Nitrogen-14 Nuclear Magnetic Resonance Study of some Diamagnetic Covalent Metal Nitrates

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^{14}N N.m.r. spectroscopy has been used to investigate the nature of species in non-aqueous solutions of some covalent diamagnetic metal nitrato-compounds. Certain covalent nitrates of non-metals have also been studied for purposes of comparison. Solutions of the metal nitrates in CCl_4 and $MeNO_2$ show chemical shifts which clearly indicate their covalent nature but fail to distinguish the bonding mode. Solutions in electron-pair donor solvents exhibit generally lower shifts, attributed to partial dissociation of nitrate ligands as a result of solvent-donor and dielectric influences. The suitability of pure nitric acid as a solvent and reaction medium for covalent metal nitrato-compounds has also been examined by the ^{14}N n.m.r. technique.

THE ability of the nitrate group to behave as a unidentate, $MONO_2$, bidentate, MO_2NO, bridging bidentate, MON(O)OM, or bridging terdentate, MON(OM)OM, ligand in solid metal nitrates and nitrato-complexes has now been amply demonstrated by recent *X*-ray crystallographic investigations [1-5] and the broad structural principles (*e.g.* the influence of *d*-electron configuration on molecular geometry) operative in such systems are beginning to emerge. Vibrational spectroscopy of solid covalent nitrates also permits recognition of covalent bonding and of specific bonding modes in favourable circumstances.[1] The structural characterisation of solid anhydrous nitrates and nitrato-complexes is essential to the understanding of their characteristic chemical and physical properties, for example their remarkably high solubility in many donor (*e.g.* $Cu[NO_3]_2$ in EtO_2CMe) [6] and non-donor (*e.g.* $Co[NO_3]_3$ in CCl_4) [7] non-

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[1] C. C. Addison, C. D. Garner, N. Logan, and S. C. Wallwork, *Quart. Rev.*, 1971, **25**, 289.

[2] T. J. King, N. Logan, A. Morris, and S. C. Wallwork, *Chem. Comm.*, 1971, 554.

[3] C. C. Addison, L. J. Blackwell, B. Harrison, D. H. Jones, N. Logan, E. K. Nunn, and S. C. Wallwork, *J.C.S. Chem. Comm.*, 1973, 347.

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[5] T. J. King and A. Morris, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 237.

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[7] R. J. Fereday, N. Logan, and D. Sutton, *J. Chem. Soc.* (*A*), 1969, 2699.

aqueous solvents. The nature of solution species is clearly of complementary interest but has been comparatively neglected. Vibrational and electronic spectroscopy are of limited applicability for this purpose, the former due to interference from solvent absorption and the latter because of difficulties in interpreting the usually broad featureless absorption bands. Electrical-conductivity measurements fulfil a useful role, but the nature of the conducting species in nitrate solutions is frequently a matter of speculation.

In seeking alternative techniques, magnetic-resonance spectroscopy of the oxygen or nitrogen nuclei of the nitrate groups appeared to be promising, since in this method attention is focussed only on the nuclei of interest (influenced by their electronic environment). The percentage natural abundances and nuclear spins of the relevant magnetic nuclei are ^{14}N (99·64, $I = 1$), ^{15}N (0·36, $I = \frac{1}{2}$), and ^{17}O (0·037%, $I = \frac{5}{2}$). The ^{17}O nucleus should be the most informative from the point of view of metal–nitrate interactions, since, in all cases observed to date, these interactions occur *via* the nitrate oxygen atoms; indeed a ^{17}O n.m.r. study of $EtO{\cdot}NO_2$ revealed the two expected resonances in the intensity ratio 1 : 2.[8] The ^{15}N nucleus also appears to be an attractive prospect, as its lack of a quadrupole moment usually results in sharp resonances and clearly observable spin–spin coupling[9] although relaxation times are rather long. However, the very low natural abundances of ^{17}O and ^{15}N are a serious drawback. Natural-abundance ^{15}N studies by pulsed Fourier-transform techniques are beginning to appear but are not as routine as corresponding ^{13}C work and ^{15}N or ^{17}O enrichment prior to conventional continuous-wave studies is expensive. The ^{14}N nucleus was therefore selected initially for the nitrate studies. The quadrupole moment of this nucleus leads to broadening of signals from nitrogen atoms in unsymmetrical molecular environments, and non-observance of spin-coupling effects. Nitrogen-14 also has extremely low sensitivity to n.m.r. detection (10^{-3} that of ^{1}H at constant field) necessitating the use of very concentrated solutions (preferably $\geqslant$1M).* Nevertheless, ^{14}N n.m.r. spectroscopy has proved an informative technique for many classes of inorganic compounds and in diverse areas of inorganic chemistry.[10]

One of the first observations of the chemical-shift phenomenon in n.m.r. spectroscopy arose during a study of the ^{14}N spectrum of an aqueous solution of ammonium nitrate.[11] The two well separated resonances (separation reported as 303 p.p.m., now known to be 355 ± 0·5 p.p.m.) due to the $[NH_4]^+$ and $[NO_3]^-$ ions were thereby revealed. In the first ^{14}N n.m.r. study of metal nitrates,[12] measurements on a series of diamagnetic compounds were carried out in aqueous solution and, not surprisingly, for each species the nitrate-resonance position and linewidth was found to be identical to that in saturated $[H_4N][NO_3]$, *i.e.* characteristic of $[NO_3]^-$. Large shifts (*ca.* +80 p.p.m.) from the $[NO_3]^-$ position were found[12] for aqueous and ethanolic solutions of paramagnetic nitrates, *e.g.* $Cu[NO_3]_2{\cdot}3OH_2$, but such shifts arise from the interaction of ^{14}N nuclei with paramagnetic environments and the studies described below have therefore been confined to diamagnetic nitrates. A ^{14}N shift of +4 p.p.m. relative to $[NO_3]^-$ has been reported[13] for the nitrate ligands in the complex $[RuNO(NO_3)_3(OH_2)_2]{\cdot}xOH_2$ in tributyl phosphate and for a solution of uranyl nitrate in methanol[14] (see Table).

RESULTS AND DISCUSSION

Due to the rapid decomposition of covalent nitrates in contact with water, it was necessary to employ pure liquid nitrates or solutions in non-aqueous media in the ^{14}N n.m.r. studies described here.

Liquid Nitrates and Solutions in CCl_4 *and* $MeNO_2$.—The ^{14}N chemical shifts (relative to aqueous $[NO_3]^-$ as external standard) and linewidths for the nitrate groups in a number of diamagnetic anhydrous metal nitrates and nitrato-complexes in CCl_4 or $MeNO_2$ as solvents, or as pure liquids, are given in the Table. Similar data for the unidentate non-metallic covalent nitrates $O_2N{\cdot}O{\cdot}NO_2$, $HO{\cdot}NO_2$, $MeCO_2{\cdot}NO_2$, $MeO{\cdot}NO_2$, and $EtO{\cdot}NO_2$ are included for purposes of comparison. Vibrational spectroscopy indicates some degree of covalent nitrate bonding in all the metallic compounds listed in the Table and the designations ONO_2 or O_2NO are used where uni- or bi-dentate bonding of nitrate oxygen atoms has been established by *X*-ray crystallography; ref. 1 gives further structural details. For each metal studied (Table), a single nitrate ^{14}N resonance was observed and the results clearly demonstrate the ready detectability of metal–nitrate covalent bonding in diamagnetic compounds, which is seen to result in an upfield shift from the $[NO_3]^-$ resonance position. It is also seen that the highest shifts observed for the covalent metal nitrates fall 10 p.p.m. below those of organic nitrates such as $MeO{\cdot}NO_2$ and $EtO{\cdot}NO_2$ and are appreciably lower than the shifts for acetyl nitrate, dinitrogen pentaoxide, and pure nitric acid. Comparison of the shifts for $Ti[O_2NO]_4$, $[NO][Au(ONO_2)_4]$, and $Sn[O_2NO]_4$ in the weak donor solvent $MeNO_2$ (in which the bonding modes found for the solids are likely to be retained and the shift values for the Ti and Sn compounds in CCl_4 support this) shows that either bi- or uni-dentate covalent bonding of nitrate to metals can lead to strikingly similar nitrogen-shielding effects, so that, unfortunately, ^{14}N n.m.r. spectroscopy does not allow a distinction between these bonding modes to be made. The extent of electronic perturbation of the nitrate group by the metal will clearly depend on the

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* 1M = 1 mol dm^{-3}.

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[12] B. M. Schmidt, L. C. Brown, and D. H. Williams, *J. Mol. Spectroscopy*, 1958, **2**, 551.

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oxidation state and polarising power of the latter as well as on the bonding mode.

The low chemical-shift values observed for Co[O$_2$NO]$_3$ are not readily interpreted, since this compound exhibits a high degree of covalency as indicated by its high volatility and solubility in CCl$_4$.[7] However, some reduction to paramagnetic Co^{II} may have occurred in solution and this could give rise to a downfield shift. The relatively small shift exhibited by [MeHgNO$_3$] in benzene solution may reflect the low electronegativity of the MeHg moiety.

^{14}N Chemical shifts of covalent nitrates and metal nitrato-complexes [a]

Compound	Solvent	^{14}N Shift [b]	Ref. to preparation
MeCO$_2$·NO$_2$ [c]	Neat	+64	*d*
O$_2$N·O·NO$_2$	CCl$_4$	+62	*e*
	MeNO$_2$	+58	
HO·NO$_2$ (100%)	Neat	+43 (7)	*f*
EtO·NO$_2$	CCl$_4$	+37 (15)	
	Neat	+36 (15)	
MeO·NO$_2$	Neat	+36 (10)	*g*
	CCl$_4$	+36 (10)	
Ti[O$_2$NO]$_4$	CCl$_4$	+25 (28)	*h*
	MeNO$_2$	+25 (58)	
	HNO$_3$ (100%)	+25	
[NO][Au(ONO$_2$)$_4$]	MeNO$_2$	+25 (51) [i]	*j*
[CrO$_2$][NO$_3$]$_2$	HNO$_3$ (100%)	+25	*k*
	Neat	+23 (32)	
	CCl$_4$	+23 (18)	
Sn[O$_2$NO]$_4$	CCl$_4$	+24 (35)	*l*
	MeNO$_2$	+24 (72)	
Al[NO$_3$]$_3$·2NCMe	MeCO$_2$Et	+22 (100)	*m*
[NO$_2$][Ga(NO$_3$)$_4$]	MeNO$_2$	+22 (38) {+125 (72), [NO$_2$]$^+$}	*n*
[VO][NO$_3$]$_3$	Neat	+21 (80)	*k*
	CCl$_4$	+21 (18)	
	MeCN	+21 (110)	
	HNO$_3$ (100%)	+21	
[MeHgNO$_3$]	C$_6$H$_6$	+14 (30)	
[H$_4$N]$_2$[Ce(O$_2$NO)$_6$]	PO(OBu)$_3$ [o]	+14 (140)	
	EtOH [o]	+11 (70)	
	H$_2$O	+8 (86)	
	MeCN [o]	+7 (50)	
	Propylene-carbonate	+5 (140)	
Co[O$_2$NO]$_3$	HNO$_3$ (100%)	+13	*p*
	CCl$_4$	+11 (28)	
[Ph$_4$As]$_2$[Zn(O$_2$NO)$_4$]	MeCN	+9 (22)	*q*
Th[O$_2$NO]$_4$·5OH$_2$	H$_2$O	+5 (100)	
[UO$_2$][NO$_3$]$_2$	MeOH	+4	
[RuNO(NO$_3$)$_3$(OH$_2$)$_2$]·xOH$_2$	PO(OBu)$_3$	+4	*r*
Cd[NO$_3$]$_2$·NCMe	MeCN	+2 (100)	*s*
[Ph$_4$As]$_2$[Cd(NO$_3$)$_4$]	MeCN	0	*t*

[a] The designations ONO$_2$ and O$_2$NO are used in the formulae of compounds for which uni- or bi-dentate bonding, respectively, of nitrate oxygen atoms has been established by *X*-ray crystallography; see ref. 1 for further structural details. [b] P.p.m. referred to external aqueous [NO$_3$]$^-$ as standard; the plus sign indicates a shift to higher magnetic field at a constant resonance frequency; linewidths (Hz) at half peak height in parentheses. It has been confirmed in these laboratories that the ^{14}N resonance position of [NO$_3$]$^-$ is unchanged in H$_2$O, MeNO$_2$, or MeCN solution with either [H$_4$N]$^+$ or [Et$_4$N]$^+$ as counter ion. It therefore seems safe to assume that the ^{14}N resonance of [NO$_3$]$^-$ is essentially independent of solvent. [c] **BEWARE**. Hazardous compound liable to decompose explosively at room temperature. [d] A Pictet and E. Khotinsky, *Compt. rend.*, 1907, **144**, 21. [e] C. C. Addison and N. Logan in 'Developments in Inorganic Nitrogen Chemistry,' ed. C. B. Colburn, Elsevier, Amsterdam, 1973, vol. 2, p. 27. [f] E. Berl and H. H. Saenger, *Monatsh.*, 1929, **53**, 1036. [g] A. P. Black and F. H. Babers in 'Organic Syntheses,' Wiley, New York, 1944, Coll. Vol. 2, p. 412. [h] B. O. Field and C. J. Hardy, *J. Chem. Soc.*, 1963, 5278. [i] The [NO]$^+$ resonance was not observed. [j] Ref. 22. [k] A. D. Harris, J. C. Trebellas, and H. B. Jonassen, *Inorg. Synth.*, 1967, **9**, 83. [l] C. C. Addison and W. B. Simpson, *J. Chem. Soc.*, 1965, 598. [m] P. M. Boorman, Ph.D. Thesis, Nottingham University, 1964. [n] D. Bowler and N. Logan, *Chem. Comm.*, 1971, 582. [o] Ammonium nitrate precipitated. [p] Ref. 7. [q] J. Drummond and J. S. Wood, *J. Chem. Soc.* (*A*), 1970, 226. [r] Ref. 13. [s] Ref. 18. [t] A. Morris, unpublished work.

The potential of the ^{14}N n.m.r. method for the identification of oxo-nitrogen species in solution is well illustrated by the spectrum of nitryl tetranitratogallate(III), [NO$_2$][Ga(NO$_3$)$_4$], in nitromethane as solvent and internal standard. Two resonances, in addition to that of the solvent, were observed and the signal at +22 p.p.m. with four times the intensity of the resonance at +125 p.p.m. is consistent with the presence of the [Ga(NO$_3$)$_4$]$^-$ anion, containing four structurally equivalent nitrate ligands, {the type of nitrate co-ordination in solid [NO$_2$][Ga(NO$_3$)$_4$] has not yet been conclusively established} and the [NO$_2$]$^+$ cation respectively. The presence of [NO$_2$]$^+$ and [Ga(NO$_3$)$_4$]$^-$ ions in MeNO$_2$ solution is also supported by i.r. and Raman studies.[15]

The linewidths quoted for the metallic species (Table) are all greater than that for the [NO$_3$]$^-$ ion (12 Hz), probably reflecting the lowering of symmetry of the electronic environment of the nitrogen nucleus on covalent bonding. The resonances in CCl$_4$ are generally narrower than those in MeNO$_2$ and the signals for the pure liquids [VO][NO$_3$]$_3$ and [CrO$_2$][NO$_3$]$_2$ are apparently viscosity broadened.

Solutions in Donor Solvents.—Inadequate solubility of species of interest in suitable solvents restricts the applicability of ^{14}N n.m.r. spectroscopy to some inorganic problems and no universally suitable solvent is available for covalent metal nitrates. Their sensitivity to aqueous environments has already been mentioned and the high reactivity of many such nitrates towards certain types of organic liquids also imposes further limitations. ^{14}N N.m.r. spectroscopy has, however, proved to be a good method for studying such reactions and the results will be presented elsewhere. For those species which are insoluble or sparingly soluble in non-polar or weakly donor media such as CCl$_4$ and MeNO$_2$, more strongly interacting donor solvents (which may also have high dielectric constants), *e.g.* MeCN, must be tolerated. The likelihood of modification of nitrate co-ordination or even the displacement of nitrate ligands by solvent molecules has then to be recognised. The Table includes results for several metal nitrates for which adequate solubility for ^{14}N n.m.r. measurements could only be achieved in solvents of this type. For [VO][NO$_3$]$_3$, the identical shifts observed for the pure liquid, a CCl$_4$ solution, and a MeCN solution are surprising since the adduct [VO][NO$_3$]$_3$·NCMe (prepared by mixing the nitrate with excess of MeCN) was recently shown by *X*-ray crystallography[16] to incorporate one uni- and two bi-dentate

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nitrate groups and a co-ordinated MeCN molecule. On the other hand, vibrational spectroscopy clearly indicates that the nitrate ligands in $[VO][NO_3]_3$ are bidentate.[17] The lower shifts observed for the compounds of Zn^{II}, Cd^{II}, Ce^{IV}, and Th^{IV} are attributable to weak covalency arising from cations of relatively low polarising power and/or partial dissociation of $[NO_3]^-$ as a result of solvent-donor and dielectric effects. Exchange between 'free' and co-ordinated nitrate will shift the resonance position towards that of $[NO_3]^-$. The nitrate groups of $Cd[NO_3]_2$ and $[Cd(NO_3)_4]^{2-}$ in MeCN solution are clearly ionic and vibrational-spectroscopic studies [18] also accord with this view.

The small positive shifts observed for aqueous solutions of $[H_4N]_2[Ce(NO_3)_6]$ and $Th[NO_3]_4 \cdot 5OH_2$ are particularly noteworthy, indicating significant interaction between nitrate and Ce^{IV} or Th^{IV} even in the presence of H_2O ligands. Support for this has also been obtained from *X*-ray diffraction [19] and Raman [20] studies on aqueous solutions of the cerium compound. *X*-Ray crystallography of $[H_4N]_2[Ce(NO_3)_6]$ shows [21] the presence of the discrete $[Ce(NO_3)_6]^{2-}$ anion in which each nitrate ligand is symmetrically bidentate. The effect of changing solvent dielectric constant and donor power on the ^{14}N resonance for this salt was investigated and the results are given in the Table. Donor solvents of relatively low dielectric constant brought about precipitation of ammonium nitrate, with $PO(OBu)_3$ (ε 6·8) immediately, with EtOH (ε 25) and MeCN (ε 38) over a period of time, effectively leaving cerium(IV) nitrate in solution. The decreasing shift with increasing solvent dielectric constant indicates increasing dissociation of $Ce[NO_3]_4$ to yield $[NO_3]^-$ ions. In propylenecarbonate (ε 69) and water (ε 81), appreciable dissociation is expected but ammonium nitrate is soluble. On addition of further nitrate ions (as $[H_4N][NO_3]$) to the aqueous solution, a single resonance in the nitrate region was still observed, but had moved downfield (^{14}N shift, +5 p.p.m.; half width, 100 Hz). This is consistent with an exchange process between co-ordinated nitrate and free nitrate ion in the high dielectric solvents.

Solutions in Pure Nitric Acid.—Pure nitric acid appears in many respects to be an ideal solvent for covalent anhydrous metal nitrates and nitrato-complexes, particularly those which are reactive towards organic compounds. For example, the salt $[NO_2][Au(NO_3)_4]$ reacts instantly with most organic solvents but can be crystallised from pure HNO_3.[22] Solutions of simple ionic nitrates in pure HNO_3 showed a single resonance line (attributable to rapid exchange of protons between HNO_3 and $[NO_3]^-$) at a position intermediate between the resonances of the pure acid (+43 p.p.m.) and nitrate ion in water (0 p.p.m.). The resonances exhibited by HNO_3 solutions of some covalent metal nitrates were clearly of interest and are recorded in the Table. The solvent resonance appeared in each case at +43 p.p.m. A second resonance, assigned to undissociated metal nitrate molecules, was observed for $Ti[NO_3]_4$, $[VO][NO_3]_3$, $[CrO_2][NO_3]_2$, and $Co[NO_3]_3$ solutions. The similarity of the chemical shifts to those observed for CCl_4 solutions of these nitrates (see Table) is striking and these observations leave no doubt that nitrate exchange between the covalent metal nitrate and HNO_3 must be absent or very slow. The possible formation of anionic species such as $[VO(NO_3)_{3+n}]^{n-}$ according to the equation (1) was explored by recording ^{14}N n.m.r.

$$[VO][NO_3]_3 + n[NO_3]^- \longrightarrow [VO(NO_3)_{3+n}]^{n-} \quad (1)$$

spectra after addition of carefully dried $Cs[NO_3]$ or $[H_4N][NO_3]$ to a solution of $[VO][NO_3]_3$ in HNO_3. In each case, the liquid separated into two layers after shaking and the ^{14}N spectra showed the lower layer to be almost pure $[VO][NO_3]_3$ and the upper layer to be a HNO_3 solution of the ionic nitrate. Thus the added ionic nitrate had merely 'salted out' the $[VO][NO_3]_3$ and no evidence for complexing was obtained. A mixture of equal volumes of HNO_3 and $[CrO_2][NO_3]_2$ after standing for 1 d showed only one broad resonance centred at +35 p.p.m. This may have been due to exchange of nitrate groups or slow reaction between the components.

No solute resonance could be observed for HNO_3 solutions of $[Be_4O][NO_3]_6$,[23] $K_2[Pd(NO_3)_4]$,[24] $Sn[NO_3]_4$, and $[NO][Au(NO_3)_4]$, probably as a result of insufficient solute concentration in the saturated solutions employed.

EXPERIMENTAL

Reference to preparative methods for the majority of the nitrates studied here is made in the Table. Other nitrates were commercially available. Solvents were purified and dried by standard techniques. Spectra were recorded at *ca.* 30 °C on a Varian HA 100 n.m.r. spectrometer operating at 7·226 MHz using standard 5 mm sample tubes, or on a Varian VF 16B variable-frequency (2—16 MHz) instrument using 15 mm sample tubes. Concentrated (preferably saturated) solutions or pure liquid samples were used, due to the low sensitivity of ^{14}N to n.m.r. detection. In the case of solid covalent nitrates, dissolution of the powdered solid in the pure dry solvent was carried out in an n.m.r. tube inside a dry-box. Chemical shifts were measured by the sample-substitution method relative to $[NO_3]^-$ ion in a saturated aqueous solution of $[H_4N][NO_3]$.

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