Preparation and Characterisation of *cis*- and *trans*-Tetra-amminebis(sulphito)cobaltate(III) Anions and the Kinetics of Redox Decomposition in Aqueous Acid Solution

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In aqueous sulphite solution, *trans*-$[Co(NH_3)_4(H_2O)(SO_3)]^+$ rapidly forms the bis(sulphito) complex which has been isolated as an unstable yellow solid, *trans*-$Na[Co(NH_3)_4(SO_3)_2],2H_2O$. The *cis*-isomer has been prepared as the brown salts *cis*-$Na[Co(NH_3)_4(SO_3)_2],2H_2O$ and *cis*-$NH_4[Co(NH_3)_4(SO_3)_2],3H_2O$. I.r. and u.v.–visible spectra are reported. The latter are in disagreement with literature spectra and *cis*–*trans*-assignments based on them are reversed. In perchloric acid solution, aquation of ligands *trans* to sulphite results in rapid formation of *trans*-$[Co(NH_3)_4(H_2O)(SO_3)]^+$ and $[Co(NH_3)_2(H_2O)_2(SO_3)_2]^-$ from the *trans*- and *cis*-isomers respectively. Rate constants, k_{obs}, for redox decomposition of the *cis*-isomer under air-free conditions are of the form (*i*) at $[H^+] = 0{\cdot}02$—$0{\cdot}20$M; at 20·0 °C and $I = 1{\cdot}00$M ($LiClO_4$), $k = (1{\cdot}39 \pm 0{\cdot}02) \times 10^{-2}$ l mol^{-1} s^{-1}, $\Delta H^\ddagger = 26{\cdot}5$

$$k_{obs} = k[H^+] + k_I \qquad (i)$$

$\pm$ 0·4 kcal mol^{-1}, and $\Delta S^\ddagger = 23{\cdot}4 \pm 1{\cdot}3$ cal K^{-1} mol^{-1}. The acid-independent term contributes only *ca.* 3% of the observed rate at 0·1 M-$HClO_4$.

BROWN and yellow forms of the complex $Na[Co(NH_3)_4(SO_3)_2]$ were reported in the early literature,[1] and assigned *cis*- and *trans*-configurations respectively. Brown crystals of the salt $NH_4[Co(NH_3)_4(SO_3)_2],3H_2O$ were also given the *cis*-configuration by Bailar and Peppard.[2] More recently Shimura[3] concluded from u.v.–visible spectra of the complexes that the assignments were incorrect and reversed the configurations.

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[1] K. A. Hofmann and A. Jenny, *Ber.*, 1901, **34**, 3855.

[2] J. C. Bailar and D. F. Peppard, *J. Amer. Chem. Soc.*, 1940, **62**, 105.

[3] Y. Shimura, *Bull. Chem. Soc. Japan*, 1952, **25**, 46.

Experience in this laboratory with cobalt(III) ammine-sulphito-complexes[4] indicated that spectra used by Shimura in his analysis were in error. This work was undertaken in order to resolve the conflicting assignments in the literature. In addition the kinetics of redox decomposition of cobalt(III) sulphito-complexes form part of a continuing interest in potential precursor complexes for electron transfer.

RESULTS

U.v.–Visible Spectra.—Spectra of the complexes were obtained as follows: (*i*) *cis*-$[Co(NH_3)_4(SO_3)_2]^-$, by dissolving either *cis*-$Na[Co(NH_3)_4(SO_3)_2],2H_2O$ or -$NH_4[Co(NH_3)_4(SO_3)_2],3H_2O$ in 0·5M-NH_3–0·5M-NH_4Cl buffer solution; (*ii*) *trans*-$[Co(NH_3)_4(SO_3)_2]^-$, by dissolving either *trans*-$[Co(NH_3)_4(H_2O)(SO_3)]Cl$ or -$Na[Co(NH_3)_4(SO_3)_2],2H_2O$ in 0·1M-Na_2SO_3 solution; and (*iii*) $[Co(NH_3)_5(SO_3)]^+$, by dissolving either $[Co(NH_3)_5SO_3]_2SO_4,2H_2O$[4] or *trans*-$[Co(NH_3)_4(H_2O)(SO_3)]Cl$ in 0·5M-NH_3–0·5M-NH_4Cl buffer solution. Visible spectra of the ions *cis*- and *trans*-$[Co(NH_3)_4(SO_3)_2]^-$ are shown in Figure 1. A ratio of 2·93 ± 0·03 : 1 for absorbances at the maximum (452 nm) and minimum (393 nm) was found to be a reliable test of satisfactory purity of samples of the *cis*-complex. The *trans*-complex has no peak in the visible region. Details of peak positions in the u.v.–visible region for the three complexes are given in Table 1.

I.r. Spectra.—Figure 2 shows i.r. spectra (KCl discs) of sodium salts of the two isomers in the region 1 400—400 cm^{-1}. For display purposes the ordinate has been offset (*ca.* 20%) for the *cis*-complex. Absorption bands (cm^{-1}) assigned to sulphite ligands occurred at 1 060vs, 950vs, 630s, 523w, and 500w for the *trans*-complex, and at 1 100vs, 1 070ms, 1 038ms, 988ms, 955vs, 642s, 628ms, and 518m for the *cis*-complex. A sample of the *cis*-complex which was exposed to light for 1 month showed no differences in its i.r. spectrum. The *trans*-complex, which visibly changes colour in a matter of days, did however show some differences in its i.r. spectrum, notably a weak band at *ca.* 1 400 cm^{-1}. This behaviour has been reported previously[5] by Babaeva *et al.* and the spectra are in reasonable agreement with those of the present study.

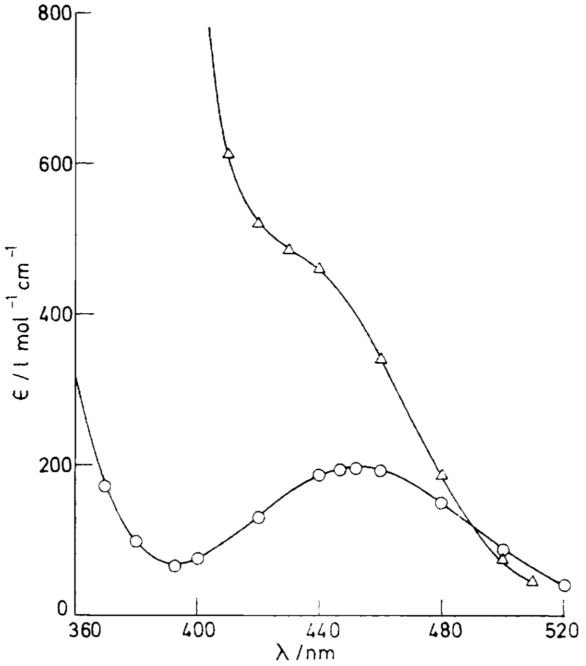

FIGURE 1 Visible absorption spectra of the ions *cis*- (○) and *trans*-$[Co(NH_3)_4(SO_3)_2]^-$ (△)

TABLE 1

Position (λ nm) and absorption coefficients (ε l mol^{-1} cm^{-1}) of maxima in u.v.–visible spectra of cobalt(III) ammine-sulphito-complexes at 25 °C

Complex	λ	log ε	λ	log ε	λ	log ε
cis-$[Co(NH_3)_4(SO_3)_2]^-$	452	2·30	295	4·32	264	4·30
trans-$[Co(NH_3)_4(SO_3)_2]^-$	*ca.* 430 (sh)	2·69	327	4·47	[a]	
$[Co(NH_3)_5(SO_3)]^+$	456	2·17	278	4·29		

[a] The sulphite background solution absorbs strongly at <270 nm.

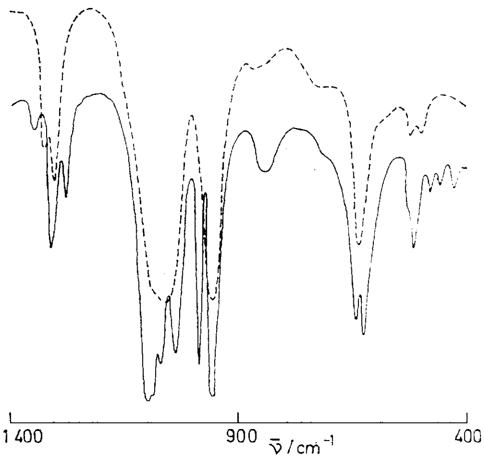

FIGURE 2 I.r. spectra (KCl discs) of the sodium salts of the ions *cis*- (——) and *trans*-$[Co(NH_3)_4(SO_3)_2]^-$ (— — —)

Kinetic Studies.—In aqueous perchloric acid solution, aquation of ligands in *trans*-positions to sulphite occurs at a rate too fast to follow by conventional techniques. Thus the spectrum of *trans*-$[Co(NH_3)_4(H_2O)(SO_3)]^+$ was obtained immediately on dissolving the complex *trans*-$[Co(NH_3)_4(SO_3)_2]^-$ in 0·1M-$HClO_4$. No studies of the ensuing redox decomposition were made since they form the subject of a recent paper.[4] When the complex *cis*-$[Co(NH_3)_4(SO_3)_2]^-$ ($\lambda_{max.}$ 452 nm) was dissolved in aqueous perchloric acid solution, the immediate spectrum showed a peak at 475 nm, consistent with rapid formation of $[Co(NH_3)_2(H_2O)_2(SO_3)_2]^-$. Thereafter redox decomposition occurred, a study of which is now described.

Preliminary runs showed that consistent results could be obtained by using both air-free conditions[4] and >150-fold excess of H^+. The redox decomposition to Co^{2+} was followed spectrophotometrically at 340 nm and plots of log (O.D.$_t$ − O.D.$_\infty$) were linear to >97% completion of reaction. Rate constants, k_{obs}, obtained from such plots are given in Table 2 for $[H^+]$ = 0·02—0·20M and I = 1·00M ($LiClO_4$). The dependence of k_{obs} on $[H^+]$ was of the form (1), with k_I barely detectable. Rate constants k and k_I

$$k_{obs} = k[H^+] + k_I \qquad (1)$$

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[4] M. A. Thacker, K. L. Scott, M. E. Simpson, R. S. Murray, and W. C. E. Higginson, *J.C.S. Dalton*, 1974, 647.

[5] A. V. Babaeva, Yu. Ya. Kharitonov, and I. B. Baranovskii, *Russ. J. Inorg. Chem.*, 1962, **7**, 643.

at 20—30 °C were computed using a least-squares program and are given in Table 3. Activation parameters for the acid-dependent path, $\Delta H^{\ddagger} = 26{\cdot}5 \pm 0{\cdot}4$ kcal mol^{-1} and $\Delta S^{\ddagger} = 23{\cdot}4 \pm 1{\cdot}3$ cal K^{-1} mol^{-1},* were computed from a least-squares plot of log (k/T) against ($1/T$). The small intercept, k_{I}, could not be measured with sufficient accuracy to allow activation parameters to be determined for this path.

TABLE 2

Observed rate constants, k_{obs}, for redox decomposition of the complex[a] *cis*-$[\mathrm{Co(NH_3)_4(SO_3)_2}]^-$ in aqueous solution, $I = 1{\cdot}00$M (LiClO$_4$), under air-free conditions

t/°C	[H$^+$]/M	10^4[Complex]/M	10^3k_{obs}/s^{-1}
20·0	0·02	1·0	0·31
20·0	0·035	1·0	0·54
20·0	0·05	2·3	0·75
20·0	0·10	1·5	1·45
20·0	0·10	2·8	1·48
20·0	0·10	3·0	1·43
20·0	0·10	3·5	1·42
20·0	0·10	5·3	1·41
20·0	0·20	1·5	2·84
20·0	0·20	3·6	2·92
20·0	0·20	*ca.* 5	2·73
25·0	0·05	3·2	1·67
25·0	0·10	1·1	3·32
25·0	0·10	2·6	3·25
25·0	0·10	3·2	3·11
25·0	0·20	6·0	6·06
30·0	0·02	1·0	1·62
30·0	0·035	1·0	2·69
30·0	0·05	2·1	3·67
30·0	0·10	1·5	7·00
30·0	0·10	3·2	6·95
30·0	0·125	1·5	8·37

[a] The form of the complex in acid solution is $[\mathrm{Co(NH_3)_2(H_2O)_2(SO_3)_2}]^-$.

TABLE 3

Summary of rate constants for redox decomposition of the complex *cis*-$[\mathrm{Co(NH_3)_4(SO_3)_2}]^-$, $I = 1{\cdot}00$M (LiClO$_4$)

t/°C	10^2k/l mol^{-1} s^{-1}	10^4k_{I}/s^{-1}
20·0	1·39 ± 0·02	0·45 ± 0·3
25·0	2·9 ± 0·1	2·9 ± 1·2
30·0	6·49 ± 0·11	4·0 ± 0·9

Considerable experimental problems prevented extension of the study to bigger ranges of [H$^+$]. The complex was slow to dissolve and not very soluble. The solubility decreased with increasing [H$^+$] and it was considered unlikely that air-free conditions would be effective with $< 1 \times 10^{-4}$M-complex. Since it has been shown[4] that at low [H$^+$] interference from the sulphite product occurs, the [H$^+$] could not be extended to lower values. Similarly the range of temperature variation was limited both by the solubility problem and the fast rate. Such extensions to the limited data in Table 2 as were obtained are shown in Figure 3. There is evidence that the general dependence on [H$^+$] is of the form (2) and that this reduces to (1) at

$$k_{\mathrm{obs}} = \frac{k[\mathrm{H^+}] + k_{\mathrm{I}}}{1 + K[\mathrm{H^+}]} \qquad (2)$$

[H$^+$] < *ca.* 0·2M. At [H$^+$] = 0·75M, the experimental points were *ca.* 25% depressed from the extrapolated line in Figure 3. Both facts are consistent with a protonation constant of *ca.* 0·4 l mol^{-1}, and that it is the protonated form of the complex which is reactive.

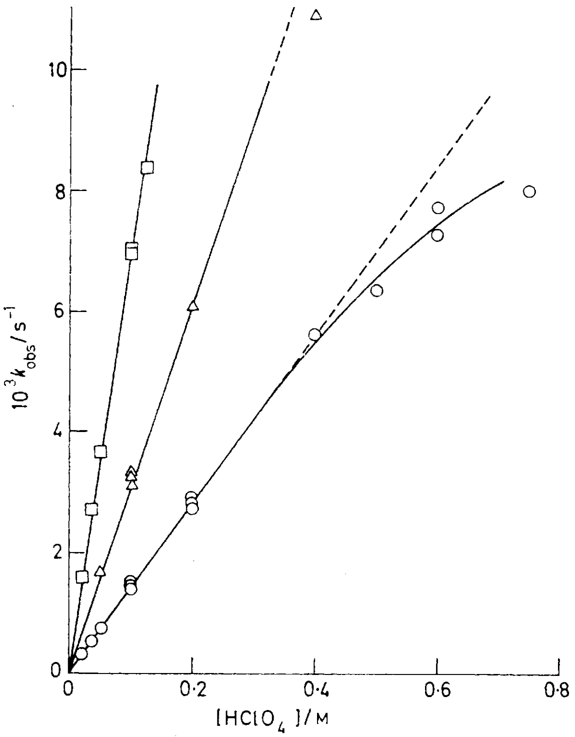

FIGURE 3 Plots of k_{obs} against [HClO$_4$] for redox decomposition of the ion *cis*-$[\mathrm{Co(NH_3)_4(SO_3)}]^-$ under air-free conditions: $I = 1{\cdot}00$M (LiClO$_4$) at 20·0 (○); 25·0 (△); and 30·0 °C (□)

DISCUSSION

The choice of solvent is of utmost importance[4] for obtaining u.v.–visible spectra of cobalt(III) sulphito-complexes, since ligand sites *trans* to sulphite are open to rapid substitution.[6] Shimura[3] assigned the configuration of the isomers of the ion $[\mathrm{Co(NH_3)_4(SO_3)_2}]^-$ purely on the basis of their spectra which were recorded in 3% NH$_3$. The *cis*-complex, with NH$_3$ ligands in *trans*-positions to sulphite, simply exchanges with the NH$_3$ of the solvent. But with the *trans*-complex a different situation obtains [equation (3)]; the estimate

$$trans\text{-}[\mathrm{Co(NH_3)_4(SO_3)_2}]^- + \mathrm{NH_3} \overset{K}{\rightleftharpoons} [\mathrm{Co(NH_3)_5(SO_3)}]^+ + \mathrm{SO_3}^{2-} \qquad (3)$$

$K = 0{\cdot}008$ has been reported.[6] Though the equilibrium favours formation of the bis(sulphito) complex, it is obvious that under the conditions used by Shimura[3] to obtain his spectra (*ca.* 1×10^{-4}M-complex dissolved in 3% NH$_3$ solution and no free sulphite initially) the absorbing species is predominantly $[\mathrm{Co(NH_3)_5(SO_3)}]^+$. Indeed the peak positions, 455 and 278 nm, correspond to those recently reported for the penta-ammine[4] (Table 1). The spectrum[3] said to correspond to the

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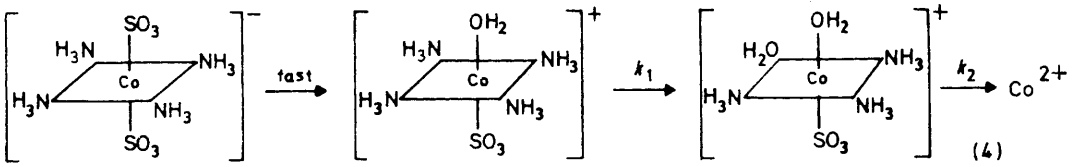
* 1 cal = 4·184 J.

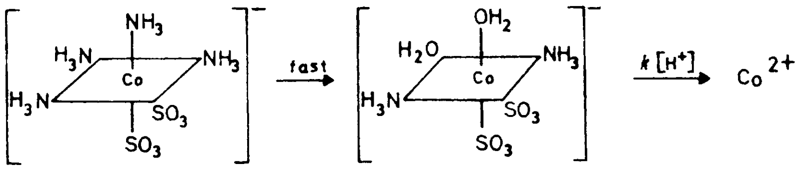
[6] J. E. Byrd and W. K. Wilmarth, *Inorg. Chem. Acta Rev.* 1971, **5**, 7.

latter has now been shown[4] to correspond to the ion *trans*-$[Co(NH_3)_4(H_2O)(SO_3)]^+$. The original assignments of Hofmann and Jenny[1] and in other references[2,5] are therefore correct; those in ref. 3 are in error. The various spectra suggest that the sulphite ligand is *S*-bonded. The distinction between isomers in terms of their colour is misleading, since finely ground samples of the brown *cis*-complex appear yellow whilst samples of the yellow *trans*-complex turn brown with time.

The redox decompositions of the two bis(sulphito) isomers proceed as shown in equations (4) and (5).



(4)



(5)

In neither case was a first-order rate constant obtained for electron transfer. The *trans*-isomer decomposes[4] by an isomerisation process, $k_1 = 1{\cdot}1 \times 10^{-4}$ s^{-1} at 25 °C and $I = 1{\cdot}00$M ($LiClO_4$), followed by a second reaction, $k_2 =$ *ca.* 6×10^{-4} s^{-1}, which is shown as the electron-transfer step but may in fact be a second isomerisation. The *cis*-isomer decomposes with second-order kinetics, $k = 2{\cdot}9 \times 10^{-2}$ l mol^{-1} s^{-1} at 25 °C and $I = 1{\cdot}00$M ($LiClO_4$). Again the reaction has been depicted as involving electron transfer, since there is no evidence to the contrary. Nevertheless it cannot be ruled out that the process involves some other H^+-assisted reaction followed by electron transfer at a faster rate. Activation parameters are similar in magnitude to typical values for substitution in cobalt(III) ammine complexes. It may be that the essential process involved in an electron-transfer reaction of this type is similar to that in a substitution reaction.

EXPERIMENTAL

Preparations.—Ammonium cis-*tetra-amminebis(sulphito)-cobaltate*(III) *trihydrate.* The complex was prepared by Bailar's method[2] {Found: H, 6·1; N, 19·45; S, 17·95. $NH_4[Co(NH_3)_4(SO_3)_2],3H_2O$ requires H, 6·1; N, 19·5; S, 17·8%}.

Sodium cis-*tetra-amminebis(sulphito)cobaltate*(III) *dihydrate.* The ammonium salt of the complex (0·9 g) was dissolved in 0·05M-NH_3–0·05M-NH_4Cl solution (80 cm^3) and added to a short column (height 2 cm) of Dowex 50W X12 resin in the Na^+ form. After passing through the column, the complex was precipitated by adding methanol (*ca.* 20 cm^3), filtered off, and washed with ethanol and then diethyl ether. Yield 0·5 g {Found: H, 4·8; N, 16·1; S, 18·2. $Na[Co(NH_3)_4(SO_3)_2],2H_2O$ requires H, 4·6; N, 16·2; S, 18·5%}.

Sodium trans-*tetra-amminebis(sulphito)cobaltate*(III) *dihydrate.* The complex *trans*-$[Co(NH_3)_4(H_2O)(SO_3)]Cl$ (0·5 g), prepared as previously reported,[4] was dissolved in a solution of Na_2SO_3 (1·1 g in 30 cm^3 water), and filtered. An equal volume of methanol was added to the filtrate and the precipitated bright yellow complex filtered off and washed well with ethanol and ether. Yield 0·6 g {Found: H, 4·6; N, 15·8; S, 18·5. $Na[Co(NH_3)_4(SO_3)_2],2H_2O$ requires H, 4·6; N, 16·2; S, 18·5%}.

Whereas solid samples of the *cis*-isomer were found to be stable, and need not be stored in the dark, those of the *trans*-isomer became orange-brown within *ca.* 2 days, even when shielded from light. Impure samples were prepared by Shimura's method. Ignoring the dubious practice of recrystallisation from water it was possible by using ion-exchange to obtain a product identical to the above trihydrate of the *cis*-isomer.

Dehydration experiments revealed that none of the complexes lost all the water of crystallisation over P_2O_5. Microanalyses were carried out by Pascher Mikroanalytisches Laboratorium, Bonn. Lithium perchlorate was obtained from the carbonate and recrystallised three times. A Unicam SP 500 manual spectrophotometer fitted with a thermostatted cell-housing was used for u.v.–visible spectra and kinetic runs. Scan spectra were obtained on a Unicam SP 800 spectrophotometer and i.r. spectra on a Perkin-Elmer 457 grating spectrophotometer.

Reaction solutions for kinetic runs were prepared as follows. A solution of perchloric acid, $I = 1{\cdot}00$M ($LiClO_4$), was degassed by a vacuum-freezing technique and thermostatted at the required temperature. A solid sample of the complex *cis*-$Na[Co(NH_3)_4(SO_3)_2],2H_2O$ was then introduced, dissolved, and some of the reactant solution then transferred to an air-free optical cell using a syringe.

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