

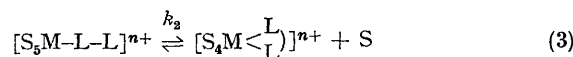
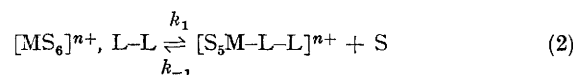
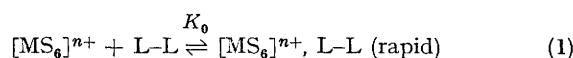
# Direct Evidence for a Rate-Determining Chelate Ring Closure Mechanism during the Reaction of 2,2'-Bipyridine with the Hexakis(dimethyl sulphoxide)-aluminium(III) Ion in Nitromethane Solution

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**Summary** Stopped-flow Fourier-transform n.m.r. experiments reveal two distinct stages in the reaction between the  $[\text{Al}(\text{Me}_2\text{SO})_6]^{3+}$  ion and 2,2'-bipyridine in  $[\text{H}_3\text{N}]$ -nitromethane solution, substitution of the first solvent molecule (at 298.2 K,  $10^{-3} k_1 = 2.0 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $\Delta H^\ddagger = 75.9 \pm 4.3 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = +73 \pm 16 \text{ J K}^{-1} \text{ mol}^{-1}$ ) being much faster than the rate of displacement of the second solvent molecule (at 298.2 K,  $10^2 k_2 = 3.9 \text{ s}^{-1}$ ,  $\Delta H^\ddagger = 92.0 \pm 1.7 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = 36.6 \pm 6.3 \text{ J K}^{-1} \text{ mol}^{-1}$ ).

THE rates of metal chelate formations [reactions (1)–(3), L–L = bidentate ligand, S = solvent molecule,  $\text{M}^{n+}$  = metal ion] are usually obtained by following the changes in



the u.v.-visible spectra of the metal ion or the ligand, or for negatively charged ligands by means of conductivity measurements (*e.g.*, in pressure-jump experiments).<sup>1</sup> These techniques do not give a very good indication of the structural changes which occur, and it is usually not possible to follow the course of the reactions by directly detecting the expulsion of the co-ordinated solvent molecules.

For the reaction between the  $[\text{Al}(\text{Me}_2\text{SO})_6]^{3+}$  ion and 2,2'-bipyridine (bipy) in nitromethane solution, u.v.-visible spectrophotometry is not possible because the solvent obscures the u.v. bands of the ligand, and there are no changes in the visible region of the spectrum. However, it is possible to follow the kinetics of the reaction by detecting the expulsion of two  $\text{Me}_2\text{SO}$  molecules from the co-ordination sphere of the  $\text{Al}^{III}$ , using stopped-flow Fourier-transform  $^1\text{H}$  n.m.r. spectroscopy,<sup>2</sup> since co-ordinated and unco-ordinated  $\text{Me}_2\text{SO}$  molecules have well separated proton resonances. Previously we showed how this technique could be used to measure the rate of solvent exchange between the  $[\text{Al}(\text{Me}_2\text{SO})_6]^{3+}$  ion and an excess of  $(\text{CD}_3)_2\text{SO}$ , and thereby we extended the temperature range over which the solvent exchange process could be studied.<sup>3</sup> Com-

bination of our results between 262 and 297 K with those from a previous line-broadening study<sup>4</sup> between 313 and 338 K gives the activation parameters shown in the Table.

One other advantage of following reactions (1)–(3) by  $^1\text{H}$  n.m.r. spectroscopy is that the two stages [reactions (1) and (2), and (3)] are accompanied by equal changes in the height of the  $^1\text{H}$  resonance associated with the free and bound  $\text{Me}_2\text{SO}$  molecules, and when  $k_1 \gg k_2$  (the case observed here), this makes it easier to determine the point at which these two reactions are complete. Usually, for metal complex formations involving multidentate ligands, chelate-ring closure [reaction (3)] is much faster than the reactions leading to first bond formation [reactions (1) and (2)]. Only in a few cases has evidence been found for a slow chelate-ring-closure, or sterically controlled substitution (SCS mechanism).<sup>5,6</sup> Usually such a conclusion is reached by comparing the rates of a range of related reactions involving 5-, 6-, or 7-membered chelate rings, or by the indirect approach of examining the rates of the reverse, dissociation reactions under acidic and neutral conditions.<sup>6,7</sup> There have been very few studies of labile metal ions in which the intermediate formed in reaction (2) has been detected, although for inert metal ions such as  $\text{Pt}^{II}$ ,  $\text{Co}^{III}$ , or  $\text{Cr}^{III}$  these intermediates can sometimes be isolated (*e.g.*, with 1,2-diaminoethane,<sup>8,9</sup> or 2,2'-bipyridine<sup>10</sup>). For inert systems the intermediates can be stabilised by protonation of the unco-ordinated donor atom, and the ring closure reaction can then be initiated by rapid prior deprotonation.<sup>8,11</sup>

For the reaction between the  $[\text{Al}(\text{Me}_2\text{SO})_6]^{3+}$  ion and 2,2'-bipyridine in  $[\text{H}_3\text{N}]$ -nitromethane solution, reactions (2) and (3) have markedly different rates, and it is possible to examine the two stages independently. The first stage is second-order overall, and with  $[\text{Al}(\text{Me}_2\text{SO})_6]^{3+} = [\text{bipy}] = 5 \times 10^{-3} \text{ mol dm}^{-3}$ , at 268.3 K the half-life is *ca.* 3.5 s, whereas the second stage (ring closure) is first-order and has a half-life of *ca.* 1240 s at this temperature. The first stage is surprisingly fast and could only be examined by flow-n.m.r. spectroscopy over a narrow temperature range (253–268 K), this being limited at the lower end by the freezing point of the solvent, and at the upper end by the rapidity of the reaction. The second stage was studied between 253 and 293 K, and the rates and activation parameters for the two stages are compared with those for the solvent exchange process in the Table.

TABLE. Comparison of rate data at 298.2 K for reactions (1)–(3) (L–L = 2,2'-bipyridine) with that for solvent exchange between the  $[\text{Al}(\text{Me}_2\text{SO})_6]^{3+}$  ion and unco-ordinated  $\text{Me}_2\text{SO}$  ( $k_{\text{ex}}$ )

Rate constant	Temperature range/K	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J K}^{-1} \text{ mol}^{-1}$	$\Delta G^\ddagger/\text{kJ mol}^{-1}$
$10^2 k_{\text{ex}} = 5.3 \text{ s}^{-1}$ <sup>a</sup>	262–338	$85.2 \pm 1.8$	$16.4 \pm 6.1$	$80.3 \pm 3.6$
$k_{\text{ex}} = 0.318 \text{ s}^{-1}$ <sup>b</sup>	262–338	$85.2 \pm 1.8$	$31.3 \pm 6.1$	$75.9 \pm 3.6$
$10^{-3} k_1 K_0 = 2.0 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ <sup>c</sup>	253–268	$75.9 \pm 4.3$	$72.9 \pm 16.2$	$54.2 \pm 9.1$
$10^2 k_2 = 3.9 \text{ s}^{-1}$ <sup>d</sup>	253–293	$92.0 \pm 1.7$	$36.6 \pm 6.3$	$81.1 \pm 3.6$

<sup>a</sup> Rate constant for the exchange of a single solvent molecule.

<sup>b</sup> Rate constant for total solvent exchange ( $k_{\text{ex}} = 6k_{\text{ex}}^{\text{I}}$ ).

<sup>c</sup> Reactions (1) and (2). <sup>d</sup> Reaction (3).

The rapidity of the first bond formation is seen to arise from a somewhat lower enthalpy of activation, and a significantly larger entropy of activation when compared with the overall solvent exchange process. This can be understood if reaction (1) (ion-dipole formation) is slightly exothermic (*ca.* 9 kJ mol<sup>-1</sup>) and is associated with a large positive entropy change (*ca.* 42 J K<sup>-1</sup> mol<sup>-1</sup>), possibly arising from desolvation of the [Al(Me<sub>2</sub>SO)<sub>6</sub>]<sup>3+</sup> ion. However, if we equate  $k_1$  with  $k_{\text{ex}}$ ,  $\Delta G^\circ (K_0) = 21.7$  kJ mol<sup>-1</sup>, and this is very much larger than values normally associated with ion-dipole interactions. Factors which have been observed previously to cause an enhancement in the values of  $K_0$  include aromatic stacking interactions,<sup>12</sup> internal conjugate-base formation (ICB mechanism),<sup>13</sup> and hydrophobic interactions between methyl groups and aromatic molecules [*e.g.*, the methyl groups of 3-(trimethylsilyl)propionate ion and the ligands 2,2'-bipyridine and 1,10-phenanthroline in their aqueous zinc(II) complexes].<sup>14</sup> Of these factors only hydrophobic interactions between the methyl groups of Me<sub>2</sub>SO and the incoming ligands is possible here, and such an effect would not be expected to be as important in nitromethane solution as it is in an aqueous medium. We believe, therefore, that either some new phenomenon is causing an enhancement in the values of  $K_0$ , or the hydrophobic interaction and desolvation processes are much more pronounced for a metal ion of charge +3 in nitromethane solution. The alternative explanation, namely that reaction (2) proceeds by an I<sub>a</sub> mechanism seems very unlikely for Al<sup>III</sup>, and this conclusion is supported by the large positive value of  $\Delta S^\ddagger$ .

Activation parameters associated with the ring-closure reaction (3) are very similar to those for the solvent exchange process, and we conclude that solvent exchange dominates the rate of this reaction. This conclusion is interesting since it has often been suggested that chelate-ring-closures are rapid because of the high effective concentration of the free end of the partially co-ordinated ligand,<sup>8</sup> such reactions even possibly having a degree of associative character. If the ring closure occurred at the same rate as solvent exchange, for the [S<sub>6</sub>Al-L-L]<sup>3+</sup> ion we would expect  $k_2 = 5k_{\text{ex}}^{\text{I}}$  (or  $4k_{\text{ex}}^{\text{I}}$  if only those solvent molecules in a *cis*-position to L-L are involved). Since we observe  $k_2 = \text{ca. } 1.4 k_{\text{ex}}^{\text{I}}$  at 298.2 K, it can be seen that at this temperature ring closure is rather slower than the total solvent exchange process, and this is in line with previous studies which indicated that there is significant steric hindrance to chelate-ring-closure for reactions of metal ion-Me<sub>2</sub>SO solvates.<sup>6,15</sup>

Preliminary results show that the reaction of the [Al-(Me<sub>2</sub>SO)<sub>6</sub>]<sup>3+</sup> ion with 1,10-phenanthroline (phen) occurs in a single step as expected, with the expulsion of two co-ordinated Me<sub>2</sub>SO molecules, whereas the reaction with 2,2':6',2''-terpyridine proceeds in three distinct stages, each stage involving the loss of a single co-ordinated Me<sub>2</sub>SO molecule.

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<sup>1</sup> R. G. Wilkins, 'The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes,' Allyn and Bacon, Boston, 1974

<sup>2</sup> D. A. Couch, O. W. Howarth, and P. Moore, *J. Phys. (E): Scientific Instruments*, 1975, **8**, 831.

<sup>3</sup> A. J. Brown, D. A. Couch, O. W. Howarth, and P. Moore, *J. Magnetic Resonance*, 1976, **21**, 503.

<sup>4</sup> S. Thomas and W. L. Reynolds, *J. Chem. Phys.*, 1966, **44**, 3148.

<sup>5</sup> K. Kustin, R. F. Pasternack, and E. M. Weinstock, *J. Amer. Chem. Soc.*, 1966, **88**, 4610; K. Kustin and J. Swinehart, *Progr. Inorg. Chem.*, 1970, **13**, 107; U. Nickel, H. Hoffmann, and W. Jaenicke, *Ber. Bunsengesellschaft Phys. Chem.*, 1968, **72**, 526; S. Harada, Y. Okuue, H. Kan, and T. Yasunaga, *Bull. Chem. Soc. Japan*, 1974, **47**, 769; H. Tomiyasu and G. Gordon, *Inorg. Chem.*, 1976, **15**, 870; Y. Ukei and M. Tanaka, *ibid.*, p. 964; R. H. Voss and R. B. Jordon, *J. Amer. Chem. Soc.*, 1976, **98**, 2173.

<sup>6</sup> P. Moore and D. M. W. Buck, *J.C.S. Dalton*, 1973, 1602.

<sup>7</sup> Ref. 1, pp. 196–200; R. G. Wilkins, *Accounts Chem. Res.*, 1970, **3**, 408.

<sup>8</sup> M. J. Carter and J. K. Beattie, *Inorg. Chem.*, 1970, 1233.

<sup>9</sup> H. Ogino and N. Tanaka, *Chem. Letters*, 1975, 687.

<sup>10</sup> S. Y. J. Ng and C. S. Garner, *Inorg. Chim. Acta*, 1971, **5**, 365; R. J. Watts, J. S. Harrington, and J. van Houten, *J. Amer. Chem. Soc.*, 1977, **99**, 2179.

<sup>11</sup> L. M. Volshtein, *Zhur. neorg. Khim.*, 1975, **20**, 2758, 3388.

<sup>12</sup> G. R. Cayley and D. W. Margerum, *J.C.S. Chem. Comm.*, 1974, 1002.

<sup>13</sup> D. B. Rorabacher, *Inorg. Chem.*, 1966, **5**, 1891; T. S. Turan, *ibid.*, 1974, **13**, 1584; R. B. Jordan, *ibid.*, 1976, **15**, 748.

<sup>14</sup> P. R. Mitchell and H. Sigel, *Angew. Chem. Internat. Edn.*, 1976, **15**, 548; E. Frieden, *J. Chem. Educ.*, 1975, **52**, 754.

<sup>15</sup> D. M. W. Buck and P. Moore, *J.C.S. Chem. Comm.*, 1974, 60.