δ 212 with no spinning sidebands. The ^{13}C CP wideline spectrum of $Fe(CO)_5$ in its β-CD intercalation compound shows a narrow peak with a bandwidth at half-height of *ca.* 20 ppm. It seems that the close

DOI: 10.1039/b005226o

Fig. 1 Solid state ^{13}C CP/MAS NMR spectrum recorded at 64.7 MHz for a ^{13}CO enriched sample of the $Cr(CO)_6$/γ-CD adduct with cross polarization (contact time 5 ms) and a recycle delay of 3 s. The sample spinning speed was 5000 Hz.

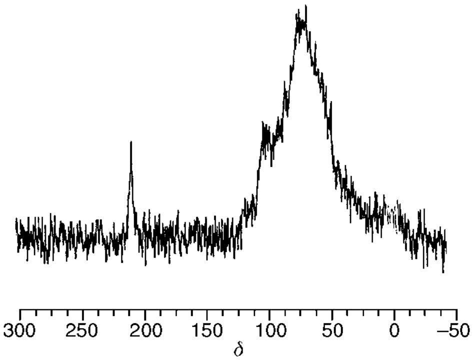

Fig. 2 Solid state ^{13}C wideline NMR spectrum recorded at 64.7 MHz for a ^{13}CO enriched sample of the $Cr(CO)_6$/γ-CD adduct, with cross polarization (contact time 5 ms) and a recycle delay of 3 s.

to spherical shape of the molecule creates a situation similar to that for $Cr(CO)_6$ and there is effectively isotropic molecular reorientation. The two likely motional processes[13] are (a) an intramolecular motional process of axial–equatorial carbonyl exchange *via* a Berry pseudorotation mechanism which would equivalence axial and equatorial environments and also lead to extensive averaging of the CSA, and (b) effectively isotropic reorientation of the whole $Fe(CO)_5$ molecule within the CD cavity which will completely average the CSA. It is likely that an $Fe(CO)_5$ molecule that is relatively free to reorient will also be stereochemically non-rigid and undergo Berry pseudorotation at a significant rate in the temperature range studied. At −80 °C the ^{13}C CP/MAS NMR spectrum is identical to that recorded at ambient temperature.

$Mn_2(CO)_{10}$ in γ-CD

The ^{13}C CP/MAS NMR spectrum at a MAS rate of 5 kHz is similar at temperatures from ambient temperature (Fig. 4) to 423 K and as in the case of $Cr(CO)_6$ and $Fe(CO)_5$ included in CDs no spinning side bands are observed for the carbonyl resonance. The isotropic band at around δ 220 shows (largely unresolved) structure, which may indicate different shifts for axial and equatorial carbonyls, and probably reflects scalar and residual dipolar couplings amongst ^{13}C and ^{55}Mn nuclei in the variety of isotopomers expected at the 20–25% ^{13}C-enrichment level. At the lowest temperature studied, 133 K, low intensity spinning sidebands are observed for the carbonyl resonance in the 5 kHz CP/MAS spectrum (Fig. 5), but they are certainly not as extensive as those observed in the ambient temperature spectrum of un-included $Mn_2(CO)_{10}$. The averaging of the carbonyl CSA for included molecules is consistent with motion of $Mn_2(CO)_{10}$ in the γ-CD complex. Simple rotation about the Mn–Mn bond, which would not average the CSA of the axial carbonyls, doesn't account for the degree of CSA averaging actually observed. Clearly the super-cage like structure, created by a complex of stoichiometry 1 $Mn_2(CO)_{10}$: 2 γ-CD, allows more extensive motion of the included $Mn_2(CO)_{10}$ molecules such as a gyration around the cavity axis. However, the loss of symmetry and increased bulk as compared to the more spherical complexes of $Fe(CO)_5$ and $Cr(CO)_6$ appears to create a situation where effectively isotropic reorientation of the guest molecules does not occur under the conditions examined.

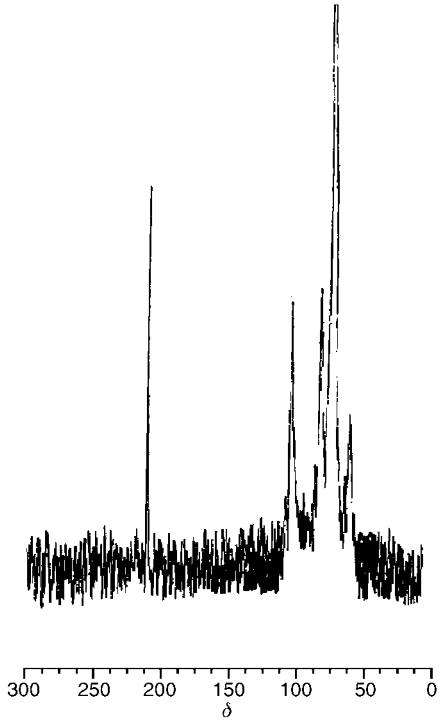

Fig. 3 Solid state ^{13}C NMR spectrum recorded at 64.7 MHz for a ^{13}CO enriched sample of the $Fe(CO)_5$/β-CD adduct. Details as in Fig. 1.

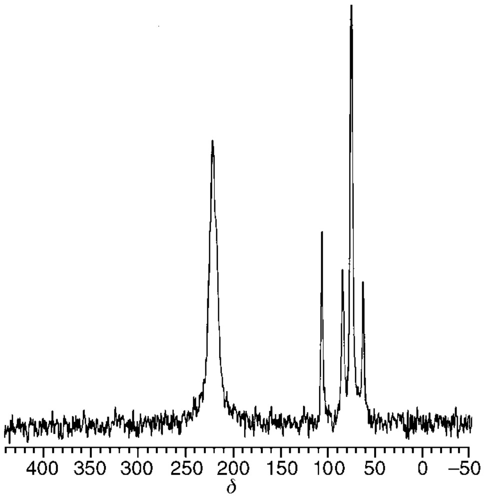

Fig. 4 Solid state ^{13}C NMR spectrum recorded at 50.32 MHz for a ^{13}CO enriched sample of the $Mn_2(CO)_{10}$/γ-CD adduct, with cross polarization (contact time 2 ms) and a recycle delay of 3 s. The sample spinning speed was 5000 Hz.

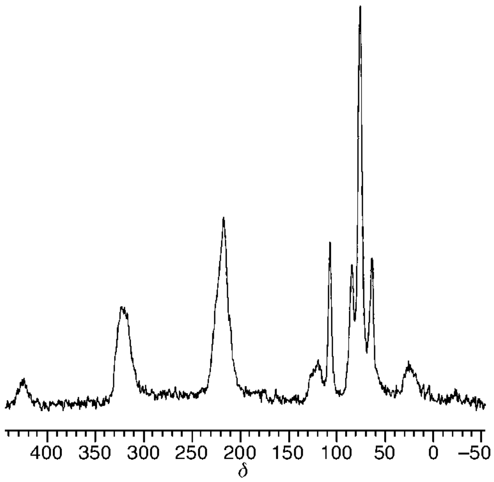

Fig. 5 Solid state ^{13}C NMR spectrum recorded at 50.32 MHz for a ^{13}CO enriched sample of the $Mn_2(CO)_{10}$/γ-CD adduct at 133 K. Details as in Fig. 4.

Conclusion

Metal carbonyl complexes studied by ^{13}C solid state NMR are shown to have altered reorientational dynamics when included in the host CD cavity compared to that of the parent molecular crystals. The high degree of symmetry associated with $Cr(CO)_6$ appears to give rise to rapid effectively isotropic reorientation, when included in γ-cyclodextrin, as demonstrated especially in the ^{13}C wideline spectrum. The stereochemical non-rigidity of $Fe(CO)_5$ and its almost spherical shape facilitate essentially isotropic reorientation in a way similar to that seen for $Cr(CO)_6$. However the loss of symmetry associated with the super-cage structure defined by the $Mn_2(CO)_{10}$ complex and the two γ-cyclodextrin molecules allows the guest molecule less mobility especially at temperatures below ambient where the motion is shown not to be effectively isotropic reorientation. It follows that in the previous study the "fast" axial reorientation of $Cr(C_6H_6)(CO)_3$, presumably coincident with the principal axis of the CD, is consistent with the same principles of host–guest interaction.

We believe the information provided in this study may be used to provide evidence that, in general, guest dynamics in host–guest complexes may be increased by the presence of higher orders of symmetry in the guest molecule.

Experimental

Preparation of cyclodextrin inclusion compounds of metal carbonyls

Table 1 Cavity and substrate dimensions

Cavity or substrate	Dimension/Å
β-Cyclodextrin	$7.80_{\text{(maximum cavity width)}}$[14]
γ-Cyclodextrin	$9.50_{\text{(maximum cavity width)}}$[14]
$Cr(CO)_6$	7 (CO–Cr–CO)[a]
$Fe(CO)_5$	6.8 (CO–Fe–CO)[a]
$Mn_2(CO)_{10}$	11 (CO–Mn–Mn–CO)[a] 7.5 (CO–Mn–CO)[a]

[a] Data obtained using inertial tensors.

Using the method of Harada *et al.*[1] originally communicated for ferrocene inclusion complexes with cyclodextrins, the finely powdered metal carbonyl was stirred in a saturated solution of CD in distilled water in a 2:1 (CD:carbonyl) molar ratio at 60 °C for 8–12 hours. The suspension was collected by centrifugation and washed with 3 × 5 ml aliquots of distilled water to remove any remaining non-included CD hydrate, and 3 × 5 ml aliquots of benzene to remove non-included carbonyl compound. A final washing with distilled water produced the desired intercalation compounds (See Table 1). $Cr(CO)_6$·γ-CD·$5H_2O$:† white; Cr 3.7 (theoretical 3.2), C 38.80–38.70 (40.17), H 6.86–6.95 (5.95%). $Fe(CO)_5$·β-CD·$6H_2O$: pale orange; Fe 3.1–3.3 (3.94), C 37.52 (39.86), H 7.27–7.24 (5.93%). $Mn_2(CO)_{10}$·γ-CD·$9H_2O$: pale beige; Mn 4.13–4.25 (3.57), C 42.68–42.70 (41.30), H 5.18–5.29 (6.23%). The deviations from the theoretical values observed for the recorded analytical data are indicative of, as in the case of $Cr(CO)_6$ and $Mn_2(CO)_{10}$ where the metal values found where seen to be higher than expected, the presence of some un-included metal carbonyl complex. Imperfections in the final washing process meant the loss of a small proportion of weakly included $Fe(CO)_5$ and a lower than expected metal value. The elemental analysis ‡ found for each of the three inclusion compounds is consistent with a 1:1, 1:1 and 2:1 CD to metal carbonyl complex ratio for $Cr(CO)_6$, $Fe(CO)_5$ and $Mn_2(CO)_{10}$ respectively.

^{13}C Enrichment

^{13}C-Enriched carbonyl compounds were prepared by irradiation of a benzene solution under 1 atm of ^{13}CO (99% enriched) using a 125 W high pressure mercury arc lamp for 2 hours.[15]

Solid state NMR spectroscopy

^{13}C CP/MAS and MAS spectra (Figs. 1, 2 and 3) were acquired on a JEOL GSX270 (6.34 T) spectrometer operating at 64.7 MHz, except for all $Mn_2(CO)_{10}$ spectra (Figs. 4 and 5) which were acquired on a Chemagnetics CMX Infinity 200 (4.7 T) instrument operating at 50.32 MHz.

Acknowledgements

This work has been carried out with the support of the EU-TMR Program (Contract No. FMRX CT96-0091) and the EPSRC.

References

1 A. Harada, K. Saeki and S. Takahashi, *Organometallics*, 1989, **8**, 730.
2 A. E. Aliev and K. D. M. Harris, *J. Phys. Chem.*, 1997, **101**, 4541.
3 K. G. Orrell, *Annu. Rep. Nucl. Magn. Reson. Spectrosc.*, 1999, **37**, 1.
4 D. Braga, *Chem. Rev.*, 1992, **92**, 633.
5 S. Aime, H. C. Canuto, R. Gobetto and F. Napolitano, *Chem. Commun.*, 1999, 281.
6 E. B. Brouwer, G. D. Enright, C. I. Ratcliffe, G. A. Facey and J. A. Ripmeester, *J. Phys. Chem. B*, 1999, **103**, 10604.
7 E. B. Brouwer, G. D. Enright and J. A. Ripmeester, *J. Am. Chem. Soc.*, 1997, **119**, 5404.
8 J. L. Atwood, L. J. Barbour, P. J. Nichols, C. L. Raston and C. A. Sandoval, *Chem. Eur. J.*, 1999, **5**, 990.
9 S. Aime, W. Dastru', R. Gobetto and G. E. Hawkes, *Advanced Applications of NMR to Organometallic Chemistry*, eds. R. W. M. Gielen and B. Wrackmeyer, John Wiley and Sons, New York, 1996.
10 T. H. Walter, L. Reven and E. Oldfield, *J. Phys. Chem.*, 1989, **93**, 1320.
11 A. Whitaker and J. W. Jeffery, *Acta Crystallogr.*, 1967, **23**, 977.
12 B. E. Hanson and K. H. Whitmire, *J. Am. Chem. Soc.*, 1990, **112**, 974.
13 H. W. Spiess, R. Grosescu and U. Haeberlen, *Chem. Phys.*, 1974, **6**, 226.
14 A. Harada, M. Takeuchi and S. Takahashi, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 4367.
15 T. C. Flood, E. Rosenberg and A. Sarhangi, *J. Am. Chem. Soc.*, 1977, **99**, 4334.

---

† The number of water molecules was found by TGA analysis using a Shimadzu DT-30 thermal analyser from the proportion of mass lost in the temperature range 75–150 °C. The relatively low number can be regarded as consistent with the assumption that water is displaced from the CD cavity during metal carbonyl inclusion.

‡ All elemental analyses were performed by the Analytical Service of the Inorganic Chemistry Laboratory, University of Oxford, using combustion for C and H and ICP-AES for Cr, Fe and Mn.