

A Cation-exchange Investigation of the Association between Tris(ethylenediamine)cobalt(III) Ions and Thiosulphate Ions in 2 M NaClO₄ Medium

RAGNAR LARSSON and GENNARO NUNZIATA*

*Division of Inorganic Chemistry, Chemical Center, University of Lund,
S-220 07 Lund 7, Sweden*

The association between Coen₃³⁺ and S₂O₃²⁻ ions in a sodium perchlorate medium (*I*=2 M) has been determined with a cation-exchange method. It is found that $\beta_1 = 5 \pm 0.5 \text{ M}^{-1}$. If a second complex exists, $\beta_2 \approx 2.5 \text{ M}^{-2}$.

In a series of investigations¹⁻⁵ one of the present authors has studied the association of cobaltammine ions, Co(NH₃)₅³⁺ and Coen₃³⁺, with various negatively charged ions such as SO₄²⁻, S₂O₃²⁻, SeO₃²⁻, and Br⁻. In many cases coordination numbers up to four were found and it has been suggested that the association could be described in terms of outer-sphere coordination rather than in terms of the ion-pair theory of N. Bjerrum.⁶ Thus the outer-sphere ligands were assumed to occupy specific coordination sites in close analogy with the situation in the inner coordination sphere.

Recently some of these investigations have been criticized by J. Bjerrum and his coworkers.^{7,8} This criticism is especially concerned with the magnitudes of the stability constants found for the Coen₃³⁺ association with thiosulphate and selenite ions. Thus Larsson and Johansson³ reported $K_1 \approx 150 \text{ M}^{-1}$ for the S₂O₃²⁻ system and Larsson, Mason and Norman⁵ found $K_1 = 130 \pm 5 \text{ M}^{-1}$ for the SeO₃²⁻ one (both values at *I*=2 (NaClO₄)). Olsen and Bjerrum,⁸ on the other hand, have reported the values $K_1 = 1.3 \pm 0.1 \text{ M}^{-1}$ and $K = 1.2 \pm 0.5 \text{ M}^{-1}$ for the two systems, respectively, at *I*=2.88 (NaClO₄). Later Bjerrum and Romano⁹ determined β_1 for the Coen₃³⁺-S₂O₃²⁻ system at a total sodium ion concentration = 1 M from a spectrophotometric investigation. They found $\beta_1 = 6 \text{ M}^{-1}$.

The large variation in β_1 determined with different methods has prompted us to employ other methods of investigation.

* Present address: Product Research Department, European Technical Center, Procter and Gamble Co., Brussels, Belgium.

A useful method for studying complex formation when no suitable potentiometric method can be used is the one of distribution of metal ions between a cationic exchange resin and the aqueous phase, developed by Fronæus.¹⁰⁻¹²

This method has been applied to the present problem, using a cation exchange resin saturated with sodium ions and keeping the concentration of sodium ions in the aqueous phase constant and equal to 2 M. It is obvious that one has to consider the sorption on the resin phase of the free central group, M, and the first complex, ML, only. This facilitates the calculations. Using the notations of Ref. 12, we can write the distribution function ϕ as

$$\phi = \frac{C_{\text{MR}}}{C_{\text{M}}} = l_0 \frac{1 + l[\text{L}]}{X} \quad (1)$$

Furthermore, the function ϕ_1 is defined as

$$\phi_1 = (l_0\phi^{-1} - 1)[\text{L}]^{-1} \quad (2)$$

It holds,¹³ that

$$\phi_1 = (\beta_1 - l) + [\beta_2 - (\beta_1 - l)l][\text{L}] + \frac{K[\text{L}]^2}{1 + l[\text{L}]} \quad (3)$$

Hence by plotting ϕ_1 against $[\text{L}]$ one should obtain the quantities $\beta_1 - l$ and $[\beta_2 - (\beta_1 - l)l]$. Furthermore if l was known one could calculate β_1 , and β_2 . If not, at least a minimum value of β_1 can be found.

Experimental details. The experiments were performed using $\text{Coen}_3(\text{ClO}_4)_3$ labelled with radioactive ^{60}Co isotope. All solutions were carefully protected from light during the whole process. The concentration of cobalt species in the aqueous phase after equilibrium was reached (C_{M}) was determined radiometrically using a Landis & Gyr scintillation counter. Not less than 10^4 counts were registered. The concentration of cobalt species in the resin phase then determined from the formula¹¹

$$C_{\text{MR}} = vm^{-1}(C_{\text{M}}' - C_{\text{M}}\delta) \quad (4)$$

where C_{M}' is the cobalt concentration of the solution (v liter) before this was shaken with the resin (m g). The cation exchanger was Dowex 50X16. It was airdried and had a swelling factor, δ , of 0.99. In the same way C_{L} was calculated from the relation $C_{\text{L}} = C_{\text{L}}'\delta^{-1}$, where C_{L}' is the thiosulphate concentration before equilibration.

RESULTS

The results of measurements at three different values of C_{M}' are given in Table 1.

It has been pointed out by Fronæus that the parameters l_0 and l can be considered as constant only if the load on the resin phase is kept constant and low. Usually this condition is reached by an interpolation between results for different values of C_{M}' . In this case, however, it is obvious from the results (Table 1) that C_{MR} is rather constant within each series of measurements. Thus calculations of ϕ_1 can be performed for each of these series separately with the assumption that l_0 and l are constants. The results are also given graphically in Figs. 1 and 2. The value of l_0 used in the calculations was the limiting value of the ϕ function for $C_{\text{L}} = 0$. The approximation $[\text{L}] = C_{\text{L}}$ was

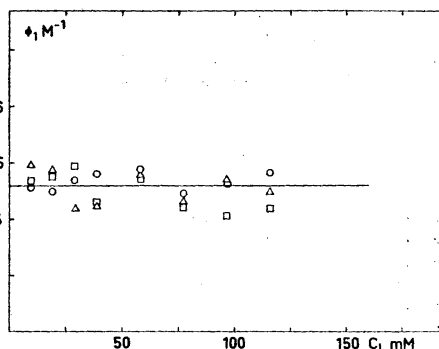
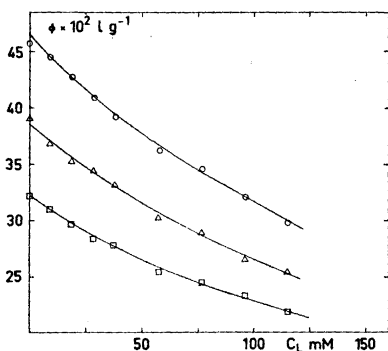


Fig. 1. ϕ as a function of $[\text{L}] \approx C_{\text{L}}$. Fig. 2. ϕ_1 as a function of $[\text{L}] \approx C_{\text{L}}$.
 $\circ: C_{\text{M}'} = 0.5$; $\triangle: C_{\text{M}'} = 1.0$; $\square: C_{\text{M}'} = 2.0$. $\circ: C_{\text{M}'} = 0.5$; $\triangle: C_{\text{M}'} = 1.0$; $\square: C_{\text{M}'} = 2.0$.

used as C_{M} was small. Fig. 2 shows that for all the three series ϕ_1 is roughly independent of $[\text{L}]$ and also has the same value within experimental errors. It follows that $\beta_1 - l = 4.6 \pm 0.5 \text{ M}^{-1}$.

DISCUSSION

Two possibilities of interpretation must now be considered. The first and straight-forward one is that only one complex exists in the range of $[\text{L}]$ used in the investigation. Then from the invariance of ϕ_1 with $[\text{L}]$ one must conclude that l has a small value and consequently that $\beta_1 = 5 \pm 0.5 \text{ M}^{-1}$. This value is in close agreement with the one reported by Bjerrum.⁹ It is then quite probable that the correct value of β_1 is 5 M^{-1} .

Nevertheless, anion exchange measurements¹ indicate the existence of higher complexes. Thus the possibility of the presence [of small amounts] of the second complex at the present values of $[\text{L}]$ must be considered.

If two complexes exist the zero slope of the ϕ_1 function must result from the relation

$$\beta_2 - (\beta_1 - l)l = 0 \quad (5)$$

In order to evaluate this equation it is necessary to know the value of l . Although a combination of the results of the measurements on the $\text{In}^{3+} - \text{SO}_4^{2-}$ system reported by Sundén^{14,15} gives a value of $l \beta_1^{-1} \approx 0.3$, this quantity is usually¹² of the order of 0.1. Thus with $\beta_1 - l \approx 5 \text{ M}^{-1}$ and $l \approx 0.5 \text{ M}^{-1}$ one can estimate $\beta_2 = 2.5 \text{ M}^{-2}$.

The present investigation strengthens the opinion⁸ that the stability of the $\text{Coen}_3^{3+} - \text{S}_2\text{O}_3^{2-}$ complexes is much lower than what has been previously³ assumed. The origin of the peculiar relation³ between the optical rotation of $(+)\text{Coen}_3^{3+}$ and the concentration of thiosulphate ions remains to be elucidated.

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