Rates and Activation Parameters for the Stepwise Formation of Mono Complexes of the Hexakis(dimethyl sulphoxide)aluminium(III) Ion with Uni-, Bi-, and Ter-dentate Nitrogen-donor Ligands in Nitromethane Solution

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Rates and activation parameters for the formation of mono complexes of the $[Al(dmso)_6]^{3+}$ ion (dmso = dimethyl sulphoxide) with pyridine, 2,2′-bipyridine (bipy), 2,2′ : 6′,2″-terpyridine (terpy), 1,10-phenanthroline (phen), and t-butylamine have been determined in nitromethane solution by following the release of the co-ordinated dmso molecules using stopped-flow Fourier-transform ^1H n.m.r. spectroscopy. Activation parameters for the solvent-exchange process (using $[^2H_6]$dmso) are also reported from data covering a wide temperature range (263—338 K). The reactions with bipy and terpy proceed in two and three distinct steps respectively, and activation parameters are reported for the first bond formations and for the subsequent slower chelate-ring closures. The reaction with pyridine is significantly retarded by the addition of a ten-fold excess of the non-ligating substrate 2,6-dibromopyridine, the rate constant decreasing from 167 to 55.6 dm^3 mol^{-1} s^{-1}. This rate retardation is in line with the observation of unusually large outer-sphere associations (K_0 in the range 2 × 10^2—75 × 10^2 dm^3 mol^{-1}) during the first bond formations, the large values of K_0 accounting for the unexpectedly rapid rates of these reactions.

SUBSTITUTION reactions of $[Al(solvent)_6]^{3+}$ ions are expected to be fairly slow since the rate constants for solvent exchange are in the range 0.1—5.1 s^{-1} at 298 K.[1] Stopped-flow Fourier-transform n.m.r. spectroscopy is a convenient way of measuring the rates of reactions which occur on this time scale,[2,3] and has several advantages over other methods which are commonly used to investigate metal complex formations (*e.g.* stopped-flow spectrophotometry). For example, complete ^1H n.m.r. spectra can be obtained every few seconds, and it is possible to follow the course of the substitution reactions by detecting the expulsion of the co-ordinated solvent molecules by the incoming ligands rather than the normal practice of following changes in the ligand u.v. absorbances; also there is no interference from strong solvent absorptions as there sometimes is in spectrophotometric studies. Nitromethane was found to be a convenient solvent in this work since it does not compete with dimethyl sulphoxide (dmso) for the inner sphere of Al^{III}, and there are no solubility problems. However, it does completely obscure the u.v. bands of the ligands, making spectrophotometric studies impossible.

By using deuteriated solvent as the incoming ligand, stopped-flow F.t. n.m.r. can also be used to extend the temperature range over which solvent-exchange data can be obtained,[4] and this enables more reliable activation parameters to be estimated. Good agreement was found previously between solvent-exchange data obtained for the $[Al(dmso)_6]^{3+}$ ion from n.m.r. line-broadening studies at high temperatures,[5] and stopped-flow F.t. n.m.r. at lower temperatures.[4]

In the present study we have extended our preliminary work on the $[Al(dmso)_6]^{3+}$ ion,[4,6] including variable-temperature studies of the reactions with $[^2H_6]$dmso, pyridine, 2,2′-bipyridine (bipy), 2,2′:6′,2″-terpyridine (terpy), 1,10-phenanthroline (phen), and t-butylamine in nitromethane solution. The reaction with bipy was found to proceed through a rate-determining chelate-

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[1] J. J. Delpeuch, M. R. Khaddar, A. A. Peguy, and P. R. Rubini, *J. Amer. Chem. Soc.*, 1975, **97**, 3373.

[2] D. A. Couch, O. W. Howarth, and P. Moore, *J. Phys.* (*E*), 1975, **8**, 831.

[3] C. A. Fyfe, M. Cocivera, and S. W. H. Domji, *Accounts Chem. Res.*, in the press.

[4] A. J. Brown, D. A. Couch, O. W. Howarth, and P. Moore, *J. Magnetic Resonance*, 1976, **21**, 503.

[5] S. Thomas and W. L. Reynolds, *J. Chem. Phys.*, 1966, **44**, 3148.

[6] A. J. Brown, O. W. Howarth, P. Moore, and W. J. E. Parr, *J.C.S. Chem. Comm.*, 1977, 586.

ring closure,[6] and in the present investigation it has also been possible to obtain activation parameters for all three stages in the formation of the 1 : 1 complex with the terdentate ligand terpy.

The first step in all of the reactions investigated was rather faster than expected on the basis of the Eigen–Wilkins mechanism.[7] Assuming that the second-order rate constants for metal complex formation (k_f) are related to the overall solvent-exchange rate constant ($k_{ex.}$) by the equation $k_f \simeq k_{ex.}K_0$, the calculated values of the outer-sphere association constants, K_0, are in the range 2×10^2—75×10^2 dm^3 mol^{-1}. These values of K_0 are significantly larger than expected for reactions with neutral ligands, and point to an unusually strong interaction in the outer sphere of the $[Al(dmso)_6]^{3+}$ ion. Accordingly we investigated the effect of an excess of the non-ligating substrate 2,6-dibromopyridine on the rate of reaction of the $[Al(dmso)_6]^{3+}$ ion with one of the simplest ligands studied, pyridine.

EXPERIMENTAL

Materials.—The salt $[Al(dmso)_6][ClO_4]_3$ was prepared from the hydrated salt by a published method.[8] It was recrystallised from anhydrous dmso, washed with dry diethyl ether to remove any unco-ordinated dmso, dried in a vacuum desiccator, and stored under dry nitrogen. Hydrogen-1 n.m.r. spectra showed the absence of water and unco-ordinated dmso. **CAUTION**: We have since abandoned the use of perchlorate salts in most of our work, having experienced a violent explosion when preparing $[Hg(dmso)_6][ClO_4]_2$. The greatest care should be exercised with complexes containing organic ligands and perchlorate ion, and we recommend the use of other weakly co-ordinating anions {*e.g.* $[BF_4]^-$, $[PF_6]^-$, $[S(CF_3)O_3]^-$, or $[BPh_4]^-$} whenever possible. In the present study, none of these alternatives was found to be satisfactory; $[BF_4]^-$ and $[PF_6]^-$ salts decompose to give the more stable fluoro-complexes of Al^{III}, tetraphenylborates (from the reaction of $AlCl_3$ + $3Na[BPh_4]$ in diethyl ether) also decompose on standing, possibly through Friedel–Crafts reactions, and the $[S(CF_3)O_3]$ salts, although stable, were too insoluble.

Other compounds used were the best available commercial materials purified by recrystallisation or distillation as necessary. [$^2H_3$]Nitromethane was recovered for future use by distillation first from anhydrous $AlCl_3$ and then from sodium hydrogencarbonate on a vacuum line, and its purity checked by ^1H n.m.r. before use.

Kinetic Studies.—It was necessary to modify our prototype, room-temperature, flow F.t. n.m.r. apparatus [2] to permit variable-temperature studies. The modified apparatus includes a shroud surrounding the inlet solutions, fed by a manifold of four temperature-controlled, pressure-regulated, nitrogen streams, the flow from each stream being adjustable to allow individual temperature control. The shroud is a few millimetres from the top of the n.m.r. spinner. A set of thermocouples are used to monitor temperatures throughout the apparatus, and the temperature control is better than ±0.5 K throughout. Satisfactory runs have been carried out with this modified apparatus at temperatures down to 210 K. Full details of the equipment are described elsewhere.[9]

RESULTS

Equilibrium Studies.—Preliminary work showed that equilibrium (1) lies entirely to the left (*i.e.* no complex formation) when dmso is used as the solvent, irrespective

$$[Al(dmso)_6]^{3+} + L \rightleftharpoons [Al(dmso)_{6-n}L]^{3+} + n\,dmso \qquad (1)$$

of the dentate number of the nitrogen-donor ligand (L) which is used. This behaviour is in accord with the known preference of Al^{III} for oxygen- rather than nitrogen-donor ligands, and the much greater concentration of dmso over L that could be achieved in dmso solution. Accordingly we investigated the reactions using nitromethane as solvent, since this greatly lowers the maximum dmso activity, and it is well known that nitromethane does not compete with dmso for the inner sphere of most metal ions.[10] In [$^2H_3$]-nitromethane, integration of the free and bound dmso resonances indicates that the complexes are almost completely formed when $[Al(dmso)_6{}^{3+}] = [L] = 10^{-2}$ mol dm^{-3}.

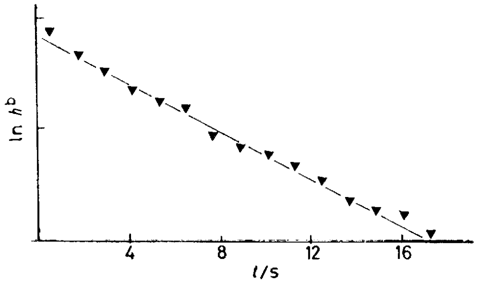

FIGURE 1 First-order rate plot for the exchange of [$^2H_6$]dmso (1 mol dm^{-3}) with the $[Al(dmso)_6]^{3+}$ ion (10^{-2} mol dm^{-3}) in [$^2H_3$]MeNO$_2$ at 293 K

Kinetic Studies.—All the reactions were studied in [$^2H_3$]nitromethane solution to avoid saturation of the spectrometer receiver.

(*a*) *Solvent exchange.* This reaction was studied as described previously [4] using concentrations of 10^{-2} mol dm^{-3} $[Al(dmso)_6]^{3+}$ and 1.0 mol dm^{-3} [$^2H_6$]dmso after mixing. The rate was measured from a linear plot of ln(peak height) against time for the decaying resonance of bound dmso at δ 2.82 p.p.m. (free dmso is found at δ 2.50 p.p.m.). A typical plot obtained at 293.0 K is shown in

TABLE 1

Rate data for the exchange of dmso with the $[Al(dmso)_6]^{3+}$ ion [a]

T/K		262.2	273.2	283.2	293.2	297.2
$10^3k_{ex.}{}^I$/s^{-1} [b]		0.52	2.0	7.4	17.8	55.0
		±0.03	±0.1	±0.2	±0.5	±3.3
T/K	313.2	318.2	323.2	328.2	333.2	338.2
$10^3k_{ex.}{}^I$/s^{-1} [c]	289	504	926	1 504	2 038	3 560
	±16	±3	±22	±3	±62	±100

[a] Rate constants refer to the exchange of a single solvent molecule. [b] Data at ⩽297.2 K obtained by flow n.m.r. spectroscopy. [c] Data ⩾313.2 K taken from ref. 5 (line-broadening studies).

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[7] R. G. Wilkins, *Accounts Chem. Res.*, 1970, **3**, 408; 'The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes,' Allyn and Bacon, Boston, 1974.

[8] F. A. Cotton and R. Francis, *J. Amer. Chem. Soc.*, 1960, **82**, 2986.

[9] A. J. Brown, Ph.D. Thesis, University of Warwick, 1977.

[10] L. S. Frankel, *Inorg. Chem.*, 1971, **10**, 814.

Figure 1, and from the gradient we obtain $k_{ex.} = 0.107 \pm 0.003$ s^{-1}. Since the co-ordination number of Al^{III} is six in this case,[5] the rate constant for the exchange of a *single* solvent molecule is $k_{ex.}{}^{I} = 1.78 \times 10^{-2}$ s^{-1} at this temperature. The results obtained at five temperatures in the range 262—297 K are summarised in Table 1, and in the Arrhenius plot (Figure 2) we show the gratifying agreement between these data and those obtained from a previous line-broadening study at higher temperatures.[5] Combination of the two sets of results gives $\Delta H^\ddagger = 85.3 \pm 1.9$ kJ mol^{-1} and $\Delta S^\ddagger = 16.7 \pm 6.1$ J K^{-1} mol^{-1} (at 298.2 K) from studies between 262 and 338 K. These activation parameters compare favourably with the values obtained from the line-broadening results alone: $\Delta H^\ddagger = 83.7 \pm 4.2$ kJ mol^{-1}, $\Delta S^\ddagger = 15.5 \pm 10.5$ J K^{-1} mol^{-1}.

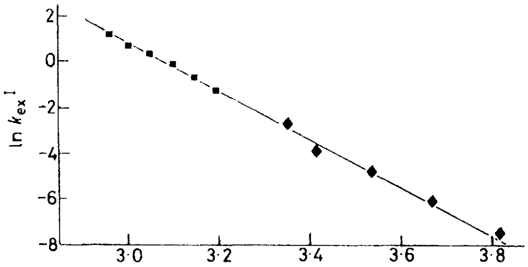


FIGURE 2 Arrhenius plot for the solvent-exchange reaction of the [Al(dmso)$_6$]$^{3+}$ ion with bulk dmso; (■) line-broadening results; (♦) flow-n.m.r. results

(*b*) *Reactions with nitrogen-donor ligands.* Previously we showed that two distinct stages are discernible in the formation of the 1 : 1 complex with 2,2′-bipyridine, the half-lives for the two successive steps being well separated ($t_{\frac{1}{2}}$ *ca.* 3.5 s for the first stage, *ca.* 1 240 s for the second stage at 268.3 K and [Al^{III}] = [bipy] = 5×10^{-3} mol dm^{-3}). Similarly, for the reaction with the terdentate ligand 2,2′:6′,2″-terpyridine, three well separated stages are apparent as shown in Figure 3. It was convenient to examine the first stages of these multistep reactions at lower temperatures (*ca.* 250—270 K), whereas the ring-closure reactions could be examined at, or above, room temperature. Field locking and signal averaging was possible for some of the slower reactions studied. It is apparent from Figure 3 that all three stages in the reaction with terpy give rise to equal changes in the heights of the resonances of free and bound dmso as expected.

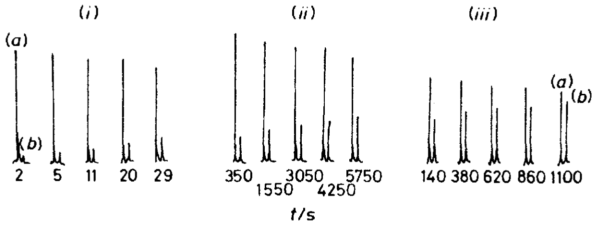


FIGURE 3 Parts of successive ^{1}H n.m.r. spectra observed for the three stages in the reaction of the [Al(dmso)$_6$]$^{3+}$ ion with terpy. (*i*) Stage one at 272.7 K; (*ii*) stage two at 272.7 K; (*iii*) stage three at 313.2 K; (*a*) δ 2.82 p.p.m.; (*b*) δ 2.50 p.p.m.

The first step in these reactions, and the single step in the reactions with 1,10-phenanthroline, pyridine, and t-butylamine, are all surprisingly fast, and we were forced to used second-order conditions and low temperatures to enable us to measure the rates by flow n.m.r. If [Al(dmso)$_6{}^{3+}$] = [ligand] = a mol dm^{-3} at time $t = 0$, it can be shown that, for a second-order process involving the formation of a single metal–ligand bond, equation (2) applies (see Appendix; h^f and h^b refer to the heights at time t of the resonances of free and bound dmso and k_1 is the second-order rate constant for first bond formation).

$$6h^f/(h^b - 5h^f) = ak_1t \qquad (2)$$

A plot of $h^f/(h^b - 5h^f)$ against time was linear with a gradient of $ak_1/6$; linear least-squares analysis was used to find the gradients of such plots and to enable values of k_1 to be estimated (Table 2).

TABLE 2

Average values of the rate constants for the reactions of the [Al(dmso)$_6$]$^{3+}$ ion (5×10^{-3} mol dm^{-3}) with nitrogen-donor ligands (5×10^{-3} mol dm^{-3}) in [^{2}H$_3$]nitromethane solution

(*a*) With 1,10-phenanthroline

T/K	271.1	267.9	265.4	263.2	257.7	250.5
k_1/dm^3 mol^{-1} s^{-1}	85.0	57.3	32.8	33.4	11.3	4.14
	±7.0	±5.1	±4.0	±4.5	±1.0	±0.15

(*b*) With 2,2′-bipyridine

First bond formation

T/K	268.3	263.4	263.2 *	253.6
k_1/dm^3 mol^{-1} s^{-1}	57.4	34.7	30.3	7.8
	±7.3	±3.9	±1.7 *	±0.8

Chelate-ring closure

T/K	293.4	283.7	273.0	263.4	252.9
10^4k_2/s^{-1}	210	58	10.0	2.2	0.44
	±20	±5	±0.6	±0.3	±0.02

(*c*) With 2,2′:6′,2″-terpyridine

First bond formation

T/K	272.7	268.1	263.1	258.4	253.3	252.7
k_1/dm^3 mol^{-1} s^{-1}	99.9	38.7	30.1	12.6	6.82	6.14
	±3.5	±2.6	±2.5	±0.5	±0.48	±0.79

First chelate-ring closure

T/K	301.4	293.2	282.8	272.7
10^4k_2/s^{-1}	63	25	5.5	1.10
	±4	±3	±0.2	±0.04

Second chelate-ring closure

T/K	343.8	334.0	333.4	323.7	313.2	303.0
10^4k_3/s^{-1}	430	100	120	66	8.8	2.4
	±4.0	±8	±13	±3	±0.5	±0.2

(*d*) With t-butylamine

T/K	273.2	263.3	253.4
k_1/dm^3 mol^{-1} s^{-1}	144.4	50.4	14.4
	±28.0	±4.3	±2.7

(*e*) With pyridine

T/K	273.5	263.5	253.3
k_1/dm^3 mol^{-1} s^{-1}	18.1	7.4	2.2
	±0.9	±0.5	±0.1

(*f*) With pyridine (5×10^{-3} mol dm^{-3}) in the presence of 2,6-dibromopyridine (5×10^{-2} mol dm^{-3})

T/K	283.2	273.2	263.3
k_1/dm^3 mol^{-1} s^{-1}	10.0	3.4	0.84
	±1.6	±0.6	±0.03

* A repeat run with [Al(dmso)$_6{}^{3+}$] = [bipy] = 0.01 mol dm^{-3} gave $k = 31.5 \pm 0.6$ dm^3 mol^{-1} s^{-1}.

The reaction with the more rigid bidentate ligand phen proceeds as expected with the simultaneous expulsion of two co-ordinated solvent molecules, and in this case equation (3) was used (Appendix; h_0^b = height of resonance of bound dmso at time $t = 0$). A plot of $h_0^b/a(3h^b - 2h_0^b)$

$$[h_0^b/a(3h^b - 2h_0^b)] - (1/a) = k_1t \qquad (3)$$

against time is shown in Figure 4 for data obtained at 250.5 K for the reaction with phen, and from the gradients

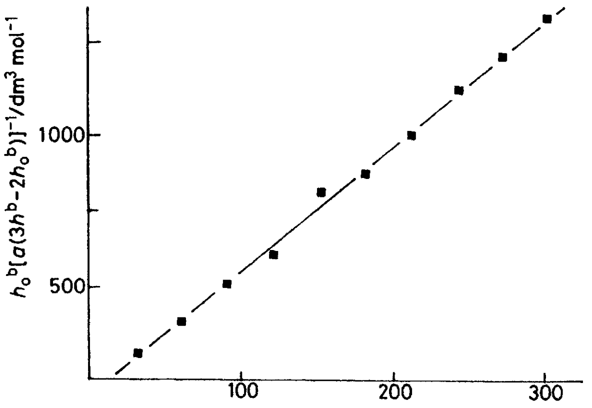


FIGURE 4 Second-order rate plot for the reaction of the $[Al(dmso)_6]^{3+}$ ion (5×10^{-3} mol dm^{-3}) with phen (5×10^{-3} mol dm^{-3}) in $[^2H_3]MeNO_2$ at 250.5 K

of plots of this kind values of k_1 (Table 2) were obtained by linear least-squares analysis.

TABLE 3

Rates and activation parameters at 298.2 K

Ligand	Rate constant	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}	$\Delta G^‡$/kJ mol^{-1}	$10^{-2}K_0$/ dm^3 mol^{-1} [a]
dmso	5.3×10^{-2} s^{-1} [b]	85.3 ± 1.9	16.7 ± 6.1	80.3 ± 3.7	
	0.318 s^{-1} [c]	85.4 ± 2.0	31.7 ± 6.1	75.9 ± 3.7	
NBu^tH_2	1.76×10^3 dm^3 mol^{-1} s^{-1}	64.9 ± 1.9	34.8 ± 7.3	54.5 ± 4.1	55
py	1.67×10^2 dm^3 mol^{-1} s^{-1}	58.1 ± 2.8	−7.6 ± 10.6	60.4 ± 6.0	5.2
py + excess of 2,6Br$_2$-py [d]	55.6 dm^3 mol^{-1} s^{-1}	76.1 ± 2.9	43.9 ± 11.0	63.0 ± 6.2	1.7
phen	2.40×10^3 dm^3 mol^{-1} s^{-1}	80.7 ± 2.2	90.6 ± 8.5	53.7 ± 4.7	75
bipy:					
first bond formation	2.04×10^3 dm^3 mol^{-1} s^{-1}	75.8 ± 3.5	72.8 ± 13.1	54.1 ± 7.4	64
chelate-ring closure	3.60×10^{-2} s^{-1}	91.1 ± 1.9	33.0 ± 7.1	81.3 ± 4.0	
terpy:					
first bond formation	1.99×10^3 dm^3 mol^{-1} s^{-1}	78.5 ± 4.5	81.4 ± 16.8	54.2 ± 9.5	63
first ring closure	4.44×10^{-3} s^{-1}	95.0 ± 2.4	28.5 ± 8.5	86.5 ± 4.9	
second ring closure	1.26×10^{-4} s^{-1}	105.5 ± 8.1	34.2 ± 24.8	95.3 ± 15.5	

[a] Calculated outer-sphere association constants assuming $K_0 \simeq k_f/k_{ex.}$. [b] Refers to the exchange of one solvent molecule. [c] Refers to the exchange of six solvent molecules. [d] A ten-fold excess of this non-ligating substrate was used.

The ring-closure reactions observed with bipy and terpy are first-order processes. The second-stage rate constants (k_2) were obtained for both ligands using equation (4), and the third-stage rate constant (k_3) for terpy was obtained from the gradients of plots of equation (5). These equations are also derived in the Appendix; they are only applicable

$$\ln[(h^b - 2h^f)/(h^b + h^f)] + \ln 2 = -k_2t \qquad (4)$$

$$\ln[(h^b - h^f)/(h^b + h^f)] + \ln 3 = -k_3t \qquad (5)$$

to consecutive reactions with well resolved rates, but this assumption is justified by the results shown in Table 2.

Activation parameters were calculated by least-squares analysis from the data in Table 2, and the results are collected in Table 3.

DISCUSSION

There can be little doubt that substitution reactions of six-co-ordinate aluminium(III) complexes such as $[Al(dmso)_6]^{3+}$ proceed by a dissociative mechanism, and this is borne out by the positive entropies of activation for solvent exchange.[1] Only for tetrahedral four-co-ordinate species such as $[Al\{P(NMe_2)_3O\}_4]^{3+}$ have negative $\Delta S^‡$ values been observed.[1]

For metal-chelate formation in aqueous media the rate-determining step is nearly always the formation of the first metal–ligand bond, and subsequent chelate-ring closures are usually very rapid. Thus reactions of the $[Ni(OH_2)_6]^{2+}$ ion with py, bipy, and terpy proceed with very similar rates,[7] and according to the Eigen–Wilkins mechanism the rate constant for complex formation (k_f) is related to the total solvent-exchange rate constant ($k_{ex.} = 6k_{ex.}^1$) and the outer-sphere ion-pair or ion–dipole constant, K_0, by an equation of type (6): [7]

$$k_f = k_{ex.}K_0f \qquad (6)$$

f is a factor which takes into account the possibility that dissociation of a solvent molecule from the ion–dipole intermediate may not lead to complex formation; it is primarily a statistical factor, and a value of $\frac{3}{4}$ has been suggested.[11] K_0 can be crudely calculated using the Fuoss equation, an assumption being made about the distance of closest approach between the solvated metal ion and the incoming ligand.[7] Reasonably good agreement has been observed between values of K_0 estimated from equation (6) and from calculations based on the Fuoss equation. For bivalent metal ions reacting with neutral ligands in aqueous media, values of K_0 are found [7] to be in the range 0.1—0.2 dm^3 mol^{-1}.

The situation observed here for reactions in nitromethane solution is very different from the 'normal' behaviour observed in aqueous solutions. Chelate-ring closure is no longer rapid (except for the reaction with a rigid bidentate ligand like phen), and the first bond formations are much more rapid than expected on the basis of equation (6). Values of K_0 calculated using equation (6) and assuming $f \simeq 1$ are in the range 1.7×10^2—75×10^2 dm^3 mol^{-1} (Table 3), much larger

[11] J. Neely and R. Connick, *J. Amer. Chem. Soc.*, 1970, **92**, 3476; P. K. Chattopadhyay and J. F. Coetzee, *Inorg. Chem.*, 1976, **15**, 400.

than expected if the Fuoss equation applies. Somewhat larger values of K_0 might be expected for the reactions of a small tripositive metal ion in a solvent of a lower dielectric constant {however, the $[Al(dmso)_6]^{3+}$ ion is not so small}, but the calculated values are much larger than predicted. The data point to some specific interaction between the ligands and the dmso molecules in the outer sphere of the $[Al(dmso)_6]^{3+}$ ion. Possibly the effect is similar to that reported to occur between the methyl groups of 3-(trimethylsilyl)propionate ion and co-ordinated aromatic molecules like phen or bipy.[12] A referee suggests that a charge-transfer interaction involving the base lone pair may be the cause.

Confirmation of the strong outer-sphere associations comes from our study of the reaction with pyridine in the presence and absence of a ten-fold excess of 2,6-dibromopyridine. This study was undertaken to see if we could swamp the outer sphere of the $[Al(dmso)_6]^{3+}$ ion with a non-ligating aromatic substrate. Control experiments showed that the bulky bromide groups which flank the pyridine nitrogen atom prevent co-ordination to Al^{III}, there being no release of co-ordinated solvent, even in the presence of a ten-fold excess of this substrate. The effect of a ten-fold excess of the substrate on the rate of reaction with py is significant as shown in Table 3. The rate constant is reduced by a factor of *ca.* 3, and the value of $\Delta G^{\ddagger}$ is increased from 60.4 to 63.0 kJ mol^{-1}. It seems, therefore, that these ligands can associate strongly in the outer sphere of the $[Al(dmso)_6]^{3+}$ ion in nitromethane solution. This association is exothermic as shown by the smaller values of $\Delta H^{\ddagger}$ for first bond formation (between 58 and 78 kJ mol^{-1}) compared with that for solvent exchange (85 kJ mol^{-1}). The multidentate ligands also co-ordinate with more positive $\Delta S^{\ddagger}$ values, indicating desolvation of the $[Al(dmso)_6]^{3+}$ ion by the strong outer-sphere association.

The chelate ring-closure reactions of bipy and terpy proceed at a rate which is significantly less than the total solvent-exchange rate (Table 3); values of $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ are somewhat larger than the values associated with k_{ex}. Steric hindrance is probably one contributing factor,[13] and for the final ring closure of terpy the very slow rate probably reflects the ring strain which is inherent in forming this meridional complex ion; values of $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ are larger by some 10 kJ mol^{-1} for the second ring-closure reaction of terpy, compared with the first ring closures of bipy and terpy, the latter two reactions having comparable activation parameters.

Flow n.m.r. spectroscopy promises to give a deeper insight into the mechanisms of metal complex formations than is evident from spectrophotometric studies, and we hope to extend our investigations to other moderately labile ions.

APPENDIX

Derivation of Equations (1)—(4).—For the reaction between a hexasolvated metal ion $[MS_6]$ and a unidentate ligand (L) we have (A1) where S^b and S^f represent bound and free solvent molecules respectively. If h^b and h^f are

$$[MS^b_6] + L \xrightarrow{k_1} [MS^b_5L] + S^f \qquad (A1)$$

the respective heights of the resonances associated with these solvent molecules, and p is a proportionality constant which relates peak heights to concentrations, making the reasonable assumption that T_2 values for S^b and S^f are the same, we have (A2) and (A3). From (A2) and (A3) we

$$h^b/p = 6[MS_6] + 5[MS_5L] \qquad (A2)$$

$$h^f/p = [S^f] = [MS_5L] \qquad (A3)$$

obtain (A4) where a = total concentration of $[MS_6]$ and of

$$(h^b + h^f)/p = 6([MS_6] + [MS_5L])$$

$$\text{or} \qquad (h^b + h^f)/p = 6a \qquad (A4)$$

L at time $t = 0$. Application to reaction (A1) of the integrated equation for a second-order process involving equal concentrations of two reactants gives (A5) where k_1

$$[MS_5L]/a[MS_6] = k_1t \qquad (A5)$$

is the second-order rate constant. Combining equations (A2)—(A5) we have (A6).

$$\frac{h^f/p}{a(h^b - 5h^f)/6p} = k_1t$$

$$\text{or} \qquad 6h^f/a(h^b - 5h^f) = k_1t \qquad (A6)$$

Similarly, for the reaction with a rigid bidentate ligand (L–L) like phen, if h_0^b is the height of the bound solvent

$$[MS^b_6] + L\text{–}L \xrightarrow{k_1} [MS^b_4(L\text{–}L)] + 2S^f \qquad (A7)$$

resonance at $t = 0$ we obtain (A8)—(A10). Now, since

$$h_0^b/p = 6a \qquad (A8)$$

$$h^b/p = 6[MS_6] + 4[MS_4(L\text{–}L)] \qquad (A9)$$

$$a = [MS_6] + [MS_4(L\text{–}L)] \qquad (A10)$$

(A11) is applicable, combining (A9)–(A11) we have (A12).

$$(1/[MS_6]) - (1/a) = k_1t \qquad (A11)$$

$$(h^b/p) - 4a = 2[MS_6] \qquad (A12)$$

Hence from (A8) and (A12) we obtain (A13). Finally,

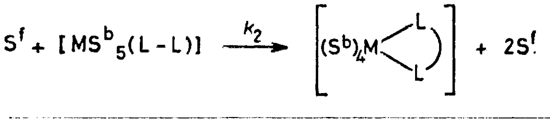
$$2[MS_6] = (6ah^b/h_0^b) - 4a$$

$$\textit{i.e.} \qquad [MS_6] = a[(3h^b/h_0^b) - 2] \qquad (A13)$$

combining (A11) and (A13) we have (A14).

$$[h_0^b/a(3h^b - 2h_0^b)] - (1/a) = k_1t \qquad (A14)$$

For the ring closure of a bidentate ligand L–L like bipy (or the first ring closure of terpy) the relevant equations are as follows, where $[MS_5(L\text{–}L)]$ represents a complex in which the ligand is unidentate, and in $[MS_4(L\text{–}L)]$ the ligand is chelated:



(A15)

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[12] P. R. Mitchell and H. Sigel, *Angew. Chem. Internat. Edn.*, 1976, **15**, 548; E. Frieden, *J. Chem. Educ.*, 1975, **52**, 754.

[13] P. Moore and D. M. W. Buck, *J.C.S. Dalton*, 1973, 1602; *J.C.S. Chem. Comm.*, 1974, 60.

Where initially $[S^f]_{t=0} = [MS_5(L\text{–}L)]_{t=0} = a$

$$h^b/p = 5[MS_5(L\text{–}L)] + 4[MS_4(L\text{–}L)] \qquad (A16)$$

$$h^f/p = a + [MS_4(L\text{–}L)] \qquad (A17)$$

and

$$[MS_5(L\text{–}L)] + [MS_4(L\text{–}L)] = a \qquad (A18)$$

Application of the integrated rate equation for a first-order process to reaction (A15) (rate constant k_2) gives (A19).

$$[MS_5(L\text{–}L)] = ae^{-k_2t} \qquad (A19)$$

Combining (A16)—(A18), we have (A20). Eliminating

$$(h^b + h^f)/p = 6a \qquad (A20)$$

$[MS_4(L\text{–}L)]$ from (A16) and (A17) we obtain (A21), and

$$(h^b/p) - (4h^f/p) + 4a = 5[MS_5(L\text{–}L)] \qquad (A21)$$

since $1/p = 6a/(h^b + h^f)$ from (A20) it follows from (A21) that:

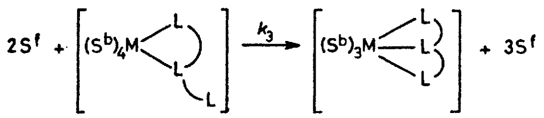
$$5[MS_5(L\text{–}L)] = [6ah^b - 24ah^f + 4a(h^b + h^f)]/(h^b + h^f)$$

$$[MS_5(L\text{–}L)] = 2a(h^b - 2h_f)/(h^b + h^f) \qquad (A22)$$

Finally, combining (A19) and (A22) and taking logarithms, we obtain equation (A23).

$$\ln 2 + \ln[(h^b - 2h_f)/(h^b + h_f)] = -k_2t \qquad (A23)$$

Similarly, for the second ring-closure reaction of a terdentate ligand (L–L–L) like terpy (first-order rate constant k_3):



(A24)

Initially, $[S^f]_{t=0} = 2a$ and $[MS_4(L\text{–}L\text{–}L)]_{t=0} = a$

$$h^b/p = 4[MS_4(L\text{–}L\text{–}L)] + 3[MS_3(L\text{–}L\text{–}L)] \qquad (A25)$$

$$h^f/p = 2a + [MS_3(L\text{–}L\text{–}L)] \qquad (A26)$$

$$[MS_4(L\text{–}L\text{–}L)] + [MS_3(L\text{–}L\text{–}L)] = a \qquad (A27)$$

$$[MS_4(L\text{–}L\text{–}L)] = ae^{-k_3t} \qquad (A28)$$

Equation (A20) still applies, and combination as before of (A20) with (A25)—(A28) then gives (A29).

$$[MS_4(L\text{–}L\text{–}L)] = 3a(h^b - h^f)/(h^b + h^f)$$

$$\text{or } \ln 3 + \ln[(h^b - h^f)/(h^b + h^f)] = -k_3t \qquad (A29)$$

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