

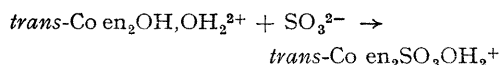
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SUBSTITUTION reactions of metal complexes containing S-bonded sulphito-ligands are remarkably rapid.<sup>1</sup> We report some substitution reactions of sulphito-complexes whose fast rates arise from abnormally low enthalpies of activation [see (2) below]. This suggests that the weakening of the ligand bond *trans* to the S-bonded sulphite-ligand is a prime cause of the *trans*-labilizing effect of this ligand. This lability is also manifested in solid-state reactions [see (3) below]. We also report the ability of the sulphite anion to substitute rapidly on co-ordinated aquo-ligands [see (1) below], and show in (4) that sulphito-ligands can undergo an unusual mutual redox reaction with a cobalt(III) centre with the production of sulphite radical anions.

(1) *The rapid addition of sulphite ion to trans-Co en<sub>2</sub>OH,OH<sub>2</sub><sup>2+</sup>*

When aqueous solutions containing *trans*-Co en<sub>2</sub>OH,OH<sub>2</sub><sup>2+</sup> and SO<sub>3</sub><sup>2-</sup> are mixed in the molar ratio 1:2 at pH 7.5 and 25°, *trans*-Co en<sub>2</sub>(SO<sub>3</sub>)<sub>2</sub><sup>-</sup> is formed quantitatively (half-time 0.7 sec.). In an equimolar mixture of the reactants, all the sulphite becomes initially bound in *trans*-Co en<sub>2</sub>(SO<sub>3</sub>)<sub>2</sub><sup>-</sup> (half-time 0.7 sec.). The resultant solution which still contains 50% unreacted *trans*-Co en<sub>2</sub>OH,OH<sub>2</sub><sup>2+</sup>, is then transformed quantitatively (half-time 6.2 sec.) to the final product *trans*-Co en<sub>2</sub>SO<sub>3</sub>OH<sub>2</sub><sup>+</sup>. This unusual sequence of reactions arises because, as is shown in (2) below, the *trans*-Co en<sub>2</sub>SO<sub>3</sub>OH<sub>2</sub><sup>+</sup> is much more labile to sulphite substitution than the reactant *trans*-Co en<sub>2</sub>OH,OH<sub>2</sub><sup>2+</sup>.

Reaction half-times for



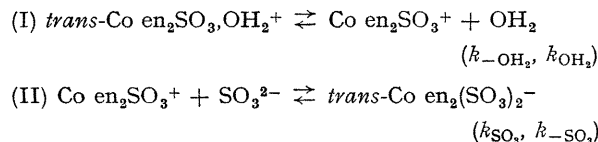
increase sharply above and below pH 7.5 where optimum concentrations of both reactive species are established.

Both *cis*- and *trans*-Co en<sub>2</sub>(OH)<sub>2</sub><sup>+</sup> undergo sulphite substitution at pH >12, with half-times of 10–100 hr. Their relative inertness to sulphite substitution compared to *trans*-Co en<sub>2</sub>OH,OH<sub>2</sub><sup>+</sup> is analogous to the much faster isomerization and water-exchange reactions of the hydroxo-aquo-complex,<sup>2</sup> but the sulphite addition reaction is at least 20 times faster than these other reactions. Since rapid substitution of SO<sub>3</sub><sup>2-</sup> only occurs in cobalt(III) complexes with aquo-ligands, it is suggested that substitution proceeds *via* addition to the oxygen of the aquo-ligand followed by rapid intramolecular rearrangement of the O-bonded sulphito-complex to the S-bonded form. We have not detected the O-bonded intermediate.

(2) *Rapid substitution reactions of trans-Co en<sub>2</sub>SO<sub>3</sub>OH<sub>2</sub><sup>+</sup>*

Experiments using H<sub>2</sub><sup>18</sup>O have shown that the aquo-ligand of *trans*-Co en<sub>2</sub>SO<sub>3</sub>OH<sub>2</sub><sup>+</sup> exchanges completely with the solvent within 45 sec. at pH 6.5 and 32°. Under the same conditions, the half-time for exchange of the oxygen atoms of the sulphito-ligand is >15 hr., very much slower than that of the free sulphite anion.

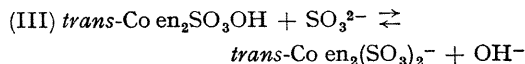
Stopped-flow measurements show that sulphite substitution of *trans*-Co en<sub>2</sub>SO<sub>3</sub>OH<sub>2</sub><sup>+</sup> proceeds with half-times in the msec. range by a dissociative mechanism:



For this reaction scheme, the rate constant for aquo-release is  $k_{-\text{OH}_2} = 13.2 \pm 0.9 \text{ sec.}^{-1}$  at 25° with  $\Delta H_{-\text{OH}_2}^\ddagger = 15.9 \pm 1.0 \text{ kcal. mole}^{-1}$  and  $\Delta S_{-\text{OH}_2}^\ddagger = 0.2 \pm 4 \text{ e.u.}$ , whilst for sulphite release from *trans*-Co en<sub>2</sub>(SO<sub>3</sub>)<sub>2</sub><sup>-</sup>,  $k_{-\text{SO}_3} = 0.111 \pm 0.004 \text{ sec.}^{-1}$  at 25° with  $\Delta H_{-\text{SO}_3}^\ddagger = 20.4 \pm 0.8$

kcal. mole<sup>-1</sup> and  $\Delta S^\ddagger_{-\text{SO}_3} = 6 \pm 3$  e.u. These activation enthalpies are much lower than those normally observed for substitution on cobalt(III) complexes.<sup>3</sup>

The relative reactivity of water and sulphite ion towards the intermediate  $\text{Co en}_2\text{SO}_3^+$  is  $k_{\text{OH}_2}[\text{H}_2\text{O}]/k_{\text{SO}_3} = 6 \times 10^{-3}$ . Azide ion and hydrogen sulphite ion also compete efficiently with water for the intermediate, and the same limiting rate constant for substitution at high nucleophile concentration is observed for  $\text{N}_3^-$  ( $12.9 \pm 0.9$  sec.<sup>-1</sup>) as for  $\text{SO}_3^{2-}$  ( $13.2 \pm 0.9$  sec.<sup>-1</sup>). Above pH 12, hydroxide ion competes very efficiently with  $k_{\text{SO}_3}/k_{\text{OH}} = 1.1 \times 10^{-2}$ . Sulphite substitution of  $\text{Co en}_2\text{SO}_3\text{OH}$  therefore involves an equilibrium



with  $K_{\text{III}} = 0.385 \pm 0.018$  at 25°. Again a dissociative mechanism operates with  $k_{-\text{OH}} > 2$  sec.<sup>-1</sup>.

### (3) Dehydration of solid $\text{trans}[\text{Co en}_2\text{SO}_3\text{OH}_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$

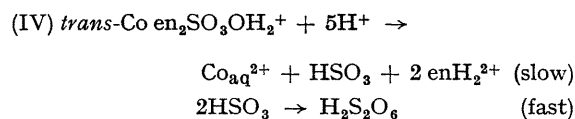
In the solid state, brown crystalline  $\text{trans}[\text{Co en}_2\text{SO}_3\text{OH}_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$  is transformed to a red amorphous powder of empirical composition  $\text{Co en}_2\text{SO}_3\text{ClO}_4$  with the loss of 2.0 moles of water. The reaction, detectable even at room temperature, is readily followed by mass spectrometry near 100°, where 10 min. is sufficient for complete reaction. The rate of loss of the aquo-ligand is at least  $10^3$  times faster than that in  $\text{cis}[\text{Co en}_2\text{SO}_4(\text{OH}_2)_2]\text{ClO}_4$  which forms  $[\text{Co en}_2\text{SO}_4]\text{ClO}_4$ .<sup>4</sup> Thus a marked *trans*-labilizing effect of the sulphito-ligand operates also in the solid state.

The u.v.-visible reflectance spectrum of red  $[\text{Co en}_2\text{SO}_3]\text{ClO}_4$  is consistent with an *O*-bonded sulphito-ligand. Although a bidentate sulphito-structure is one possibility suggested by the i.r. spectrum, a polymeric structure based on the unit  $[\dots \text{Co en}_2\text{O-SO-O} \dots]$  seems more probable.<sup>5</sup> Isotopic enrichment studies with  $\text{H}_2^{18}\text{O}$  show that, before

the aquo-ligand is eliminated, one oxygen of the sulphito-ligand becomes nonequivalent to the other two; this would suggest the intermediate formation of *trans*- $\text{Co en}_2\text{OSO}_2\text{OH}_2^+$  before polymer formation. The slow dissolution of  $\text{Co en}_2\text{SO}_3\text{ClO}_4$  in dilute  $\text{HClO}_4$  yields the *S*-bonded *trans*- $\text{Co en}_2\text{SO}_3\text{OH}_2^+$  ion.

### (4) Internal oxidation-reduction in *trans*- $\text{Co en}_2\text{SO}_3\text{OH}_2^+$ in perchloric acid

The *S*-bonded sulphito-ligand is very inert to both acid and base hydrolysis but at elevated temperatures and in perchloric acid media ranging from 0.01–7 M, *trans*- $\text{Co en}_2\text{SO}_3\text{OH}_2^+$  quantitatively forms  $\text{Co}_{\text{aq}}^{2+}$  and dithionic acid. Radical scavengers like  $\text{Fe}^{2+}$  and  $\text{O}_2$  reduce the  $\text{H}_2\text{S}_2\text{O}_6$  yield but do not affect the rate of  $\text{Co}^{2+}$  formation. The reaction can therefore be written:



At 73°,  $k_{\text{IV}} = 3.2 \times 10^{-4}$  sec.<sup>-1</sup> with  $\Delta H^\ddagger_{\text{VI}} = 32.8 \pm 0.5$  kcal. mole<sup>-1</sup> and  $\Delta S^\ddagger_{\text{IV}} = 20 \pm 2$  e.u. Check experiments have verified that, in sealed vessels, there is no measurable concentration of  $\text{Co}_{\text{aq}}^{2+}$  produced in acid solutions of  $\text{SO}_3^{2-}$  and *cis*- and *trans*- $\text{Co en}_2(\text{OH}_2)_2^{3+}$  which are possible intermediates in this decomposition. Reaction IV is therefore an example of an inner-sphere redox reaction. The alternative acid hydrolysis of *trans*- $\text{Co en}_2\text{SO}_3\text{OH}_2$  only becomes detectable in 8–11M- $\text{HClO}_4$  media.

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<sup>1</sup> J. Halpern, R. A. Palmer, and L. M. Blakely, *J. Amer. Chem. Soc.*, 1966, **88**, 2877; P. H. Tewari, R. H. Gaver, H. K. Wilcox, and W. K. Wilmarth, *Inorg. Chem.*, 1967, **6**, 611; Hon Gee Tsiang and W. K. Wilmarth, *ibid.*, 1968, **7**, 2535.

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<sup>3</sup> F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, 1967, 2nd edn., ch. 3.

<sup>4</sup> C. G. Barraclough and M. L. Tobe, *J. Chem. Soc.*, 1961, 1993.

<sup>5</sup> M. E. Baldwin, *J. Chem. Soc.*, 1961, 3123.