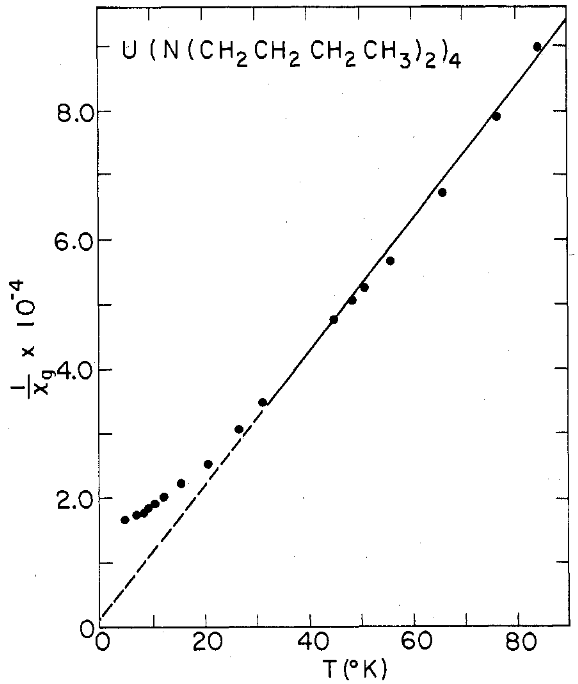

Figure 3. Inverse susceptibility of $U[N(CH_2CH_2CH_3)_2]_4$ vs. temperature. The straight line is the calculated inverse susceptibility in that temperature range with the parameters obtained from a least-squares fit as given in Table IV.

Conclusion

We have succeeded in the synthesis and characterization of some new uranium and thorium alkylamides, one of which was reported as being nondistillable in the original report of $U(NEt_2)_4$.[8] The uranium *n*-alkylamides and $U(NPh_2)_4$ have very similar spectral properties in various solvents. The ether solvents appear to complex each of the uranium *n*-alkylamides in the same fashion, while the hydrocarbon solvents do not appear to complex. The low-temperature magnetic susceptibilities in the solid state are similar. The analogous thorium *n*-alkylamides have been synthesized and appear to be light sensitive. These amides exhibit the expected diamagnetic behavior. Even though a number of new uranium and thorium amides have been synthesized and can be purified by distillation, there are d-transition-metal amides which sublime or distill for which the analogous actinide amides have not been isolated.[12,15] This may be because the uranium amides tend to oligomerize and/or be more thermally unstable than the corresponding d-transition-metal amides. Much work remains to be done on these interesting systems.

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Registry No. $U(N(CH_2CH_2CH_3)_2)_4$, 63833-51-2; $U(N(CH_2CH_2CH_2CH_3)_2)_4$, 63833-50-1; $Th(N(CH_2CH_2CH_3)_2)_4$, 63833-49-8; $Th(N(CH_2CH_2CH_2CH_3)_2)_4$, 63833-48-7; UCl_4, 10026-10-5; $LiN(CH_2CH_2CH_3)_2$, 4111-53-9; $ThCl_4$, 10026-08-1; $LiN(CH_2CH_2CH_2CH_3)_2$, 25440-26-0.

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A Nuclear Magnetic Resonance Study of Ligand Exchange on Dioxopentakis(trimethyl phosphate)uranium(VI) Ion and Its Triethyl Phosphate Analogue

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Ligand-exchange processes on $UO_2L_5{}^{2+}$ where L is either trimethyl phosphate (TMP) or triethyl phosphate (TEP) have been studied using ^1H and ^{31}P NMR techniques, respectively. In CD_2Cl_2 diluent the rate law for L exchange is rate = $5k_{ex}[UO_2I_5{}^{2+}]$, and the exchange mechanism is considered to be either D or I_d. Typical observed rate parameters are k_{ex}(260 K) = 95 ± 6 (32.2 ± 2.7) s^{-1}, $\Delta H^* = 6.0 \pm 0.3$ (10.4 ± 0.4) kcal mol^{-1}, $\Delta S^* = -26.1 \pm 2.3$ (-11.3 ± 1.4) cal deg^{-1} mol^{-1} for solutions in which $[UO_2L_5{}^{2+}] = 0.039$ (0.139) M, [L] = 0.198 (0.745) M, and $[CD_2Cl_2] = 12.18$ (11.21) M where in each case the first magnitude refers to the TMP system and that in parentheses refers to the TEP system. From a comparison of $\Delta H^*/\Delta S^*$ linear free energy relationships it is concluded that the surface charge density at the uranium center seen by the equatorial ligands in $UO_2L_5{}^{2+}$ lies between that on the tervalent aluminum and the divalent first-row transition-metal centers in $AlL_6{}^{3+}$ and $ML_6{}^{2+}$, respectively.

Introduction

The dioxouranium(VI) ion presents the unusual opportunity to study substitution processes in which transition state flexibility is likely to be restricted to the equatorial plane as a consequence of the relatively rigid dioxouranium(VI) axis.[1-6] Of considerable interest is the extent to which the two inert oxo ligands[7,8] modify the reactivity of the formally sexavalent uranium center toward ligand substitution in the equatorial plane. Ligand-substitution studies[9-11] in aqueous solution (and theoretical treatments[12]) indicate that the effective charge on the uranium center is considerably less than six, but the absence of a detailed mechanistic characterization of water exchange on $UO_2(H_2O)_4{}^{2+}$[13] necessarily injects some uncertainty into the detailed interpretation of these studies. Such difficulties are much reduced in studies of exchange of a ligand L on $UO_2L_5{}^{2+}$ species[14-16] as typified by the systems in which

Table I. Solution Compositions and Kinetic Parameters for Ligand Exchange on $UO_2L_5^{2+}$

Soln	$[UO_2L_5^{2+}]$,[a] M	[L],[b] M	$[CD_2Cl_2]$, M	CN[c]	k(260 K),[d] s^{-1}	$\Delta H^{\ddagger}$,[e] kcal mol^{-1}	$\Delta S^{\ddagger}$,[e] cal deg^{-1} mol^{-1}
	$UO_2(TMP)_5^{2+}$	TMP					
i	0.321	1.736	7.46	5.0 ± 0.1	111 ± 8	6.1 ± 0.4	−25.6 ± 2.3
ii	0.208	1.053	9.90	5.1 ± 0.1	96 ± 6	6.2 ± 0.4	−25.4 ± 2.5
iii	0.039	0.198	12.18	5.0 ± 0.1	95 ± 6	6.0 ± 0.3	−26.1 ± 2.3
iv	0.019	0.086	12.89	5.0 ± 0.1	108 ± 7	5.7 ± 0.4	−27.0 ± 2.5
v	0.012	0.062	13.15	5.1 ± 0.1	104 ± 7	5.4 ± 0.4	−28.3 ± 2.3
	$UO_2(TEP)_5^{2+}$	TEP					
vi	0.292	1.120	8.87	5.2 ± 0.1	31.8 ± 2.8	10.6 ± 0.7	−10.6 ± 2.7
vii	0.183	0.921	9.62	5.1 ± 0.1	30.8 ± 2.4	9.6 ± 0.4	−14.5 ± 1.6
viii	0.139	0.745	11.21	5.0 ± 0.1	32.2 ± 2.7	10.4 ± 0.4	−11.3 ± 1.4
ix	0.052	0.242	13.46	5.0 ± 0.1	35.7 ± 3.2	9.7 ± 0.4	−13.8 ± 1.7

[a] Added as $[UO_2L_5](ClO_4)_2$. [b] Added as L. [c] CN = number of ligands per UO_2^{2+} ion as determined from integration of the bound and free TMP and TEP resonances within the temperature ranges 180–220 K and 190–230 K, respectively. [d] k(260 K) values interpolated from the linear least-squares fit of the experimental data to eq 2; the errors quoted are typical standard deviations obtained for each solution from the best fit of the theoretical to the experimental line shape. [e] Errors quoted are the standard errors for the linear least-squares fit of the data to eq 2.

L = trimethyl phosphate (TMP) and triethyl phosphate (TEP) discussed here. A comparison of the ligand-exchange parameters of these and related $UO_2L_5^{2+}$ systems[15,16] with other metal ion systems shows that the effective surface charge density on the uranium center lies between that of tervalent aluminum and the divalent first-row transition-metal ions for predominantly dissociative ligand-exchange processes.

Experimental Section

The complexes $[UO_2(TMP)_5](ClO_4)_2$ and $[UO_2(TEP)_5](ClO_4)_2$ were prepared by refluxing hydrated dioxouranium(VI) perchlorate (3.0 g) with triethyl orthoformate[17,18] (8.0 g) for 1 h at 320 K after which either redistilled and dried (Linde 4A molecular sieves) TMP (3.5 g) or TEP (4.6 g) was added at room temperature. In the case of TMP the yellow crystalline complex precipitated immediately and was filtered off, washed with dry ether, and dried under vacuum. (Found: C, 15.35; H, 3.81; P, 13.18. $[UO_2(TMP)_5](ClO_4)_2$ requires: C, 15.39; H, 3.88; P, 13.24.) In the case of TEP a yellow oil formed at the bottom of the flask. The supernatant liquid was decanted off and the oil was stirred with successive portions of dry ether until yellow crystals were obtained. This product was filtered off, washed with dry ether, and dried under vacuum. (Found: C, 25.48; H, 5.37; P, 11.2. $[UO_2(TEP)_5](ClO_4)_2$ requires: C, 26.12; H, 5.48; P, 11.2.) Both complexes are hygroscopic. Unless under vacuum, all preparative and handling procedures were carried out under dry nitrogen, and exposure to light was kept to a minimum to reduce the possibility of photochemically induced redox processes.[19] Attempts to prepare the tributyl phosphate analogue by these methods failed. Analyses for C, H, and P were performed by the Australian Microanalytical Service, Melbourne. No explosion hazard was encountered in these preparations but it should be noted that *anhydrous perchlorate salts are potentially explosive.*

Solutions of $[UO_2(TMP)_5](ClO_4)_2$ and TMP in CD_2Cl_2, and $[UO_2(TEP)_5](ClO_4)_2$ and TEP in CD_2Cl_2 (Table I), were prepared in 5-cm^3 volumetric flasks not more than 1 h prior to commencement of a kinetic run. Portions of each solution were degassed in 5 mm o.d. NMR tubes attached to a vacuum line prior to sealing under vacuum.

^1H (90 MHz) and ^{31}P (36.4 MHz with ^1H broad band decoupling) NMR spectra were run on a Bruker HX90E spectrometer in the PFP and PFT modes, respectively, using the CD_2Cl_2 deuterium resonance as a lock signal. Up to 30 scans were computer averaged (Nicolet BNC12) at each temperature for the TMP system, and up to 700 scans were accumulated prior to Fourier transformation for the TEP system. Each spectrum was digitized onto paper tape (700–1000 data points per spectrum) prior to line shape analysis through a CDC 6400 computer. The spectrometer temperature control was better than ±0.3 K.

Results and Discussion

At 90 MHz the ^1H doublet ($J_{^{31}P-^1H}$ = 11.3 ± 0.2 Hz) of coordinated trimethyl phosphate (TMP) appears downfield of the free TMP doublet ($J_{^{31}P-^1H}$ = 11.2 ± 0.2 Hz) under slow exchange conditions as seen in Figure 1. At 36.4 MHz the broad-band proton-decoupled ^{31}P singlet of coordinated triethyl phosphate (TEP) appears upfield of the free TEP singlet under slow exchange conditions as seen in Figure 2. Over the respective temperature ranges 180–220 K and 190–230 K, in which chemical exchange induced line shape modifications were negligible, the ratios of the areas of coordinated and free resonances are consistent with $UO_2(TMP)_5^{2+}$ and $UO_2(TEP)_5^{2+}$ being the vastly predominant species over the concentration ranges shown in Table I. The absence of any deviation from this stoichiometry over these concentration ranges indicates that neither CD_2Cl_2 nor perchlorate enters the first coordination sphere, and the absence of any splitting of the coordinated resonances is consistent with the five TMP or TEP ligands occupying equivalent equatorial positions in the pentagonal bipyramidal $UO_2(TMP)_5^{2+}$ and $UO_2(TEP)_5^{2+}$ ions. Such structures are consistent with those suggested for other $UO_2L_5^{2+}$ species in solution, where L = *N*,*N*-dimethylformamide[14] (DMF), *N*,*N*-dimethylacetamide[15] (DMA), or dimethyl methylphosphonate[16] (DMMP).

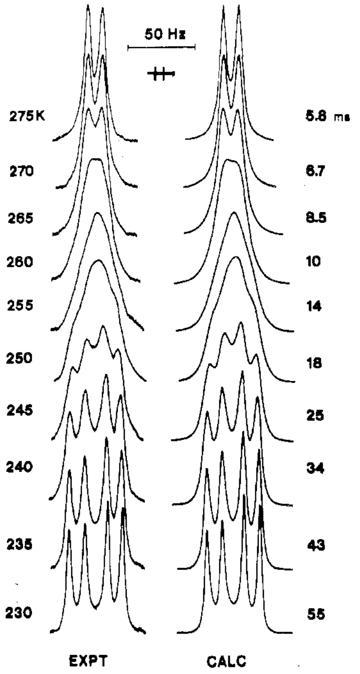

Figure 1. Experimental and calculated best fit ^1H (90 MHz) NMR line shapes of a $UO_2(TMP)_5^{2+}$ (0.039 M), TMP (0.198 M), and CD_2Cl_2 (12.18 M) solution. The experimental temperatures (K) and best fit values appear on the left- and right-hand sides of the figure, respectively. The coordinated TMP doublet is downfield.

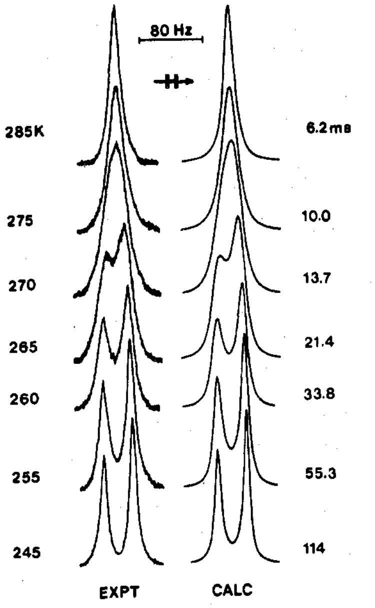

Figure 2. Experimental and calculated best fit ^{31}P (36.4 MHz, ^{1}H decoupled) NMR line shapes of a $UO_2(TEP)_5^{2+}$ (0.183 M), TEP (0.921 M), and CD_2Cl_2 (9.62 M) solution. The experimental temperatures (K) and best fit τ values appear on the left- and right-hand sides of the figure, respectively. The coordinated TEP singlet is upfield.

The kinetic parameters for ligand exchange on $UO_2(TMP)_5^{2+}$ and $UO_2(TEP)_5^{2+}$ were derived from complete line shape analyses of the exchange modified line shapes over the temperature ranges 230–280 K and 240–285 K, respectively, using a computer program described in the literature.[20] This program requires as input for each experimental temperature the line width at half amplitude and chemical shifts for each resonance, extrapolated from the low-temperature range in which no exchange modifications of the line shape occur. For the TMP system shown in Figure 1 the chemical shift between the coordinated and free resonances varied ($1/T$) from 30.70 Hz (230 K) to 31.50 Hz (280 K) and the coordinated and free line widths varied ($1/T$) respectively from 2.40 and 1.99 Hz (230 K) to 2.34 and 1.92 Hz (280 K). For the TEP system shown in Figure 2 the analogous chemical shift variations were 36.16 Hz (245 K) and 33.18 Hz (285 K), and the coordinated and free line width variations were respectively 2.60 and 3.05 Hz (245 K) and 1.46 and 1.76 Hz (285 K). Theoretical[21,22] and experimental[23] examinations reveal no difference between chemical exchange induced modifications of FT and of CW line shapes and therefore this program, which is based upon the assumption of CW conditions, is also used in treatment of the FT data. Typical experimental and computed best fit line shapes are shown in Figures 1 and 2. The mean site lifetimes of coordinated and free ligand, τ and τ_F respectively, are given in eq 1 where χ and χ_F are the coordinated and free

$$\tau/\chi = \tau_F/\chi_F = 1/k_{ex}\chi \tag{1}$$

ligand mole fractions, respectively, and the first-order rate constant k_{ex} is given by eq 2.

$$k_{ex} = (kT/h)\exp(-\Delta H^{\ddagger}/RT)\exp(\Delta S^{\ddagger}/R) \tag{2}$$
$$= \text{rate}/5[UO_2L_5^{2+}]$$

The τ values determined for the solutions listed in Table I are plotted against $1/T$ in Figure 3 from which it is seen that, while the TMP and TEP data sets are quite different, within each of the systems the τ(260 K) values exhibit only small variations with change in the concentration of free ligand, and the variations of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ within a system are contained

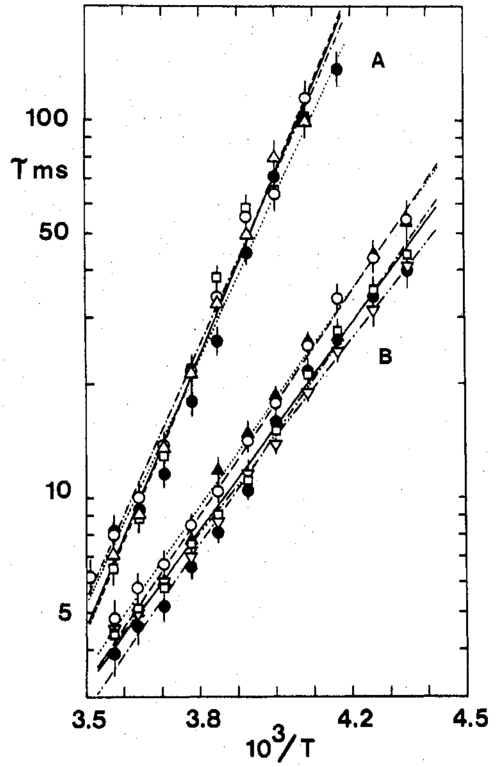

Figure 3. Semilogarithmic plots of data for the $UO_2(TEP)_5^{2+}$ (A) and $UO_2(TMP)_5^{2+}$ (B) systems. In data set (A) the individual data for solutions vi–ix are respectively represented by squares, open circles, triangles, and closed circles and their linear least-squares fits to eq 2 are represented by ---, -··-, — and ···, respectively. In data set (B) the individual data for solutions i–v are respectively represented by closed circles, squares, open circles, closed triangles, and open triangles and their linear least-squares fits to eq 2 are represented by -··-, - - -, · · ·, —, and -···-, respectively.

within two standard errors. For a given system these kinetic parameters may be considered identical, within the quoted errors, with change in free ligand concentration and are consistent with a dissociative, D, or dissociative interchange, I_d, mechanism[24] as shown in eq 3 and 4, respectively. The

$$UO_2L_5^{2+} + L^* \xrightarrow[\text{slow}]{k} UO_2L_4^{2+} + L + L^*$$
$$UO_2L_4^{2+} + L + L^* \xrightarrow[\text{fast}]{} UO_2L_4L^{*2+} + L \tag{3}$$

· ·

$$UO_2L_5^{2+} + L^* \xrightleftharpoons[\text{fast}]{K_{\text{assn}}} UO_2L_5^{2+}\cdots L^*$$
$$UO_2L_5^{2+}\cdots L^* \xrightleftharpoons[\text{slow}]{k'} UO_2L_4L^{*2+}\cdots L \tag{4}$$

(where the asterisk is a typographical distinction only)

rate-determining step in both mechanisms is the dissociation of L, but whereas the D mechanism produces an intermediate of sufficiently long lifetime to complete the exchange process through reaction with a different L molecule, the I_d mechanism proceeds through the associated species $UO_2L_5^{2+}\cdots L$ in which an L molecule resides in the second coordination sphere. For the D mechanism $k_{ex} = k$ and is independent of [L], but for the I_d mechanism the variation of k_{ex} with [L] is given by eq 5. When K_{assn} [L] << 1, k_{ex} exhibits a first-order dependence

$$k_{ex} = k'K_{assn}[L]/(1 + K_{assn}[L]) \tag{5}$$

on [L], whereas when $K_{assn}[L] >> 1$, $k_{ex} = k'$ and is independent of [L]. The variations in k_{ex} predicted by eq 5 over the extremes of the [TMP] and [TEP] concentration ranges (Table I) when $K_{assn} \geq 100$ or 15 M^{-1}, respectively, are within

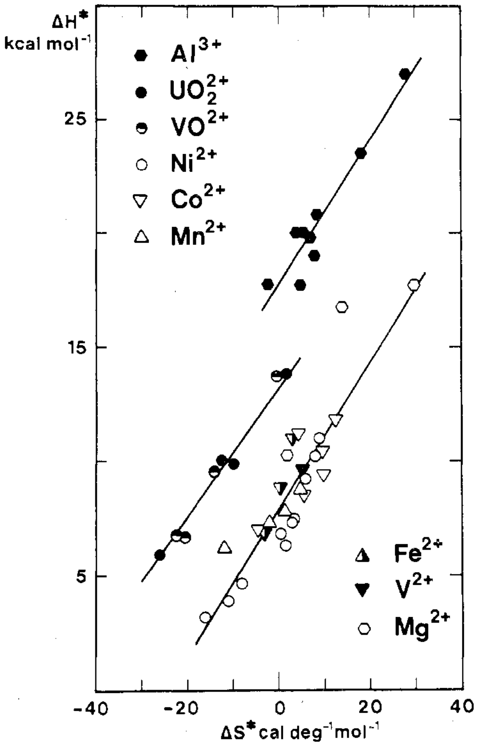

Figure 4. Linear free energy relationships for ligand (L) exchange. The central metal species are identified by symbol in the figure. The exchanging ligand in order of decreasing $\Delta S^{\ddagger}$ is: Al^{3+}: H_2O, TMP, TMP, DMMP, dimethyl hydrogenphosphite, DMSO, DMF, DMSO, DMF (ref 35c, a, b, a, a, d, e, b, b); UO_2^{2+}: DMMP, DMA, TEP, TMP (ref 16, 15, this work); VO^{2+}: H_2O, CH_3OH, DMF, CH_3CN (ref 40, 41a, c, b); Ni^{2+}: DMF, CH_3OH, DMF, H_2O, H_2O, NH_3, H_2O, CH_3CN, DMSO, DMSO, (ref 36i, j, g, c, d, f, e, h, c, a); Mn^{2+}: H_2O, H_2O, CH_3CN, CH_3OH (ref 36m, n, l, k); Co^{2+}: DMF, NH_3, DMSO, H_2O, CH_3OH, CH_3CN (ref 36i, r, o, q, p, h); Fe^{2+}: CH_3OH, CH_3CN, H_2O (ref 36k, s, t); Mg^{2+}: C_2H_5OH, CH_3OH, H_2O (ref 36u, v, w); V^{2+}: H_2O (ref 36x). (N.B. The symbol for Fe^{2+} is inverted in the key to the figure.)

the range of k_{ex}(260 K) values for these two systems (Table I). It is concluded either that a D mechanism is operative or that the above K_{assn} values, which are much greater than K_{assn} = 0.35 M^{-1} calculated from the Fuoss[25] equation for an interaction distance of 7 Å, represent the lower limits for an I_d mechanism. It is clear that if, as suggested from space filling models, approximately 15 CD_2Cl_2 and 1 TMP or TEP molecules may be accommodated in the second coordination sphere of $UO_2L_5^{2+}$, then considerable preferential solvation must occur in solutions iii–v and ix if K_{assn} = 100 or 15 M^{-1}, respectively, are lower limiting values, but as no direct determination of the solvent composition in the second coordination sphere was achieved this aspect is not further pursued. The postulation of a $UO_2L_4^{2+}$ reactive intermediate as required in a D mechanism is afforded considerable plausibility with the recent reports of the six-coordinate $UO_2(HMPA)_4^{2+}$ ground state species (HMPA = hexamethylphosphoramide) in solution[26] (the species $UO_2(HMPA)_4^{2+}$ has also been observed in CD_2Cl_2 solution in this laboratory[27]) and in the solid state[28] and also of $UO_2(H_2O)_4^{2+}$ in solution.[13]

The lower $\Delta H^{\ddagger}$ and more negative $\Delta S^{\ddagger}$ values of the $UO_2TMP_5^{2+}$ system may arise in part from the ability of four TMP ligands to increase their oxygen–uranium bond order as the fifth TMP ligand decreases its bond order in the formation of a primarily dissociative transition state, whereas in the more crowded $UO_2TEP_5^{2+}$ system such compensatory movement of the four nonleaving TEP ligands is likely to be less thereby producing a higher $\Delta H^{\ddagger}$ value and a less negative $\Delta S^{\ddagger}$ value. The extension of this simple argument from ligands with a phosphate skeleton to the analogous DMA[15] and DMMP[16] systems is of uncertain value as the variation in ligand–uranium bonding is unclear at this stage, and in addition the magnitude of contributions to $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ from solvent interaction outside the first coordination sphere is presently the subject of debate.[29-33]

The average $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for the $UO_2(TMP)_5^{2+}$ and the analogous TEP, DMA,[15] and DMMP[16] systems are plotted in Figure 4 from which it is seen that a reasonable linear relationship exists between these two activation parameters. Similar relationships exist for AlL_6^{3+} (which appears to be the only tervalent species for which the exchange rate has been shown to be independent of free ligand concentration) and ML_6^{2+} divalent metal complexes on which ligand exchange also occurs through D or I_d mechanisms. (The transition metal complex $\Delta H^{\ddagger}$ values have been corrected for crystal field contributions calculated using $\rho = 1$ as described by Companion.[34] In view of the approximate nature of such corrections no attempt has been made to distinguish between the activation parameter sets for the divalent metal complexes, and as has been done elsewhere[29] they are treated as a single data set.) This study sheds no light on the origins of these free-energy relationships, which have been debated elsewhere,[29-32] but it is clear from Figure 4 that the $UO_2L_5^{2+}$ linear least-squares line (slope ≈ 276 K, $\Delta G^{\ddagger} \approx 13$ kcal mol^{-1} (=$\Delta H^{\ddagger}$ when $\Delta S^{\ddagger}$ = 0)) lies between those of the AlL_6^{3+} systems[35] (317 K, 18 kcal mol^{-1}) and ML_6^{2+} (324 K, 8 kcal mol^{-1}) systems.[36] It is generally considered[29,37,38] that the surface charge density on the metal center is a dominant factor determining the magnitude of the kinetic parameters of ligand exchange in a metal complex, on which basis the empirical deduction that the surface charge density seen by the equatorial ligands in $UO_2L_5^{2+}$ lies between that seen in AlL_6^{3+} (Al^{3+} radius = 0.45 Å)[39] and ML_6^{2+} (the extremes of the radii of the species plotted are Ni^{2+} = 0.62 Å and Mn^{2+} = 0.91 Å)[39] may be made from Figure 4. It is interesting to note that the data[40,41] for exchange of the four equatorial ligands in VOL_5^{2+} lie close to the $UO_2L_5^{2+}$ line suggesting a similarity of surface charge density seen at the two metal centers by the equatorial ligands, but this conclusion should be treated with caution as the order of exchange in [L] has not been reported for VOL_5^{2+}, and some studies indicate that the highly labile axial L ligand may provide a pathway for substitution at the equatorial sites.[42]

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Registry No. $[UO_2(TMP)_5](ClO_4)_2$, 26201-91-2; $[UO_2(TEP)_5](ClO_4)_2$, 63609-14-3.

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Reactions of the Octaisothiocyanatodirhenate(III) Anion with Tertiary Phosphines. Cleavage of the Rhenium–Rhenium Quadruple Bond

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The reactions of the salt $(Bu_4N)_2Re_2(NCS)_8$ with monodentate and bidentate tertiary phosphines produce the green complexes $(Bu_4N)_2Re_2(NCS)_8L_2$ which contain dimeric thiocyanate-bridged anions with magnetically dilute rhenium(III) centers. The reactions of the diethylphenylphosphine product with 1,2-bis(diphenylphosphino)ethane, 2,2′-bipyridyl, and 1,10-phenanthroline lead to the breaking of the thiocyanate bridges and the formation of the six-coordinate rhenium(III) monomers $Re(NCS)_3(PEt_2Ph)(B)$, where B = dppe, bpy, or phen. This is the first extensive series of complexes which has been prepared directly from anions of the type $Re_2X_8^{2-}$ (X = Cl, Br, or NCS) where cleavage of the quadruple Re–Re bond is the rule rather than the exception. The reason for this behavior may be due to the fact that the metal–metal bond in $Re_2(NCS)_8^{2-}$ is weaker than that in the related octahalo anions, a conclusion which is based upon differences in the electronic absorption spectra of these species. The complexes of the type $(Bu_4N)_2Re_2(NCS)_8L_2$ which contain monodentate 1,2-bis(diphenylphosphino)ethane (dppe) and bis(diphenylphosphino)methane (dppm) are unstable in acetonitrile solutions due to a very rapid intramolecular attack of the unbound tertiary phosphine groups upon the thiocyanate bridges. This leads to the formation of the yellow monomeric anions $[Re(NCS)_4(dppm)]^-$ and $[Re(NCS)_4(dppe)]^-$, the latter species having been isolated in the solid state as its butylammonium salt. Its properties have been compared to those of the related derivative with triethylphosphine, $(Bu_4N)Re(NCS)_4(PEt_3)_2$, which is also reported here for the first time. The new complexes prepared in the present study have been characterized by infrared, electronic absorption, and x-ray photoelectron spectroscopy and magnetic susceptibility and concentrated range conductance measurements.

Introduction

The reactions of the octahalodirhenate(III) anions $Re_2X_8^{2-}$, where X = Cl or Br, with monodentate tertiary phosphines lead to the formation of either substitution derivatives of the type $Re_2X_6(PR_3)_2$ or the one- or two-electron reduction products $Re_2X_5(PR_3)_3$ or $Re_2X_4(PR_3)_4$.[1] The electronic and molecular structures of these species have attracted much interest[2,3] and studies on the chemical reactivity of these low oxidation state dimers are currently being pursued in our laboratory.[4-6]

While the strong metal–metal bond is more often than not retained in the products which result from reactions of $Re_2X_8^{2-}$, it is becoming increasingly apparent that under quite mild reaction conditions this bond may be disrupted to afford monomeric rhenium species. Thus the reaction of $(Bu_4N)_2Re_2Cl_8$ with ligands as different as thiourea and 1,2-bis(diphenylphosphino)ethane leads to products $(ReCl_3(tu)_3$ and $Re_2Cl_6(dppe)_2$, respectively)[7-9] in which the metal–metal bond is no longer present. More recently we have shown[5] that rhenium(II) complexes of the type $Re_2X_4(PR_3)_4$ may react with carbon monoxide to afford the rhenium(II) monomers $ReX_2(CO)_2(PR_3)_2$. However, in none of these instances is it yet clear why the reactions proceed with disruption of the metal–metal bond while related ones do not. This is in contrast to the photochemical cleavage of the quadruple bond in $Re_2Cl_8^{2-}$ which has recently been achieved[10] by ultraviolet irradiation of acetonitrile solutions of $(Bu_4N)_2Re_2Cl_8$.