Nitrogen-15 N.M.R. Characterization of Bent and Linear Nitrosyl Ligands in the Solid State by Cross-polarisation Magic-angle-spinning Spectroscopy of Complexes of Ruthenium

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High-resolution cross-polarisation magic-angle spinning (CP/MAS) ^{15}N n.m.r. spectroscopy of solid [RuCl(NO)$_2$(PPh$_3$)$_2$](BF$_4$) shows a large chemical shift anisotropy for the bent as compared with the linear nitrosyl ligand (in contrast to solution ^{15}N n.m.r. which shows a bent–linear ligand fluxionality): in solid [Ru(NO)$_2$(PPh$_3$)] the two near-linear nitrosyls, with Ru–N–O bond angles differing by 7°, are clearly distinguished.

We present the first report of high-resolution solid state ^{15}N n.m.r. spectroscopy of nitrogen-containing ligands in metal complexes. ^{15}N N.m.r. spectroscopy has proved to be a sensitive indicator of nitrosyl structures in solution.[1—4] As shown in Table 1, the nitrogen shift in related complexes of ruthenium increases (the shielding decreases) by ca. 90 p.p.m. from a linear mononitrosyl (1) to a dinitrosyl (2) with slightly bent NO ligands, and by a further 290 p.p.m. to the strongly

Table 1. Nitrogen n.m.r. and i.r. spectroscopic measurements of ruthenium nitrosyl complexes with different nitrosyl geometries.

Compound	Co-ordination geometry	M–N–O /°	v(^{14}NO)[a] /cm^{-1}	Solvent or state	δ^{15}N[b] p.p.m.
trans-[RuCl$_3$(^{15}NO)(PPh$_3$] (1)	Octahedral	180	1876	CD$_2$Cl$_2$	−36.7^c
[Ru(^{15}NO)$_2$(PPh$_3$)$_2$] (2)	Distorted tetrahedral	178, 171^d 175, 168^f	1665, 1615	C$_6$D$_6$ solid	50.7^e 37 40
trans-[RuCl(CO)(^{15}NO)(PPh$_3$)$_2$] (3)	Square pyramidal	~120		C$_6$D$_6$	342.3^e
[RuCl(^{14}NO)(^{15}NO)(PPh$_3$)$_2$](BF$_4$) (4)	Fluxional		1828, 1778 }$_g$ 1739sh,1722	(CD$_3$)$_2$CO	131.2 }$_h$ 130.2
	Square pyramidal	179.5^i 136^i	1845 1687	solid	26 303

[a] Nujol mull unless a solvent is specified. [b] Relative to neat liquid nitromethane, high frequency positive. The solid state values are from Table 2. [c] Ref. 1. [d] Ref. 15. [e] Ref. 2. [f] Ref. 14. [g] Methanol solution. [h] Ref. 7, $^2J(^{31}P^{15}N)$ 2.5 Hz. [i] Ref. 5.
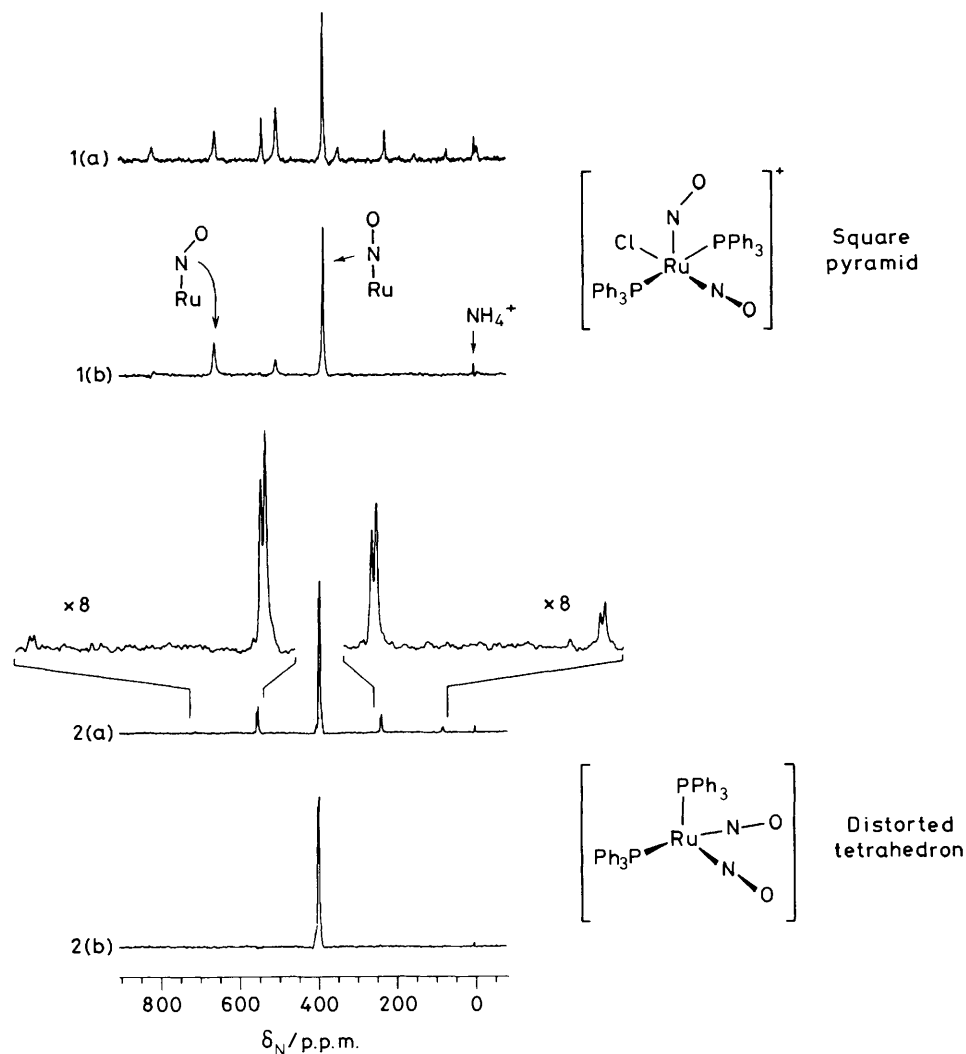
Figures 1 and 2. ^{15}N CP/MAS spectra measured at 4.70 T with MAS at 3206 Hz, without (a) and with (b) total suppression of sidebands. Figure 1: *trans*-[RuCl(^{14}NO)(^{15}NO)(PPh$_3$)$_2$](BF$_4$), (**4**). Figure 2: [Ru(^{15}NO)$_2$(PPh$_3$)$_2$], (**2**).

Table 2. ^{15}N N.m.r. shift tensor components measured by CP/MAS spectroscopy.[a]

	ω_{zz}	ω_{xx}	ω_{yy}	ω_o	δ	η	δ^{15}N[b]	Δ
(**2**)	176	508	508	397	−221	0	37	−331
	189	505	505	400	−211	0	40	−316
(**4**)	91	533	533	386	−295	0	26	−442
	1218	318	453	663	+555	0.24	303	+832

[a] The tensor components ω_{ii} are in p.p.m. (high frequency positive) relative to (NH$_4$)$_2$SO$_4$(s), for which δ ^{15}N is −360 p.p.m. relative to MeNO$_2$(l) and +20 p.p.m. relative to NH$_3$(l). The uncertainty in the line positions is 0.5 p.p.m., and in the tensor components *ca.* 2 p.p.m. (relative), 20 p.p.m. (absolute), 30 p.p.m. for the bent nitrosyl. The tensor components are ordered by the inequalities $|\omega_{zz} - \omega_o| \geqslant |\omega_{xx} - \omega_o| \geqslant |\omega_{yy} - \omega_o|$, where the isotropic shift ω_0 is defined by $\omega_0 = (\omega_{xx} + \omega_{yy} + \omega_{zz})/3$; the anisotropy Δ is equal to $3\delta/2$, where $\delta = \omega_{zz} - \omega_0$, and the anisotropy factor η is given by $\eta = (\omega_{yy} - \omega_{xx})/\delta$ (ref. 16). [b] Relative to Me$_3$NO$_2$(l), high frequency positive.

bent apical nitrosyl in (**3**). In our solution studies of the 5-co-ordinate complex [RuCl(^{15}NO)$_2$(PPh$_3$)$_2$](BF$_4$),[3] however, we obtained a single ^{15}N resonance over the range

183—300 K, although single crystal X-ray crystallographic work had shown the presence of bent apical and linear equatorial nitrosyl ligands.[5] A fluxional process interconverting bent and linear nitrosyl sites had been proposed to explain the complexity of i.r. spectra of a 50% ^{15}N-enriched sample, (**4**).[6] Consistent with this proposal, we observed a doubling of the ^{15}N resonance in such solutions, demonstrating a ^{14,15}N equilibrium isotope effect in the fluxionality.[7] We therefore undertook cross-polarisation magic-angle-spinning (CP/MAS) ^{15}N n.m.r. spectroscopy[8] of these metal complexes to explore its potential for defining nitrosyl geometries in the solid state, as well as to supply the nitrogen shifts of the bent and linear ligands with which to interpret the averaged resonances given by the solutions.[7]

Figures 1 and 2 show two types of spectra, obtained with standard CP/MAS, the first (a) giving spinning sidebands from which the components of the shift tensor may be derived,[9] the second (b) with total suppression of sidebands[10] to identify the isotropic shifts. The [RuCl(^{14}NO)(^{15}NO)(PPh$_3$)$_2$](BF$_4$) spectra (Figure 1) establish that it is not fluxional in the solid at ambient temperatures. Two shift tensors are obtained which are characteristic of a linear and a bent nitrosyl (Table 2). One is axially symmetric with quite a large anisotropy, −442 p.p.m., which is comparable with that of the middle nitrogen

in N_2O, -508 p.p.m.[11] The other shift tensor, that of the bent nitrosyl, is asymmetric ($\eta \neq 0$) and its anisotropy, $+832$ p.p.m., represents a larger (absolute) value than the largest previously observed for nitrogen, -603 (or -657) p.p.m. in the N_2 molecule[12a] and 672 p.p.m. in pyridine.[12b] For a linear geometry the highest shielding (lowest shift) component is the axial one, corresponding to free diamagnetic circulation. In the bent nitrosyl the most extreme component corresponds to *deshielding*, by excitations of $n(N) \rightarrow \pi^*$ type; the latter effect is particularly strong for the low-lying $\pi^*(NO)$ orbital.[13] The two observed isotropic shifts, 26 and 303 p.p.m., are characteristic of the linear and bent geometries, as shown by the comparison with compounds (1)—(3), (3) and (4) being isoelectronic.

The ^{15}N spectra of $[Ru(^{15}NO)_2(PPh_3)_2]$, (2), show the sensitivity of the CP/MAS technique as a probe of nitrosyl geometry. No crystallographic symmetry is imposed on the molecule, and the Ru–N–O bond angles differ by (only) 7° in the solid (*cf.* Table 1).[14,15] The ^{15}N CP/MAS spectra (Figure 2) show resonances with isotropic shifts of 40 and 37 p.p.m. arising from the different nitrosyl environments, and shift tensors which are comparable to that of the linear nitrosyl in (4). The mean of the shifts, 38.5 p.p.m., involves a shift of *ca.* -12 p.p.m. (increased shielding) relative to the shift in benzene solution, which can be attributed to effects of solvation. In the 5-co-ordinate complex (4), however, the mean of the linear and bent nitrosyl shifts in the solid state represents a shift of *ca.* $+35$ p.p.m. (*deshielding*) relative to the solution shift. This accords with the evidence, from the temperature-dependence of the equilibrium isotope effect, for an additional contribution to the fluxional process in solution, probably from a trigonal bipyramidal structure with two linear nitrosyls.[7]

Clearly, CP/MAS n.m.r. spectroscopy is a useful, and sensitive, alternative to single crystal X-ray crystallography for distinguishing the bent and linear geometries in the solid state. In the $[RuCl(NO)_2(PPh_3)_2]^+$ studies a knowledge of the solid state isotropic shifts has been essential to the analysis of the fluxional equilibrium system in solution.[7]

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