380. *The Preparation and Properties of Chelated Sulphatobis(ethylenediamine)cobalt(III) Salts.*

By C. G. BARRACLOUGH and M. L. TOBE.

The preparation of the bromide and the perchlorate of one of the isomeric $[Co\,en_2SO_4OH_2]^+$ cations is described. The sulphate group occupies one co-ordination position. When heated, these salts lose water and the sulphate group acts as a chelate. The characteristic infrared absorption frequencies of the chelated sulphato-group are reported.

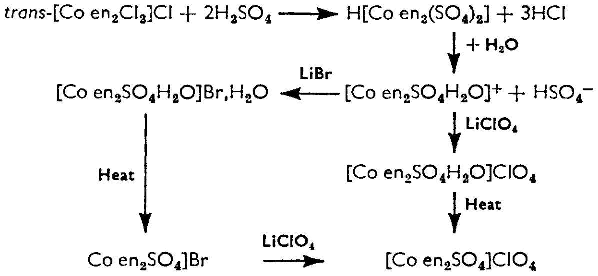
IN a recent paper[1] on the infrared spectra of sulphato-complexes, the characteristic features of the spectra of monodentate and bridging sulphato-groups were described. We have considered the possibility of extending this work to the characterisation of chelated sulphato-groups but have been handicapped by the lack of well-defined complexes of this type. Thus, in Weinland and Sierp's sulphato-complexes[2] only analytical data had been used to support the formulation of the sulphato-group as a chelate. The infrared spectra of these compounds suggest that the sulphato-group is bound in one co-ordination position only, the other being occupied by a water molecule. Duff[3] reported the complex $[Co\,en_2SO_4]Br,H_2O$ but the compound that we obtained on using his procedure appeared to have the structure $[Co\,en_2SO_4H_2O]Br$, the infrared spectrum being characteristic of monodentate sulphate and the compound having a titratable proton. Heating this complex to drive off the water does not result in ring closure.

The chelate complexes $[Co\,en_2SO_4]Br$ and $[Co\,en_2SO_4]ClO_4$ have now been prepared from more accessible reagents, the aquo-complexes, $[Co\,en_2SO_4H_2O]Br$ and

---

[1] Nakamoto, Fujita, Tanaka, and Kobayashi, *J. Amer. Chem. Soc.*, 1957, **79**, 4904.
[2] Weinland and Sierp, *Z. anorg. Chem.*, 1921, **117**, 59.
[3] Duff, *J.*, 1922, **121**, 450.

$[Co\ en_2SO_4H_2O]ClO_4$ being characterised as intermediates. These compounds are prepared in accordance with the following scheme:



The anionic nature of the complex ion isolated from the sulphuric acid treatment was demonstrated by passing a freshly prepared solution through a cation-exchange resin in the sodium form. The effluent was highly coloured and freeze-drying yielded a violet powder which was the sodium salt contaminated with large amounts of sodium sulphate. The complex salt was extremely soluble in water and aquated readily, so that we were unable to purify a sample for further examination and characterisation.

FIG. 1.

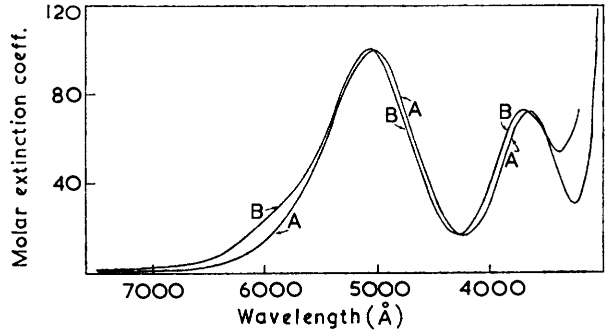


FIG. 2.

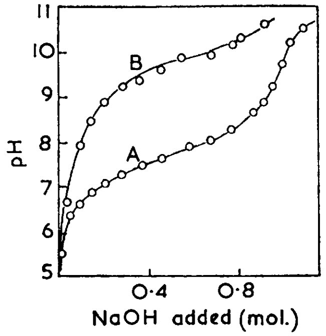


FIG. 1. *The visible absorption spectra of* (A) $[Co\ en_2SO_4H_2O]Br,H_2O$ (*or the analogous perchlorate*) *and* (B) $[Co\ en_2SO_4]Br$.

FIG. 2. pH *titration curves for the addition of* NaOH *solution to an aqueous solution of* (A) $[Co\ en_2SO_4H_2O]Br,H_2O$ *and* (B) $[Co\ en_2SO_4]Br$ *at* 0°.

When an aqueous solution of this complex was left at room temperature for 24 hr. and then poured into a solution of lithium bromide in acetone a very deliquescent purplish powder was obtained. This powder gave positive tests for ionic bromide and co-ordinated sulphate. The infrared spectrum was consistent with presence of a monodentate sulphate group and was not greatly changed when the material was heated at 110°. The extreme solubility of this complex in water and the ease with which it formed oils discouraged further investigation. When the aqueous solution of the disulphato-complex was saturated with lithium bromide or lithium perchlorate it deposited, in 2—3 days at 0°, purplish-pink crystals of $Co\ en_2SO_4Br,2H_2O$ (I) or $Co\ en_2SO_4ClO_4,H_2O$ (II) respectively. The visible absorption spectra of these two salts are identical and are shown in Fig. 1. A pH titration of the complex with dilute alkali indicates the presence of one co-ordinated water molecule (Fig. 2). The infrared absorption spectrum of the bromide (I) in a Nujol mull (detailed below) is consistent with a monodentate sulphato-complex, the three bands assigned to the sulphato-group and required by the symmetry are: 1130s, 1070s; 978s; 645s, 625m.

Compounds I and II lose all their water at 110—120° and their colours change from pink to purple. The heated products can be recrystallised and have the composition Co en_2SO_4Br (III) and Co $en_2SO_4ClO_4$ (IV). Compound (III) contains ionic bromine * and both have co-ordinated sulphate. The visible absorption spectrum of the bromide differs significantly from that of the aquosulphato-complexes (I) and (II) and is given in Fig. 1. The perchlorate is insoluble in water. The infrared spectrum of the bromide (III) is given below; the maxima assigned to the sulphate group are at 1211s, 1176vs, 1075vs; 993s; 647s, 632s; and 515m cm.$^{-1}$. The number of bands (four) is in agreement with that predicted by Nakamoto *et al.*[1] for a chelated sulphato-group with C_{2v} symmetry. It appears that it is not possible to distinguish between a bridging and a chelated sulphato-group on the basis of the infrared spectrum.

The molecular weight of the bromide corresponds to that expected for a mononuclear complex that splits into two ions, and the conductivity of an aqueous solution is that expected for a 1 : 1 electrolyte (110 ohm cm.$^{-1}$ at 22° for a 0·001M-solution). The pH titration curve for an aqueous solution differs from that of the aquo-sulphato-bromide (I) and indicates that an aquo-group is absent although the complex reacts readily with hydroxide ions.

The visible absorption spectrum of an aqueous solution of bromide (III) changes, with a half-life of 3 hr. at 20°, to that of the aquo-sulphato-complex (I). No free sulphate can be detected in this time. Over much longer periods the spectrum changes towards that of *cis*-$[Co\ en_2(H_2O)_2]^{3+}$ and free sulphate ions can then be detected in the solution. Semiquantitative measurements indicate that the opening of the chelate ring is about twenty times faster than the subsequent loss of the sulphate.

EXPERIMENTAL

Aquosulphatobis(ethylenediamine)cobalt(III) *Bromide*.—*trans*-Dichlorobis(ethylenediamine)-cobalt(III) chloride (10 g.) was added to concentrated sulphuric acid (20 ml.) in a beaker and, when the initial effervescence had subsided, the mixture was gently warmed. The complex slowly dissolved, evolving hydrogen chloride and forming a violet solution. The temperature was raised to 120° until the gas evolution had ceased and the oil was then allowed to cool and poured into alcohol (1 l.) which was continuously stirred to prevent the formation of an oil. The solid was filtered off, washed with alcohol and ether, and dried in a vacuum. The deliquescent solid was dissolved in water (20 ml.), treated with lithium bromide (5 g., anhydrous) in water (5 ml.), and set aside at 0°. After 3 days the purple crystals of the *bromide* were filtered off, washed with alcohol and ether, and air-dried (yield, 1·6 g.) [Found: Br, 20·1; SO_4, 24·7; H_2O, 9·6. $Co(C_2H_8N_2)_2SO_4Br,2H_2O$ requires Br, 20·5; SO_4, 24·5; H_2O, 9·6%]. A second crop (1·8 g.) was obtained after a further 3 days. When the mother-liquor was kept too long the bromine entered the co-ordination sphere and crystals of *cis*- and *trans*-$[Co\ en_2Br_2]Br$ were deposited.

Infrared maxima were at 1282s, 1208w, 1147sh, 1130s, 1099m, 1070s, 1052s, 1000m, 978s, 893w, 881w, 800sh, 794s, 645s, 625m, 595sh, 585s.

Aquosulphatobis(ethylenediamine)cobalt(III) *perchlorate* was made by an analogous method, hydrated lithium perchlorate (10 g.) being added to the solution (yield, 7 g.). It is less soluble in water than the bromide [Found: H_2O, 5·4. $Co(C_2H_8N_2)_2SO_4ClO_4,H_2O$ requires H_2O, 4·6%].

Sulphatobis(ethylenediamine)cobalt(III) *Bromide*.—A powdered specimen of the aquosulphato-bromide was heated at 110° for 24 hr. in an electric oven and lost weight equivalent to two water molecules per cobalt atom. The *product* was recrystallised by dissolving it in the minimum amount of cold water and adding solid sodium bromide, then forming short purple-red needles [Found: SO_4, 27·2; Br, 21·9. $Co(C_2H_8N_2)_2SO_4Br$ requires SO_4, 27·0; Br, 22·5%]. The apparent molecular weight was determined by measuring the freezing-point depression [4] of a 0·015M-aqueous solution (Found: *M*, 187. $[Co\ en_2SO_4]^+Br^-$ requires *M*, 177). Since the

---

* The complex $[Co\ en_2SO_4Br]$ can be prepared by heating the salt *cis*-$[Co\ en_2H_2OBr]SO_4$. This does not initially give a positive reaction for ionic bromide.

[4] Cf. Richards, *Z. phys. Chem.*, 1903, **44**, 563.

activity coefficients of these ionic species may be well removed from unity at these concentrations the method was calibrated by means of 0·015M-potassium bromide (Found: *M*, 67. Calc. for K^+Br^-: *M*, 59).

Infrared maxima were at 3229s, 3175m, 3151m, 3037s, 2943m, 2884m, 1590sh, 1570s, 1451s, 1391w, 1370w, 1323sh, 1314w, 1299sh, 1282sh, 1277m, 1224sh, 1211s, 1176vs, 1136m, 1111w, 1088sh, 1075vs, 1053s, 993s, 948w, 936w, 910w, 903w, 893w, 879w, 827m, 806s, 667m, 647s, 632s, 585s, 573w, 515m, 505w, 480w cm.$^{-1}$ (Nujol and hexachlorobutadiene mulls).

Sulphatobis(ethylenediamine)cobalt(III) *perchlorate* can be made by heating the aquosulphatoperchlorate. It is insoluble in water and cannot be recrystallised without decomposition. A better crystalline specimen was obtained by carefully adding lithium perchlorate solution to a saturated aqueous solution of the bromide. Short purple-red needle crystals were obtained [Found: SO_4, 26·0. $Co(C_2H_8N_2)_2SO_4,ClO_4$ requires SO_4, 25·6%].

One of us (C. G. B.) acknowledges the award of a travelling scholarship from the University of Melbourne.

William Ramsay and Ralph Forster Laboratories,
University College,
Gower Street, London, W.C.1.

[*Received, November 4th*, 1960.]