

SOLVENT EXCHANGE RATES IN COBALT(III) COMPLEXES MEASURED  
BY N.M.R. SPECTROSCOPY\*

By I. R. LANTZKE† and D. W. WATTS†

The mechanism of substitution reactions in octahedral cobalt(III) complexes of the type  $[\text{CoXY en}_2]^{n+}$ , where en represents 1,2-diaminoethane, and X and Y monodentate ligands, has been extensively reviewed.<sup>1-4</sup> In aquation studies, where studies of oxygen exchange in aquo complexes would have been useful in the interpretation of mechanism, the techniques are difficult, and not a great amount of work has been attempted.<sup>5,6</sup> In most of the non-aqueous solvent studies<sup>7-10</sup> the differentiation between unimolecular ( $S_N1$ ) and bimolecular solvolytic ( $S_N2_{\text{SOL}}$ ) mechanisms of substitution has proved difficult because intermediates containing the coordinated solvent have not been isolated.

Recent work in dipolar aprotic solvents,<sup>11-14</sup> where stable complexes containing the coordinated solvent have been prepared, has emphasized the need for solvent exchange results, and in these systems n.m.r. spectroscopy will prove a useful technique in that proton resonances in such ligands as dimethyl sulphoxide (DMSO) and *NN*-dimethylformamide (DMF) are shifted significantly by coordination.<sup>15</sup>

We have studied exchange of the solvent DMSO- $d_6$  for DMSO in complex ions of the type *cis*- $[\text{CoX}(\text{DMSO})_2 \text{en}_2]^{2+}$  where X = Cl<sup>-</sup>, Br<sup>-</sup>, and NO<sub>2</sub><sup>-</sup>, and in the complex ion *cis*- $[\text{Co}(\text{DMSO})_2 \text{en}_2]^{3+}$  at the probe temperature (35°) in a Varian A60 analytical n.m.r. spectrometer. (DMSO- $d_6$  was used as supplied by Merck, Sharpe & Dohme at 99.9% purity.) Rate constants were calculated from the areas of the methyl proton resonances of the coordinated and free dimethyl sulphoxide molecules.

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† School of Chemistry, University of Western Australia, Nedlands, W.A.

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<sup>7</sup> Brown, D. D., Ingold, C. K., and Nyholm, R. S., *J. chem. Soc.*, 1953, 2674.

<sup>8</sup> Pearson, R. G., Henry, P. M., and Basolo, F., *J. Am. chem. Soc.*, 1957, **79**, 5379, 5382.

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<sup>13</sup> Fitzgerald, W., and Watts, D. W., *Aust. J. Chem.*, 1966, **19**, 935.

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The results are presented in Table 1. The solvolysis reaction



is negligible under these conditions.<sup>15</sup>

These rates parallel the results on aquation of complexes of the type  $[CoClX en_2]^+$ , where  $X = Br^-, Cl^-,$  and  $NO_2^-$ , and support the duality of mechanism proposed by Asperger and Ingold<sup>16</sup> in that although  $Br^-$  is expected to promote ionization more than  $Cl^-$ ,  $NO_2^-$  by electron withdrawal must inhibit ionization and thus the formation of an  $S_N1$  transition state. The greater rate for  $NO_2^-$ , however, correlates with the stabilization of an  $S_N2$  transition state by the  $NO_2^-$  ligand.

The results also suggest that Adamson<sup>17</sup> in suggesting a hydrogen bonded intermediate in aquation is in error, in that in the present system no comparable

TABLE 1  
RATE CONSTANTS ( $k_{ex}$ ) FOR SOLVENT EXCHANGE IN  $DMSO-d_6$  AT 35°  
 $k_{ex}$  calculated from  $d(DMSO)/dt$

Complexes (all <i>cis</i> )	Concn. (M)	$\delta$ (p.p.m.)		$k_{ex}$ ( $min^{-1}$ )	
		Coord.* DMSO	Free DMSO	From Coord.	From Free
$[CoCl(DMSO) en_2](ClO_4)_2$	0.41	2.77	2.57	$4.1 \times 10^{-3}$	$4.2 \times 10^{-3}$
$[CoBr(DMSO) en_2](ClO_4)_2$	0.39	2.75	2.57	$4.6 \times 10^{-3}$	$4.7 \times 10^{-3}$
$[Co(NO_2)(DMSO) en_2](ClO_4)_2$	0.50	2.74	2.57	$1.80 \times 10^{-2}$	$1.88 \times 10^{-2}$
$[Co(DMSO)_2 en_2](ClO_4)_3$	0.34	2.94	2.57	$2.65 \times 10^{-3}\dagger$	$2.65 \times 10^{-3}\dagger$

\* Centre of doublet.

† Half the measured rate of removal and release of DMSO to allow for the two identical ligands.

intermediate could exist involving the DMSO molecule. However, like Stranks (ref.<sup>2</sup>, p. 123) we find it difficult to understand a duality of mechanism and feel that this present work must be extended to a greater variety of ligands X and to the measurement of activation parameters.

The slower exchange with the trivalent complex  $cis-[Co(DMSO)_2 en_2]^{3+}$  is consistent with the requirement of greater energy to achieve charge separation for a dissociative reaction of an ion of greater charge.

It is also possible to follow comparable displacement reactions of the type



by following the aldehyde proton resonance of DMF which occurs in this system at 7.77 p.p.m. when coordinated, and 8.00 p.p.m. when free. This reaction was conveniently studied at higher temperatures than that of the probe and thus the

<sup>16</sup> Asperger, S., and Ingold, C. K., *J. chem. Soc.*, 1956, 2862.

<sup>17</sup> Adamson, A. W., *J. Am. chem. Soc.*, 1958, 80, 3183.

activation energy was easily determined. The results presented below give an activation energy of  $24.6 \pm 0.5$  kcal mole<sup>-1</sup> and an entropy of activation of  $0.6 \pm 1.6$  cal deg<sup>-1</sup> mole<sup>-1</sup>:

Complex concn. (M)	0.200	0.271	0.204
10% (min <sup>-1</sup> )	0.94	2.76	9.0
Temperature	44.8°	54.0°	64.4°

These activation parameters are consistent with those measured previously for  $S_N1$  reactions of  $cis$ -[CoCl(DMF) $_2$ ] $^{2+}$  involving a trigonal bipyramidal transition state (e.g. aquation,<sup>18</sup> 25.2 kcal mole<sup>-1</sup> and 0.5 cal deg<sup>-1</sup> mole<sup>-1</sup>; anation<sup>14</sup> by Cl<sup>-</sup> to give *trans*-product, 25.4 kcal mole<sup>-1</sup> and 0.7 cal deg<sup>-1</sup> mole<sup>-1</sup>; anation<sup>14</sup> by SCN<sup>-</sup> to give *trans*-product, 25 kcal mole<sup>-1</sup> and 3 cal deg<sup>-1</sup> mole<sup>-1</sup>; and are similar to the parameters for the aquation<sup>18</sup> of  $cis$ -[CoCl(DMA) $_2$ ] $^{2+}$  (DMA = *NN*-dimethylacetamide) and  $cis$ -[CoCl(DMSO) $_2$ ] $^{2+}$  which are 23.5 kcal mole<sup>-1</sup> and 4.7 cal deg<sup>-1</sup> mole<sup>-1</sup> and 25.2 kcal mole<sup>-1</sup> and 1.5 cal deg<sup>-1</sup> mole<sup>-1</sup>, respectively. These aquation reactions have been shown to involve an  $S_N1$  rate determining step.<sup>18</sup>

<sup>18</sup> Lantzke, I. R., and Watts, D. W., *Aust. J. Chem.*, 1966, **19**, 1821.