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Swinging of the Bent Nitrosyl Ligand in [Co(^{15}NO)(TPP)]: A Solid-State Motion Detected by ^{15}N CPMAS NMR Spectroscopy

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In our studies of a range of bent (and linear) nitrosyl complexes by ^{15}N CPMAS NMR spectroscopy,[1] we observed partially averaged spectra for the *meso*-tetraphenylporphinato complex [Co(^{15}NO)(TPP)] above 220 K, showing that the nitrosyl is spinning, or more probably swinging, in the solid state.

[Co(^{15}NO)(TPP)] was shown by X-ray crystallography[2] to have square pyramidal coordination of the cobalt with a bent apical nitrosyl. Solution spectra (Table I) are as expected for a bent nitrosyl.[3] [Co(^{15}NO)(TPP)], octaethylporphinate [Co(^{15}NO)(OEP)], and [Co(^{15}NO)(esal)$_2$] (in which bidentate Schiff base ligands form the basal plane and the CoNO angle is 129°)[1] all show strong deshielding of the nitrosyl nitrogen (δ 740–770 ppm), and also of cobalt (δ 8000–9000 ppm). In the solid state [Co(^{15}NO)(TPP)] gives a normal isotropic ^{15}N shift; but CPMAS spectroscopy at temperatures down to 220 K yields an unexpectedly narrow pattern of spinning sidebands, as shown in Figure 1, with a span ($\delta_{11} - \delta_{33} = \Omega$) of 242 ppm; furthermore, the shielding tensor[4] has axial symmetry. These properties are quite inappropriate to a bent nitrosyl: thus the shielding tensor for [Co(^{15}NO)(esal)$_2$] has a span of 1933 ppm, and is markedly asymmetric[1] (Table I).

At 200 K, however, [Co(^{15}NO)(TPP)] shows the larger manifold of sidebands that was expected, with a span of 1655 ppm. The shielding tensor no longer has axial symmetry and is comparable to those observed for other bent nitrosyls of cobalt, [Co(^{15}NO)(esal)$_2$] for example. Yet there is no significant change in the isotropic shift, and the infrared absorption (1800–650 cm^{-1}, Nujol mull) is unchanged from room temperature to well below 200 K. There must, therefore, be an internal motion which partially averages the shielding tensor at higher temperatures and involves only bent conformers, since the isotropic shift and the infrared absorption are unaffected. It cannot be a bent–linear or "kicking" motion as observed for the 5-coordinate complex [RuCl(NO)$_2$(PPh$_3$)$_2$]$^+$, which has one bent and one linear nitrosyl in the crystal,[5] but in solution shows averaging of the nitrogen shift and an ^{14}N,^{15}N equilibrium isotope effect in the semienriched compound.[6] The only degree of freedom of the nitrosyl in [Co(^{15}NO)(TPP)] is change in the torsion angle relative to the C_4 axis of [Co(TPP)], i.e. nitrosyl swinging or spinning.

The sideband line widths are constant at all temperatures (Figure 1), whereas intermediate exchange rates would broaden the lines.[7] We concluded that the change is discontinuous: that some relaxation of the crystal packing, perhaps movement of the pendent phenyl groups, in a phase transition in the range 200–220 K, allows the nitrosyl to swing or spin above this temperature. This conclusion was confirmed by differential scanning calorimetry[8] over the range 163–273 K, which clearly showed a phase change (only) at 206.7(4) K, with $\Delta H = 649(3)$ J mol^{-1}. The barrier to the motion is likely to be intermolecular, or largely so.

In the absence of intermediate rate behavior the NMR evidence does not distinguish discrete swings from free spinning; but the disorder revealed by the X-ray structure of [Co(NO)(TPP)], as in the "hydra"[9] picture (Figure 2) from Scheidt and Hoard's paper,[2] suggests swinging between four sites. As well as 2-fold disorder of the cobalt, there is 4-fold disorder of the nitrosyl (in a given molecular orientation). The nitrosyl oxygen (which avoids electron donors in the plane) lies above a gap between two CoN$_4$ bond directions, so pointing in the direction of a phenyl group.

A full theory of spinning sideband patterns with motional exchange is difficult, and computations are lengthy, but limiting slow and fast cases can be calculated simply,[10] giving Euler angles for the tensor components relative to the motional axis (C_4). Principal axes of the shielding tensor are expected to be near the NO bond axis for the axis of greatest deshielding δ_{11}, because of the low energy of the $n_N \rightarrow \pi^*$ circulation; with the δ_{33} axis perpendicular to the CoNO plane, so that this paramagnetic circulation is orthogonal to the low-lying π^*NO orbital.[1,3] Transformation of the components measured at 200 K to a set of principal axes defined by C_4 symmetry and simple averaging of the four positions give the apparent chemical shift tensor components, for rapid four-site exchange, as

$$\delta_{\parallel} = 1717 \cos^2 \theta + 490 \sin^2 \theta$$

$$\delta_{\perp} = {}^{1}/_{2}(62 + 1717 \sin^2 \theta + 490 \cos^2 \theta)$$

where θ is the angle between the C_4 and δ_{11} axes. A mean value

Table I. Spectroscopic Properties of Square Pyramidal Complexes of Cobalt with Bent Apical Nitrosyl

	^{59}Co params^a			^{15}N params^b							
nitrosyl compd	T (K)	δ_{soln}	$W_{1/2}$ (Hz)	$\delta_{soln}{}^d$	δ_{solid}	$\delta_{\parallel}$		$\delta_{\perp}$	Ω^e	κ^f	$\nu(^{14}NO)^c$ (cm^{-1})
[Co(^{15}NO)(TPP)]	298	7909	4250	770.7	765.0	926(20)		684(10)	242(30)	1.0	1690
	260				760.8	929(26)		677(13)	252(50)	1.0	
	220				757.6	936(30)		668(15)	268(45)	1.0	
						δ_{11}	δ_{22}	δ_{33}			
	200				757.2	1717(48)	490(33)	62(65)	1655(76)	0.48(0.10)	1690
[Co(^{15}NO)(OEP)]	298	8113	3000	760.1							1675
[Co(^{15}NO)(esal)$_2$]^g	298	9662	1150	739.7	741.9	1959(13)	240(21)	26(16)	1933(25)	0.78(0.03)	1645

^{a} Cobalt shifts are in ppm relative to [Co(CN)$_6$]$^{3-}$(aq). ^{b} Nitrogen shifts are in ppm relative to neat liquid nitromethane. Uncertainties in the tensor parameters express 95% confidence intervals. Where none are given, the fit was constrained to axial symmetry. ^{c} KBr disk. ^{d} In CD$_2$Cl$_2$. ^{e} Ω = span = $\delta_{11} - \delta_{33}$. ^{f} κ = skew = $3(\delta_{iso} - \delta_{22})/(\delta_{11} - \delta_{33})$. ^{g} Reference 1.

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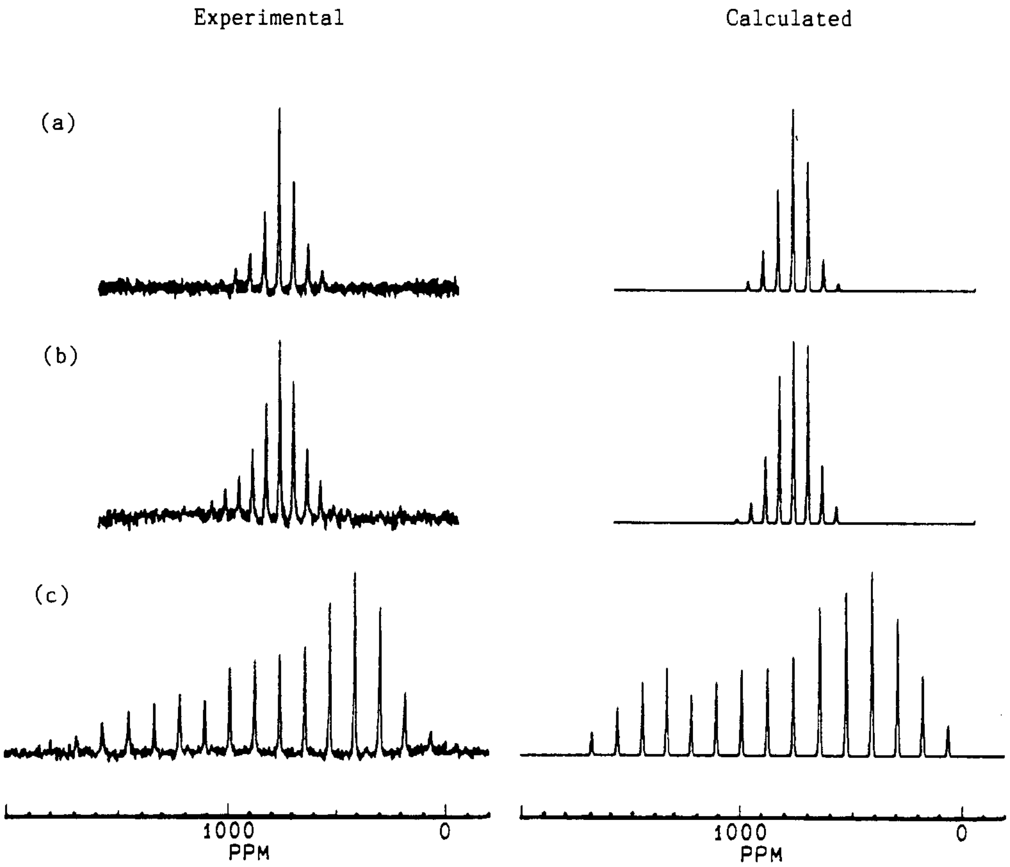

Figure 1. ^{15}N CPMAS solid-state NMR spectra of [Co(^{15}NO)(TPP)]: experimental and calculated spinning sideband patterns. The computed sideband intensities were obtained from the principal components (in Table I): (a) 260 K (spinning rate 2.03 kHz); (b) 220 K (1.91 kHz); (c) 200 K (3.55 kHz).

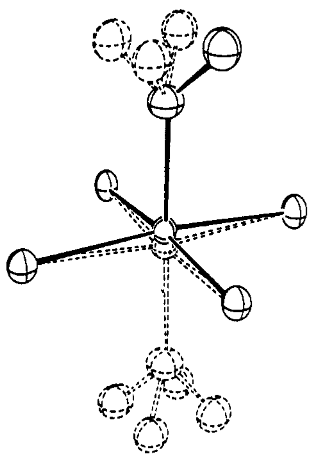

Figure 2. Diagram showing the statistical disorder of the $Co(N_4)(NO)$ group in the tetragonal crystal of [Co(NO)(TPP)]; a single orientation is given in solid lines. Figure reproduced with permission from ref 2.

of 254 ppm for the span ($\delta_{\parallel} - \delta_{\perp}$) observed at 220 K and above gives $\theta = 53°$, corresponding to ∠CoNO = 127°.

In the X-ray determination, indirect evidence gave the cobalt displacement from the centre of the statistically averaged C_{4h} molecule as 0.094(52) Å and of the nitrosyl nitrogen from the C_4 axis as ≥0.10 Å.[2] The averaged model gives ∠CoNO = 135.2° and an NO bond length which is too short. When the authors allow for the displacement of the cobalt and the nitrogen they obtain a normal NO bond length and a CoNO angle ≤128.5°,[2] in agreement with our value of 127°.

Our work suggests that apparent anisotropies recorded for bent nitrosyls may be reduced somewhat by small-angle oscillations of the nitrosyl ligand.

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