

Communications

Evidence for Fluxionality in Solid $\text{Co}_4(\text{CO})_{12}$

Sir:

The use of variable-temperature magic angle spinning carbon-13 NMR spectroscopy has helped elucidate many interesting dynamic processes in the solid state. For example, the metal carbonyls $\text{Co}_2(\text{CO})_8$ ¹ and $\text{Fe}_3(\text{CO})_{12}$ ² undergo rapid bridge-terminal CO exchange in the solid state, ring whizzing of metal-coordinated cyclooctatetraene rings is fast in the solid,³ and many organic molecules have been observed to be fluxional in the solid state.^{4,5} Here we show experimental results for $\text{Co}_4(\text{CO})_{12}$ that are consistent with a rapid molecular reorientation in the solid state which results in exchange of carbonyl ligands.

The structure of $\text{Co}_4(\text{CO})_{12}$ ⁶ is closely related to that of $\text{Fe}_3(\text{CO})_{12}$ ⁷ both are defined by a nearly icosahedral arrangement of carbonyls with the metal cluster located inside. It has been postulated⁸ and proven^{2,9} that the Fe_3 cluster may rotate within the carbonyl framework of $\text{Fe}_3(\text{CO})_{12}$. The iron triangle rotates between the two crystallographically observed orientations. At 25 °C the rotation is rapid on the NMR time scale while at -93 °C the motion is in the slow-exchange limit.⁹

Tetracobalt dodecacarbonyl also exhibits a crystallographic disorder with two orientations of the Co_4 tetrahedron within the icosahedron of carbonyls. In light of the behavior of $\text{Fe}_3(\text{CO})_{12}$ it seems likely that a similar reorientation is possible for $\text{Co}_4(\text{CO})_{12}$.

The MAS ¹³C NMR spectra for $\text{Co}_4(\text{CO})_{12}$ are shown in Figure 1 from -62 to +63 °C. The spectrum at 35 °C was obtained with proton decoupling to allow the observation of the rotor material, Delrin, which serves as a chemical shift reference. Spinning sidebands are designated by asterisks; the spinning rate varied from 3.7 kHz at -62 °C to 4.4 kHz at 25 °C and above.

At 63 °C a single broad line is observed at 202.8 ppm. This is similar to the room-temperature spectrum of $\text{Co}_2(\text{CO})_8$ and is consistent with all 12 carbonyls in $\text{Co}_4(\text{CO})_{12}$ exchanging rapidly on the NMR time scale. The line shape changes from +63 to -62 °C are completely reversible; however, above 65 °C considerable decomposition occurs during the NMR experiment so further line narrowing could not be observed. The chemical shift

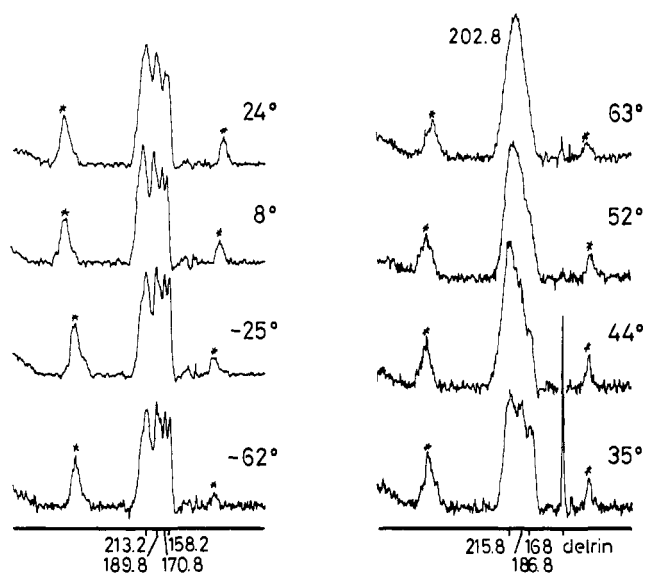


Figure 1. Variable temperature carbon-13 NMR spectra from -62 to +63 °C. These were recorded at 22.6 MHz by using a Chemagnetics superconducting magnet and probe interfaced to a JEOL FX60QS spectrometer. Proton decoupling was used to record the spectrum at 35 °C to give the Delrin signal as a chemical shift reference.

observed at 63 °C (202.8 ppm) is close to that calculated from the low-temperature solution ¹³C NMR spectrum reported for $\text{Co}_4(\text{CO})_{12}$ ¹⁰ and observed at 61 °C in a highly viscous solvent (206.1 ppm).¹¹

As the sample is cooled to 24 °C, three peaks are observed. Only one set of spinning sidebands are seen at all temperatures. In the 24 °C spectrum and at all lower temperatures the spinning sidebands are associated with the peak at ca 213 ppm. This is easily seen in Figure 1 but is also confirmed by variable spinning rate experiments.

When the sample is cooled further, four lines appear at 213.2, 189.8, 170.8, and 158.2 ppm. These are quite anomalous for bridging and terminal carbonyls in neutral cobalt carbonyl derivatives.¹⁰ Also the center-of-mass for the NMR spectrum shifts distinctly upfield as the sample is cooled. In solution the bridging CO's are observed at 243.1 ppm while the terminal CO's come at 195.9 and 181.98 ppm.^{10a} One complicating factor in interpreting the low-temperature spectra is ⁵⁹Co-¹³C dipolar coupling. A Co-C distance of 1.83 Å for a terminal carbonyl gives a calculated dipolar coupling of 2.56 kHz. Spinning rates of 3.7 kHz at the magic angle may not be sufficient to completely average

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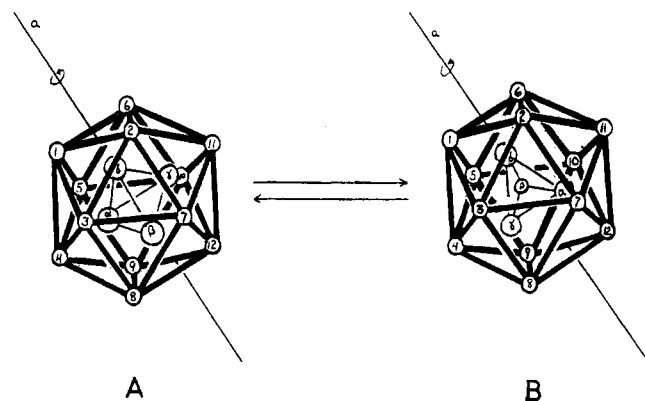


Figure 2. Schematic representation of the structure of $\text{Co}_4(\text{CO})_{12}$ showing the 2-fold disorder observed crystallographically. Rotation of the cobalt tetrahedron about the 2-fold axis, a , is not sufficient to exchange all 12 carbonyls.

the ^{59}Co - ^{13}C dipolar interactions. Thus the spectra at temperatures from -62 to $+24$ °C probably exhibit some dipolar broadening. Also some selective site exchange may still be taking place at -62 °C.

Although the spectra below 24 °C appear to be consistent with a static molecule, we do not have a satisfactory explanation for the chemical shifts at this time. It is clear that above 24 °C chemical shifts differences as well as dipolar couplings are lost as the signals broaden and finally coalesce at about 52 °C. This can only be explained by a reorientation of the molecule.

The nearly spherical icosahedra of carbonyls in $\text{Co}_4(\text{CO})_{12}$ pack very efficiently in the solid. The carbonyl ligands mesh to some extent, and the closest contact between adjacent molecules is between carbonyl oxygens at 2.86 Å.^{6a} Thus it seems unlikely that the reorientation involves the rotation of the entire icosahedron. Furthermore, rotation of the entire icosahedron will not make all 12 carbonyl ligands equivalent.

Figure 2 shows a schematic representation of the molecular structure of $\text{Co}_4(\text{CO})_{12}$. The numbering scheme is consistent with that given by Johnson and Benfield, who have considered polytopal rearrangements of $\text{Co}_4(\text{CO})_{12}$ and its derivatives in solution.¹² In structure A of Figure 2 the cobalt labeled α represents the apical cobalt and is directed at face 4,5,9. Cobalts β , γ , and δ are directed at edges 7,8, 10,11, and 1,2, respectively. The bridging carbonyls are represented by the vertices 3, 6, and 12. Crystallographically the molecule occupies a site of two-fold symmetry. This gives rise to the disorder of the Co_4 tetrahedron. In Figure 2 the observed 2-fold axis is designated a ; structures A and B are related by the 2-fold axis and represent half-molecules in the crystal structure.

The result of the 2-fold rotation is to interchange carbonyls 1,2, 9,12, 4,11, 5,7, 8,10, and 3,6. Therefore this rotation is not sufficient to interchange all carbonyl sites. However at the temperatures reached in recording the NMR spectra (63 °C), it is possible that all possible orientations of the cobalt tetrahedron are observed, or, in other words, the apical cobalt, α , may be directed at any triangular face in the ligand icosahedron. Reorientation of the tetrahedron to point at an adjacent face requires a rotation of 36°. Adjacent faces, for example, are represented by 4,5,9 and 4,9,8 in structure A.

The activation energy for exchange in the solid, as estimated by the apparent coalescence temperature, ~ 52 °C, is not significantly greater than observed in solution, where the coalescence temperature may be estimated to be 30 °C.^{13,14} Thus it appears

that the intramolecular motion described here is only a slightly higher energy process than the fluxional process observed in solution. Also it should be noted that the proposed mechanisms to explain the solution dynamics^{12,15} involve expansion of the ligand icosahedron to a cuboctahedron, and this clearly cannot occur in the solid because of the constraints imposed by the lattice.

The reported temperatures in this study were measured by a thermocouple placed in the spinner air stream prior to the sample. Thus these represent an upper limit for the true sample temperature. Also it should be noted that 63 °C is above the reported melting point of $\text{Co}_4(\text{CO})_{12}$ (60 °C).¹⁶ Significant line broadening and coalescence, however, occur well below this temperature. Finally, when the rotor was opened after the high-temperature experiment, the sample showed no evidence of having melted; i.e., it was still a polycrystalline solid.

Acknowledgment. We thank the National Science Foundation for support of this work (Grant DMR-8211111).

Registry No. $\text{Co}_4(\text{CO})_{12}$, 17786-31-1.

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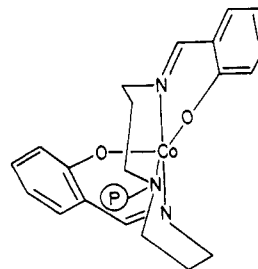
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Received November 21, 1985

Cobalt(II)-Facilitated Transport of Dioxygen in a Polystyrene Membrane

Sir:

Recently there has been considerable interest in the production of oxygen-enriched air by permselective polymer membranes.¹ We report here the enrichment of oxygen in an air sample that is passed through polystyrene which contains a supported Co(II) Schiff base complex as an additive. Subsequent to the start of our work selective transport of gases by metal complexes has been reported in liquid membranes.² Our work is novel in concept and mechanism for it incorporates addition of cross linked polymer bound CoSMDPT (SMPDT = *N,N*-bis(3-(salicylideneamino)-propyl)methylamine) particles



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- (13) The coalescence temperature for the carbon-13 NMR spectra of $\text{Co}_4(\text{CO})_{12}$ is not reported in the literature.¹¹ However, in the variable-temperature oxygen-17 NMR for $\text{Co}_4(\text{CO})_{12}$, coalescence is observed at ca. 57 °C at 54.25 MHz.¹⁴ Because of the greater chemical shift dispersion in oxygen-17 NMR coalescence is observed at a higher temperature.

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