Oxygen-17 N.M.R. Study of Linkage Isomerization in Nitritopenta-amminecobalt(III): Evidence for Intramolecular Oxygen Exchange

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[17]O N.m.r. spectroscopy of specifically labelled $Co(NH_3)_5(ONO)^{2+}$ shows that spontaneous intramolecular O-to-O exchange in the nitrite ligand occurs at a rate comparable to that of the spontaneous O-to-N isomerization.

Extensive studies of the kinetics and mechanisms of the nitrito-to-nitro intramolecular linkage isomerization of co-ordinated nitrite have been reported,[1] but despite this activity it was only recently that both base catalysis[2] and metal ion catalysis[3] of the isomerization were detected. The base-catalysed path also occurs by an intramolecular path and presumably is effected by the same labilizing process which leads to loss of some ligands from the conjugate base (S_N1cb process). However, ^{18}O-labelling experiments produced a surprising result. The presumed specifically-labelled $[Co(NH_3)_5(ON^{18}O)]^{2+}$ or $[Co(NH_3)_5(^{18}ONO)]^{2+}$ ions, prepared by allowing $[Co(NH_3)_5(OH)]^{2+}$ to react with $N^{18}O^+$ or $[Co(NH_3)_5(^{18}OH)]^{2+}$ with NO^+, respectively, were subsequently decomposed either in acid solution or in the presence of acid and N_3^-. Cleavage of the nitrito-ligand before rearrangement produced

in each case $[Co(NH_3)_5(^{18}OH_2)]^{3+}$ containing 50% of the original label.[2]

There appear to be three possible ways in which the observed oxygen scrambling can occur in these experiments: i, during formation of $[Co(NH_3)_5(ONO)]^{2+}$, if NO^+ attacks a filled non-bonding d-orbital and then captures either of the bound oxygen atoms; ii, if rapid intramolecular oxygen exchange occurs spontaneously; iii, if facile acid-catalysed scrambling occurs during the cleavage process.

In elucidating this problem, we have applied [17]O n.m.r. spectroscopy, using complexes labelled with [17]O (20% enriched) at different sites.

The complexes $[Co(NH_3)_5(^{17}ONO)]^{2+}$ and $[Co(NH_3)_5(ON^{17}O)]^{2+}$ were prepared from labelled $[Co(NH_3)_5(^{17}OH_2)]^{3+}$ and unenriched $[Co(NH_3)_5(OH_2)]^{3+}$, respectively, by reaction
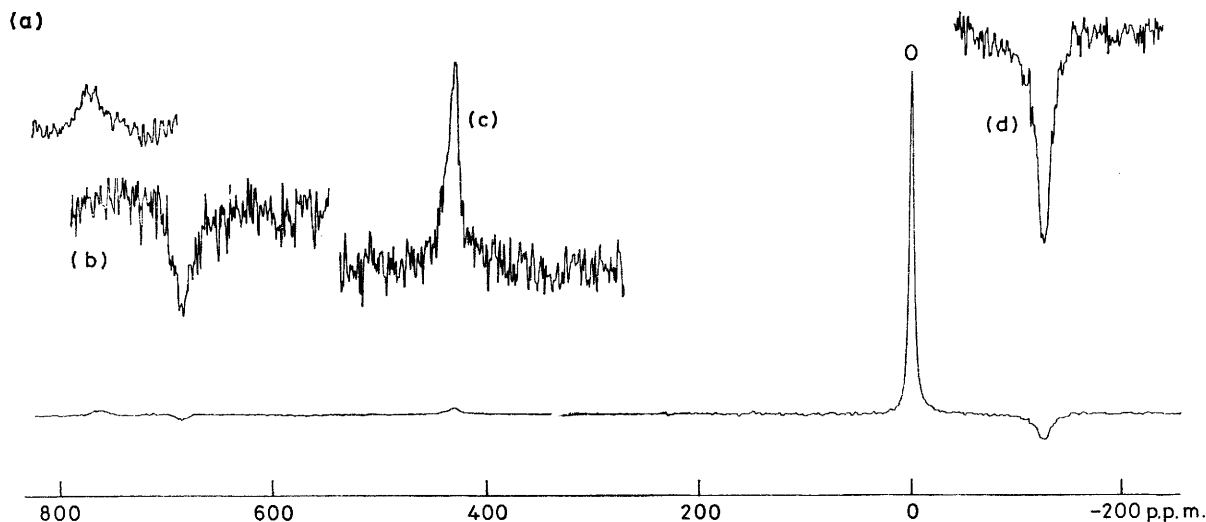
Figure 1. [17]O N.m.r. spectra of (a) $[Co(NH_3)_5(ON^{17}O)]^{2+}$, (b) $[Co(NH_3)_5(N^{17}O_2)]^{2+}$, (c) $[Co(NH_3)_5(^{17}ONO)]^{2+}$, and (d) $[Co-(NH_3)_5(^{17}OH_2)]^{3+}$, measured relative to $^{17}OD_2$ at 25 °C using saturated solutions of 20% enriched samples and an accumulation time of only 10 min. (In low field instruments, the pulse sequence introduces phase correction problems for multiple line spectra, and hence some peaks are inverted.[11])

with either HNO_2 or $HN^{17}O_2$, as described for the ^{18}O-analogues.[2] The nitrito-complex was converted into the nitro-complex in solution by heating. Spectra were recorded in D_2O on a Jeol FX90Q FT-n.m.r. spectrometer with natural abundance $D_2{}^{17}O$ as internal reference. The three complexes exhibited well separated characteristic single ^{17}O-chemical shifts (Figure 1), corresponding to resonances reported for organic analogues[4] (Table 1). Clearly, the complexes were regio-specifically labelled by the synthetic routes employed, which excludes the possibility of rapid oxygen scrambling during formation, and rapid spontaneous oxygen scrambling. Further, when either $[Co(NH_3)_5(^{17}ONO)]^{2+}$ or $[Co(NH_3)_5-(ON^{17}O)]^{2+}$ was cleaved with acid in the n.m.r. tube, a signal due to $[Co(NH_3)_5(^{17}OH_2)]^{3+}$ was observed in each case (Figure 2). For identical concentrations of the initial complexes, the aqua-product ^{17}O-signal intensities were the same. These observations parallel the results of earlier ^{18}O experiments,[2] and establish that the scrambling of oxygen atoms occurs during acid cleavage.
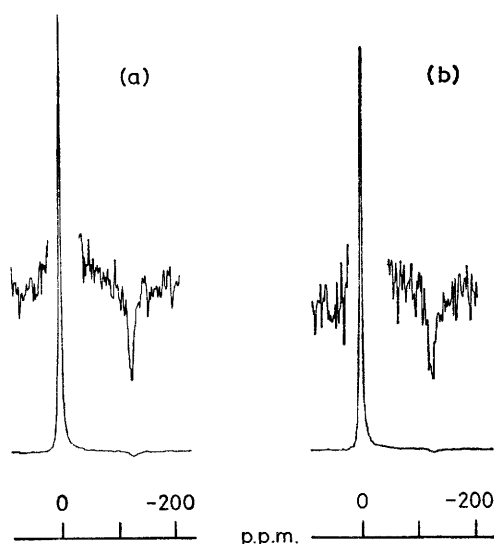
While very rapid oxygen scrambling in solution was not observed, we pursued the prospect of slow $O \rightarrow O$ site exchange further. When a solution of specifically labelled nitrito-complex was allowed to isomerize spontaneously in solution and consecutive ^{17}O n.m.r. spectra were recorded, two observations were made. First, the expected signal due to the N-bound isomer appeared. Secondly, an additional peak due to the alternately-labelled nitrito-isomer grew and subsequently decayed to that of the nitro-isomer with time. Clearly, slow $O \rightarrow O$ scrambling of the ligand competes with the $O \rightarrow N$ process, although the nitro-isomer is present to $>99\%$ at equilibrium (Scheme 1).

$$M-^{17}ONO \overset{k_e}{\underset{k_e}{\rightleftharpoons}} M-ON^{17}O$$

$$M-NO^{17}O$$
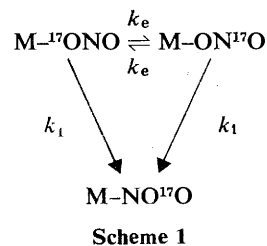
Scheme 1

From peak areas of different isomers in consecutive spectra, and a graphical analysis of these experimental data for the type of scheme previously described,[5] we have obtained a rate ratio for the $O \rightarrow O$ vs. the $O \rightarrow N$ process, k_e/k_1, determined as 1·2 at 25 °C (error ca. 10%). Further, k_1 measured by this method agrees with that reported previously. Since $k_e = 1·2 \times k_1$, it is clear that both O and N are effective competitors for the metal ion during the spontaneous isomerization. Although O-to-O interconversion has been observed previously in other complexes,[6] this is the first evidence for competitive capture of different atoms on the same donor ligand.

Figure 2. [17]O N.m.r. spectrum of $[Co(NH_3)_5(^{17}OH_2)]^{3+}$ obtained following in situ acid cleavage of identical concentrations of (a) $[Co(NH_3)_5(ON^{17}O)]^{2+}$ and (b) $[Co(NH_3)_5(^{17}ONO)]^{2+}$.

Table 1. [17]O Chemical shifts of nitrito- and nitro-compounds.[a]

Compound[b]	δ/p.p.m.	Compound[c]	δ/p.p.m.
$[Co(NH_3)_5(^{17}ONO)]^{2+}$	430	$Me^{17}ONO$	420
$[Co(NH_3)_5(ON^{17}O)]^{2+}$	790	$MeON^{17}O$	790
$[Co(NH_3)_5(N^{17}O_2)]^{2+}$	690	$MeN^{17}O_2$	590
$[Co(NH_3)_5(^{17}OH_2)]^{3+}$	—125	$Me^{17}OH$	—40

[a] Relative to $^{17}OD_2$. [b] This work. [c] Refs. 4, 11.

(I)   (II)

(III)
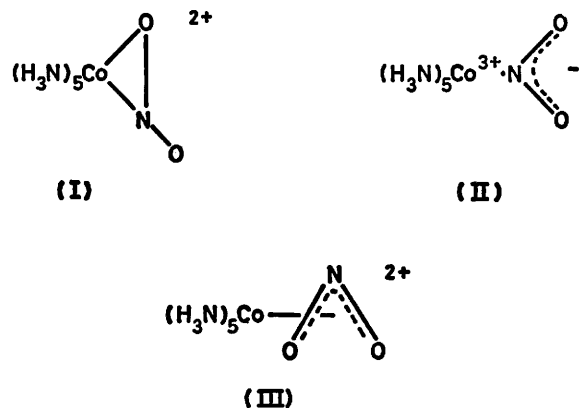
At least three possible intermediates consistent with the intramolecular nature of the O → N spontaneous isomerization can be contemplated; these are a heptaco-ordinate transition state (I), a pentaco-ordinate tight ion-pair (II), or a hexaco-ordinate π-bonded species (III). The ion-pair formulation is unlikely, since ion pairs readily dissociate in water, and no exchange with added labelled nitrite occurs.[7] Such an intermediate assemblage would require a lifetime equal to or less than the collision-to-collision lifetime, and very efficient donor atom capture. Further, the negative volume of activation is inconsistent with an expanded transition state.[8] An intermediate like (I), although consistent with the known O → N process,[9] cannot accommodate the spontaneous O → O scrambling we observed. Likewise, a heptaco-ordinate intermediate with both O-donors bound could accommodate the O → O but not the O → N process. However, a π-bonded intermediate (III) would accommodate all the observations reported. It would allow an almost equally effective competition by both oxygen atoms and the nitrogen atom for the

metal ion from the activated state. It is also consistent with the negative volume of activation[8] and the retention of a cobalt–nitrite bond.[7] Independent experiments clearly show that both O and N of NO_2^- can compete for the $[Co(NH_3)_4-(NH_2)]^{2+}$ pentaco-ordinate intermediate,[10] hence the similar competition abilities of O and N in intermediate (III) are reasonable in the light of this evidence.

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References

1 W. G. Jackson and A. M. Sargeson, 'Rearrangements in Co-ordination Complexes' in 'Rearrangements in Ground and Excited States,' ed. P. de Mayo, Academic Press, New York, 1979.
2 W. G. Jackson, G. A. Lawrance, P. A. Lay, and A. M. Sargeson, *Inorg. Chem.*, 1980, **19**, 904.
3 W. G. Jackson, G. A. Lawrance, P. A. Lay, and A. M. Sargeson, *Aust. J. Chem.*, to be published.
4 L.-O. Andersson and J. Mason, *J. Chem. Soc., Dalton Trans.*, 1974, 202.
5 M. L. Bender, *J. Am. Chem. Soc.*, 1951, **73**, 1626; R. A. Alberty and W. G. Miller, *J. Chem. Phys.*, 1957, **26**, 1231.
6 C. Anrade, R. B. Jordan, and H. Taube, *Inorg. Chem.*, 1970, **9**, 711; L. M. Jackman, J. F. Dormish, R. M. Scott, R. H. Portman, and R. D. Minard, *ibid.*, 1979, **18**, 1503.
7 R. K. Murmann and H. Taube, *J. Am. Chem. Soc.*, 1956, **78**, 4886; R. K. Murmann, *ibid.*, 1955, **77**, 5190.
8 M. Mares, D. A. Palmer, and H. Kelm, *Inorg. Chim. Acta*, 1978, **27**, 153.
9 F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1968.
10 W. G. Jackson, unpublished work.
11 J.-P. Kintzinger, 'Oxygen-17 NMR,' in 'NMR: Basic Principles and Progress,' eds. P. Diehl, E. Fluck, and R. Kosfield, Springer–Verlag, Berlin, 1980, vol. 17, pp. 1—65.