Inorganica Chimica Acta, *166* (1989) 13–15

Natural Abundance ^{17}O NMR Spectra of Molybdenyl, Uranyl and Zirconyl Complexes

JAN M. CODDINGTON, RUSSELL F. HOWE
and MICHAEL J. TAYLOR*

Department of Chemistry, University of Auckland, Auckland (New Zealand)

(Received July 25, 1989)

NMR spectroscopy has been increasingly used to study the hydrolysis of cations of metals such as aluminium [1], gallium [2], vanadium [3] and molybdenum [4]. Aside from the general objective of characterising oxyanions and polynuclear oxo- and hydroxy-cations in aqueous solutions, there is also interest in identifying solution precursors which are important in the preparation of supported metal oxide [5] or pillared clay catalysts [6].

In a recent NMR study of molybdenum(VI) solutions, we attempted without success to detect ^{17}O NMR signals from the molybdenyl cation (either MoO_2^{2+} or $Mo_2O_5^{2+}$) believed to exist in strongly acidic Mo(VI) aqueous solutions [7]. ^{17}O data have been reported for oxo-bridged anions such as dichromate $Cr_2O_7^{2-}$ [8] and $Mo_7O_{24}^{6-}$ [9]. Heptamolybdate $Mo_7O_{24}^{6-}$ displays terminal ^{17}O chemical shifts in the range 750–830 ppm [7, 9] but we were uncertain of the values to expect for terminal oxygens in neutral or cationic oxo-complexes. Despite unequivocal evidence from ^{95}Mo NMR and vibrational spectra of the presence of molybdenyl halide complexes, $MoO_2X_2(H_2O)_2$, in aqueous HCl or HBr solutions [7], no ^{17}O signals could be found apart from that of the solvent. It is possible that oxygen exchange between the molybdenyl complex and water is rapid on the NMR time scale. We therefore reinvestigated $MoO_2Cl_2(H_2O)_2$ and $MoO_2Br_2(H_2O)_2$, taking advantage of ether extraction to transfer these complexes into a less polar medium. The ^{17}O NMR spectra of diethyl ether extracts containing the molybdenyl group in the form of $MoO_2X_2(H_2O)_2$ reveal sharp peaks at 1015 ppm (X = Cl) or 1019 ppm (X = Br) attributable to the *cis*-MoO_2 unit, in addition to the solvent signal at *c.* 15 ppm which includes resonance due to both diethyl ether [10] and water molecules.

Another cationic oxo-complex which has been well characterized in aqueous solutions UO_2^{2+}. Aqueous solutions of uranyl salts are known from X-ray scattering measurements [11], Raman spectra [12] and other evidence [13] to contain the hydrated complex $UO_2(H_2O)_6^{2+}$. An early NMR study of acidified uranyl perchlorate solutions located the ^{17}O signal from the UO_2^{2+} ion 1115 ppm downfield from that of water [14]. The uranyl oxygen resonance peak was markedly asymmetric, but this could not be explained and was probably due to instrumental factors associated with the continuous-wave NMR technique then employed. We have measured the ^{17}O NMR spectrum, at natural abundance, of 0.5–2.0 mol l^{-1} uranyl nitrate solutions in H_2O (containing 10% D_2O to provide a lock signal). Two sharp signals were observed in addition to that of the solvent (*c.* 10 ppm in aqueous acid conditions), at 415 ppm due to nitrate ion [10] and at 1121 ppm (line width <50 Hz) attributed to UO_2^{2+}. An identical chemical shift for UO_2^{2+} was observed in aqueous perchloric acid. No ^{17}O NMR signal was observed from coordinated H_2O ligands of $UO_2(H_2O)_6^{2+}$, presumably because these molecules are highly labile and their resonance merges with the solvent water peak.

Structure determinations of uranyl nitrate in the solid state show both nitrate ions to be coordinated as bidentate ligands to the UO_2^{2+} ion, which also retains two H_2O ligands [15, 16]. A uranyl complex of this kind probably exists in solutions of $UO_2(NO_3)_2 \cdot 6H_2O$ in acetone, the Raman spectra of which showed that the nitrate anions are coordinated [17]. For solutions of uranyl nitrate in acetone we find ^{17}O signals at 15 ppm (H_2O), 420 ppm, broad (coordinated NO_3^-), 560 ppm (acetone), and 1118 ppm (UO_2^{2+}). The acetone signal has moved from its usual position at 572 ppm [10], and we also find that its ν(CO) Raman frequency has decreased from 1710 to 1700 cm^{-1}. Both these effects can be attributed to solvation of the uranyl complex by acetone.

Hydrolysis of uranium(VI) aqueous solutions is reported to result in formation initially of $(UO_2)_2(OH)_2^{2+}$ and subsequently higher nuclearity species such as $(UO_2)_3(OH)_5^+$ [13, 18, 19]. We have prepared these polynuclear cations by adding KOH to aqueous uranyl nitrate solution initially at pH 1. At pH 2.5, the Raman spectrum of the solution showed the ν_{sym}(U–O) bands of UO_2^{2+} and $(UO_2)_2(OH)_2^{2+}$ at 872 and 850 cm^{-1}, respectively, to have an intensity ratio of approximately 3:1, whereas at pH 3 the Raman intensities of these bands were approximately equal and a shoulder at 836 cm^{-1} indicated the presence of some $(UO_2)_3(OH)_5^+$ [18]. The sharp UO_2^{2+} signal at 1121 ppm in the ^{17}O spectrum of uranyl nitrate was, however, unchanged on addition of alkali. No new signals due to coordinated hydroxide ligands and no changes in shape of the solvent peak were detected. We infer that the hydroxide ligands are labile on the ^{17}O NMR time scale at room temperature, undergoing rapid exchange with the

---

*Author to whom correspondence should be addressed.

0020-1693/89/$3.50

TABLE 1. ^{17}O NMR data for some metal–oxo complexes (δ/ppm)

Species	Solvent	Oxo–ligand resonance	Other ^{17}O resonances
$MoO_2Cl_2(H_2O)_2$	diethyl ether	1015	15(H_2O), 7(Et_2O)
$MoO_2Br_2(H_2O)_2$	diethyl ether	1019	15(H_2O), 7(Et_2O)
$UO_2(NO_3)_2(H_2O)_2$	acetone	1118	15(H_2O), 420 broad (NO_3^-), 560(Me_2CO)
$UO_2(H_2O)_6^{2+}$	water (pH 1)	1121	10(H_2O), 415 sharp (NO_3^-)
$(UO_2)_2(OH)_2^{2+}$	water (pH 3)	1121	10(H_2O), 415(NO_3^-)
$UO_2(H_2O)_6^{2+}$	aqueous $HClO_4$	1121	10(H_2O), 290 sharp (ClO_4^-)
UO_2Cl_2(aq)	aqueous HCl	1122	10(H_2O)
UO_2Br_2(aq)	aqueous HBr	1121	10(H_2O)
$Zr_4(OH)_{12}^{4+}/NO_3^-$	aqueous HNO_3	[a]	14(H_2O), 425 (coordinated NO_3^-)
CrO_2Cl_2	liquid	1460[b]	

[a]Not observed. [b]Ref. 8.

solvent. Evidence for facile exchange of hydroxide ligands with H_2O has been presented for Al^{3+} hydrolysis products by Oldfield *et al.* [20], although in this case distinct ^{17}O signals from hydroxide ligands could be detected which had δ values of 20–30 ppm. The ^{17}O signal of terminal oxo-groups in UO_2^{2+} and $(UO_2)_2(OH)_2^{2+}$ appears to be insensitive to the state of hydrolysis of the uranium(VI) species. The insensitivity of the oxygen resonance frequency of UO_2^{2+} to the presence of other ligands is further demonstrated by the observation that the ^{17}O chemical shifts of UO_2Cl_2 in concentrated HCl, or UO_2Br_2 in concentrated HBr, given in Table 1, hardly differ from that of $UO_2(H_2O)_6^{2+}$, despite the fact that a displacement of the ν_{sym}(UO) Raman frequency from 872 cm^{-1} in uranyl nitrate or perchlorate solutions to 860 cm^{-1} in halogen acid solutions shows that complexing of the UO_2^{2+} ion by halide has occurred [21].

A polynuclear cation which contains no terminal oxo-ligands is $Zr_4(OH)_{12}^{4+}$. This species, believed to be present in aqueous solutions of $ZrOCl_2$, contains bridging and terminal hydroxide ligands [12, 22]. In aqueous HNO_3 solutions of $ZrOCl_2$ (2 mol l^{-1}) we could find no ^{17}O NMR signals to attribute to hydroxide ligands and assumed that this resonance contributes to the solvent water peak at 14 ppm. However, in the presence of the zirconyl complex, the ^{17}O signal of NO_3^- was shifted from 415 ppm to become a broad peak at 425 ppm, and the Raman spectrum showed evidence of coordinated nitrate. These changes in the NMR and Raman spectra resemble those observed for nitrate coordinated to UO_2^{2+}.

Experimental

Molybdenum(VI) solutions were prepared by dissolving $Na_2MoO_4 \cdot 2H_2O$ in concentrated HCl or HBr. These solutions were shaken with an equal volume of diethyl ether to prepare solvent extracts in which the Mo(VI) concentration was *c.* 1 mol l^{-1}. Uranyl solutions were made using $UO_2(NO_3)_2 \cdot 6H_2O$. Aqueous KOH was added to precipitate $UO_2(OH)_2$ which was separated by centrifuging, washed free of nitrate, and redissolved in $HClO_4$, HCl or HBr solution. Zirconium(IV) solutions were prepared by dissolving $ZrOCl_2$ in dilute aqueous HNO_3.

NMR spectra were obtained using a 10 mm broadband probe in a Bruker AM400 spectrometer operating at 295 K. Natural abundance ^{17}O spectra at 54.24 MHz were collected with 4K data points over 84000 Hz using a 50° pulse (7 μs). The pulse repetition rate was 0.11 s. Line broadening of 50 Hz was employed. D_2O was added to aqueous solutions to provide a locking signal. For ether extracts, $CDCl_3$ was added as an internal lock. Spectra were referenced to external water at 295 K for ^{17}O. Raman spectra of samples in glass tubes were recorded using a Jasco R300 spectrometer with Coherent Radiation argon (488 or 514 nm) laser excitation (50–200 mW of power at the sample).

Conclusions

We conclude from these studies that cationic or neutral oxo-complexes are likely to have high positive ^{17}O chemical shifts associated with a relatively deshielded environment of the oxygen atom. With oxygen ligand concentrations of 0.5 mol l^{-1} or more, there was no difficulty in obtaining satisfactory NMR spectra from ^{17}O at the natural abundance level of 0.04%. This is particularly convenient in the case of the uranyl ion since it enables the spectra to be obtained without recourse to isotopic labelling of this kinetically stable species.

Acknowledgements

We thank the New Zealand Universities Grants Committee and the Medical Research Council for financial support.

References

1 J. W. Akitt and J. M. Elders, *J. Chem. Soc., Dalton Trans.*, (1988) 1347.
2 J. W. Akitt and D. Kettle, *Magn. Reson. Chem., 27* (1989) 377.
3 W. G. Klemperer and W. Shum, *J. Am. Chem. Soc., 99* (1977) 3544.
4 M. Filowitz, W. G. Klemperer, L. Messerle and W. Shum, *J. Am. Chem. Soc., 98* (1976) 2345.
5 P. Sarrazin, B. Mouchel and S. Kasztelan, *J. Phys. Chem., 93* (1989) 904.
6 D. Plee, F. Borg, L. Gatineau and J. J. Fripiat, *J. Am. Chem. Soc., 107* (1985) 2362.
7 J. M. Coddington and M. J. Taylor, *J. Chem. Soc., Dalton Trans.*, (1989), in press.
8 R. G. Kidd, *Can. J. Chem., 45* (1967) 605.
9 M. Filowitz, R. K. C. Ho, W. G. Klemperer and W. Schum, *Inorg. Chem., 18* (1979) 93; O. W. Howarth and P. Kelly, *J. Chem. Soc., Chem. Commun.*, (1988) 1236.
10 J. Mason (ed.), *Multinuclear NMR Spectroscopy*, Plenum Press, New York, 1987.
11 S. Pocev and G. Johansson, *Acta Chem. Scand., 27* (1973) 2146.
12 M. H. Booker, C.-H. Huang and J. Sylwestrowicz, *J. Inorg. Nucl. Chem., 42* (1980) 1431.
13 C. F. Baes, Jr. and R. E. Mesmer (eds.), *The Hydrolysis of Cations*, Wiley-Interscience, New York, 1976.
14 S. W. Rabideau, *J. Phys. Chem., 71* (1967) 2747.
15 J. C. Taylor and M. H. Mueller, *Acta Crystallogr., 19* (1965) 36.
16 G. Xinmin, T. Ning, W. Xin, Z. Yin and T. Minyu, *J. Coord. Chem., 20* (1989) 21.
17 G. V. Kozhevnikova and G. Keresztury, *Inorg. Chim. Acta, 98* (1985) 59.
18 L. M. Toth and G. M. Begun, *J. Phys. Chem., 85* (1981) 547; J. R. Bartlett and R. P. Cooney, *Spectrochim. Acta, Part A, 45* (1989) 549.
19 W.-S. Jung, M. Harada, H. Tomiyasu and H. Fukutomi, *Bull. Chem. Soc. Jpn., 61* (1988) 3895.
20 A. R. Thompson, A. C. Kunwar, H. S. Gutowsky and E. Oldfield, *J. Chem. Soc., Dalton Trans.*, (1987) 2317.
21 M. Gál, P. L. Goggin and J. Mink, *J. Mol. Struct., 114* (1984) 459.
22 M. Aberg, *Acta Chem. Scand., Ser. B, 31* (1977) 171.