

## Studies on Cobaltamines

### I. Equilibrium Measurements of Inner-Sphere Thiocyanato- and Nitro-Complexes

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The exchange of ammonia in the hexammine cobalt(III) ion for one and two thiocyanate ions or one nitrite ion has been achieved by the use of active carbon as a catalyst. By measurement of the total cobalt concentration in solutions saturated with hexammine cobalt (III) perchlorate, the equilibrium constants at ionic strength 1 M have been calculated. The influence of outer-sphere complexes has been considered.

Ever since the beginning of coordination chemistry in the days of Jørgensen and Werner the ammino compounds of trivalent cobalt have been intensely studied. Little has been known, however, about the equilibrium constants of reactions between these compounds. This situation is obviously related to those properties that made Co(III) complexes so suitable for preparative work; the low solubility of many of them and — above all — their sluggish reaction.

Until the work of J. Bjerrum<sup>1</sup>, no reactions had been quantitatively studied, involving an ammonia displacement from the hexammine cobalt(III) ion. In the present paper, equilibrium measurements of the reaction of the hexammine cobalt(III) ion with thiocyanate and nitrite ions, respectively, will be presented.

#### METHOD OF INVESTIGATION

To overcome the slow attainment of equilibrium J. Bjerrum<sup>1,2</sup> has used active carbon as a catalyst. Other workers have also studied this catalytic effect.<sup>3,4</sup> They agree that the efficiency of the carbon is gradually decreased as time progresses. The probable explanation is that the carbon is poisoned by a layer of cobalt(III) hydroxide; a proposal strengthened by the observation of Bjerrum<sup>1, p. 255</sup>, that there is a decrease in the total concentration of cobalt when equilibrium has been attained. Though experiments of the

present author have shown platinum black and finely dispersed silver to be catalysts as well, active carbon has been used in this investigation because of its cheapness and (compared to silver) greater inertness.

The measurements should be performed in a medium of high and constant ionic strength in order to justify the assumption that the coefficients of activity are constant, so that the law of mass action may be expressed in concentration units instead of activities.

Furthermore, the concentration of ammonium ions should be as great as possible in order to suppress the hydrolysis:



As the neutral salt, therefore, 1 M  $\text{NH}_4\text{ClO}_4$  has been used. At the temperature of measurement, 20°C, the solubility of  $\text{Co}(\text{NH}_3)_6(\text{ClO}_4)_3$  in 1 M  $\text{NH}_4\text{ClO}_4$  is 0.21 mM.

It therefore seemed natural to measure the degree of complex formation from the increase in solubility of this rather sparingly soluble salt.

For easy concentration determinations the hexammine cobalt(III) salt was labelled with radioactive  $^{60}\text{Co}$ .

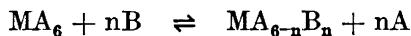
#### NOTATIONS AND GENERAL FORMULAE

The notations used and methods of calculation will conform as closely as possible to those used by Fronæus<sup>5</sup>.

In formulae M will stand for Co, A for ammonia and B for thiocyanate or nitrite.

$C_A$  will mean the total and [A] the free concentration of A. Equivalent notations apply to other molecular species.

The equilibrium constant for the reaction

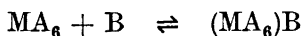


will be denoted by  $\gamma_n$

$$\gamma_n = \frac{[\text{MA}_{6-n}\text{B}_n][\text{A}]^n}{[\text{MA}_6][\text{B}]^n} \quad (1)$$

In recent years the conception of "outer-sphere complexes" has been used in connection with the explanation of kinetical data on cobalt(III) complexes<sup>6-8</sup>. The eventual formation of such outer-sphere complexes will be duly accounted for in this investigation.

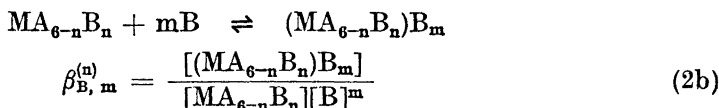
An outer-sphere coordination of the ligand B to the unsubstituted ion  $\text{MA}_6$  may be written:



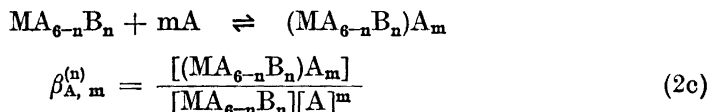
The equilibrium constant is denoted

$$\beta_{\text{B},1}^{\circ} = \frac{[(\text{MA}_6)\text{B}]}{[\text{MA}_6][\text{B}]} \quad (2a)$$

In the general case, with  $n$  ligands B in the inner (hexacoordination-) sphere and  $m$  ligands B in the outer sphere we write:



Analogously, with ammonia in the outer coordination sphere we write in the general case



It is further defined:

$$X_{\text{A}}^{(n)} = \sum_{m=1}^M \beta_{\text{A}, m}^{(n)} [\text{A}]^m \quad (3a)$$

$$X_{\text{B}}^{(n)} = \sum_{m=1}^M \beta_{\text{B}, m}^{(n)} [\text{B}]^m \quad (3b)$$

Combining the expressions (1), (2 b), (2 c), (3 a) and (3 b) we may write the total metal concentration  $C_{\text{M}}$

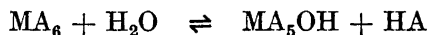
$$C_{\text{M}} = [\text{MA}_6] \left[ 1 + X_{\text{A}}^{\circ} + X_{\text{B}}^{\circ} + \gamma_1 \frac{[\text{B}]}{[\text{A}]} (1 + X_{\text{A}}^{(1)} + X_{\text{B}}^{(1)}) + \dots + \gamma_n \frac{[\text{B}]}{[\text{A}]} (1 + X_{\text{A}}^{(n)} + X_{\text{B}}^{(n)}) \right] \quad (4)$$

For the sake of simplicity in writing, we denote the expression inside the large brackets as  $Y$ .

$$\text{Thus} \quad C_{\text{M}} = [\text{MA}_6] Y \quad (5)$$

Though the concentration of ammonium ions is kept high, the hydrolytic reactions may still be of significance.

For the first step of hydrolysis



we put

$$k_{\text{OH}}^{\overline{\text{---}}} = \frac{[\text{MA}_5\text{OH}][\text{HA}]}{[\text{MA}_6]}$$

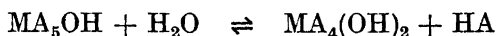
Now

$$[\text{HA}] = C_{\text{NH}_4} = 1 \text{ M}$$

Thus

$$[\text{MA}_5\text{OH}] = [\text{MA}_6] k_{\text{OH}}^{\overline{\text{---}}} \quad (6)$$

From the value of the second constant of hydrolysis reported by Bjerrum <sup>1</sup>, p. 272 (for another temperature and another ionic medium) it may be inferred that the second hydrolytic step



will not contribute to an appreciable amount.

Adding eqn. (6) to the expression (5) for the total metal concentration we finally get

$$C_M = [\text{MA}_6](Y + k_{\text{OH}}) \quad (7)$$

As the solution is saturated with  $\text{MA}_6(\text{ClO}_4)_3$  we have

$$[\text{MA}_6][\text{ClO}_4]^3 = l \quad (8)$$

where  $l$  is the solubility product of  $\text{MA}_6(\text{ClO}_4)_3$  in the actual solution. When  $C_B = C_A = 0$  we write

$$[\text{MA}_6]_0[\text{ClO}_4]_0^3 = l_0 \quad (9)$$

By dividing eqn. (8) with eqn. (9) we get

$$[\text{MA}_6] = [\text{MA}_6]_0 \cdot \frac{[\text{ClO}_4]_0^3}{[\text{ClO}_4]^3} \cdot \frac{l}{l_0} \quad (10)$$

Inserting eqn. (10) in eqn. (7) we get

$$C_M = (Y + k_{\text{OH}}) \cdot [\text{MA}_6]_0 \cdot \frac{[\text{ClO}_4]_0^3}{[\text{ClO}_4]_3^3} \cdot \frac{l}{l_0} \quad (11)$$

As previously mentioned the cobalt determination was a radiometric one. The counting intensity for a given volume of the saturated solution ( $I$  cpm) is proportional to  $C_M$ .

$$\text{Thus} \quad I = \text{const.} \cdot C_M \quad (12 \text{ a})$$

$$I_0 = \text{const.} \cdot [\text{MA}_6]_0 \quad (12 \text{ b})$$

Combining eqns. (11), (12 a) and (12 b) we get

$$Y + k_{\text{OH}} = \frac{I}{I_0} \cdot \frac{[\text{ClO}_4]_0^3}{[\text{ClO}_4]_3^3} \cdot \frac{l_0}{l} \quad (13)$$

The above deduction is made under the assumption that no polynuclear complexes are formed. This may be regarded as reasonable, because of the small value of  $C_M$ . Furthermore, as it is known that most polynuclear Co(III) complexes involve the formation of OH or  $\text{NH}_2$  bridges<sup>9</sup>, and only a small contribution to  $C_M$  is due to hydrolytic products, the assumption made is so much more plausible.

#### EXPERIMENTAL

*Chemicals used.* Unlabelled  $\text{Co}(\text{NH}_3)_6\text{Cl}_3$  was prepared from analytical grade  $\text{CoCl}_2$  aq, following the prescriptions of Bjerrum<sup>1</sup>, p. 241.

$\text{Co}(\text{NH}_3)_6(\text{ClO}_4)_3$ , labelled with  $^{60}\text{Co}$ , was prepared from neutron irradiated metallic cobalt (from AERE, Harwell) which was dissolved in dilute hydrochloric acid, some platinum black acting as a catalyst. Thereafter  $\text{Co}(\text{NH}_3)_6\text{Cl}_3$  was prepared as above, and the perchlorate was precipitated with concentrated perchloric acid, filtered and washed with alcohol and ether.

From these two preparations a stock solution was made containing 5 mM  $\text{Co}^*(\text{NH}_3)_6(\text{ClO}_4)_3$  and 55 mM  $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ .

*Ammonium thiocyanate* and *sodium nitrite*. Analytical grade reagents were used and the stock solutions were checked by titration according to Volhard and by cerimetric titration, respectively.

*Ammonium perchlorate* was of analytical grade. The concentration of the stock solution was checked by evaporation of a sample on the steam bath. No loss of weight could be detected on prolonged heating at this temperature.

*Sodium perchlorate*. A *purum* quality preparation was recrystallized once from hot water and dried at 110°.

Carbon dioxide-free *ammonia* was used together with ammonium perchlorate to make buffer solutions ( $C_{\text{NH}_3}:C_{\text{NH}_4} = 1:5, 1:0.5$  and  $1:0.05$ ), the ammonia content of which was determined by acidimetric titration using bromocresol green as indicator.

*Active carbon*. A gas adsorption carbon was used. Once every month it was heated in an oven to 150 °C to increase the accurate attainment of equilibrium. (Cf. Fig. 1 and the foot-note on p. 217 of Ref.<sup>10</sup>)

*Procedure*. In 100 ml flasks with ground glass stoppers 30 ml aliquots of solutions of the following general composition were mixed from stock solutions:

$C_B$  M ammonium thiocyanate (or sodium nitrite)  
 $C_A$  M ammonia  
 1.000 —  $C_B$  M ammonium perchlorate  
 2.0 mM  $\text{Co}^*(\text{NH}_3)_6^{3+}$

The amount of  $\text{Co}(\text{NH}_3)_6(\text{ClO}_4)_3$  will then be about ten times that of a saturated solution. After a while a precipitation takes place. In the experiments aiming at an inner-sphere equilibration, weighed amounts of active carbon were added. Three (or sometimes four) flasks were charged with solution of the same composition, each flask being charged with different amounts of active carbon, approximately 25, 40 and 70 mg. The flasks, with the stoppers shielded and kept in place by a rubber nipple, were placed in a shaker and vigorously shaken for some days.

Thereafter a 10 ml sample was withdrawn from each flask, using a pipette with two small disks of filter paper kept in place at the tip of the pipette by means of a set of small cut rubber tubings. The samples were poured into small Petri dishes and the activity was measured with a Tracerlab P-20 QG Scintillation Counter, combined with a Tracerlab SC-18 Superscaler. The Petri dishes used were internally calibrated with an equal amount of a solution of known activity.

At no time less than 10 000 counts, more often 20 000 counts, were registered. Thus the error of counting was always less than 1 %.

Using the value of 5.3 years for the half-life of  $^{60}\text{Co}$ , the measured intensities ( $I$  cpm) have been corrected to a common time.

Sodium nitrite was chosen instead of ammonium nitrite because of its easy availability. This choice does not invalidate the assumptions made on the constancy of the ammonium ion concentration, as the concentration of sodium nitrite will in no case be more than 3 % of the total salt concentration. Furthermore, an extrapolation to  $C_{\text{NO}_2^-} = 0$  is undertaken in the course of calculation, thus completely eliminating any errors introduced.

*Temperature control*. The shaking of the flasks and the separation of aliquots to be measured, were made in a thermostatically controlled room, the temperature of which was  $20.0^\circ \pm 0.2^\circ$ . The pipettes used had been stored in the same room and had thus attained the same temperature.

The temperature dependency of the solubility of  $\text{Co}(\text{NH}_3)_6(\text{ClO}_4)_3$  was determined by raising the temperature of the room to 22.9°. The increase in the solubility was then 25 %, corresponding to 0.9 % for every tenth of a degree.

*Calculation of the concentration of perchlorate ions*. As seen from the composition of the solutions examined and the stock solution of hexammine cobalt(III) salts, the perchlorate concentration will depend on  $C_B$  and on the amount of cobalt complexes formed. The following formula may be derived:

$$[\text{ClO}_4] = 1000 - 5.5 - C_B + 3 \times 0.21 \times I/I_0 = 994.5 - C_B + 0.63 \times I/I_0 \text{ mM}$$

The second term on the right side of the formula corresponds to the chloride ions brought into the solution from the cobalt stock solution. The fourth term represents the increase in  $[\text{ClO}_4]$  as the solubility rises.

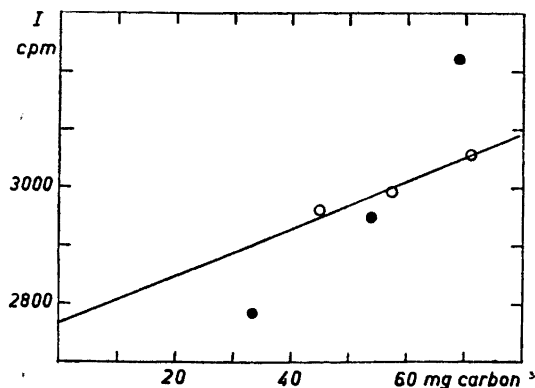


Fig. 1. The dependency of the equilibration on the amount of carbon in the thiocyanate measurements. Filled circles denote experiments with carbon that had long been exposed to air, unfilled circles denote experiments with carbon heated to 150° for several hours.

The solubility of  $\text{Co}(\text{NH}_3)_6(\text{ClO}_4)_3$  in pure 1 M  $\text{NH}_4\text{ClO}_4$  was determined by radiometric isotope dilution analysis to be 0.21 mM.

*On the action of carbon.* The criterion that equilibrium has been reached should be that the intensities of the solutions equilibrated by different amounts of carbon are the same. As long as the solution is saturated with respect to  $\text{Co}(\text{NH}_3)_6(\text{ClO}_4)_3$ , any adsorption of cobalt on the carbon would not affect this result. As a matter of fact this criterion has been found to be fulfilled in the measurements on the nitrite-substitution and the hydrolysis. In these cases the value of  $I$ , recorded in the following, is the mean value of the measurements with different amounts of carbon.

In the case of the thiocyanate-substitution, however, it was found that  $I$  increased as the carbon amount was increased. This effect was most prominent in experiments with low ammonia concentration. Those values of  $I$  reported in this system and denoted by an asterisk are attained by a linear extrapolation to zero amount of carbon. For series, notably those at high ammonia concentration, where the spreading is  $< \pm 2\%$ , the mean values have been reported. In Fig. 1 this effect is illustrated together with the effect of heating the carbon.

The nature of this effect is rather dubious. A probable explanation is perhaps that there occurs a catalytic decomposition of the thiocyanate ions on carbon, yielding cyanide ions, which react with the cobaltamine ions. This reaction may well be favoured by a decrease in the pH, as it is known that the thiocyanic acid is not stable in acid solution. It is strengthened by the fact that the slope of the line  $I$  versus the amount of carbon is increased on prolonged shaking, indicating the occurrence of a time reaction.

## RESULTS

In order to obtain information on the hypothetical existence of outer-sphere complexes of the hexammine cobalt(III) ion, measurements were made of the solubility of the perchlorate at varying concentrations of thiocyanate or nitrite ions and of ammonia, *without any addition of carbon*. For the two first-mentioned ligands the value of  $\frac{I}{I_0} \cdot \frac{[\text{ClO}_4]_0^3}{[\text{ClO}_4]_s^3}$  are reported in Figs. 2 and 3.

Within the limits of experimental error the quotient is found to have a constant

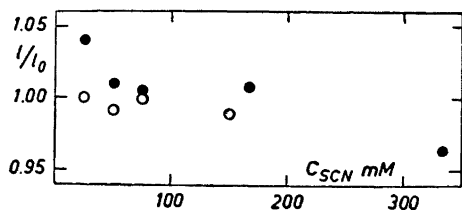


Fig. 2. The function  $l/l_0$  plotted against  $C_{SCN}$ . Filled circles correspond to  $C_{NH_3} = 194$  mM, unfilled circles to  $C_{NH_3} = 0$ .

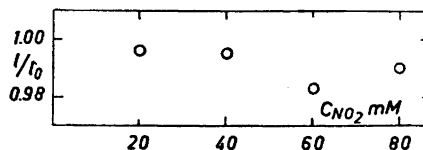


Fig. 3. The function  $l/l_0$  plotted against  $C_{NO_2} \cdot C_{NH_3} = 69$  mM.

value of 1. Thus it might be concluded that no outer-sphere complexes with charged ligands are formed and secondly that there is no medium effect affecting the solubility product  $l$ . However, the possibility of these two factors just compensating each other over the rather small concentration range used, must still be kept in mind. Two facts favour such an explanation.

Firstly, there has been observed quite distinct changes of the absorption spectrum of the hexammine cobalt(III) perchlorate, when part of the perchlorate ions is exchanged for halide or azide ions (Ref. <sup>12,13</sup>) and also for thiocyanate ions (Sonesson <sup>14</sup>).

Secondly, it is seen from Table 1, that an exchange of one fifth of the ammonium perchlorate for sodium perchlorate effects a distinct change of the solubility of  $Co(NH_3)_6(ClO_4)_3$ . As thiocyanate and nitrite ions are more unequally shaped compared to perchlorate ions than sodium ions are compared to ammonium ions, the change in solubility in the cases considered might be expected to be at least as large as that indicated in Table 1.

In the case of ammonia, conditions are quite different. The measurements are recorded in Table 1, showing a steady increase of solubility as  $C_{NH_3}$

Table 1. The influence of the ammonia concentration on the solubility of  $Co(NH_3)_6(ClO_4)_3$ .

$C_{NH_4ClO_4} = 1$ M						$C_{NH_4ClO_4} = 0.8$ M $C_{NaClO_4} = 0.2$ M		
$C_{NH_3}$ M	$I$ cpm	$x_A^\circ$	$C_{NH_3}$ M	$I$ cpm	$x_A^\circ$	$C_{NH_3}$ M	$I$ cpm	$x_A^\circ$
0.0	1 387					0.0	1 267	
0.1976	1 409	0.016	2.122	1 882	0.36	0.499	1 336	0.055
0.355	1 430	0.031	2.217	1 936	0.40	1.239	1 493	0.136
0.503	1 461	0.053	2.992	2 266	0.63	2.124	1 717	0.36
0.739	1 509	0.088	3.24	2 465	0.78	3.01	2 037	0.61
1.047	1 596	0.151	3.70	2 712	0.96			
1.770	1 815	0.31	3.94	2 903	1.09			

increases. This effect may be due to any of two causes; an increase in the solubility product of  $\text{Co}(\text{NH}_3)_6(\text{ClO}_4)_3$  as the solvent dielectric constant is changed with increasing ammonia, or an outersphere complex formation with one or more molecules of ammonia. As no value of the dielectric constant of ammonia water solutions has been found in literature, we are not able to tell the direction of such a change of solubility. However, some data of J. Bjerrum<sup>11</sup> on the solubility of  $\text{Ba}(\text{IO}_3)_2$  in 2 M  $\text{NH}_4\text{NO}_3$  and varying  $C_{\text{NH}_3}$ , suggests that this medium effect should be one to decrease the solubility, not to increase it. The possibility of outer-sphere ammine complexes has then been accepted as a working-hypothesis.\* In the third column of Table 1 the function  $x_A^\circ$  is recorded.

$$x_A^\circ = \frac{I}{I_0} - 1$$

This notation is chosen to distinguish the thus defined quantity from the quantity  $X_A^\circ$  defined by eqn. (3 a).  $X_A^\circ$  might be calculated from  $x_A^\circ$ , if the dependency of the solubility product on  $C_{\text{NH}_3}$  was known. Then, however, this correction would have to be used also when calculating  $Y$  in the inner-sphere equilibration measurements.

In the following the quantity  $Y - x_A^\circ$  is used in calculation,  $Y$  being formed under the assumption that  $l/l_0 = 1$ , *i.e.* is independent of  $C_{\text{NH}_3}$ . The measurements recorded in Table 1 with the ionic medium 0.2 M  $\text{NaClO}_4$ , 0.8 M  $\text{NH}_4\text{ClO}_4$  show that the increase in solubility is independent of the pH, thus there is (at this pH) no reaction like  $\text{Co}(\text{NH}_3)_6^{3+} \rightleftharpoons \text{Co}(\text{NH}_3)_5\text{NH}_2^{2+} + \text{H}^+$ .

#### THE HYDROLYTIC EQUILIBRIUM

By adding active carbon to an ammonium perchlorate solution with  $C_B = 0$  we can get an estimation of the constant of hydrolysis, defined by eqn. (6). As this constant will be obtained at a difference of two almost equal quantities, the random error will be consequently large. The values reported in Fig. 4 are mean values of five or more independent determinations. It is seen that there is a slight increase in the values as  $C_{\text{NH}_3}$  increases. However, it is uncertain if this is a real effect or follows from experimental error. If the change is significant, it is of interest to note that the trend is the inverse to that found by Bjerrum<sup>1, p. 257</sup>. This might be seen as a support of the hypothesis of outersphere ammonia complexes.

#### THE THIOCYANATE SYSTEM

Measurements were made at the thiocyanate concentrations 25.0, 75.0 and 166.7 mM. The results are tabulated in Table 2. The values of  $x_A^\circ$  are obtained by a graphical interpolation of the data given in Table 1, and those of  $k_{\text{OH}}$  from the line drawn in Fig. 4.

\* Light absorption measurements of the present author, the results of which are soon to be published, strengthen this view.



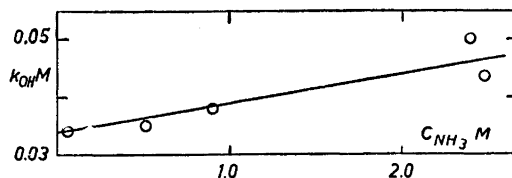


Fig. 4. The experimentally determined values of  $k_{OH}$  plotted against  $C_{NH_3}$ . The line is drawn to fit the points as closely as possible.

In Fig. 5 the quantity  $Y-x_A^0$  is plotted against  $C_B/C_A$ . Actually the quotient  $[B]/[A]$  should be used in the subsequent calculations, but for small values of  $C_B/C_A$  the number of  $B$  bound per metal atom,  $\bar{n}$ , is small and thus  $[B] = C_B - \bar{n} C_M$  is almost equal to  $C_B$ . (Analogous reasoning, of course, is to be applied to  $C_A$  and  $[A]$ .) For greater values of  $C_B/C_A$  where  $\bar{n}$  is rather large and a distinct difference exists between  $[B]$  and  $C_B$ , the degree of reproducibility of measurements is rather low, so there is no point in making extra corrections of the quotient  $C_B/C_A$ . Thus  $C_B/C_A$  will be used as the ligand quotient throughout the calculations.

Table 2. The thiocyanate system. Calculation of  $Y-x_A^0$  as a function of  $C_B/C_A$ .

$I_0 = 1\ 387\ \text{cpm}; [\text{ClO}_4]_0 = 995\ \text{mM}$							
Time of shaking (h)	$C_B$ mM	$C_A$ mM	$\frac{C_B}{C_A}$	$I$ cpm	$[\text{ClO}_4]$ mM	$Y+k_{OH}$	$Y-x_A^0$
27	25.0	274.6	0.0910	1 680	970	1.122	1.065
17		113.1	0.2210	1 737	970	1.160	1.119
60		56.5	0.442	1 856*	970	1.240	1.202
55		35.5	0.704	2 060*	970	1.376	1.340
60		25.0	1.00	2 440*	971	1.64	1.60
55		19.36	1.29	2 875*	971	1.93	1.89
60		15.33	1.63	3 900*	971	2.74	2.7
60		12.91	1.94	4 000*	971	2.81	2.8
71	75.0	1 532	0.0490	2 260	921	1.292	1.018
71		1 140	0.0658	2 178	921	1.245	1.046
71		796	0.0942	2 116	921	1.210	1.075
118		274.6	0.2731	2 170	920	1.237	1.180
118		193.8	0.387	2 265	921	1.295	1.240
133		112.7	0.665	2 500	921	1.430	1.389
66		79.9	0.94	3 004	921	1.72	1.68
100		56.5	1.33	3 250	921	1.86	1.82
> 150	166.7	1 409	0.1183	3 493	829	1.457	1.206
> 150		488	0.342	3 358	829	1.400	1.316
115		274.6	0.607	3 580	829	1.493	1.436
41		113.1	1.47	5 370*	830	2.25	2.21
> 150		100.5	1.66	4 912*	829	2.05	2.0
88		79.7	2.09	7 290	831	3.1	3.0

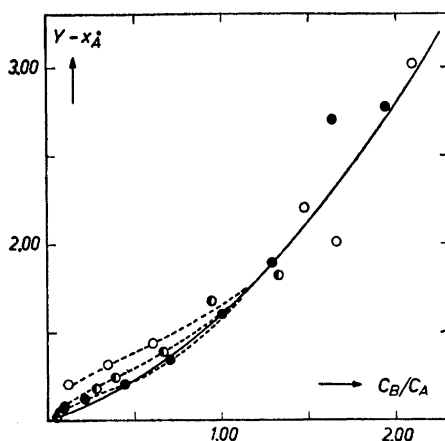


Fig. 5. The thiocyanate system.  $Y - x_A^0$  as a function of  $C_B/C_A$ . Filled, half-filled and unfilled circles correspond to  $C_B = 25.0, 75.0$  and  $167$  mM, respectively. The dotted lines are those used for the extrapolation of Table 3. The full-drawn curve is obtained from the reported constants.

However, there is no difficulty in calculating  $\bar{n}$ , and for systems where greater accuracy might be obtained, this correction may be worth while.

Applying the method of calculation used by Fronaeus<sup>5</sup>, we get

$$\bar{n} \approx \frac{[B]}{[A]} \cdot \frac{1}{Y} \cdot \frac{dY}{d([B]/[A])}$$

From graphical estimation on the curve  $Y - C_B/C_A$  we can get an approximate value of  $\frac{dY}{d([B]/[A])}$  and of  $[B]/[A]$  and thus the more correct expression:

$$\frac{[B]}{[A]} = \frac{C_B - \bar{n}C_M}{C_A + \bar{n}C_M}$$

It is seen in Fig. 5 that we obtain different curves for the different values of  $C_B$ . At about  $C_B/C_A = 1.3$  they seem to coalesce. This means that in the expression  $Y$  of eqn. (4) *either* we have still some terms dependent on  $[A]$  or  $[B]$  only and not on  $[B]/[A]$ , *i.e.* the correction with  $x_A^0$  corresponding to outer-sphere ammonia attachment to the  $MA_6^{3+}$  ion has not made account for all possible outer-sphere complexes, so that there may also exist, *e.g.*,  $(MA_6)B^-$  and  $(MA_6)A^+$  complexes, *or*, and this is as plausible an explanation as the preceding one, the equilibrium constants  $\gamma_n$  will be effected by the change in the dielectric constant of the solvent as  $C_{NH_3}$  increases. Such an effect is well known for dissociation constants of weak acids<sup>15</sup>, and has also been observed in studies on complex formation<sup>16,17</sup>.

Both these effects may be thought to combine to give the effect of Fig. 5. Whatever the cause, however, an extrapolation to  $C_A = C_B = 0$  for constant values of  $C_B/C_A$  will make all these effects vanish, *i.e.* the function  $Y$  will transform to

$$Y_0 = 1 + \gamma_1 \frac{C_B}{C_A} + \gamma_2 \left( \frac{C_B}{C_A} \right)^2 + \dots$$

where the constants  $\gamma$  are valid in 1 M  $NH_4ClO_4$ .

Table 3. The thiocyanate system. Extrapolation to  $C_B = 0$  and calculation of equilibrium constants.

$$\gamma_1 = 0.3 \pm 0.1 \quad \gamma_2 = 0.3 \pm 0.1$$

$\frac{C_B}{C_A}$	$Y - x_A^0$			$Y_0$	$\frac{C_A}{C_B} (Y_0 - 1)$
	$C_B = 167 \text{ mM}$	$C_B = 75.0 \text{ mM}$	$C_B = 25.0 \text{ mM}$		
0.100	1.182	1.091	1.063	1.037	0.37
0.250	1.265	1.179	1.131	1.106	0.42
0.400	1.337	1.245	1.186	1.160	0.40
0.600	1.432	1.348	1.277	1.254	0.42
0.900	1.592	1.538	1.490	1.477	0.53
1.300	1.89	1.88	1.88	1.88	0.67
1.47	2.21			2.21	0.82
1.63			2.7	2.7	1.04
1.66	2.0			2.0	0.61
1.94			2.8	2.8	0.93
2.09	3.0			3.0	0.96

In Table 3 such an extrapolation is performed for  $C_B/C_A \leq 1.3$ , above this region of coalescence the experimental  $Y - x_A^0$  values have been used. The function  $\frac{C_A}{C_B} (Y_0 - 1)$  are, within the limits of the rather large experimental errors, linear, showing the existence of the first and second substituted complex to be formed for these values of the ligand quotient.

#### THE NITRITE SYSTEM

As the nitro-ligand was found to be more strongly attached to the Co(III) nucleus, much smaller values of the ligand quotient had to be used than was the case in the preceding investigation on the thiocyanate system. The nitrite concentrations used were 9.00, 18.00 and 27.00 mM. In Table 4 the experimental results are recorded. As before,  $C_B/C_A$  is used instead of  $[B]/[A]$ . In Fig. 6 a line with the slope 43 has been drawn through the upper points.

The points corresponding to  $(Y - x_A^0)$ -values less than about 2.5 are found to lie above that line and the ones corresponding to  $C_B = 27 \text{ mM}$  and  $C_B = 18 \text{ mM}$  are lying progressively higher than those corresponding to  $C_B = 9 \text{ mM}$ . An extrapolation to  $C_B = 0$  would, within the limits of experimental error, bring about a complete coincidence with the above-mentioned line. Thus it may be concluded that at these values of the ligand quotient only the first substitution complex exists,  $\gamma_1$  being  $43 \pm 2$ . The colour of the solutions when the carbon had been filtered off was clear yellow. Thus the nitropentamine complex is formed and not the nitritopentamine one.

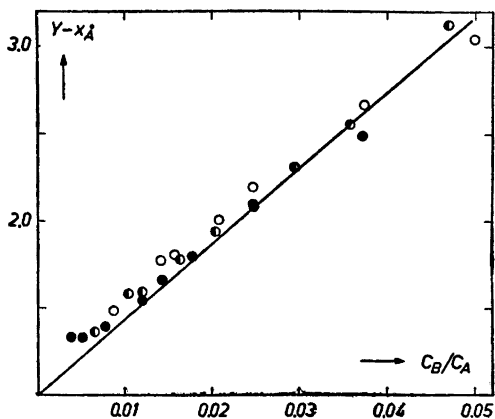


Fig. 6. The nitrite system.  $Y - x_A^0$  as a function of  $C_B/C_A$ . Filled, half-filled and unfilled circles correspond to  $C_B = 9.00$ , 18.00 and 27.0 mM, respectively.

Table 4. The nitrite system. Calculation of  $Y - x_A^0$  as a function of  $C_B/C_A$ .

$I_0 = 1\ 387\ \text{cpm}; [\text{ClO}_4]_0 = 995\ \text{mM}$								
Time of shaking (h)	$C_B$ mM	$C_A$ M	$\frac{C_B}{C_A} \cdot 10^3$	$I$ cpm	$[\text{ClO}_4]$ mM	$Y + k_{\text{OH}}$	$Y - x_A^0$	
87	9.00	0.2419	37.2	3 710	986	2.54	2.49	
87		0.363	24.8	3 061	986	2.15	2.08	
61		0.509	17.7	2 688	986	1.89	1.80	
61		0.629	14.3	2 524	986	1.77	1.66	
61		0.750	12.0	2 385	986	1.67	1.55	
64		1.155	7.8	2 284	985	1.60	1.40	
64	18.00	1.774	5.1	2 364	986	1.66	1.33	
64		2.393	3.8	2 594	986	1.82	1.33	
63		0.383	47.0	4 669	978	3.20	3.13	
63		0.503	35.8	3 862	977	2.64	2.55	
63		0.608	29.6	3 533	977	2.41	2.31	
63		0.729	24.7	3 243	977	2.21	2.09	
63		0.882	20.4	3 064	977	2.09	1.94	
63		1.107	16.3	2 887	977	1.97	1.78	
63		1.501	12.0	2 726	977	1.86	1.59	
63		1.727	10.4	2 787	977	1.90	1.59	
72		27.00	2.767	6.5	2 888	977	1.97	1.36
64			0.601	49.9	4 721	969	3.14	3.04
64	0.721		37.4	4 195	968	2.79	2.66	
52	0.920		29.4	3 719	968	2.47	2.31	
64	1.099		24.6	3 595	968	2.39	2.20	
52	1.299		20.8	3 360	968	2.23	2.01	
64	1.719		15.7	3 195	968	2.12	1.81	
52	1.918		14.1	3 217	968	2.14	1.78	
72	3.10	8.7	3 353	968	2.23	1.48		

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