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Is the Fe–C–O Moiety Linear or Bent in Heme Model Compounds? Evidence for Non-Axially Symmetric Shielding Tensors from ^{13}C CP MAS NMR Spectroscopy

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Heme model compounds have been widely used to understand the bonding of small molecules such as carbon monoxide to hemoproteins. The Fe–CO unit has been established crystallographically as being linear normal to the heme plane for several protein-free CO adducts of iron(II) porphyrins.[1–4] By contrast, crystallographic studies of several CO hemoproteins have been interpreted in favor of bent and/or tilted Fe–C–O moieties.[4–7] In this communication we report for the first time slow-spinning ^{13}C CP MAS NMR spectra of ^{13}CO (99% ^{13}C-enriched) in the structurally unhindered "picket-fence" model, Fe(CO)(TpivPP)(1-MeIm),[8,9] **1**, and in the structurally hindered complexes Fe(CO)(hybrid-C_{12})(1-MeIm),[3,9] **2**, Fe(CO)PBC$_{14}$(1-MeIm),[9] **3**, and Fe(CO)(C_2Cap)(1-MeIm),[9,10] **4** (Scheme I). The spectra enable the principal components of the ^{13}C shielding tensor to be calculated, which provide a sensitive probe of local Fe–CO geometry.

A typical spectrum of ^{13}CO in a heme model compound is shown in Figure 1. Spectra were recorded at several different speeds using both conventional cross-polarization and the nonquaternary suppression technique[11] to minimize overlap of sidebands with residual signals of the porphyrin skeleton. The intensities of the sidebands were analyzed using the method of Herzfeld and Berger[12,13] to yield values of the shielding tensor components σ_{11}, σ_{22} and σ_{33}. The results are summarized in Table I.

The ^{13}C shielding tensor for the picket-fence model **1** shows a small asymmetry ($\eta = 0.07$). Accurate X-ray structural data is not yet available on this compound, though Collman and collaborators have unpublished results suggesting that the Fe–CO linkage is strictly linear;[14] they indicated, however, that the accurate determination of the carbon atom position in the Fe–CO linkage demanded X-ray data of much higher resolution than currently available. It is worth noting that the shielding tensor components for CO in **1** (Table I) are significantly different from those obtained indirectly by variable field T_1 relaxation time measurements on the closely related complex of 1-MeIm-iron-protoporphyrin dimethyl ester ($\sigma_{11} = \sigma_{22} = -400.8$; $\sigma_{33} = 183.2$ ppm).[15]

An asymmetry in the shielding tensor must result either from a nonlinear Fe–C–O moiety or alternatively from molecular asymmetry or crystal packing affecting the electronic distribution at the carbon atom. However, detailed X-ray structural studies of deoxy and oxygenated picket-fence porphyrins show that there are no intermolecular contacts less than 3.5 Å,[8] and the geometry of the porphyrin nitrogens around the iron center is close to square symmetry. We therefore conclude that the major effect on the anisotropy is due to a bending of the Fe–C–O group. For CO in compound **1**, the small asymmetry observed may be ascribed to weak dipole–dipole interactions with the distal amide groups of the pickets. This interpretation is supported by the fact that there is an increase in the CO dissociation rate constant from the picket-fence porphyrin with reversed (PhCONH) amide pickets.[16] It is also supported by approximate CFF calculations which indicate weak attractive interactions between the CO ligand and the pickets.[17]

For CO in the sterically hindered hybrid model compound **2**, which has two pivalamido pickets, one on each side of a C_{12} diamido handle, linked in a cross configuration, the shielding tensor was found to be symmetric within experimental error. This is consistent with X-ray structural data which shows that the Fe–C–O group is linear in this compound.[3] All contacts with the terminal oxygen atom and polymethylene chain were found to be larger than 4 Å and so not capable of inducing an Fe–C–O deformation.

For the CO in the sterically hindered compound **3** there is a significant increase in the asymmetry of the shielding tensor ($\eta = 0.23$). There are a shift to high frequency of the σ_{11} shielding component and a shift to low frequency of the σ_{22} component, while the σ_{33} component remains unchanged relative to CO in compounds **1** and **2**. Thus while the isotropic chemical shift remains essentially the same, a change in local geometry is manifested by the change in the asymmetry of the shielding tensor. This asymmetry provides strong evidence for a large deviation from linearity of the Fe–C–O unit due to steric interactions with the distal protecting chain. This deviation from linearity, with associated bond weakening, is probably the cause of the markedly higher CO desorption rate from compound **3** compared to that of structurally unconstrained compounds.[18]

There has been an X-ray structure determination of CO in compound **4** at −150 °C which suggested that there are two Fe–

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(9) Abbreviations: TpivPP, $\alpha,\alpha,\alpha,\alpha$-*meso*-tetrakis(*o*-pivalamidophenyl)porphinato; 1-MeIm, 1-methylimidazole; hybrid-C_{12}, 5,15-[decanediylbis[*o*-carbonylamino)phenylene]]-α,α-10,20-bis[*o*-(pivaloylamino)phenyl]porphyrin; PHC$_{14}$, porphyrin bridged with C_{14} polymethylene "handle" in a cross configuration; C_2Cap, 5,10,15,20-[pyromellitoyltetrakis[*o*-(oxypropoxy)phenylene]] porphyrin.

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(18) The dissociation rate constant for CO desorption from Fe(CO)PHC$_{14}$(1-MeIm) is 0.12 s^{-1}.

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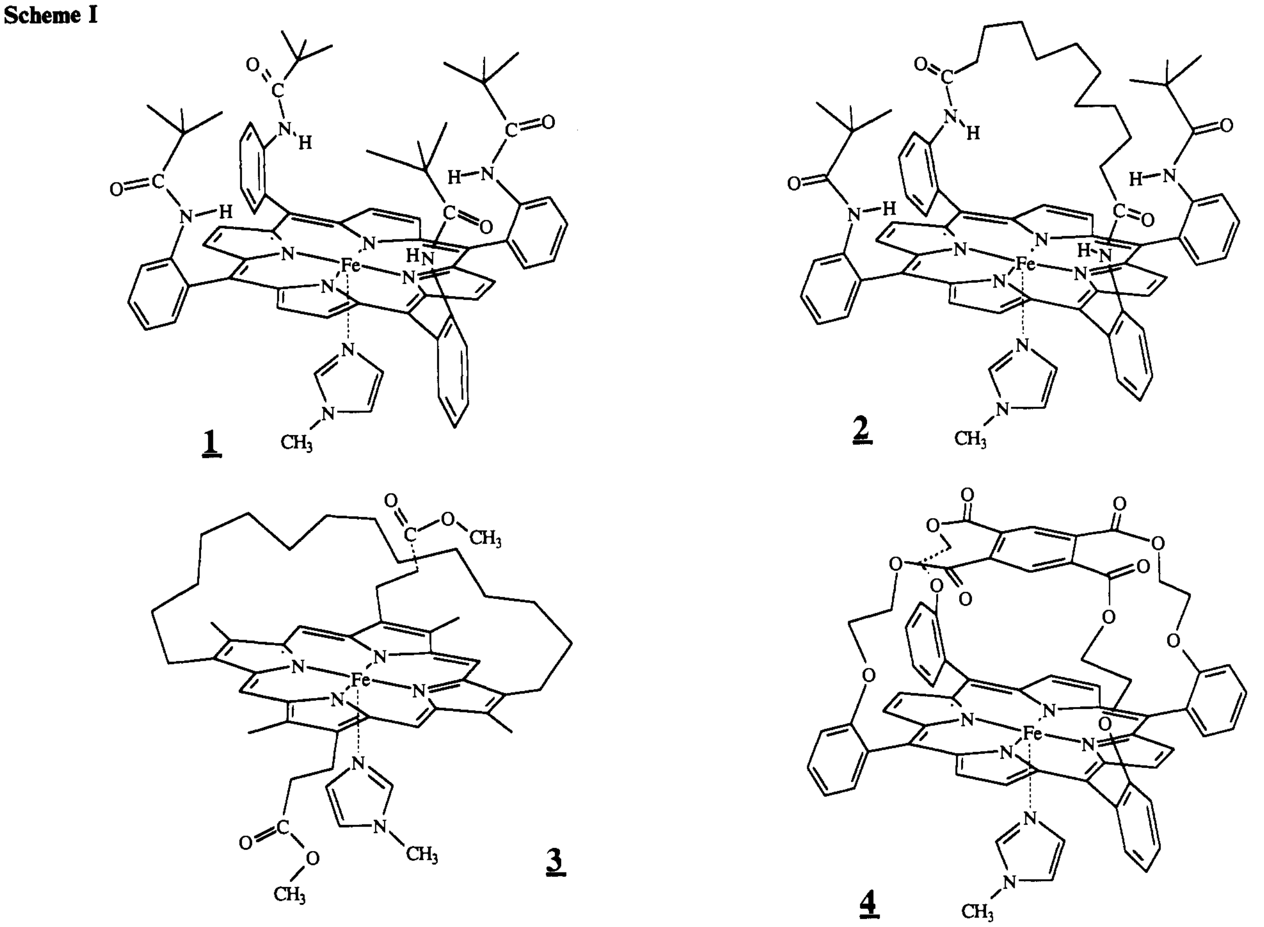
Scheme I



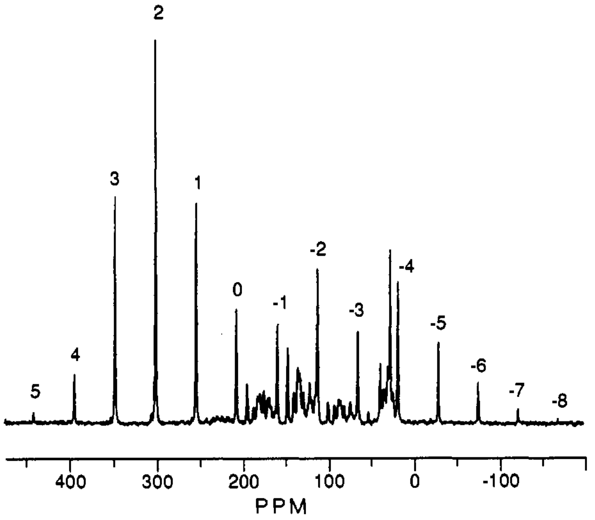


Figure 1. ^{13}C CP MAS NMR spectra of ^{13}CO in compound **2** (spinning speed 3538 Hz, 8-ms contact time, 1-s recycle delay, number of scans 18 000, and line broadening 20 Hz). The assignment of spinning sidebands is shown. All spectra were acquired on a Bruker MSL-300 spectrometer at a frequency of 75.46 MHz. The samples were spun in sealed glass ampules at speeds of between 2.4 and 4 kHz.

Table I. Principal Components of the Shielding Tensor of ^{13}CO in the Compounds Shown in Scheme I[a,b]

compd	temp/K	σ_{iso}	σ_{11}	σ_{22}	σ_{33}	$\Delta\sigma$	η
1	297	−205.0	−364	−346	+95	450	0.07
2	297	−205.0	−355	−354	+94	449	0.00
3	297	−205.0	−389	−320	+94	449	0.23
4	297	−202.5	−361	−335	+90	443	0.10

[a] Shieldings, σ, are given in parts per million relative to TMS. Note that the sign of shielding is opposite to that of chemical shift on the δ scale. The anisotropy $\Delta\sigma$ is defined as $\sigma_{33} - 0.5(\sigma_{11} + \sigma_{22})$, and the asymmetry parameter, η, by $(\sigma_{22} - \sigma_{11})/(\sigma_{33} - \sigma_{iso})$, where $\sigma_{iso} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$. [b] The estimated uncertainty in the σ values is ±15 ppm. The estimated uncertainty in η is ±0.07.

C–O geometries present, one with a bond angle of 175.9° and the other with an angle of 172.9°.[19] The NMR spectrum shows only a single peak, possibly because any different CO environments have the same isotropic chemical shift (within 0.5 ppm). The shielding tensor does show a small deviation from axial symmetry, but surprisingly this is still comparable with that of the picket-fence model.

In conclusion, ^{13}C CP MAS NMR spectroscopy has been used for the first time to gain detailed information on the local electronic environment of the ^{13}C nucleus of CO in heme model compounds.

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