High-resolution Solid-state Oxygen-17 Nuclear Magnetic Resonance Spectroscopy of Transition Metal Carbonyls

Eric Oldfield,* Max. A. Keniry, Sumio Shinoda, Suzanne Schramm, Theodore L. Brown, and H. S. Gutowsky
School of Chemical Sciences, University of Illinois at Urbana-Champaign, 505 South Mathews Avenue, Urbana, IL 61801, U.S.A.

We have obtained the first high-resolution solid-state oxygen-17 n.m.r. spectra of a series of transition metal carbonyls and the results indicate that the principal elements of the ^{17}O chemical shift tensors may be determined, that the anisotropies are very large ($\Delta\delta$ *ca.* 600—700 p.p.m.) while the ^{17}O quadrupole coupling constants are very small (*ca.* 1 MHz), and that magnetically nonequivalent $C^{17}O$ groups may be detected.

Carbon monoxide is an important ligand in organometallic chemistry, and an important precursor in the synthesis of a wide range of chemical species. There is thus much interest in the nature of metal–CO bonding. N.m.r. spectroscopy can in principle provide much detailed structural information. While there have been previous reports of carbon-13 and oxygen-17 chemical shifts of metal carbonyls in solution,[1] there have been no reports of ^{17}O spectra in the crystalline solid-state, where the potentially informative individual components of the chemical shift tensor (δ_{11}, δ_{22}, and δ_{33}) may be evaluated, and only a few reports of ^{13}C shielding tensors (see *e.g.* refs. 2, 3, and references cited therein). We present in this paper the first observation of high-resolution solid-state ^{17}O n.m.r. spectra of several transition metal carbonyls, together with, for comparison, their corresponding ^{13}C n.m.r. spectra.

We show in Figures 1(a) and (b) the ^{17}O n.m.r. spectra of

Table 1. Carbon-13 and oxygen-17 chemical shift tensor elements for group 6B metal carbonyls.

	Oxygen-17[a]					Carbon-13[b]				
	Tensor elements[c]			Anisotropy[d]	Isotropic	Tensor elements[c]			Anisotropy[d]	Isotropic
	δ_{11}	δ_{22}	δ_{33}	$\Delta\delta$	shift[e]	δ_{11}	δ_{22}	δ_{33}	$\Delta\delta$	shift[e]
$Cr(CO)_6$	615	579	−94	−691	367	369	335	−69	−421	212
$Mo(CO)_6$	585	556	−79	−650	354	338	332	−65	−400	202
$W(CO)_6$	567	536	−67	−619	348	326	319	−70	−393	192

[a] Spectra obtained at 67.8 MHz (11.7 T). Chemical shifts are in p.p.m. from external H_2O. High frequency (low field, paramagnetic, deshielded) shifts are positive. [b] Spectra obtained at 90.5 MHz (8.45 T). Chemical shifts are in p.p.m. from external Me_4Si, same sign convention as in footnote a. [c] Obtained using the Herzfeld–Berger method (ref. 5). Accuracies are ±10—20 p.p.m. for ^{17}O and ±5—10 p.p.m. for ^{13}C. [d] Defined as $\Delta\delta = \delta_{33} - 1/2(\delta_{11} + \delta_{22})$ with $|\delta_{33}-\delta_i| \geq |\delta_{11}-\delta_i| \geq |\delta_{22}-\delta_i|$. [e] $\delta_i = 1/3(\delta_{11} + \delta_{22} + \delta_{33})$. Measured from centreband positions, errors are ±1 p.p.m.

crystalline Mo($C^{17}O$)$_6$ and Mo(bpy)($C^{17}O$)$_4$, (bpy = bipyridine), obtained at 67.8 MHz (11.7 T). Only the (1/2, −1/2) spin transition is observed in (a), while in (b) there are additional contributions from the satellite transitions, which can be removed by spinning slightly off the 'magic-angle', Figure 1(c). Also shown in Figure 1, (d) and (e), are the 37.8 MHz ^{13}C magic-angle spinning n.m.r. spectra of Mo(^{13}CO)$_6$ and Mo(bpy)(^{13}CO)$_4$.

The ^{17}O linewidths in Figure 1 are remarkably narrow ($\leq$500 Hz) and show no sign of second-order quadrupolar structure, as seen in the simulated spectrum of CO [inset in Figure 1(a)] in which an ^{17}O nuclear quadrupole coupling constant (e^2qQ/h) of 4.34 MHz has been determined.[4] This width and lack of observable structure implies that the ^{17}O e^2qQ/h values are $\leq$1 MHz. The correspondingly small electric field gradients at oxygen presumably arise from *increased* π back-donation and formation of co-ordinate σ-bonds, increasing the electron density perpendicular to the CO-bond axis. However, further experiments in which the extent of π-bonding is varied (and at several field strengths to determine e^2qQ/h accurately) are required in order to quantify these effects.

The sideband intensities of Figure 1 may be analysed to yield the principal elements of the respective chemical shift tensors, δ_{ii}. Combination of magic-angle sample-spinning and the Herzfeld–Berger method[5] provides increased sensitivity over non-spinning techniques,[3] and resolution of non-equivalent CO residues, as shown with the *cis* and *trans* carbonyl groups in Mo(bpy)(CO)$_4$, both in ^{17}O and ^{13}C n.m.r. spectroscopy.

We tentatively assign the Mo(bpy)(CO)$_4$ ^{17}O resonance at 346 p.p.m. to *cis* carbonyls and that at 367 p.p.m. to *trans* carbonyls, based on the observation of an intense centreband at 349 p.p.m. together with a weak one at 366 p.p.m., in Mo(pyridine)(CO)$_5$ (data not shown). The ^{17}O shifts observed in Mo(*o*-phenanthroline)(CO)$_4$ are about the same as in the bipyridine adduct, 346 and 365 p.p.m. The chemical shift of Mo(mesitylene)(CO)$_3$ is 362 p.p.m., close to that attributed to the *trans* ligands in the other species studied.

Determination of the ^{17}O shift tensor elements of the more shielded component of the spectrum of Mo(bpy)(CO)$_4$, Figure 1(b), yields δ_{11} = 544, δ_{22} = 533, and δ_{33} = −40 p.p.m. using the Herzfeld–Berger method. However, contributions from the satellite transitions are more pronounced for the less shielded component and we cannot accurately determine its δ_{ii}s.

We show in Table 1 tensor elements for the group 6B carbonyls. There is a large increase in shielding but a decrease in shielding anisotropy for both ^{13}C and ^{17}O nuclei, on going from Cr to Mo to W. Although uncertainties in individual tensor elements are quite large (^{17}O *ca.* ± 10—20 p.p.m.; ^{13}C *ca.* ±5—10 p.p.m.), the results suggest that these changes are brought about by a basically similar shielding of δ_{11} and δ_{22} for both ^{13}C and ^{17}O, however, δ_{33} (along the C–O bond) is constant for ^{13}C, while it becomes deshielded for ^{17}O.

The results presented above show that it is now feasible to obtain *both* ^{13}C and ^{17}O chemical shift tensors for CO in metal carbonyls, and suggest that lower field operation may yield ^{17}O e^2qQ/h information. Taken together, these parameters should help clarify our understanding of the chemical shifts and structures of such systems,[3,6] and may provide new structural probes for studying the adsorption of CO, and metal carbonyls, onto various surfaces.

This work was supported by a U.S.–N.S.F. Solid State Chemistry Grant (S. Schramm) and in part by the Mobil Foundation. S. Shinoda was on leave from the Institute of Industrial Science, University of Tokyo, 22-1, Roppongi 7

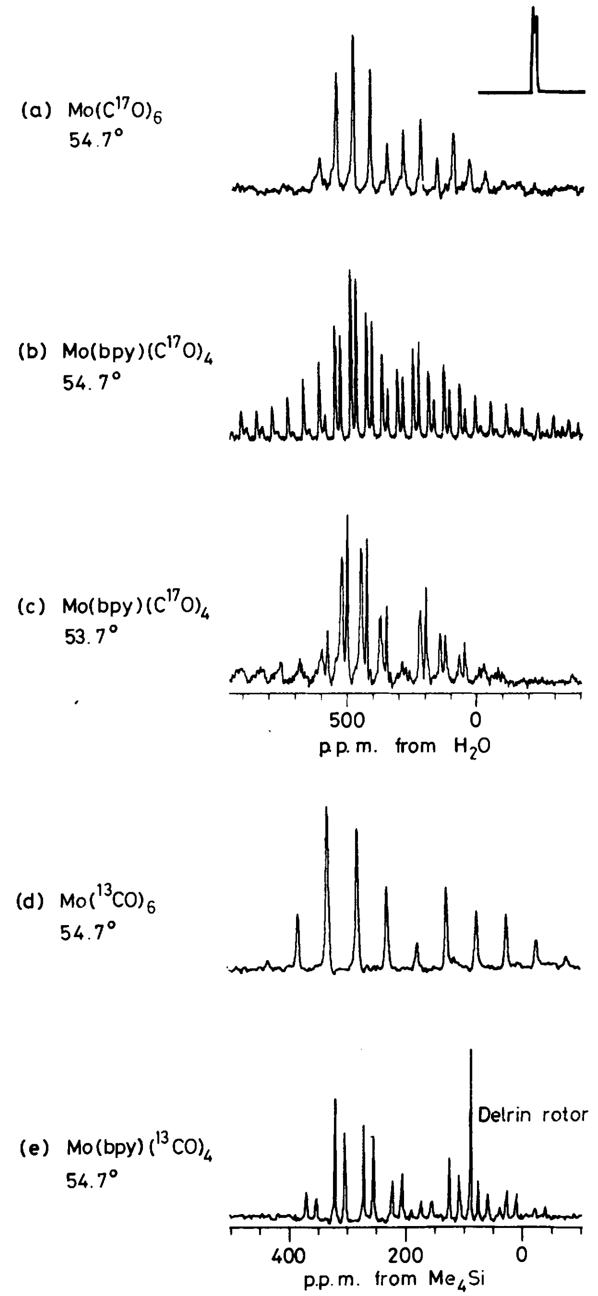

Figure 1. ^{17}O and ^{13}C Solid-state n.m.r. spectra of Mo(CO)$_6$ and Mo(bpy)(CO)$_4$ obtained using 'magic-angle' sample-spinning (m.a.s.s.). (a) ^{17}O M.a.s.s. n.m.r. spectrum of Mo($C^{17}O$)$_6$ at 67.8 MHz (11.7 T). The inset is a computer simulation of solid $C^{17}O$ under 'magic angle' spinning conditions, using a quadrupole coupling constant of 4.34 MHz. (b) ^{17}O M.a.s.s. n.m.r. spectrum of Mo(bpy)($C^{17}O$)$_4$ at 67.8 MHz. (c) as (b) but at 53.7° to broaden the satellite transitions. (d) ^{13}C M.a.s.s. n.m.r. spectrum of Mo(^{13}CO)$_6$ at 37.8 MHz (3.52 T). (e) ^{13}C Cross-polarization m.a.s.s. n.m.r. spectrum of Mo(bpy)(^{13}CO)$_4$ at 37.8 MHz (3.52 T). Values of between 20 and 100 Hz line broadening due to exponential multiplication were used to improve spectral signal-to-noise ratios. Chemical shifts are reported with respect to external water (^{17}O) or Me_4Si (^{13}C). Metal carbonyls were enriched in ^{17}O by exchange from *ca.* 40% ^{17}O enriched water following the method of Darensbourg *et al.*, ref. 7. ^{13}C Enrichment was performed using the method of Kirtley *et al.*, ref. 8. MoL(^{13}CO)$_4$ (L = bipyridine, phenanthroline) were synthesized from Mo(^{13}CO)$_6$ following the methods of Stiddard (ref. 9) and Angelici and Graham (ref. 10).

Chome, Mintao-ku Tokyo 106, Japan. E. O. is a U.S.P.H.S. Research Career Development Awardee, 1979—1984.

Received, 14th August 1984; Com. 1183

References

1 R. Bramley, B. N. Figgis, and R. S. Nyholm, *Trans. Faraday Soc.*, 1962, **58**, 1893; G. M. Bodner, S. B. Kahl, K. Bork, B. N. Storhoff, J. E. Wuller, and L. J. Todd, *Inorg. Chem.*, 1973, **12**, 1071; D. Cozak, I. S. Butler, J. P. Hickey, and L. J. Todd, *J. Magn. Reson.*, 1979, **33**, 149; J. P. Hickey, J. R. Wilkinson, and L. J. Todd, *J. Organomet. Chem.*, 1979, **179**, 159; S. Aime, L. Milone, D. Osella, G. E. Hawkes, and E. W. Randall, *ibid.*, 1979, **178**, 171; S. Aime, R. Gobetto, D. Osella, L. Milone, G. E. Hawkes, and E. W. Randall, *J. Chem. Soc., Chem. Commun.*, 1983, 794.

2 H. C. Dorn, B. E. Hanson, and E. Motell, *J. Organomet. Chem.*, 1982, **224**, 181.

3 J. W. Gleeson and R. W. Vaughan, *J. Chem. Phys.*, 1983, **78**, 5384.

4 M. A. Frerking and W. D. Langer, *J. Chem. Phys.*, 1981, **74**, 1990.

5 J. Herzfeld and A. E. Berger, *J. Chem. Phys.*, 1980, **73**, 6021.

6 W. Buchner and W. A. Schenk, *J. Magn. Reson.*, 1982, **48**, 148.

7 D. J. Darensbourg, B. J. Baldwin, and J. A. Froelich, *J. Am. Chem. Soc.*, 1980, **102**, 4688.

8 S. W. Kirtley, M. A. Andrews, R. Bau, G. W. Grynkewich, T. J. Marks, D. L. Tipton, and B. R. Whittlesey, *J. Am. Chem. Soc.*, 1977, **99**, 7154.

9 M. H. B. Stiddard, *J. Chem. Soc.*, 1962, 4712.

10 R. J. Angelici and J. R. Graham, *Inorg. Chem.*, 1967, **6**, 972.