

DYNAMIC NMR STUDIES OF THE DIOXOURANIUM(VI) ION IN NON-AQUEOUS SOLUTION.  
INSIGHTS INTO THE PROCESSES OF SOLVENT AND LIGAND EXCHANGE ON METAL IONS IN  
GENERAL.

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**Abstract** - Dynamic NMR studies of ligand exchange on  $\text{UO}_2\text{S}_5^{2+}$  and  $\text{UO}_2\text{S}_4^{2+}$  species (where the ligand S is often a widely used solvent such as trimethylphosphate or dimethylacetamide) have facilitated the kinetic characterisation of the dioxouranium(VI) ion. Two rate laws are observed for the ligand exchange process, the first being independent of the free ligand concentration [S], whilst the second is a two term rate law for which the observed first order exchange rate constant may be expressed:  $k_{\text{ex}} = k_1 + k_2[\text{S}]$ . These observations are rationalised in terms of the ability of uranium(VI) to maintain coordination numbers of six, seven and eight. It is also shown, from comparisons of linear free energy relationships, that the surface charge density at the uranium(VI) centre experienced by the equatorial ligands lies between that on six-coordinate aluminium(III) and a series of six-coordinate divalent metal ions. It is suggested that the variability of coordination number and kinetic behaviour observed in the dioxouranium(VI) system may also be observed with other metal ions, and preliminary studies of scandium(III) appear to support this suggestion.

INTRODUCTION

The solvated metal ion is the ubiquitous precursor of metal complexes in solution, and as a consequence a knowledge of the dynamics of this species in solution is of particular interest. Early studies (1-3) established a characteristic pattern in the lability of metal ions towards ligand substitution reactions and indicated, furthermore, that this lability was often closely related to the lifetime of solvent molecules in the first coordination sphere of the metal ion. Nuclear magnetic resonance studies (4-7) have largely confirmed this correlation between the coordinated solvent lifetime and the lability to substitution of a metal ion, and have also established that the solvated metal ion is a species of definite stoichiometry (for all but the more labile species) and may be regarded as a metal complex in which the ligands are solvent molecules (8,9). The desire for a better understanding of the factors determining the lability of metal ions has led to NMR studies of solvent exchange processes in a range of non-aqueous solvents, and much excellent work has been reported (e.g. 10-12 amongst many). A perusal of the literature, however, reveals that the great majority of these studies have been concerned with the early main group and first row transition metal ions which tend to exhibit the ground state stoichiometry  $\text{MS}_6^{n+}$  (where S is a solvent molecule), apart from beryllium(II) for which  $\text{BeS}_4^{2+}$  appears to be the most common ground state stoichiometry (13-16). It is tempting to speculate upon the additional understanding of solvent and ligand exchange processes which might be gained through a study of a metal ion which exhibits a variation in ground state coordination number (and by implication transition state coordination number) with change in ligand character. Such a species is the dioxouranium(VI) ion,  $\text{UO}_2^{2+}$ , which exhibits coordination numbers six, seven and eight in the solid state (17-20) and which provides the central theme of this discussion. Surprisingly few studies of ligand substitution on dioxouranium(VI) in aqueous solution have been reported (21-23) probably as a consequence of the difficulty encountered with protolysis - a phenomenon which does not arise in non-aqueous solution.

COORDINATION CHEMISTRY OF SIMPLE DIOXOURANIUM(VI) SPECIES

Crystallographic studies (17,18) show that the  $\text{UO}_2(\text{HMPA})_4^{2+}$  (where HMPA is hexamethylphosphoramide) and  $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$  species have structures in which the oxo ligands occupy the axial positions, and HMPA and  $\text{H}_2\text{O}$  occupy the four and five equatorial positions respectively. It is reasonable to assume that similar structures persist both in the solid state and in solution for a number of recently reported species (24-33) which are listed in Table 1. It may be seen that in these species the equatorial ligands are often widely used solvents and further that when S = FPP (30) and TMU (31) the solid state stoichiometry,  $\text{UO}_2\text{S}_4^{2+}$ , differs from the solution stoichiometry  $\text{UO}_2\text{S}_5^{2+}$ . (It is also interesting to note that, whereas  $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$  persists in the solid state,  $\text{UO}_2(\text{H}_2\text{O})_4^{2+}$  is the predominant solution species (28,34).)

TABLE 1. Dioxouranium(VI) Species

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Isolated as  $[\text{UO}_2\text{S}_5](\text{ClO}_4)_2$  and existing as  $\text{UO}_2\text{S}_5^{2+}$  in solution<sup>a</sup>

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S = trimethylphosphate<sup>b</sup> (TMP, 23.0°C); triethylphosphate<sup>b</sup> (TEP); dimethylmethylphosphonate<sup>d</sup> (DMMP); dimethylsulphoxide<sup>e</sup> (DMSO, 29.8°C); N,N-dimethylformamide<sup>f</sup> (DMF, 30.9°C); N,N-dimethylacetamide<sup>g</sup> (DMA, 32.2°C); N-methylacetamide<sup>h</sup> (NMA i.e. isomer with methyl groups in trans positions<sup>i</sup>); dimethylbenzamide<sup>j</sup> (DMB) and N-formylpyrrolidine<sup>k</sup> (FPR).

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Isolated as  $[\text{UO}_2\text{S}_4](\text{ClO}_4)_2$  and existing as  $\text{UO}_2\text{S}_4^{2+}$  in solution<sup>a</sup>

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S = tetramethylurea<sup>l</sup> (TMU, 29.6°C); N-formylpiperidine<sup>k</sup> (FPP).

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Isolated as  $[\text{UO}_2\text{S}_4](\text{ClO}_4)_2$  and existing as  $\text{UO}_2\text{S}_4^{2+}$  in solution<sup>a</sup>

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S = hexamethylphosphoramide<sup>m</sup> (HMPA, 38.8°C); (TMU); (FPP).

- a) Solution in  $d_2$ -methylenechloride only except for S = TMU and NMA where  $d_3$ -acetonitrile solutions were also prepared, and for S = DMSO where  $d_6$ -acetone and  $d_2$ -methylenechloride/ $d_3$ -acetonitrile solutions were prepared. The mole ratio of dissolved S: dissolved  $[\text{UO}_2\text{S}_5](\text{ClO}_4)_2$  or  $[\text{UO}_2\text{S}_4](\text{ClO}_4)_2$  was varied from 0:1 to 10:1. When this ratio is 0:1 and S = TMU or FPP the stoichiometry  $\text{UO}_2\text{S}_4^{2+}$  of necessity persists, but when the ratio becomes 1:1 the stoichiometry becomes  $\text{UO}_2\text{S}_5^{2+}$ , whereas the stoichiometry  $\text{UO}_2\text{S}_4^{2+}$  persists for all values of this ratio when S = HMPA.
- b) ref. 24.
- c) Gutmann donor number. ref. 36, 37.
- d) ref. 25.
- e) ref. 28.
- f) ref. 27, 29.
- g) ref. 26.
- h) ref. 33.
- i) L.A. La Planche and M.T. Rogers, *J. Amer. Chem. Soc.*, **85**, 3728 (1963).
- j) J. Carver, private communication.
- k) ref. 30.
- l) ref. 31.
- m) ref. 32.
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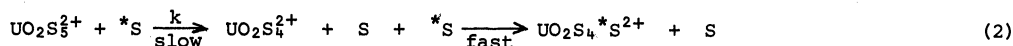
The solution stoichiometries were determined by comparisons of the integrated areas of the NMR signals arising from the coordinated and free ligands in either  $d_2$ -methylenechloride or  $d_3$ -acetonitrile inert diluents (these diluents are defined as inert in that they do not compete with the ligands of interest for sites in the first coordination sphere under the experimental conditions). The only ligand for which the stoichiometry  $\text{UO}_2\text{S}_4^{2+}$  persists in the solid state (17) and in solution is HMPA (32,35) which is the most bulky of the ligands listed in Table 1, and one which also has the highest Gutmann donor number (36,37) DN (=38.8). The balancing of these two factors is just the condition under which a low coordination number might be expected to be imposed upon a metal centre (the observation of the stoichiometry  $\text{Al}(\text{HMPA})_4^{3+}$  in solution (38), whereas  $\text{AlS}_6^{3+}$  is the more usual stoichiometry of aluminium (III) species, appears to justify this expectation also).

The structure of  $\text{UO}_2(\text{HMPA})_4^{2+}$ , in which the mean axial O-U and equatorial O-U distances are 1.74(4) Å and 2.27(5) Å respectively (17), makes an interesting comparison with that of  $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$  in which the analogous distances are 1.71(7) Å and 2.45(6) Å respectively (18). These data suggest that, whilst the axial bond distances in the two structures may not be meaningfully distinguished between, the lengthening of the equatorial bonds for the smaller and weaker donor  $\text{H}_2\text{O}$  ligand (DN = 18) indicates a tendency to minimise the change in the total bond order as the coordination number changes. Unfortunately these are the only two published structures of dioxouranium(VI) species in which the equatorial sites are occupied solely by a single type of oxygen donor ligand, but crystallographic studies of dioxouranium(VI) species, in which the equatorial plane is occupied by both uni- and bidentate oxygen donor ligands, indicate that there is a general tendency for equatorial, and sometimes the axial, bond distances to increase as the number of oxygen donor atoms in the equatorial plane increases from four to five to six (19,20). This has important mechanistic implications, as is discussed later.

#### LIGAND EXCHANGE ON DIOXOURANIUM(VI) SPECIES

The rates of ligand exchange on the  $\text{UO}_2\text{S}_n^{2+}$  species are readily determined from exchange induced modifications of the NMR spectra arising from the coordinated and free ligands. A

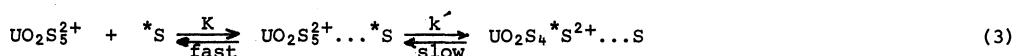
within experimental error over the 28 fold variation of [TMP]. The addition of LiClO<sub>4</sub> such that the solution most dilute in UO<sub>2</sub>S<sub>5</sub><sup>2+</sup> was of the same ionic strength as that most concentrated in UO<sub>2</sub>S<sub>5</sub><sup>2+</sup> had no effect upon k<sub>ex</sub>. This type of kinetic behaviour is characteristic of a dissociative, (D), mechanism (39) in which the rate determining step is the formation of a reactive intermediate UO<sub>2</sub>S<sub>4</sub><sup>2+</sup> as shown in equation 2.



(where the asterisk is a typographical distinction only)

For this mechanism k<sub>ex</sub> = k. (N.B. The oxo ligands are inert (40,41) and thus S exchange involving the axial sites is improbable.)

An alternative explanation of the observed kinetics is available in terms of the dissociative interchange (I<sub>d</sub>) mechanism (39) in which the major energetic step in the formation of the transition state is still bond rupture but, in contrast to the D mechanism, the incipient reactive UO<sub>2</sub>S<sub>4</sub><sup>2+</sup> intermediate is insufficiently stable to survive several molecular collisions prior to reaction, and exchange with a different ligand S will not occur unless that ligand is present in the second coordination sphere at the opportune time. If this species is represented as UO<sub>2</sub>S<sub>5</sub><sup>2+</sup>...\*S the I<sub>d</sub> mechanism may be represented as in equation 3:



where  $K = [\text{UO}_2\text{S}_5^{2+} \dots *S][\text{UO}_2\text{S}_5^{2+}]^{-1}[S]^{-1}$  and: -

$$k_{\text{ex}} = k'K[S]/(1 + K[S]) \quad (4)$$

Two limiting forms of equation (4) exist: -

- $K[S] \gg 1$  and  $k_{\text{ex}} = k'$
- $K[S] \ll 1$  and  $k_{\text{ex}} = k'K[S]$

Obviously limiting form a) need only be considered in the present case. This limit requires that every UO<sub>2</sub>S<sub>5</sub><sup>2+</sup> species must have at least one S species in the second coordination sphere. An inspection of Table 2 indicates that this is an unlikely situation in the less concentrated solutions unless TMP is able to preferentially occupy the second coordination sphere. (Molecular models suggest that approximately fifteen CD<sub>2</sub>Cl<sub>2</sub> and one TMP molecule may be accommodated in the second coordination sphere of UO<sub>2</sub>(TMP)<sub>5</sub><sup>2+</sup>.) At present there is no experimental evidence for such preferential occupancy of the second coordination by S in any of the UO<sub>2</sub>S<sub>n</sub><sup>2+</sup> systems studied. In the UO<sub>2</sub>(TMU)<sub>5</sub><sup>2+</sup> system the independence of k<sub>ex</sub> on [S] holds over a 59.4 fold range of [TMU] in which the most dilute solution studied was 0.0012, 0.0068 and 15.46 mol dm<sup>-3</sup> in [UO<sub>2</sub>(TMU)<sub>5</sub><sup>2+</sup>], [TMU] and [CD<sub>2</sub>Cl<sub>2</sub>] respectively (31). In this latter system the existence of the ground state species UO<sub>2</sub>(TMU)<sub>4</sub><sup>2+</sup>, generated when [UO<sub>2</sub>(TMU)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub> is dissolved alone in either d<sub>2</sub>-methylenechloride or d<sub>3</sub>-acetonitrile (Table 1), lends considerable plausibility to the choice of the D mechanism as the operative mechanism in the UO<sub>2</sub>S<sub>5</sub><sup>2+</sup> systems for which k<sub>ex</sub> is independent of [S]. The D mechanism has also been postulated as being operative in the exchange reactions of AlS<sub>5</sub><sup>3+</sup> on the basis of a similar kinetic pattern (10,38).

#### Activation enthalpy/entropy linear free energy relationships and the UO<sub>2</sub>S<sub>5</sub><sup>2+</sup> systems

The variation of ΔH<sup>#</sup> and ΔS<sup>#</sup> characterising the UO<sub>2</sub>S<sub>5</sub><sup>2+</sup> species as the nature of S is changed is consistent with a linear free energy relationship (LFER) existing between these two kinetic parameters as is shown in Figure 2. The datum points represent the mean ΔH<sup>#</sup> and ΔS<sup>#</sup> values for a series of determinations over a given concentration range for each UO<sub>2</sub>S<sub>5</sub><sup>2+</sup> species, and the bars represent the extremes of the data included in calculating the mean values. The slope of the linear regression line shown in Figure 2 is 296 ± 15 K and the intercept, ΔG<sup>#</sup>, = 54.2 + 0.9 kJ mol<sup>-1</sup>. There is no obvious relationship between the position of a given UO<sub>2</sub>S<sub>5</sub><sup>2+</sup> species on the LFER line and the DN value for S probably as a consequence of steric interactions between adjacent ligands. Nevertheless, it appears from the data obtained in d<sub>2</sub>-methylenechloride diluent (which in all solutions was in great excess over the free ligand S) that the complementary changes in ΔH<sup>#</sup> and ΔS<sup>#</sup> are predominantly controlled by the nature of the coordinated ligand, S. However, upon changing the diluent from d<sub>2</sub>-methylenechloride to d<sub>3</sub>-acetonitrile it is seen (Figure 2) that both ΔH<sup>#</sup> and ΔS<sup>#</sup> characterising UO<sub>2</sub>(NMA)<sub>5</sub><sup>2+</sup> decrease significantly in magnitude (whilst at the same time remaining on the LFER line) whereas the same parameters characterising UO<sub>2</sub>(TMU)<sub>5</sub><sup>2+</sup> may not be significantly differentiated between. Modifications of activation parameters resulting from a change in bulk environment may indicate that solvent outside the first coordination sphere influences the stability of the transition state (42), or may be manifestations of the solvation phenomena incorporated into the model of Bennetto and Caldin (43,44) in which it is proposed that rearrangements of bulk solvent, occurring synchronously with the formation of the transi-

typical set of such spectra observed for the  $\text{UO}_2(\text{DMA})_5^{2+}$  system (26) is shown in Figure 1.

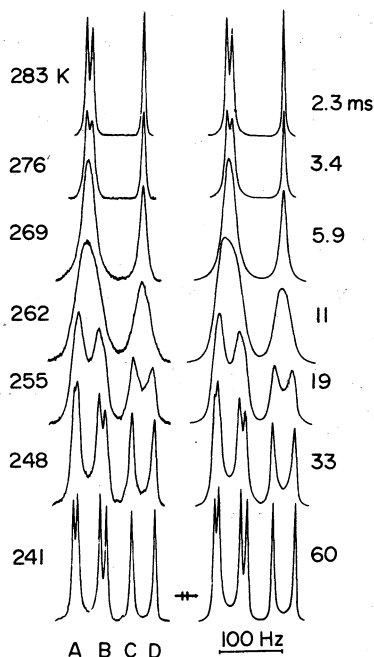


Fig. 1. Experimental (left hand side) and computed best fit  $^1\text{H}$  (90 MHz) NMR spectra of a  $\text{UO}_2(\text{DMA})_5^{2+}$  ( $0.1518 \text{ mol dm}^{-3}$ )-DMA ( $0.7108 \text{ mol dm}^{-3}$ )- $\text{CD}_2\text{Cl}_2$  ( $14.15 \text{ mol dm}^{-3}$ ) solution. Experimental temperatures and the corresponding  $\tau_c$  (ms) values appear at the left and right hand sides of the figure respectively. Resonances A (doublet) and C (singlet) arise from coordinated DMA and the remaining resonances arise from free DMA (from ref. 26).

The parameter directly determined from exchange modified spectra is the mean site lifetime of the coordinated ligand,  $\tau_c$ , which is directly related to more familiar kinetic parameters through equation 1:

$$\frac{1}{\tau_c} = k_{\text{ex}} = \text{ligand exchange rate}/(n[\text{UO}_2\text{S}_n^{2+}]) = \frac{k_B T}{h} e^{-\Delta H^\ddagger/RT} e^{\Delta S^\ddagger/R} \quad (1)$$

where  $k_{\text{ex}}$  is the observed first order rate constant and the other parameters have their usual meaning. No net chemical reaction occurs during the ligand exchange process and the observed rate constant,  $k_{\text{ex}}$ , is necessarily first order under these conditions. The studies of ligand exchange on  $\text{UO}_2\text{S}_n^{2+}$  have been carried out in inert diluents, however, which permits the variation of the concentration of the exchanging species such that the overall exchange rate law may be determined.

Ligand exchange on  $\text{UO}_2\text{S}_n^{2+}$  exhibiting a rate independent of [S]. For  $\text{UO}_2\text{S}_5^{2+}$ , where S = TMP (24), TEP (24), DMMP (25), DMSO (28), DMF (29), DMA (26), NMA (33) and TMU (31),  $k_{\text{ex}}$  is found to be virtually independent of the free ligand concentration [S]. A typical set of data for  $\text{UO}_2(\text{TMP})_5^{2+}$  is shown in Table 2 from which it is seen that  $k_{\text{ex}}$ ,  $\Delta H^\ddagger$ , and  $\Delta S^\ddagger$  are identical

TABLE 2. Exchange of TMP on  $\text{UO}_2(\text{TMP})_5^{2+}$

$[\text{UO}_2(\text{TMP})_5^{2+}]$ $\text{mol dm}^{-3}$	$[\text{TMP}]$ $\text{mol dm}^{-3}$	$[\text{CD}_2\text{Cl}_2]$ $\text{mol dm}^{-3}$	$k_{\text{ex}}(260\text{K})^*$ $\text{s}^{-1}$	$\Delta H^\ddagger$ $\text{kJ mol}^{-1}$	$\Delta S^\ddagger$ $\text{J K}^{-1} \text{mol}^{-1}$
0.3214	1.736	7.46	$111 \pm 8$	$25.5 \pm 1.6$	$-107 \pm 10$
0.2082	1.053	9.90	$96 \pm 6$	$26.1 \pm 1.6$	$-105 \pm 10$
0.0392	0.1981	12.18	$95 \pm 7$	$25.2 \pm 1.5$	$-109 \pm 10$
0.0192	0.0856	12.89	$108 \pm 8$	$23.8 \pm 1.6$	$-113 \pm 10$
0.0122	0.0616	13.15	$104 \pm 7$	$22.6 \pm 1.8$	$-119 \pm 10$

\* (data from ref. 24)

tion state, make contributions to the observed  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values. Our data are not sufficiently extensive at present to explore these possibilities in greater depth.

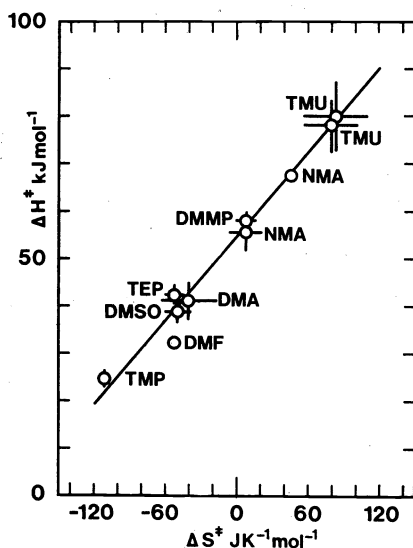


Fig. 2. Linear free energy relationship for the exchange of S on  $\text{UO}_2\text{S}_5^{2+}$ . The acronym adjacent to each datum point identifies S for that system, and the bars indicate the extremes of the values taken to determine the mean value represented by each datum point. The solid curve is the linear regression line.

The diluent used in each study was  $\text{d}_2$ -methylenechloride except in the cases of the TMU and NMA systems indicated by the datum points corresponding to the lower  $\Delta H^\ddagger$  values in each case, which were studied in  $\text{d}_3$ -acetonitrile, and the DMSO system which was studied in a  $\text{d}_6$ -acetone.

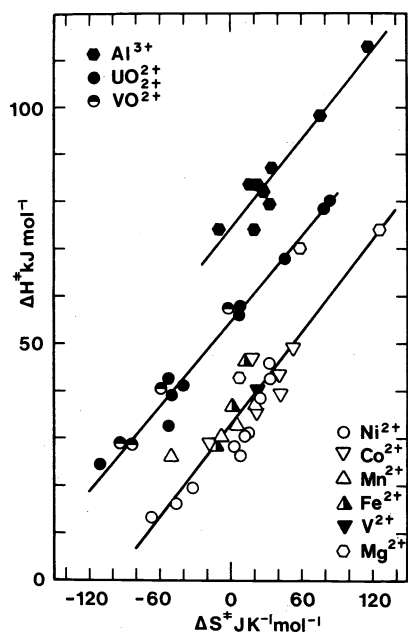


Fig. 3. Linear free energy relationships for ligand exchange. The  $\text{UO}_2\text{S}_5^{2+}$  data are as shown in Fig. 2 and the original sources of the data for the other metal ions are given in ref. 24.

The LFER shown in Figure 2 may be used empirically to compare the kinetic characteristics of ligand exchange on  $\text{UO}_2\text{S}_5^{2+}$  with such reactions at other metal centres. In Figure 3 the  $\text{UO}_2\text{S}_5^{2+}$  data are plotted together with similar data for  $\text{AlS}_6^{3+}$  and  $\text{MS}_6^{2+}$  systems, which are also considered to undergo S exchange through predominantly dissociative mechanisms. The LFER line for  $\text{AlS}_6^{3+}$  is characterised by  $T \approx 317 \text{ K}$  and  $\Delta G^\ddagger \approx 75 \text{ kJ mol}^{-1}$ , and that for  $\text{MS}_6^{2+}$  is characterised by  $T \approx 324 \text{ K}$  and  $\Delta G^\ddagger \approx 33 \text{ kJ mol}^{-1}$ . It is generally considered (5,24,43,45) that the surface charge density at the metal centre is the dominant factor determining  $\Delta G^\ddagger$  for ligand exchange, and on this basis it may be concluded that the surface charge density experienced by the equatorial ligands in  $\text{UO}_2\text{S}_5^{2+}$  lies between that on  $\text{Al}^{3+}$  and  $\text{M}^{2+}$ . (It should be noted that the  $\text{MS}_6^{2+}$  data have been corrected for crystal field contributions (46) where necessary, and that the ionic radii range from  $\text{Ni}^{2+} = 0.62 \text{ \AA}$  to  $\text{Mn}^{2+} = 0.91 \text{ \AA}$ .) It is also interesting to note that the data for exchange of the four equatorial ligands in  $\text{VO}_5^{2+}$  lie close to the  $\text{UO}_2\text{S}_5^{2+}$  line suggesting similar surface charge densities at the two metal centres, but as the mechanism of ligand substitution on  $\text{VO}_5^{2+}$  is subject to debate (24 and references therein) this conclusion should be treated with caution.

#### Ligand exchange on $\text{UO}_2\text{S}_n^{2+}$ characterised by a two term rate law

For the species  $\text{UO}_2(\text{HMPA})_4^{2+}$ ,  $\text{UO}_2(\text{FPR})_5^{2+}$  and  $\text{UO}_2(\text{FPP})_5^{2+}$  in  $d_2$ -methylenechloride diluent a two term ligand exchange rate law is observed (32,33) as exemplified by equation 5:

$$k_{\text{ex}} = k_1 + k_2[\text{S}] \quad (5)$$

Typically for  $\text{UO}_2(\text{HMPA})_4^{2+}$   $k_1(273 \text{ K}) = 12.5 \pm 1.1 \text{ s}^{-1}$ ,  $\Delta H_1^\ddagger = 14.0 \pm 3.0 \text{ kJ mol}^{-1}$  and  $\Delta S_1^\ddagger = -172 \pm 11 \text{ J K}^{-1} \text{ mol}^{-1}$ ; and  $k_2(273 \text{ K}) = 173 \pm 15 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ ,  $\Delta H_2^\ddagger = 22.2 \pm 3.0 \text{ kJ mol}^{-1}$  and  $\Delta S_2^\ddagger = -120 \pm 9 \text{ J K}^{-1} \text{ mol}^{-1}$  (32). The  $k_1$  term may be ascribed to a D type ligand exchange process in which the reactive intermediates  $\text{UO}_2(\text{HMPA})_3^{2+}$ ,  $\text{UO}_2(\text{FPR})_4^{2+}$  and  $\text{UO}_2(\text{FPP})_4^{2+}$  are generated. The first intermediate represents a stoichiometry not so far reported in the ground state, but the relatively large DN and size of HMPA makes its postulation plausible, whereas  $\text{UO}_2(\text{FPP})_4^{2+}$  is known as a ground state species (see Table 1). The  $k_2$  term is consistent with either an  $\text{I}_d$  mechanism (equations 3 and 4) under limiting conditions (b), or an associative (A) mechanism in which the rate determining step is the formation of a transition state in which the coordination number is increased by one. If the A mechanism is operative, the  $\text{UO}_2(\text{HMPA})_4^{2+}$  system requires a transition state stoichiometry  $\text{UO}_2\text{S}_5^{2+}$ , which is a well established ground state for other ligands (Table 1), whilst when  $\text{S} = \text{FPP}$  and  $\text{FPR}$  the required transition state stoichiometry is  $\text{UO}_2\text{S}_6^{2+}$ . This latter stoichiometry has not been reported for a ground state species with monodentate oxygen donor ligands, but six oxygen donor atoms can be accommodated in the equatorial plane of dioxouranium(VI) when the ligands are bidentate (19,20) and hence a transition state stoichiometry,  $\text{UO}_2\text{S}_6^{2+}$ , seems possible. The usual tests for an A mechanism whereby the dependence of the magnitude of  $k_2$  upon the nature of the incoming group is observed is not possible for these ligand exchange processes, and thus a definitive choice between the A and  $\text{I}_d$  mechanisms cannot be made. Nevertheless the existence of two pathways for ligand exchange indicates a similarity in free energy changes along the reaction coordinate, which (in view of the ability of the dioxouranium(VI) species to adopt various stoichiometries in the ground state) is not particularly surprising as through variation of both the axial and equatorial bond distances different transition states of similar free energy, and presumably similar overall bond order, may be generated.

The foregoing discussion of the dioxouranium(VI) ion demonstrates, to a reasonable degree, that those metal ions which exhibit different coordination numbers in the presence of different ligands may also be expected to exhibit a corresponding variation in their ligand exchange behaviour. Apart from the dioxouranium(VI) ion and other actinon ions, the lanthanon ions and the rather enigmatic scandium(III) ion are species of this type; and it is with a brief consideration of this latter ion that this discussion will be concluded.

#### LIGAND EXCHANGE ON SCANDIUM(III)

The unexpected lability of scandium(III) ion towards ligand substitution in aqueous solution (3,47) has been attributed to the aqua-scandium(III) species having a coordination number greater than six. Crystallographic studies show that six (48) or eight (49) oxygen donor ligands may be accommodated in the first coordination sphere of scandium(III), but only 5.1 aqua ligands have been detected by NMR methods (50) in the first coordination sphere of scandium(III) probably as a consequence of displacement of aqua ligands by anionic ligands. In non-aqueous solution, however, the picture is less obscured. Solutions of  $[\text{Sc}(\text{TMP})_6](\text{ClO}_4)_3$  and  $\text{TMP}$  in  $d_3$ -acetonitrile,  $d_3$ -nitromethane, or tetrachloroethane are characterised by NMR spectra in which the separate signals of coordinated and free  $\text{TMP}$  are observed. From these data it is clear that  $\text{Sc}(\text{TMP})_6^{3+}$  is the vastly predominant scandium(III) species in solution, and in  $d_3$ -acetonitrile the following ligand exchange parameters have been determined:  $-k_{\text{ex}}(300 \text{ K}) = 65.7 \pm 2.6 \text{ s}^{-1}$ ,  $\Delta H^\ddagger = 29.8 \pm 0.4 \text{ kJ mol}^{-1}$  and  $\Delta S^\ddagger = -110.9 \pm 1.5 \text{ J K}^{-1} \text{ mol}^{-1}$  where  $k_{\text{ex}}$  is virtually independent of  $[\text{TMP}]$  (51). The  $\Delta G^\ddagger = 63 \text{ kJ mol}^{-1}$  value for this process indicates that six coordinate scandium(III) behaves much as expected for a tri-positive ion with an ionic radius ( $0.68 \text{ \AA}$ ) greater than that for aluminium(III) ( $0.45 \text{ \AA}$ ).

However, when solutions of  $[\text{Sc}(\text{DMSO})_6](\text{ClO}_4)_3$  and DMSO in  $d_3$ -nitromethane are examined it is apparent that the rate of ligand exchange in this system is too great to be determined by NMR methods at the lowest temperature (250 K) studied (51). This may be a consequence of scandium(III) assuming a coordination number greater than six in DMSO solution as is believed to be the case in aqueous solution. Whatever the truth may be it is clear that examination of such systems in non-aqueous solution is likely to provide fascinating insights into ligand exchange processes.

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