

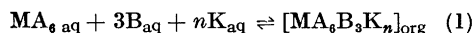
Studies on Cobaltamines
VII. An Investigation of the Coordination Number of Outer-sphere Complexes

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The estimation of the number of coordination sites available for ligands, coordinated in the outer sphere of cobaltamines, is a difficult task. Most complex systems of this kind are so weak that it is not possible to reach the saturated complex in aqueous solution. In order to escape this difficulty an extraction technique has been employed.

The cobalthexammine(III) ion is easily extracted into cyclohexanone from aqueous solutions of sodium salicylate. This probably corresponds to the following reaction



where $\text{MA}_6 = \text{Co}(\text{NH}_3)_6^{3+}$

B = salicylate ion
K = cyclohexanone

In order to determine n it is necessary to vary the concentration of K in the organic phase. As a diluent 2-octanol has been used. This solvent is a rather poor extracting agent in this case. The cobalt concentration in the two phases was determined radio-metrically¹. The organic solvents were the same as before² and the sodium salicylate was recrystallized from ethanol.

If $[\text{MA}_6\text{B}_3]_{\text{org}}$ is the concentration of the salicylate complex in the organic phase that does not contain any ketone (but probably water and octanol), we define the complex-ity constants of the ketone complexes in the organic phase as

$$\beta_{n \text{ org}} = \frac{[\text{MA}_6\text{B}_3\text{K}_n]_{\text{org}}}{[\text{MA}_6\text{B}_3]_{\text{org}} [\text{K}]_{\text{org}}^n} \quad (2)$$

$$\text{Furthermore } D = \frac{[\text{MA}_6\text{B}_3]_{\text{org}}}{[\text{MA}_6\text{B}_3]_{\text{aq}}} \quad (3)$$

and $\varphi = C_{\text{M org}}/C_{\text{M aq}}$

We then have

$$\varphi = D \cdot \alpha_3 \text{ aq} \cdot (1 + \sum \beta_{n \text{ org}} [\text{K}]_{\text{org}}^n) \quad (4)$$

where α_3 is the portion of the cobalt in the aqueous phase which exists as the third salicylate complex.

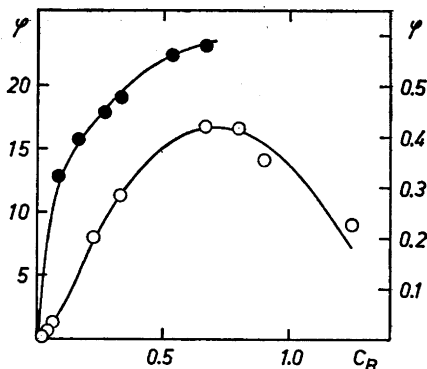


Fig. 1. The partition quotient φ as a function of the salicylate concentration in the aqueous phase.

O: $\text{Co}(\text{NH}_3)_6^{3+}$; $C_K = 1.9 \text{ M}$; left ordinate scale.

●: $\text{Co en}_2(\text{NCS})_2^+$; $C_K = 1.0 \text{ M}$; right ordinate scale.

For constant $[\text{B}]_{\text{aq}}$, we obtain

$$\varphi = \varphi_0(1 + \sum \beta_{n \text{ org}} [\text{K}]_{\text{org}}^n) \quad (5)$$

From this equation $\beta_{n \text{ org}}$ can be determined.

In order to determine a suitable $[\text{B}]$, φ was determined at $[\text{K}]_{\text{org}} = 1.93 \text{ M}$ (Fig. 1). (In all cases $[\text{B}]$ and $[\text{K}]$ were taken to be the respective total concentrations.) Obviously, the measurements should be performed at a value of $[\text{B}]$ near the position of the maximum in Fig. 1, as φ is then not very dependent on $[\text{B}]$. In Fig. 2 measurements of φ are given for $C_B = 0.67 \text{ M}$ and 0.80 M . The linear rise of φ indicates the presence of only one ketonic complex; eqn. 5 gives $\beta_{1 \text{ org}} = 0.9 \pm 0.1 \text{ M}^{-1}$. φ deviates strongly from linearity at high values of $[\text{K}]_{\text{org}}$. This, as well as the drastic drop of φ in Fig. 1, may be caused by changes in activity coefficients as some cyclohexanone dissolves in the aqueous phase. A still more likely explanation, however, is to assume the existence of an anionic complex MA_6B_4 in the aqueous phase. This explains at once the decrease of φ in Fig. 1. Regarding the deviation from linearity in Fig. 2, it is illuminating that we obtain a greater deviation for a greater C_B . This must mean that the tendency towards the formation of an anionic complex is increased

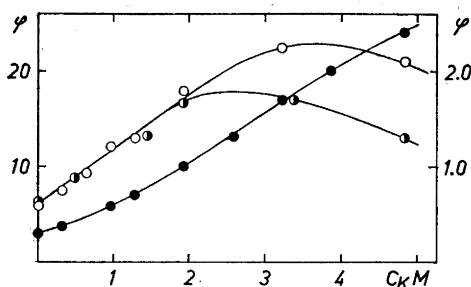


Fig. 2. The partition quotient φ as a function of the ketone concentration in the organic phase.

- : $\text{Co}(\text{NH}_3)_6^{3+}$; $C_B = 0.67 \text{ M}$; left ordinate scale.
 ◐: $\text{Co}(\text{NH}_3)_6^{3+}$; $C_B = 0.80 \text{ M}$; left ordinate scale.
 ●: $\text{Co en}_2(\text{NCS})_2^+$; $C_B = 0.67 \text{ M}$; right ordinate scale.

as some cyclohexanone dissolves in the aqueous phase (cf. Ref.², p. 709).

Analogous measurements were also performed by using the *trans*- $\text{Co en}_2(\text{NCS})_2^+$ ion as the inert cobalt complex ion. Then the extracted species contains probably only one salicylate ion and more space should be available for the ketonic ligands. The cobalt concentration in the two phases was determined colorimetrically. The results are given in Figs. 1 and 2. $C_B = 0.67 \text{ M}$ was used for the measurements of Fig. 2. It is easily deduced that eqn. 5 should also apply here. In Fig. 3 $(\varphi/\varphi_0 - 1) [\text{K}]^{-1}_{\text{org}}$ is plotted against $[\text{K}]_{\text{org}}$. The linearity indicates the presence of two complexes. $\beta_{1 \text{ org}} = (0.76 \pm 0.05) \text{ M}^{-1}$ and $\beta_{2 \text{ org}} =$

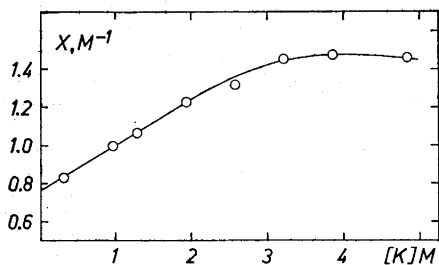


Fig. 3. $X_1 = (\varphi/\varphi_0 - 1) [\text{K}]^{-1}_{\text{org}}$ plotted against $[\text{K}]_{\text{org}}$.

$(0.24 \pm 0.05) \text{ M}^{-2}$. Also here deviation from linearity occurs at high $[\text{K}]_{\text{org}}$.

If we assume that each salicylate ion uses two coordination sites, which is likely but not quite certain, at least seven coordination sites are filled in the outer sphere of the $\text{Co}(\text{NH}_3)_6^{3+}$ ion and four sites in that of the $\text{Co en}_2(\text{NCS})_2^+$ ion.

It is interesting to note that the coordination number found in this case, for the cobalthexammine ion is very near the number eight expected from geometrical considerations. In the anionic complex discussed above, we should indeed have an example of outer-sphere coordination number eight. It is also interesting to note the similar magnitude of $\beta_{1 \text{ org}}$ for the two central groups studied. The possibility of an association of ketones with cobaltamines has been suggested earlier³ from other measurements.

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1. Larsson, R. *Acta Chem. Scand.* **11** (1957) 1405.
2. Larsson, R. *Acta Chem. Scand.* **14** (1960) 697.
3. Larsson, R. *Acta Chem. Scand.* **12** (1958) 708.

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Pteroylglutamic Acid as a Growth Factor for a Strain of *Rhodotorula*

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In a study of fungi occurring on slime-flux of tree stumps, a strain of *Rhodotorula*, called 18 b, was isolated. This appeared to require *p*-aminobenzoic acid (PAB) as an essential factor for growth¹. Since such a requirement is extremely rare among fungi, the nutrition of strain No. 18 b was more closely studied. This strain does not belong to *Rhodotorula aurantiaca*, the PAB-requirement of which has been investigated by Robbins and Ma², nor does it seem to be identical with any other earlier described species of the genus *Rhodotorula*.