Stereochemical Rigidity and Geometrical Isomerism in Nine-co-ordinate Complexes of Th^{IV} and U^{IV} in Aqueous Solution

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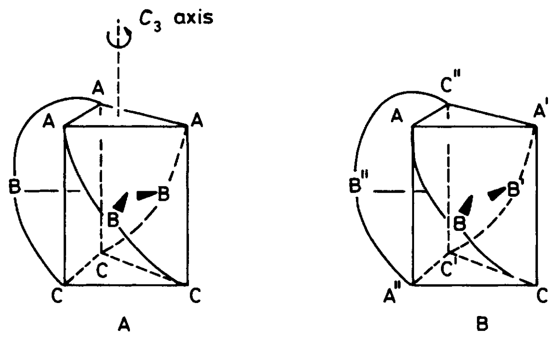
The ^{1}H n.m.r. spectra, in aqueous solution at room temperature, of tris-complexes of Th^{IV} and U^{IV} with an asymmetric tridentate Schiff base ligand show the presence of two isomers, which are assigned to the symmetric and asymmetric forms of a tricapped trigonal prism.

The great majority of metal complexes with co-ordination number greater than 6 are fluxional on an n.m.r. timescale at room temperature.[1,2] We report the ^{1}H n.m.r. spectra of complexes of Th^{IV} and U^{IV} in aqueous solution. These spectra not only indicate stereochemical rigidity in 9-co-ordination, but also a previously uncharacterised form of geometrical isomerism.



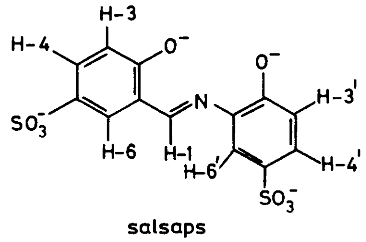
Symmetric isomer

Asymmetric isomer

Figure 1

For 9-co-ordinate complexes of the type ML_3, where L is a symmetrical tridentate ligand, the idealised structure expected on theoretical grounds,[3] and found experimentally in those cases which have been studied by *X*-ray diffraction,[3] is the *mer*-isomer of a tricapped trigonal prism. If the ligand is asymmetric, then there are two possible isomers: a symmetric isomer A, and an asymmetric isomer B (Figure 1). In A the three ligands are equivalent, but in B all the ligands are different.

The tridentate Schiff base ligand salsaps (Figure 2) formed *in situ* in aqueous solution from equimolar quantities of salicylaldehyde-5-sulphonate (sals) and 2-aminophenol-4-sul-



salsaps

Figure 2

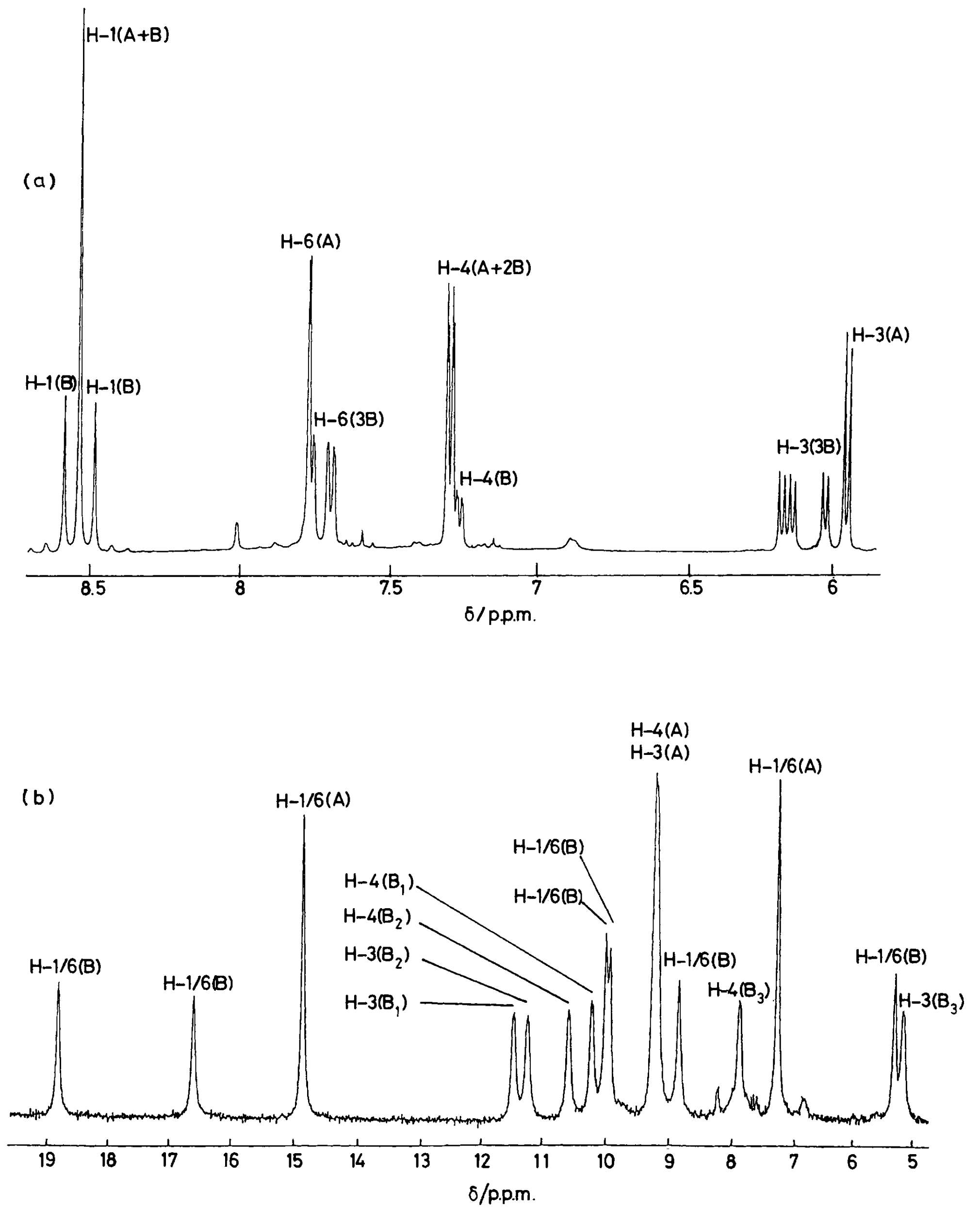


Figure 3. The 500 MHz ^1H n.m.r. spectrum (D_2O, pH = 7.0, 295 K) of (a) Th^{IV} + [$^2H_3$]salsaps (mole ratio 1:3), (b) the 250 MHz ^1H n.m.r. spectrum (D_2O, pH = 7.0, 295 K) of U^{IV} + [$^2H_3$]salsaps (mole ratio 1:3).

phonate (aps) has been shown to give very stable 2:1 octahedral complexes with a number of 'hard' metal ions such as Al^{III}, Ga^{III}, and Fe^{III}.[4] Figure 3a shows the ^1H n.m.r. spectrum of a D_2O solution containing salsaps and Th^{IV} in a 3:1 molar ratio.† In order to simplify the spectrum, the salsaps was prepared from aps which had been fully deuteriated in the aromatic ring.[4] When the salsaps:Th^{IV} ratio was 4:1, the same spectrum was obtained but with the addition of free ligand peaks. This not only shows that intermolecular exchange is slow on an n.m.r. timescale, at 295 K, but also, from the observed intensity ratios, confirms the 3:1 ligand:metal stoicheiometry of the Th^{IV} species.

It is clear from Figure 3a that two isomers are present in solution. One of these gives single resonances, or groups of resonances, for the salsaps protons, and can be assigned to the symmetric isomer A. In the other (isomer B) the resonances occur in groups of three of equal intensity, as is clearly shown for the H-3 and H-6 resonances. In the methine region (H-1) intensity measurements indicate that the third resonance from isomer B is coincident with the single resonance of isomer A. The concentrations of the asymmetric and symmetric species are in the ratio 1.4:1 (at 295 K) as compared to the 'statistical' value of 3:1.

The H-3 resonance occurs in the range δ 6.7—6.9 for the

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† An aqueous solution of $Th^{IV}(NO_3)_4$, the sodium salt of sals and [$^2H_3$]2-aminophenol-4-sulphonic acid was adjusted to pH = 7.0 with dilute $KOH_{aq.}$, evaporated to dryness and the residue dissolved in D_2O. The U^{IV} complex was prepared by a similar method but starting with $U^{IV}Cl_4$.

free salsaps ligand and its 2 : 1 metal complexes.[4] However for the Th^{IV} $(salsaps)_3{}^{8-}$ species, δ lies between 5.96—6.20 (5.96 for the symmetric isomer). Inspection of models based on structures A and B shows that H-3 in one ligand lies above the plane of a benzene ring from another ligand, and will experience appreciable shielding from the aromatic ring current.[5]

^1H N.m.r. spectra (250 MHz) were recorded over the temperature range 278—323 K for a D_2O solution containing a salsaps : Th^{IV} ratio of 5 : 1. As the temperature was raised considerable broadening and eventual partial coalescence of the complexed ligand resonances was observed. However, the free ligand resonances also broadened, and it seems likely that 'scrambling' of the ligands in the Th^{IV} complexes in this temperature range largely occurs by an intermolecular, rather than a intramolecular, exchange process. The stereochemical rigidity of the Th^{IV} complexes can be partly attributed to the preferred planar configuration of the salsaps ligand.

Figure 3b shows the ^1H n.m.r. spectrum of the corresponding U^{IV} complex. Four strong peaks are observed (two overlapping but completely resolved at lower temperatures) and twelve weaker peaks of equal intensity, again indicating the presence of two isomers with an asymmetric : symmetric ratio of 1.6 : 1 at 295 K. The resonances are broadened and shifted by the paramagnetism of the U^{IV} ion ($5f^2$), and could not be assigned directly. The partial assignment given in Figure 3b is based on a 2D ^1H n.m.r. correlated shift (COSY) spectrum (500 MHz),[6] together with a normal spectrum obtained using sals selectively deuteriated in the 3-position.‡

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References

1 E. L. Muetterties and C. M. Wright, *Quat. Rev. Chem. Soc.*, 1967, **21**, 109; M. G. B. Drew, *Prog. Inorg. Chem.*, 1977, **23**, 67; C. R. Fay, D. F. Lewis, and J. R. J. Weir, *J. Am. Chem. Soc.*, 1975, **97**, 7179.

2 For exceptions to reference 1: J. F. Desreux and M. F. Loncin, *Inorg. Chem.*, 1986, **25**, 69; M. V. R. Stainer and J. Takats, *J. Am. Chem. Soc.*, 1983, **105**, 410; R. C. Fay, J. R. Weir, and A. H. Bruder, *Inorg. Chem.*, 1984, **23**, 1079.

3 D. L. Kepert, 'Inorganic Stereochemistry,' Springer-Verlag, Berlin, 1982.

4 D. F. Evans and D. A. Jakubovic, *Polyhedron*, in the press.

5 *C.f.* C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, 1958, **29**, 1012.

6 W. Peters, M. Fuchs, H. Sicius, and W. Kuchen, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 231.

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‡ Obtained by heating the sodium salt of sals (0.3 g) in D_2O (5 cm^3), at 170 °C for 60 h (glass ampoule under Ar), and evaporating to dryness. The formulation was confirmed by ^1H n.m.r. spectroscopy.