Iodine-127 Nuclear Magnetic Resonance Spectra of Transition-metal Periodate Complexes

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^{127}I N.m.r. spectra have been recorded in solution for $[M\{IO_5(OH)\}_2]^{5-}$ (M = Cu, Ag, or Au), $[MO_2\{IO_5(OH)\}_2]^{6-}$ (M = Ru or Os), $[Co_4I_3O_{24}H_{12}]^{3-}$, and in addition for H_5IO_6, $NaIO_4$, and $[I(OH)_6]^+$. The presence of a very broad resonance at *ca.* 2 800—3 100 p.p.m. is suggested to be characteristic of the presence of an orthoperiodate group $[H_{5-n}IO_6]^{n-}$. The syntheses and properties of $Na_6[OsO_2L_2]\cdot nH_2O$ [L = $IO_5(OH)$ or $TeO_4(OH)_2$] are reported.

The ^{127}I nucleus has a natural abundance of 100% and a high relative receptivity [D_c (sensitivity relative to ^{13}C) = 5.41 × 10^2][1] but despite this few reports of ^{127}I n.m.r. chemical shifts have appeared. This is largely a consequence of the quadrupolar nature ($I = \frac{5}{2}$) of this nucleus and of the substantial quadrupole moment ($Q = -0.79 \times 10^{-28}$ m^2) which combine in most cases to render the lines too broad to observe. Whilst there are many reports of relaxation measurements of I^- ions,[2] reported ^{127}I n.m.r. chemical shifts in solution are restricted to those of I^- in a variety of solvents under different conditions and to the metaperiodate ion (IO_4^-).[1–3] Solid-state measurements for I^- and IO_4^- are numerous[1] and isolated reports of the chemical shifts of solid IO_3^- salts,[4] $CsICl_2$,[5] $[IF_6][AsF_6]$,[6] and IF_7[7] have appeared. The optimum situation for the observation of n.m.r. spectra of quadrupolar nuclei is when they are in sites of cubic symmetry, and thus in addition to the tetrahedral IO_4^- ion spectra for the 'pseudo-octahedral' orthoperiodates in H_5IO_6 and its salts may be obtainable. Previous failures to observe such spectra have been ascribed to chemical exchange effects between different forms of periodate {IO_4^-, $H_4IO_6^-$, $[I_2O_8(OH)_2]^{4-}$, *etc.*}.[3] However orthoperiodate is known to form heteropolyanions with many of the transition metals [often in unusually high oxidation states *e.g.* Cu^{III} (ref. 8) and Ni^{IV} (ref. 9)] and in these complexes it was thought that chemical exchange was unlikely. Hence we attempted to record ^{127}I n.m.r. spectra for various orthoperiodate derivatives and now report the results.

Experimental

N.m.r. spectra were recorded for saturated solutions in H_2O–D_2O (5:1 v/v) in tubes of 10 mm outside diameter, except for $[I(OH)_6][HSO_4]$ which was run in concentrated sulphuric acid solution with a co-axial insert (outside diameter 5 mm) containing D_2O to provide the lock. Data were collected using a Bruker AM 360 spectrometer operating at 48.8 (^{17}O), 85.4 (^{59}Co), 113.6 (^{125}Te), and 72.5 MHz (^{127}I), with measurements referenced respectively to neat water, 1 mol dm^{-3} aqueous $K_3[Co(CN)_6]$, neat Me_2Te, and 1 mol dm^{-3} aqueous KI (subsequently corrected to infinite dilution using published data).[3] Typically the ^{127}I n.m.r. spectra required *ca.* 5 000 scans with a pulse interval of 0.08 s. They were also recorded upon a JEOL FX90Q spectrometer at 17.9 MHz. Energy dispersive *X*-ray fluorescence (EDX) data were obtained upon a Cambridge Stereoscan 150 scanning-electron microscope, thermal gravimetric analysis (t.g.a.) measurements from a Stanton-Redcroft TG760 instrument, i.r. spectra on a Perkin-Elmer 1710 FT spectrometer, and u.v.–visible spectra on a Perkin-Elmer PE554 spectrometer.

The compounds $Na_5[M\{IO_5(OH)\}_2]\cdot nH_2O$ (M = Cu, Ag, or Au),[10,11] $Na_6[RuO_2\{IO_5(OH)\}_2]\cdot nH_2O$, and $Na_6[RuO_2\{TeO_4(OH)_2\}_2]\cdot nH_2O$,[12] $H_3[Co_4I_3O_{24}H_{12}]\cdot 3H_2O$,[13] and $[I(OH)_6][HSO_4]$[14] were made by literature methods. All had satisfactory heavy-atom ratios by EDX. The water content in the complexes can vary from preparation to preparation, hence the use of 'nH_2O' in the formulae. Periodic acid and $NaIO_4$ were obtained commercially.

Preparation of $Na_6[OsO_2\{IO_5(OH)\}_2]\cdot 18H_2O$.—To a solution of $K_2[OsO_2(OH)_4]$ (0.20 g, 0.53 mmol) in 1 mol dm^{-3} aqueous NaOH (18 cm^3) was added $NaIO_4$ (0.23 g, 1.05 mmol) in water (5 cm^3). A bright orange solution resulted. This was concentrated *in vacuo* until a pale yellow solid began to separate, and then placed in a refrigerator overnight. The pale yellow solid which precipitated was filtered off, washed with cold water (10 cm^3), and dried *in vacuo*. Yield >95%. Atom ratio (EDX): Os:I:Na 0.94:2.00:5.79; 28.4% H_2O (t.g.a.) (Calc. 28.6%).

Preparation of $Na_6[OsO_2\{TeO_4(OH)_2\}_2]\cdot 8H_2O$.—A solution of $K_2[OsO_2(OH)_4]$ (0.20 g, 0.53 mmol) in 1 mol dm^{-3} aqueous NaOH was treated with H_6TeO_6 (0.25 g, 1.09 mmol) in water (5 cm^3). A yellow-brown solution formed, which on cooling in a refrigerator overnight deposited a fawn solid. This was filtered off, washed with cold water (5 cm^3), and dried *in vacuo*. Yield >95%. Atom ratio (EDX): Os:Te:Na 0.92:2.00:5.99; 14.8% H_2O (t.g.a.) (Calc. 15.1%).

Results and Discussion

Saturated solutions of $NaIO_4$ in dimethyl sulphoxide exhibit a moderately sharp ^{127}I n.m.r. resonance at +4 150 p.p.m. ($W_{\frac{1}{2}}$ = 500 Hz), consistent with a previous study.[1,3] In water (pH 7) the spectrum consists of a strong resonance at +4 120 p.p.m. ($W_{\frac{1}{2}}$ = 850 Hz) and a very broad weak feature at *ca.* +3 080 p.p.m. ($W_{\frac{1}{2}}$ = 13 kHz). Spectra were also obtained from solutions of H_5IO_6 at pH 1.9, 2.5, 6.0, and 10.5. These solutions showed broad resonances at *ca.* 4 100 ($W_{\frac{1}{2}}$ *ca.* 8—20) and *ca.* 3 100 p.p.m. ($W_{\frac{1}{2}}$ *ca.* 20—28 kHz). The relative intensities of these two resonances and the linewidths varied with pH, consistent with the presence of equilibria between several

Table. Multinuclear n.m.r. data

Complex	$\delta(^{127}I)^a$	$\delta(^{17}O)^b$	$\delta(^{125}Te)^c$
$[Cu\{IO_5(OH)\}_2]^{5-}$	2 940(28 000)	—	—
$[Ag\{IO_5(OH)\}_2]^{5-}$	2 930(28 000)[d]	—	—
$[Au\{IO_5(OH)\}_2]^{5-}$	2 910(28 000)	—	—
$[RuO_2\{IO_5(OH)\}_2]^{6-}$	2 950(30 000)	1 244	—
$[OsO_2\{IO_5(OH)\}_2]^{6-}$	2 905(29 000)	751	—
$[Co_4I_3O_{24}H_{12}]^{3-}$	2 890(18 000)[e]	—	—
$[RuO_2\{TeO_4(OH)_2\}_2]^{6-}$	—	1 251	917
$[OsO_2\{TeO_4(OH)_2\}_2]^{6-}$	—	751	903

[a] Saturated aqueous solutions relative to aqueous I^- (extrapolated to infinite dilution); $W_{\frac{1}{2}}$ in parentheses (Hz). [b] Relative to external water. [c] Relative to external neat Me_2Te; H_6TeO_6 has δ 713 p.p.m. [d] $\delta(^{109}Ag)$ = 2 802 p.p.m. (W. Levason, M. D. Spicer, and M. Webster, *J. Chem. Soc., Dalton Trans.*, 1988, 1377). [e] $\delta(^{59}Co)$ = 13 200 and 12 560 p.p.m. relative to $K_3[Co(CN)_6]$ in water (the *X*-ray structure reveals two cobalt environments[13]).

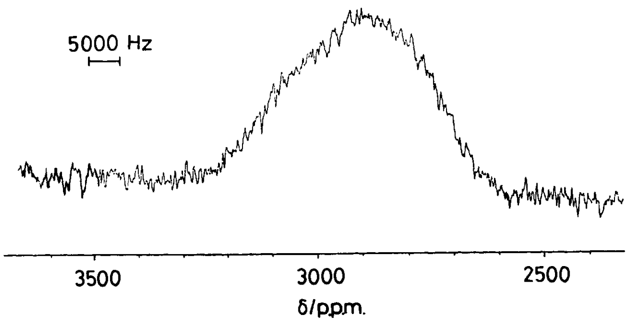

Figure. The ^{127}I n.m.r. spectrum of $[OsO_2\{IO_5(OH)\}_2]^{6-}$ in H_2O–D_2O solution

different forms of periodate in solution.[15] Raising the temperature to 95 °C does not appreciably sharpen the lines. The linewidths in spectra of some quadrupolar nuclei, including ^{59}Co,[16] have been observed to broaden with increased magnetic field strength, and in order to check whether this high-field anisotropy effect was significant in the present case spectra of H_5IO_6 solutions were recorded at 8.45 and 2.11 T, but again no significant linewidth difference was apparent. From these results it seems that an ^{127}I resonance at *ca.* 4 100 p.p.m. is due to the tetrahedral IO_4^- ion, and the broad feature at *ca.* 3 100 p.p.m. corresponds to an 'octahedral' orthoperiodate $[H_{5-n}IO_6]^{n-}$ (or possibly dinuclear $[H_{6-n}I_2O_{10}]^{n-}$) species.

The $[I(OH)_6]^+$ ion which is formed by dissolution of H_5IO_6 in concentrated sulphuric acid[14] had $\delta(^{127}I)$ at 3 100 p.p.m. ($W_{\frac{1}{2}}$ = 20 kHz). In this case both the high viscosity of the solution and hydrogen bonding with the solvent will contribute to the linewidth.

The ^{127}I n.m.r. data for six transition-metal periodate complexes are listed in the Table. The $[M\{IO_5(OH)\}_2]^{5-}$ (M = Cu, Ag, or Au) contain planar metal centres with chelating bidentate $O_2IO_3(OH)^{4-}$ ligands,[8,17] whilst $[RuO_2\{IO_5(OH)\}_2]^{6-}$ has a *trans* octahedral ruthenium(VI) centre chelated by the same periodate groups.[12] The osmium(VI) complex prepared from $[OsO_2(OH)_4]^{2-}$ and $NaIO_4$ in alkaline solution is formulated as a *trans* osmyl $[OsO_2\{IO_5(OH)\}_2]^{6-}$ complex on the basis of the spectroscopic properties, particularly the (OsO_2) stretch in the i.r. spectrum at 820 cm^{-1} characteristic of an osmyl group.[18] The $\delta(^{127}I)$ of these complexes were found in the range *ca.* 2 900—2 950 p.p.m. with $W_{\frac{1}{2}}$ *ca.* 28—30 kHz. A typical spectrum is shown in the Figure. Ligand exchange is likely to be very slow in these high-oxidation-state complexes, and the broad lines are readily ascribed to the fast relaxation of the iodine nuclei resulting from the considerable deviations from cubic symmetry which arise from the chelation of the periodates to the metal. The $[Co_4I_3O_{24}H_{12}]^{3-}$ ion which is known from an *X*-ray study[13] to contain octahedral Co^{III} and IO_6 groups has $\delta(^{127}I)$ = 2 890 p.p.m. The large linewidths in the spectra of these complexes limit the accuracy with which the chemical shifts can be measured, and errors of ±30 p.p.m. on the data in the Table would be a reasonable estimate. It is thus debatable whether the small differences in chemical shift 'observed' as the metal is changed have any significance. However since the ^{127}I n.m.r. chemical shift range is large (>4 000 p.p.m. on the basis of the few known examples) it appears that the observation of a broad resonance at *ca.* 3 000 p.p.m. is a useful fingerprint for the presence of an orthoperiodate ligand. Even for moderately soluble complexes, spectra with good signal/noise ratio are achieved in less than 30 min accumulation at 72.54 MHz, and hence this appears a convenient diagnostic tool.

The complexes in the Table contain several other n.m.r.-active nuclei, and the appropriate data are also included. We were unable to observe convincing ^{17}O resonances for the oxygen atoms of the periodate ligands, presumably due both to the low natural abundance of ^{17}O (0.037%), and to the line broadening caused by the relaxation of the iodines. However sharp resonances were observed at 751 p.p.m. for the OsO_2^{2+} groups in the periodate and tellurate complexes which may be compared with values of 785 p.p.m. for OsO_4 (CCl_4 solution) and 725 p.p.m. for $Rb_2[OsO_2(OH)_4]$ (1 mol dm^{-3} NaOH solution). Similar resonances were present at 1 244 and 1 251 p.p.m. for the ruthenyl periodate and tellurate complexes which may be compared with that[19] of RuO_4 at 1 106 p.p.m. The ^{125}Te resonances of the tellurate ligands in the osmium and ruthenium complexes (903 and 917 p.p.m. respectively) are sharp. The corresponding resonances of $[M\{TeO_4(OH)_2\}_2]^{5-}$ were found at 774.5, 774, and 753 p.p.m. for M = Cu, Ag, and Au, and at 713 p.p.m. for H_6TeO_6. It is notable that the trends in the tellurium chemical shift with metal parallel those observed in the ^{127}I chemical shifts of the corresponding periodates, despite the reservations expressed above.

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