

Studies on Cobaltamines

V. Anion-Exchange Investigations of the Outer-Sphere Complexity of the Cobalthexammine(III) Ion

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The distribution of the $\text{Co}(\text{NH}_3)_6^{3+}$ ion between an anion exchanger and water has been determined for varying concentrations in the aqueous phase of sulphate, thiosulphate, fluoride, chloride, bromide and acetate ions. From the distribution curves obtained the existence of the third sulphate and thiosulphate complexes is deduced as well as the fourth chloride and bromide complexes.

The tendency towards the formation of anionic complexes follows the order $\text{S}_2\text{O}_3^{2-} > \text{SO}_4^{2-}$ and $\text{Br}^- > \text{Cl}^- > \text{F}^-$. These results seem to support the concept of a second coordination sphere of the $\text{Co}(\text{NH}_3)_6^{3+}$ ion, which is closely analogous with the inner coordination sphere.

In recent years many reports have appeared concerning the association between various anions and complex ions, such as $\text{Co}(\text{NH}_3)_6^{3+}$ and $\text{Cr}(\text{NH}_3)_6^{3+}$. The association products have sometimes been described as "ion-pairs", sometimes as "outer-sphere complexes". The first term was introduced by Bjerrum¹ and formally describes the effect of the long-range electrostatic forces around such highly charged ions. These effects, however, can also be treated in other ways (Gronwall *et al.*², Mayer³, Guggenheim⁴).

On the other hand, if the concept of "outer-sphere complexes" shall be used sensibly, we cannot confine ourselves to the mere existence of such association products, as they can be described as indicated above. The term "sphere" is intimately related to the coordination theory of Werner⁵, and if the term "outer-sphere complexes" should have any pragmatic sense, we must demand that the same criteria shall apply to the *outer sphere of coordination* as to the *inner* one. That is, the ligands must be assumed to occupy a limited number of so-called coordination sites, and moreover, these should be spatially well defined. Such a situation obviously arises if some kind or kinds of specific interaction is at hand.

As in the case of coordination in the inner sphere, it is not necessary to specify the "forces" of interaction.

It seems to the present authors that an indication of the usefulness of the concept of outer-sphere coordination would be the detection of association products that cannot be explained in terms of "ion-pairing". Such association products would be anionic complexes, *e.g.* $[\text{Co}(\text{NH}_3)_6\text{Cl}_4]^-$ or $[\text{Co}(\text{NH}_3)_6(\text{SO}_4)_3]^{3-}$, *i.e.* of a composition that corresponds to an association between negatively charged ligands and uncharged or negatively charged central groups.

A method for the detection of anionic complexes has been devised by Fronæus⁶. This method has been used in this investigation to study the association between the cobalthexammine(III) ion and fluoride, chloride, bromide, acetate, sulphate and thiosulphate ions, respectively.

THEORY

The distribution of the hexammine cobalt complex, here denoted MA_6 , between the anion exchange resin, saturated with the ligand B, and the aqueous solution with the total concentration of ligand C_B , is designated as:

$$\varphi = C_{(\text{MA}_6)_R} / C_{\text{MA}_6} \quad (1)$$

The subscript R indicates the resin phase.

It can be shown⁶ that

$$\varphi = K \cdot \frac{X([\text{B}]_R)}{[\text{B}]_R^\nu} \cdot \frac{[\text{B}]^\nu}{X([\text{B}])} \quad (2)$$

Here

$$X = 1 + \sum_{n=1}^N \beta_n [\text{B}]^n \quad (3)$$

K is the constant of the Donnan equation, and ν is the quotient between the absolute values of the ionic charge of the central group and that of the ligand.

Further-more it has been shown⁶ that φ has a maximum value for such a $[\text{B}]$ that the mean ligand number $\bar{n} = \nu$. This holds true whether ν is a whole number or not.

It can be seen from eqn. (2) that for two systems, for which K can be regarded as approximately equal, φ will be greatest — at corresponding values of $[\text{B}]$, *e.g.* at the maximum — for the system that exhibits the greatest anion complexity in the resin phase (*cf.* Ref.⁶, p. 3).

Thus there are two possible indications of the formation of the anionic complexes alluded to in the introduction: the appearance of a maximum, which indicates the formation of anionic complexes in the aqueous phase, and the magnitude of that maximum, which is a measure of the degree of formation of anionic complexes at the very high ligand concentrations that exist in the resin phase.

Furthermore, if we assume that $[\text{B}]_R$ is constant, it is easily deduced (Ref.⁷, p. 1449) that

$$d \ln \varphi / d \ln [\text{B}] = \nu - \bar{n} \quad (4)$$

from which relation \bar{n} may be estimated also beyond the value of ν .

MEASUREMENTS

Experimental technique. In 50 ml glass bottles with well ground stoppers a weighed amount (w g) of resin was added to 15 ml of a solution with a ligand concentration C'_B and a concentration C'_{MA} of $\text{Co}(\text{NH}_3)_6(\text{ClO}_4)_3$. w was always 1.00 g. The bottles were carefully closed and put into brass cylinders, which were kept rotating in a water thermostat (20°C) for 30 h at least.

The brass cylinders had the twofold purpose of preventing the bottles from breaking and of protecting the solutions from light, that might have produced decomposition of the cobalt complex⁸.

After the indicated time, the solution was separated as completely as possible from the resin phase by backway filtration using a large-porous filterstick. The cobalt concentration was determined for both phases. As the φ values were in all cases $< 10^{-2}$ l/g, the cobalt charge of the resin phase could be quantitatively extracted by shaking with a certain volume v_1 (15 ml) of water. The cobalt used contained an amount of ^{60}Co (Harwell) and the determinations of the cobalt concentrations could thus be easily performed radiometrically.

Measurement of radioactivity. The detector and the scaler were the same as before⁹. In addition, auxiliary equipment, constructed in this laboratory, was used, which, together with a Tracergraph Printing Timer, allowed automatic registration of a series of samples. The reproducibility was 1 %.

Chemicals used. Sodium (in one case lithium) salts of *pro analysi* quality were used. Stock solutions were made by dissolution of weighed amounts in distilled water. The concentrations were checked for the NaCl and NaBr solutions with argentometric titration, for Na_2SO_4 solution with alkalimetric titration after cation exchange and for the $\text{Na}_2\text{S}_2\text{O}_3$ solution with iodometric titration.

The anion exchange resin was Dowex 1 \times 4, 50–100 mesh. It was converted to the proper ionic form and air-dried.

Calculation of [B]. The swelling factor of the resin, $\delta = C'_B/C_B$, was determined by a titration of the liquid phase for the chloride, bromide and thio-sulphate systems (Fig. 1). For the sulphate system the values for the thio-sulphate system were used. From these curves C_B could be calculated for any C'_B (the concentration of ligand before equilibration). As C'_M was kept very low (0.2 mM), [B] was put equal to C_B in all cases but those of very low sulphate and thiosulphate concentrations, where $[\text{B}] = (C_B + 3 C'_M) \delta^{-1}$ (cf. Ref.⁶, p. 5).

Calculation of φ . To calculate C_{MR} we use the relation $C_{(\text{MA})R} = v_1 \cdot C''_{MA} \cdot w^{-1}$ where C''_{MA} is the cobalt concentration of the washing-solution.

Thus

$$\varphi = C_{(\text{MA})R}/C_{MA} = v_1 C''_{MA} w^{-1}/C_{MA} \quad (5)$$

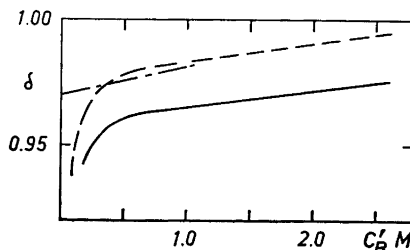


Fig. 1. Swelling factor $\delta = C'_B/C_B$ of the resin: chloride (—), bromide (---) and thiosulphate (- · - · -) solutions.

As $C_{MA_6}'' = \text{Const} \cdot I_2$ and $C_{MA_6} = \text{Const} \cdot I_1$ where I_1 and I_2 are the γ -intensities of 10 ml of the first filtrate and the washing-solution, respectively, we then obtain

$$\varphi = v_1 I_2 w^{-1} / I_1 \text{ l/g} \quad (6)$$

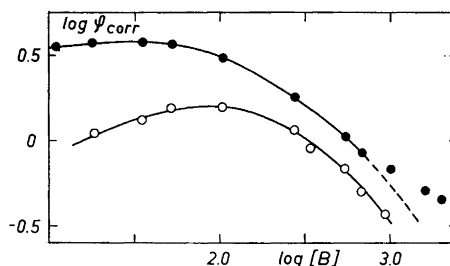
A reproducibility of 5 % or better was obtained. As the resin particles could not be completely freed from adherent solution, there is a certain contribution, φ_a , in the thus calculated φ values. (cf. Sonesson, Ref.⁷, p. 1448). In order to obtain the real φ we must make an estimate of φ_a . Sonesson⁷ used the value 0.5 ml/g, a value obtained from his measurements of the gadolinium acetate system. This choice was based on the assumption that the tendency to form anionic complexes was very small within this system so that the φ obtained could be regarded as almost a pure φ_a -contribution. In the present investigation the estimate of φ_a is based upon the measurements of the fluoride and acetate systems, where very low and rather constant φ values are found (Table 3). As φ_a must be equal to or less than the smallest φ found, we make the estimate $\varphi_a = 0.45$ ml/g. This is in good agreement with the value used by Sonesson⁷, as it should be for the same type of resin. Some difference must be expected caused by variations in particle size and separation effectivity.

Another correction, φ_s , that must be made, arises from the adsorption on the surface of the resin (Ref.⁶, p. 4). This effect is more difficult to determine, as it must be expected that several factors are at hand. First, the most strongly adsorbed ionic species is of course, the trivalent uncomplexed MA_6 , and so φ_s will decrease more rapidly the stronger the complexity of the system is. On the other hand, the adsorption must depend on the nature of the surface and thus on the ionic form of the resin. For this reason different correction terms have been used for φ_s in this paper. For the sulphate and thiosulphate systems the correction used by Sonesson⁷ has been used, only slightly modified. This

Table 1. The distribution quotients for the sulphate and thiosulphate systems. ($C'_M = 0.2$ mM).

a. The sulphate system				b. The thiosulphate system			
[B] M	φ ml . g ⁻¹	$(\varphi_a + \varphi_s)$ ml . g ⁻¹	φ_{corr} ml . g ⁻¹	[B] M	φ ml . g ⁻¹	$\varphi_a + \varphi_s$ ml . g ⁻¹	φ_{corr} ml . g ⁻¹
1.6	1.32	1.3	—	1.6	3.30	1.3	2.0
18.4	2.73	1.63	1.10	11.0	5.20	1.65	3.55
34.9	2.48	1.16	1.32	17.9	5.36	1.62	3.74
51.8	2.37	0.82	1.55	35.2	4.94	1.16	3.78
103	2.13	0.54	1.59	52.5	4.52	0.82	3.70
273	1.60	0.45	1.15	104	3.62	0.54	3.08
340	1.35	0.45	0.90	276	2.25	0.45	1.80
543	1.14	0.45	0.69	345	1.94	0.45	1.49
678	0.95	0.45	0.50	550	1.51	0.45	1.06
945	0.82	0.45	0.37	686	1.30	0.45	0.85
				1020	1.13	0.45	0.68
				1620	0.96	0.45	0.51
				2015	0.90	0.45	0.45

Fig. 2. The logarithms of the corrected distribution quotients of the sulphate (O) and thiosulphate (●) systems plotted against $\log[B]$.



correction was made, as it has been found to work properly for the system (gadolinium glycolate) studied by Sonesson ⁷, a system, which seems to be of about the same complexity as those two mentioned above (*vide infra*). For the chloride and bromide systems of a much weaker complexity the excessive value of φ for small C_B is much less, that is, φ_s does not contribute to any greater extent. Any correction in these cases is very much a question of choice, and the reported values (Fig. 3) have not been corrected for the adsorption effect.

RESULTS

The measurements of the sulphate and thiosulphate systems are given in Table 1. It can clearly be seen that both these systems exhibit a maximum of φ . In Fig. 2 $\log \varphi_{corr}$ is plotted against $\log[B]$. The maximum of the thiosulphate system is greater and appears at a lower value of $[B]$ than the one of the sulphate system.

From Fig. 2 one can obtain $d \log \varphi_{corr} / d \log [B]$ and thus from eqn. (4) one can calculate \bar{n} . Such a calculation is very uncertain because of the many corrections made and also because of the unvalidity of the assumption of a constant $[B]_R$ at higher C_B values *. Nevertheless it has been attempted and can be found in Table 2. As the \bar{n} values for large $[B]$ are greater than 2, we must also assume the presence of the third complex.

It must be pointed out that the calculation of \bar{n} for values of $[B] > 0.1$ M is independent of the correction φ_s , as this function decreases rapidly for

Table 2. The sulphate and thiosulphate systems. \bar{n} calculated from eqn. (4).

	a. The sulphate system			b. The thiosulphate system		
$[B]$ M	0.2	0.5	0.9	0.14	0.2	0.5
\bar{n}	2.0	2.4	2.7	2.0	2.1	2.4 **

* Furthermore, the β_n values for the aqueous phase probably vary somewhat, as the ionic strength is not kept constant.

** This value is probably too low because of a beginning variation of $[B]_R$, which causes the experimental points to lie above the expected curve for greater C_B values (Fig. 2).

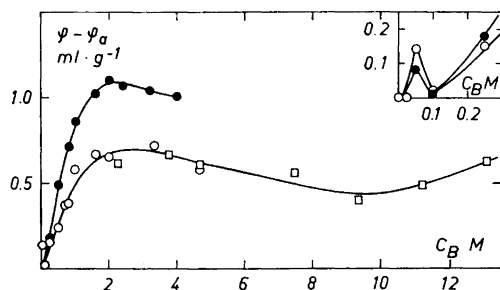


Fig. 3. The chloride and bromide systems. The distribution quotients corrected for the φ_a -contribution NaCl: O, LiCl: \square , NaBr: \bullet . (In the bromide case, precipitation occurred for $C_B > 4$ M.)

$[B] < 0.1$ M and is almost negligible for $[B] > 0.1$ M. The choice of the value of the correction φ_a is more critical. However, even if such a low value as 0.3×10^{-3} l/g is used, we obtain, *e.g.*, $\bar{n} = 2.35$ for $[\text{SO}_4^{2-}] = 0.7$ M. Thus the conclusion regarding the existence of the third complex is still valid.

The results of the measurements of the chloride and bromide systems are given graphically in Fig. 3. In both cases a slight maximum is observed, followed by an increase of φ at very high C_B values in the chloride case

The maxima indicate the presence of anionic complexes. The subsequent increase of φ must be attributed to a complete invalidity of the assumption of the constancy of $[\text{B}]_R$. It is interesting to note the greater value of the maximum for the bromide system. This indicates a greater tendency towards formation of anionic complexes in the resin phase for this system as compared to the chloride system.

The measurements of the fluoride and acetate systems are given in Table 3. As it has been mentioned before, the estimate of φ_a is based upon these results. The low values of φ makes it probable that the tendency to formation of anionic complexes is negligible.

Table 3. The distribution quotients of the fluoride and acetate systems. ($C'_M = 0.2$ mM).

a. The fluoride system		b. The acetate system	
C'_B mM	φ ml · g ⁻¹	C'_B mM	φ ml · g ⁻¹
16	0.53	42	0.49
32	0.57	83	0.43
48	0.49	170	0.43
95	0.53	330	0.52
260	0.48	670	0.50
320	0.46	1330	0.59
510	0.53	1870	0.65
640	0.54		

DISCUSSION

From the existence of not only the second but also the third complex of the sulphate and thiosulphate systems, it follows that the criterion of outer-sphere coordination that was suggested in the introduction, is actually fulfilled. Also the existence of the fourth chloride and bromide complexes gives weight to the use of the concept of "outer-sphere coordination".

It is interesting to note that the order of increasing strength of the anionic complexity is $\text{Br}^- > \text{Cl}^- > \text{F}^-$ and $\text{S}_2\text{O}_3^{2-} > \text{SO}_4^{2-}$. The last sequence at least, is based both on the complexity in the aqueous phase (the position of the maximum) and in the resin phase (the magnitude of the maximum). This order is reverse to that reported by Evans and Nancollas¹⁰ for the first complexity constant, $\text{Cl}^- > \text{Br}^- > \text{I}^-$. This fact may seem astonishing at first, but an inspection of the data of Evans and Nancollas¹⁰ shows that this order of the free energy change, $\text{Cl}^- < \text{Br}^- < \text{I}^-$, is a consequence of very large positive entropy terms. The enthalpies of reaction were¹⁰ all positive and followed the sequence $\text{Cl}^- > \text{Br}^- > \text{I}^-$. If we use this order of the enthalpies also for the formation of the higher complexes and use a rather small positive entropy term, we may very well obtain an order of the free energy changes $\text{Cl}^- > \text{Br}^- > \text{I}^-$ which is in accordance with the sequence of anionic complexity that has been found here.

In this connection some words can be said in favour of the measurements of Evans and Nancollas¹⁰. These authors have used a method which is known to yield reliable results (Olerup¹¹, p. 63) and their result for the iodide system ($\beta_1 = 17 \text{ M}^{-1}$, $I = 0.054 \text{ M}$) agrees well with that, which was reported independently by Kubota¹², ($\beta_1 = 16 \text{ M}^{-1}$, $I = 0.03-0.1 \text{ M}$). Recently this work has been criticized by other authors¹³. They, however, use a method, which is also known to yield very uncertain information in the case of weak complexity, (Olerup¹¹, p. 58). We therefore chose to base our discussion on the work of Evans and Nancollas¹⁰.

The observed trend for the complexity is contrary to the one that was expected for pure electrostatic attraction. The degree of complex formation rather follows the same order as the polarizabilities of the ligands do: $\text{Br}^- > \text{Cl}^- > \text{F}^-$; $\text{S}_2\text{O}_3^{2-} > \text{SO}_4^{2-}$. This may be taken as an indication of a partial charge transfer from the ligands towards the cobalt centre. This is in agreement with the absorption spectra in the ultraviolet region¹⁴, typical of "charge transfer complexes".

Thus, in conclusion, we may state that the studied association products have so many features in common with ordinary coordination complexes that the use of the concept of the second coordination sphere is well justified.

This work has been financially supported by the *Swedish Natural Science Research Council*, a fact which is gratefully acknowledged.

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Received May 12, 1962.