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Two-dimensional nutation ^{59}Co NMR of solid $Co_4(CO)_{12}$ *

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Abstract

^{59}Co 2D nutation NMR experiments were conducted at 47.485 MHz in order to determine the quadrupole coupling constants (e^2Qq/h) of ^{59}Co nuclei in solid $Co_4(CO)_{12}$. The 2D spectrum observed clearly indicates the presence of two inequivalent ^{59}Co nuclei, Co(apical) and Co(basal). The magnitude of e^2Qq/h and the asymmetry parameter of the electric field gradient, η, were determined to be 9 ± 2 MHz and 0 for Co(basal), and 15 ± 3 MHz and 0.8 for Co(apical). The large value of η for Co(apical) suggests that the apical Co occupies the site on a pseudo-C_3 axis in the crystalline lattice. These facts are consistent with our previous proposal that a symmetry conserved reorientation of the Co_4-tetrahedron occurs in the solid state.

Introduction

$Co_4(CO)_{12}$ undergoes fast carbonyl exchange in solution [1]. In the solid state, the ^{13}C MAS NMR spectra reported for this compound are surprisingly different from each other and, although variable temperature measurements indicated some fluxionality, the exact mechanism of CO and/or Co motion has not been unequivocally defined [2–4]. In order to gain further insight into this behaviour we recently reported variable temperature ^{13}C and ^{59}Co NMR spectral data in the solid state; these measurements [5] showed that some restricted motion of the Co_4-tetrahedron occurs at higher temperatures and the motion was assigned to a reorienta-

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tion of the Co_4-tetrahedron about a C_3 axis running through the apical Co rather than the interconversion between the apical and basal Co's as proposed previously [2–4].

The C_{3v} structure of $Co_4(CO)_{12}$ in solution has now been well established by ^{17}O NMR [6] but interpretation of ^{13}C and ^{59}Co NMR data has proved to be less straightforward [7]. Difficulties have also been experienced in the X-ray crystallographic determination of $Co_4(CO)_{12}$ which adopts a disordered structure [8].

In order to assign the ^{59}Co NMR spectrum unambiguously and to understand better both the physical properties associated with the static structure and the dynamic behaviour of the cluster, we carried out measurements to obtain both the quadrupole coupling constants (e^2Qq/h) and the asymmetry parameters (η) for the different ^{59}Co nuclei in crystalline $Co_4(CO)_{12}$. The 2D nutation NMR technique [9] can distinguish such inequivalent nuclei and determine the values of quadrupole coupling constants from the FID signals of the central transitions ($m = +1/2 \leftrightarrow -1/2$) in a powdered specimen. We now describe application of this technique to polycrystalline $Co_4(CO)_{12}$.

Experimental

^{59}Co NMR spectra were measured on a Bruker MSL-200 spectrometer at the Larmor frequency of 47.485 MHz. $Co_4(CO)_{12}$ (1.5 g) was sealed into a glass ampoule (10 mm $\phi \times 30$ mm) with a small amount of He gas. In order to obtain the nutation spectrum [9], the pulse length was increased from 2 to 256 μs every 2 μs in the time domain t_1 using the automation program. Data points (1k) were collected every 0.8 μs for each FID in the time domain t_2. Each FID was quadrature-detected and accumulated 100 times. The recycle time for the accumulation was set to be longer than *ca.* 5 s, to allow for recovery of magnetization to its thermal equilibrium value. The temperature of the sample was controlled within ±1 K using the VT-1000 system (Bruker) and measured by Cu-Constantan thermocouples.

The data acquired were two-dimensionally Fourier transformed into the frequency domain ($t_1 \rightarrow F_1$; $t_2 \rightarrow F_2$) by means of an ASPECT-3000 computer.

Preparation of $Co_4(CO)_{12}$

$Co_2(CO)_8$ (8.52 g) was dissolved in hexane (150 cm^3) and heated under reflux for 3 h. The reaction mixture was then concentrated to 75 cm^3, and cooled to −30°C to give small black crystals of the product 6.1 g (86%). ν(CO stretching modes) in hexane were 2065(s), 2060(s), 2040(w), 2030(w) and 1879(s) cm^{-1}.

Results and discussion

In the past, there have always been problems assigning to Co(apical) and Co(basal), the two cobalt resonances observed for $Co_4(CO)_{12}$ in solution. Integration always proved imprecise but the general suggestion was that the low field resonance was the less intense and therefore could be assigned to Co(apical). Solid state NMR studies now show that there is a unique pulse-length dependence of the ^{59}Co NMR lineshape (as shown in Fig. 1) which clearly shows the presence of two resonances due to Co(apical) and Co(basal). The interpretation of this is

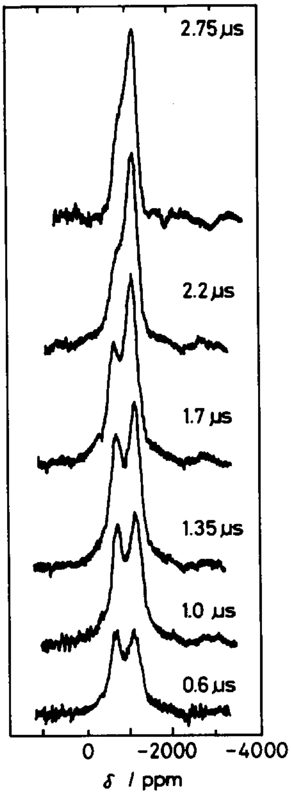

Fig. 1. Dependence of the lineshape on the pulse-length for the central ^{59}Co NMR resonances in solid $Co_4(CO)_{12}$. The chemical shift reference for ^{59}Co is $K_3[Co(CN)_6]$.

presented below, and coupled with the previously observed variation of t_1 and ^{59}Co chemical shift with temperature [5], it strongly supports the idea of the resonance at the lowest field being due to Co(apical) as earlier suggested from studies in solution.

In order to determine the first-order quadrupolar splitting in $Co_4(CO)_{12}$, we carried out the usual 1D NMR measurements by expanding the spectral width to 800 kHz. The spectra observed at room temperature and 176 K are shown in Fig. 2. Two pairs of satellite peaks (one at ± 600 kHz and another at ± 200 kHz from the central peaks) can be recognized at 176 K. This indicates that the central transitions arise from two inequivalent ^{59}Co nuclei in the solid, although the quadrupole parameters, e^2Qq/h and η, for each ^{59}Co cannot be obtained from only a consideration of the position of each of these satellite peaks.

Figure 3 shows a contour plot of the 2D nutation spectrum of the ^{59}Co nuclei in solid $Co_4(CO)_{12}$ at room temperature. From Fig. 3, the chemical shift values of Co(apical) and Co(basal) in the F_2 dimension can be obtained and are indicated by the two arrows; the values are -715 and -1125 ppm respectively which are identical to those obtained previously [5] and to those in Fig. 1.

In the case of quadrupolar nuclei, the F_1 dimension of the nutation spectrum contains information about the quadrupole parameters for both inequivalent nuclei [9,10]. Figure 4 shows the projections of the nutation pattern onto the F_1

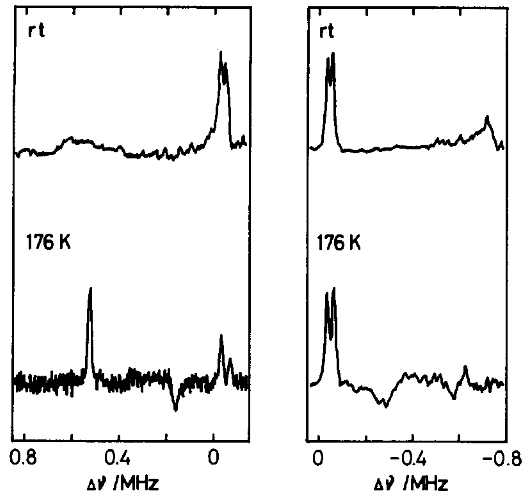

Fig. 2. ^{59}Co NMR spectra showing first order splittings for solid $Co_4(CO)_{12}$.

axis for the two different ^{59}Co nuclei. Since peaks are observed below 50 kHz, the value of the e^2Qq/h must be < 20 MHz [10]. We carried out a computer simulation of the 2D nutation spectrum in Fig. 4 and showed that the spectrum is insensitive to η, and the best values of e^2Qq/h for Co(apical) and Co(basal) are 15 ± 3 MHz and 9 ± 2 MHz respectively.

Adopting these values of e^2Qq/h, we attempted to simulate the first order splitting of the resonances in Fig. 2. The spectrum extends over an extremely wide frequency range, so neither the observed intensities nor the phase-corrections of each peak are reliable; we therefore simulated only the peak positions. We then found that the outer satellites must result from the quadrupolar coupling of

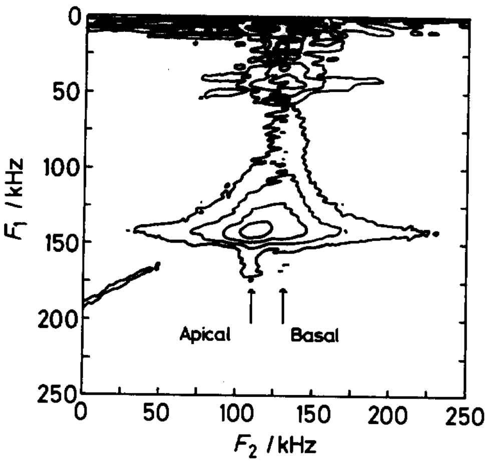

Fig. 3. Two-dimensional contour plot of the ^{59}Co nutation spectrum of solid $Co_4(CO)_{12}$. The exact positions of the apical and basal cobalt resonances are indicated by arrows.

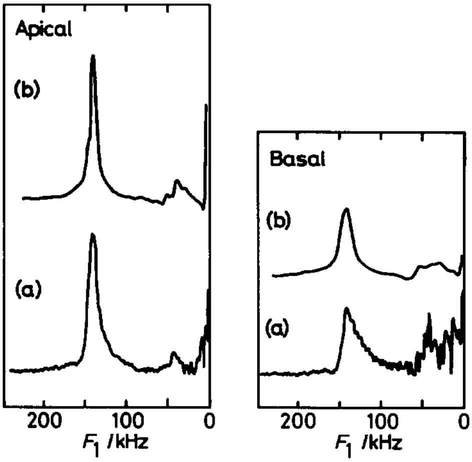

Fig. 4. (a) The projections of the two-dimensional nutation spectrum onto the F_1 axis at the F_2(apical) and F_2(basal) frequencies indicated by the arrows in Fig. 3. (b) Simulated spectra for Co(apical) $e^2Qq/h = 15 \pm 3$ MHz and Co(basal) $e^2Qq/h = 9 \pm 2$ MHz.

Co(basal) and the inner satellites from coupling of Co(apical) which allowed values of η to be estimated as 0.8 for Co(apical) and 0 for Co(basal) at 176 K.

It is interesting to compare these quadrupole parameters with those observed in other cobalt compounds. In the case of ^{59}Co, both the quadrupole coupling constant and the asymmetry parameter of the electric field gradient depend strongly not only on the electronic state but also on the static and time-averaged local symmetry around the cobalt site in the crystal lattice; in the case of the regular octahedral Co^{III} complexes e.g. $K_3[Co(CN)_6]$ crystals, values of e^2Qq/h = 5.88 MHz and $\eta = 0.9$ have been reported [11]. In crystalline $[Co(NH_3)_6]Cl_3$ there are four inequivalent ^{59}Co nuclei in the unit cell which give rise to four different values of e^2Qq/h = 0.9, 1.8, 31.0, 17.5 MHz, and η = 0.9, 0.8, 0.5, 0.4 respectively [12]. Thus, although the Co nuclei are approximately at the centres of regular octahedra of NH_3 groups, only a slight deformation of the octahedron is necessary to cause the quadrupole parameters to vary over a wide range. Such a slight reduction in symmetry is probably also responsible for the hexagonal closed-packed alloy, Co_2Zr, having a non-zero value of e^2Qq/h (14.04 MHz and $\eta = 0$) [13]. The effect of this reduction in symmetry is clearly demonstrated in crystalline *trans*-$[Co(en)_2Cl_2]NO_3$ (en = $H_2NCH_2CH_2NH_2$) which has a significantly larger quadrupole coupling constant (e^2Qq/h = 62.78 MHz) and $\eta = 0.132$ [14].

Much larger values of e^2Qq/h are found for cobalt carbonyl compounds, e.g. the values of e^2Qq/h and η for $Co_2(CO)_8$ are 90.23 MHz and 0.315 respectively [15] and similar values have been reported for a variety of trinuclear clusters of the type $Co_3(CO)_9(\mu_3\text{-}CR)$ [16].

The cobalt atoms in $Co_4(CO)_{12}$ are bonded to each other and are associated with either three or four CO's resulting in site symmetries which are obviously lower than octahedral symmetry; these local symmetries within an individual cluster are further reduced in the unit cell. It is therefore rather surprising that all the Co nuclei in $Co_4(CO)_{12}$ have relatively small values of e^2Qq/h when compared to the examples above. In contrast to the structure of $Co_4(CO)_{12}$ in solution

[1], it is also worth noting that the observed apparent symmetry is higher for the Co(basal) atoms than for Co(apical).

In accord with our previous ^{59}Co T_1 measurements [5] which revealed that the Co_4 tetrahedron undergoes rapid reorientation above 250 K, the quadrupole parameters observed at room temperature obviously correspond to motionally averaged values and since the values of e^2Qq/h and η of Co(apical) differ from those of Co(basal) a reorientation about one axis only is strongly supported by the present data. This motion is thus ascribed to the reorientation about a pseudo C_3-axis incorporating the Co(apical) atom in a single molecule as described previously [5]. The zero value of η for Co(basal) is also entirely in accord with such a reorientation [17]. The large η value of 0.8 for Co(apical) could be explained by consideration of the unit cell, rather than just the single cluster unit, since the unit cell lacks a C_3-axis.

To sum up, the two-dimensional nutation NMR clearly distinguishes two inequivalent ^{59}Co nuclei in crystalline $Co_4(CO)_{12}$ and we cannot confirm the disorder suggested from X-ray crystallographic studies [7]. The quadrupole parameters are determined to be $e^2Qq/h = 15 \pm 3$ MHz and $\eta = 0.8$ for Co(apical) and $e^2Qq/h = 9 \pm 2$ MHz and $\eta = 0$ for Co(basal). These values further support our previous proposal that the symmetry conserved reorientation of the Co_4-tetrahedron occurs about the pseudo-C_3 axis incorporating Co(apical) of a single molecule in the solid state.

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