On the Outersphere Association of Tris(ethylenediamine)cobalt(III) Ion with Thiosulphate and Selenite Ions

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Recently Larsson *et al.*[1-3] from measurements of optical and circular dichroism have drawn the conclusion that the D-tris(ethylenediamine)cobalt(III) ion with divalent anions such as thiosulphate and selenite forms association products with rather high stability constants in about 2 M sodium perchlorate solutions. Thus Larsson *et al.* estimate the following stability constants for the Co en$_3$$^{3+}$, S$_2O_3$$^{2-}$-system:[1,2]

$$K_1 = 150 \quad \text{M}^{-1}, \quad \beta_2 = 7.5 \times 10^3 \quad \text{M}^{-2},$$
$$\beta_3 = 1.5 \times 10^5 \quad \text{M}^{-3}, \quad \beta_4 = 1.5 \times 10^5 \quad \text{M}^{-4}$$

and for the Co en$_3$$^{3+}$,SeO$_3$$^{2-}$-system:[3]

$$K_1 = 130 \pm 5 \text{ M}^{-1}, \beta_2 = (8.3 \pm 0.3) \times 10^3$$
$$\text{M}^{-2}, \beta_3 = (2.9 \pm 0.6) \times 10^4 \text{ M}^{-3},$$
$$\beta_4 = (1.4 \pm 0.8) \times 10^5 \text{ M}^{-4}$$

in both cases at 20°C for $I = 2$ (NaClO$_4$).

According to N. Bjerrum's electrostatic theory of ion-association such a stepwise second-sphere association is quite unexpected, and disagrees also with experimental data from more traditional methods. Thus Posey and Taube[4] from spectrophotometric measurements in the ultraviolet, obtain the following expression for the association constant of the ion-pair [Co(NH$_3$)$_6$]SO$_4$$^+$ in solutions with $\sqrt{I}$ varying from 0.04 to 0.3:

$$\log K_1 = 3.32 - \frac{6.1\sqrt{I}}{1 + 2.0\sqrt{I}}$$

corresponding to $K_1 \sim 10$ for $I = 2$. The rather polarizable thiosulphate ion has a much higher influence on the ultraviolet absorption of the cobalt(III)-amine complexes than the much less polarizable sul-

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phate ions,[5] but it is noteworthy that the stability of the ion-pairs formed with the first-mentioned ion is even smaller than those formed with the sulphate ion.[6] This supports the electrostatic nature of the second-sphere association.

In order to further examine this problem, the ultraviolet absorption of the tris(ethylenediamine)cobalt(III) ion has been studied in solutions of Na$_2$S$_2$O$_3$ and Na$_2$SeO$_3$ in which the sodium ion concentration was kept constant at 2.88 M with NaClO$_4$. The measurements were made at selected wavelengths in the near-ultraviolet where the thiosulphate and selenite ions have a considerable influence on the absorp-
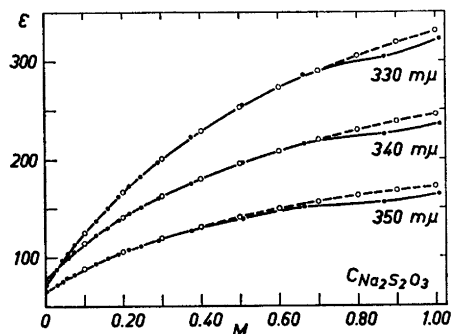

Fig. 1. The molar extinction coefficient ε of Co en$_3$$^{3+}$ as function of the thiosulphate concentration for selected wavelengths.
$C_{\text{Co en}_3^{3+}} \sim 0.0025$ M, 2 $C_{\text{Na}_2\text{S}_2\text{O}_3}$ + C_{NaClO_4} = = 2.88 M. ● Exptl. points, ○ Calc. points.
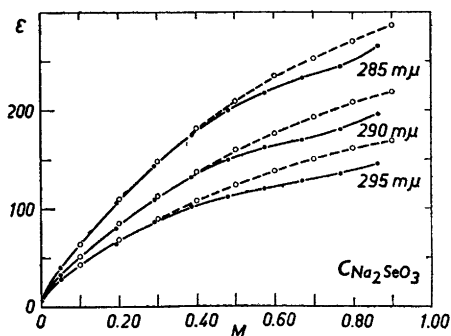

Fig. 2. The molar extinction coefficient ε of Co en$_3$$^{3+}$ as function of the selenite concentration for selected wavelengths.
$C_{\text{Co en}_3^{3+}} \sim 0.0025$ M, 2 $C_{\text{Na}_2\text{SeO}_3}$ + C_{NaClO_4} = = 2.88 M. ● Exptl. points, ○ Calc. points.

Table 1. Relative increases of the absorption in the Co en$_3$$^{3+}$, S$_2O_3$$^{2-}$-system at various wavelengths. ε(0.2 M S$_2$O$_3$$^{2-}$)$-$ ε(0.1 M S$_2$O$_3$$^{2-}$) is taken as unity.

$C_{Na_2S_2O_3}$	330	335	340	345	350 mμ	Average
0.05—0.10 M	0.596	0.594	0.604	0.613	0.620	0.605
0.10—0.20 M	1	1	1	1	1	1
0.20—0.25 M	0.448	0.415	0.448	0.443	0.458	0.442
0.25—0.30 M	0.367	0.380	0.388	0.387	0.386	0.382
0.30—0.40 M	0.703	0.667	0.653	0.646	0.681	0.670
0.40—0.50 M	0.584	0.570	0.560	0.566	0.542	0.564

tion although their own absorption is negligible. Some of the absorption curves, ε_λ versus $C_{Na_2,X}$, are given in Figs. 1 and 2. In Table 1 the relative increases in absorption for selected increases in the thiosulphate concentration are compared for various wavelengths in order to examine as to what extent the formation of one ion-pair could sufficiently explain the data. The fact that the relative increase in absorption seems to be independent of the wavelength supports the idea that the solutions in the concentration range examined contain only two species, viz. Co en$_3$$^{3+}$ and [Co en$_3$]S$_2$O$_3$$^+$. Under this assumption it is possible to estimate the ion-pair constant $K_1 = [[$Co en$_3$]X$^+$]/[$Co en$_3$$^{3+}$][X^{2-}]$ following the procedure given by J. Bjerrum.[7] In this way it was found that $K_1 = 1.3 \pm 0.1$ M^{-1} for the thiosulphate system, and $K_1 = 1.2 \pm 0.5$ M^{-1} for the selenite system. The calculation gives further values for the extinction coefficient of the ion-pair, and the possibility of calculating the absorption curves. The results of such a calculation for the anions in question are shown in Figs. 1 and 2. The computed curves show that the assumption of only one ion-associate [Co en$_3$]X$^+$ is sufficient to reproduce satisfactorily the absorption change of the thiosulphate solutions up to $C_{S_2O_3}{}^{2-} = 0.6$ M, and that of the selenite solutions up to $C_{SeO_3}{}^{2-} = 0.3$ M. The deviations found at high anion concentrations are most likely caused by the formation of triple ions [Co en$_3$]X$_2$$^-$, but irregularities caused by the large change in the salt medium must also be considered.

Our results seem to confirm the electrostatic picture of the second-sphere association, and are in complete disagreement with the results of Larsson et al.

In his rotation studies,[1,8] Larsson studied the influence of various anions on the optical rotation of D-Co en$_3$$^{3+}$, and found in thiosulphate and sulphate solutions a minimum in the rotation curve from which he draws conclusions about the second-sphere association. As discussed elsewhere,[9] another explanation is possible considering that the dextro as well as the levo-form of Co en$_3$$^{3+}$ exist as an equilibrium mixture of four conformations [10] each with its own optical rotation. For this reason the measurements ought to be repeated with the optically active tris(diamine) complex of trans-cyclohexane-1,2-diamine which exists in one conformation only. The minimum in the rotation curve is less pronounced in solutions with a high concentration of NaClO$_4$, and the authors of this
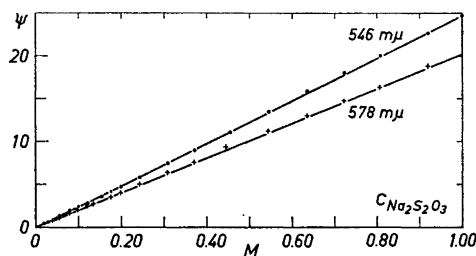
Fig. 3. Increase in rotation Ψ of D-Co en$_3$$^{3+}$ with $C_{Na_2S_2O_3}$ at two wavelengths in solutions with $C_{Na_2SO_4} + C_{Na_2S_2O_3} = 1$ M. $\Psi = \Delta$ degrees/$d \times C_{Co\ en_3}{}^{3+}$ ($C_{Co\ en_3}{}^{3+} = 0.032$ M, $d = 1$ dm, 20°C).

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communication have found that it disappears completely in mixtures of $Na_2S_2O_3$ and Na_2SO_4 at a constant molarity of one. In this medium the rotation of D-Co en$_3^{3+}$ at 546 and 578 mμ shows no anomaly and changes linearly with the mole fraction from 1 M Na_2SO_4 to 1 M $Na_2S_2O_3$ (see Fig. 3).

Experimental. A preparation of the double salt (+)$_D$—[Co en$_3$]Cl$_3$, $\frac{1}{2}$NaCl, 3 H$_2$O prepared by a modified method[11] was used. (Found: C 16.70; N 19.86; Cl 29.18. Calc.: C 16.80; N 19.60; Cl 28.93). All other chemicals were commercial products of AnalaR grade.

The absorption measurements were made with a Cary 14 spectrophotometer. The reference cells contained a cobaltfree solution of the same saltmedia.

The polarimetric measurements were made with a Perkin-Elmer polarimeter, model 141, in a 1 dm cell at 20°C.

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Heats of Reaction of Antimony Pentachloride with Propionyl Chloride and Ethyl Chlorocarbonate

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In previous communications values have been reported of the enthalpy of formation of adducts between antimony pentachloride and compounds having the general formula $R_1R_2C=O$.[1-3] The experiments reported in this paper conclude the study of the effects of systematic variations in R_1 and R_2 such that the two atoms attached to the carbonyl group are any two of the elements carbon, nitrogen, oxygen, and chlorine. It includes the cases where R_1 is a chlorine atom and R_2 an ethyl or an ethoxy group.**

Experimental. Materials. Ethylene chloride was treated as given in Ref. 1 and *antimony pentachloride* as given in Ref. 3. *Propionyl chloride* (Fluka) was fractionally distilled and purity checked by potentiometric titration after hydrolysis and also by NMR measurements. NMR spectra were run on the pure sample and on a sample to which 0.7 % (mole) water had been added. The purity was judged to be better than 99.5 %. d_4^{25} 1.0505. *Ethyl chlorocarbonate* (Fluka) was distilled in an all-glass apparatus and transferred to break-off ampoules. Titration after alkaline hydrolysis indicated purity of 99 $\pm$ 1 %.

Apparatus. Calorimetric and infrared equipment see Ref. 4. The NMR spectra were recorded on a Varian A 60 spectrometer.

Calibration and *corrections to standard states*, see Ref. 1.

Calorimetric procedure, see relevant parts of Ref. 4.

Units of measurements. The results of the calorimetric experiments are expressed in terms

** The interaction between antimony pentachloride and $COCl_2$ is certainly very weak. No attempts have therefore been made to measure the enthalpy of adduct formation with phosgene as donor.