282.   *Complexes of Cobalt*(III) *with Hydroxyethylethylenediamine-triacetic Acid.*

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The visible spectra and some qualitative aspects of the equilibrium properties and kinetic behaviour of solutions of cobalt(III)–hydroxyethyl-ethylenediaminetriacetate complexes are described and discussed. Sexidentate complexes in which the oxygen of the hydroxyethyl group of the ligand is co-ordinated to cobalt are postulated as well as quinquedentate mono-aquo-complexes. Geometrical isomers appear to be present in solutions of both the sexidentate and the quinquedentate complexes.

FOLLOWING an earlier investigation [1] of the kinetics of reduction of the ethylenediamine-tetra-acetic acid (edta) complex $Co^{III}(HY)Cl^-$ to Co^{II} by ferrous ions in aqueous solution, we studied the reduction of other cobalt(III)–edta complexes and of related cobalt(III)–heta complexes [heta $= H_3(YOH) = N'$-hydroxyethylethylenediamine-NNN'-triacetic acid]. Unexpected behaviour of the heta complexes led us to postulate various isomers, and here we summarise the evidence.

We prepared a solution of a cobalt(III)–heta complex by oxidising an aqueous solution of cobalt(II) sulphate with molecular bromine in the presence of heta, followed by removal of bromine from the $Co^{III}(YOH)Br^-$ so produced by treating it with silver oxide. After acidification, this solution contained complex A, which gave a visible spectrum fairly similar to that of the quinquedentate edta complex, $Co(HY)H_2O$ (Fig. 1). Originally we assumed that complex A was the quinquedentate complex, $Co(YOH)H_2O$, in which the hydroxyethyl group is free (compare ref. 2). When the pH of a solution of complex A was increased to *ca.* 7, a change in spectrum occurred corresponding to the formation of complex B. Since the change from A to B was instantaneous and reversible and gave a

[1] Pidcock and Higginson, *J.*, 1963, 2798.
[2] Morris and Busch, *J. Phys. Chem.*, 1959, **63**, 340.

pH-titration curve typical of a weak monobasic acid, we concluded that complex B is the conjugate base of A. However, the spectrum of B differs markedly from that of $Co(Y)OH^{2-}$ (Fig. 1) and whereas the pK corresponding to the change $Co(Y)H_2O^- \longrightarrow Co(Y)OH^{2-} + H^+$ is *ca.* 8·1,[3] we found that for $A \longrightarrow B + H^+$ was *ca.* 5·2. When a solution of complex A in 1M-perchloric acid was kept at 50° for several days we obtained a new complex, C, shown by the spectrum becoming very similar to that of $Co(HY)H_2O$. Solutions of compounds with apparently identical spectra to complex C could be produced directly from $Co(YOH)Br^-$ by (i) heating it in aqueous solution at *ca.* 85° for several minutes, (ii) treating it in acid solution (pH ∼ 2) at room temperature with silver nitrate followed by filtration, (iii) warming it gently in aqueous solution with powdered charcoal. A pH titration of complex C showed the corresponding pK value to be *ca.* 8·2 and gave complex D, the spectrum of which was almost identical with that of $Co(Y)OH^{2-}$. We have not shown the spectra of complexes C and D in Fig. 1 for although they differ slightly from
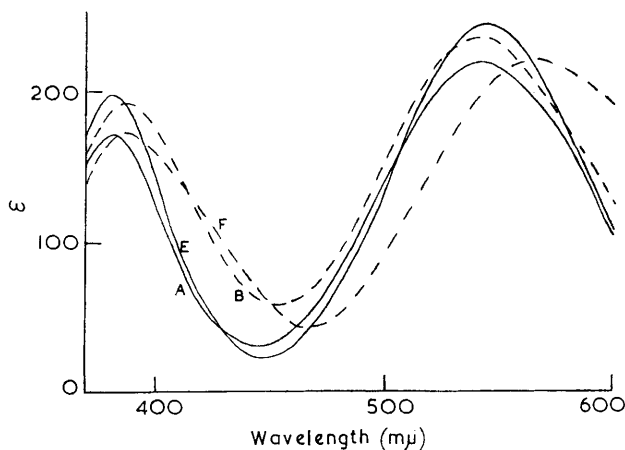

FIG. 1. Spectra of edta and heta complexes of cobalt(III).

A, $Co(YOH)$; B, $Co(YO)^-$; E, $Co(HY)H_2O$; F, $Co(Y)OH^{2-}$; the spectra of $Co(YOH)H_2O$ and $Co(YOH)OH^-$ are very similar to E and F, respectively.

the spectra of $Co(HY)H_2O$ and $Co(Y)OH^{2-}$, respectively, it is not possible to distinguish corresponding pairs in a small-scale figure. When complex D in alkaline solution (pH ∼ 9) was kept at room temperature, the spectrum gradually changed to that of complex B.

We conclude that complex C is quinquedentate $Co(YOH)H_2O$ and D is quinquedentate $Co(YOH)OH^-$, the hydroxyethyl group of the ligand being free in both cases. We suggest that complex A is the sexidentate complex $Co(YOH)$, in which the oxygen atom of the hydroxyethyl group is co-ordinated to cobalt, while complex B is the conjugate base $Co(YO)^-$ in which the hydroxyl hydrogen atom of the bound hydroxyethyl group has ionised. The suggestion that a hydroxyethyl group can co-ordinate to a metal ion in a chelate complex has previously been made;[4] in the case of heta, the behaviour of its complex with iron(III) is consistent with this possibility.[5] It appears that the quinquedentate complex $Co(YOH)H_2O$ is more stable than sexidentate $Co(YOH)$, but that this order of stability is reversed with the conjugate bases, the sexidentate form being the more stable. We have not established the values of the mass-action constants relating to the

[3] Schwarzenbach, *Helv. Chim. Acta*, 1949, **32**, 839; Shimi and Higginson, *J.*, 1958, 260.
[4] Schwarzenbach, Anderegg, Schneider, and Senn, *Helv. Chim. Acta*, 1955, **38**, 1147; Thompson and Loraas, *Inorg. Chem.*, 1963, **2**, 594.
[5] Gustafson and Martell, *J. Phys. Chem.*, 1963, **67**, 576.

equilibria between the corresponding quinquedentate and sexidentate forms, but from the pH-titration curves we conclude that at least 95% of the more stable form is present at equilibrium.

When a solution of Co(YOH), prepared directly from Co(YOH)Br$^-$, was allowed to react with a large excess of Fe^{2+}, a curved plot of the logarithm of the Co(YOH) concentration against time was obtained instead of the expected linear plot. Morris and Busch [2] found a similar kinetic behaviour in the hydrolysis of Co(Y)Br^{2-} and showed that it was consistent with the presence of two geometrical isomers, one of which reacted more rapidly than the other. They also showed that if the spectra of the two isomers are identical it is possible to determine their proportions by analysing the kinetic data. By making a similar assumption, we found that our results with Co(YOH) could be interpreted to show the presence of two isomers, the proportion of the less reactive isomer being *ca.* 63% of the total Co(YOH). This value is the mean obtained from 20 experiments, extreme values being 59 and 69%; the uncertainty in individual values is *ca.* $\pm4\%$. Isomeric forms are present in the original Co(YOH)Br$^-$ since both the hydrolysis of this complex (loss of bromide ion) at pH $\sim$5 and its reduction by ferrous ion at pH 1·7 gave curved logarithmic plots of the concentration of the complex against time. From the hydrolysis reaction we estimate the proportion of the less reactive isomer was *ca.* 60%. On the other hand, solutions of Co(YOH)H$_2$O produced by any of the methods described above, except (ii), gave linear logarithmic plots for their reduction by an excess of ferrous ions and hence in these cases the kinetic criterion does not indicate the presence of geometrical isomers. [We did not use solutions of Co(YOH)H$_2$O produced by method (ii) for kinetic experiments owing to the presence of Ag$^+$.] Next, we converted a solution of Co(YOH)H$_2$O, obtained by method (i), into Co(YOH): the solution of Co(YOH)H$_2$O was made alkaline, the Co(YOH)OH$^-$ initially formed changed slowly into Co(YO)$^-$, and acidification of the latter then gave Co(YOH). When this solution of Co(YOH) was allowed to react with an excess of ferrous ions we again obtained curved logarithmic plots showing the presence of *ca.* 60% of a less reactive isomer.

We conclude that two geometrical isomers are present in the original Co(YOH)Br$^-$ and that normally these maintain their configurations in the various interconversions between quinquedentate and sexidentate forms. The kinetic simplicity of the reaction between Co(YOH)H$_2$O and Fe^{2+} might be taken to indicate that only one isomer is present for this complex, and that two isomers reappear at some stage in its conversion into Co(YOH). We have rejected this interpretation on account of the behaviour of Co(YOH) solutions obtained from Co(YOH)H$_2$O which had been prepared by using charcoal [method (iii)]. Although the spectrum and kinetic behaviour of the parent Co(YOH)H$_2$O solution were identical with those of Co(YOH)H$_2$O solutions prepared by the other methods, linear logarithmic plots were obtained when such Co(YOH) solutions were reduced by an excess of ferrous ions. Moreover, the second-order rate constant, $k = -(\text{d}\ln[\text{Co(YOH)}]/\text{d}t)[\text{Fe}^{2+}]^{-1}$, obtained from these plots was equal to the rate constant obtained under comparable conditions for the less reactive isomer present in Co(YOH) solutions, produced by methods which did not involve the use of charcoal. If the simple kinetics observed with Co(YOH)H$_2$O solutions necessarily indicate that only one isomer is present, it would be difficult to understand why samples produced with and without the use of charcoal should show different behaviour after conversion into Co(YOH). Evidently the use of charcoal leads only to the geometrical isomer of higher stability and this is in accord with its usual action.[6] Since the spectra of corresponding solutions containing a single, or both, geometrical isomers are identical, the assumption made in calculating the proportions of the two isomers is justified.

It seems that in the quinquedentate monoaquo-complex the energies of the geometrical

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[6] Dwyer, " Advances in the Chemistry of the Co-ordination Compounds," ed. Kirschner, Macmillan, New York, 1961, p. 28.

isomers are very similar, otherwise we should expect kinetic differentiation in their reaction with ferrous ions. The formation of the less stable sexidentate complex is likely to confer strain upon certain of the chelate rings [7] and in these circumstances the energies of the geometrical isomers may differ more markedly. It is also notable that in the quinquedentate complex $Co(YOH)Br^-$ sufficient strain must be introduced by the presence of the bromine atom to cause kinetic differentiation between the isomers. Unlike the bromo-complex, the corresponding chloro-complex $Co(YOH)Cl^-$ showed no kinetic evidence for isomers in its reaction with an excess of ferrous ions. On conversion of the chloro-complex into $Co(YOH)$ by treatment with silver oxide and acidification, the curved logarithmic plot for the reaction of this $Co(YOH)$ with excess of ferrous ions showed that the parent $Co(YOH)Cl^-$ contained two isomeric forms, *ca.* 67% of the more stable isomer being present. Presumably the chlorine ligand does not cause as much strain in a quinquedentate complex as does the larger bromine ligand. This behaviour is similar to that of the related edta complexes, $Co(HY)Br^-$ and $Co(HY)Cl^-$. In their hydrolysis the former complex shows evidence of isomers of different reactivity [2] whereas the latter does not.[8]

The relative stabilities of the various structures possible for geometrical isomers of quinquedentate edta complexes have been discussed previously,[2,9] and two of the forms are

FIG. 2. Structures suggested for geo-
metrical isomers of quinquedentate
heta complexes of cobalt(III).

trans   *cis*
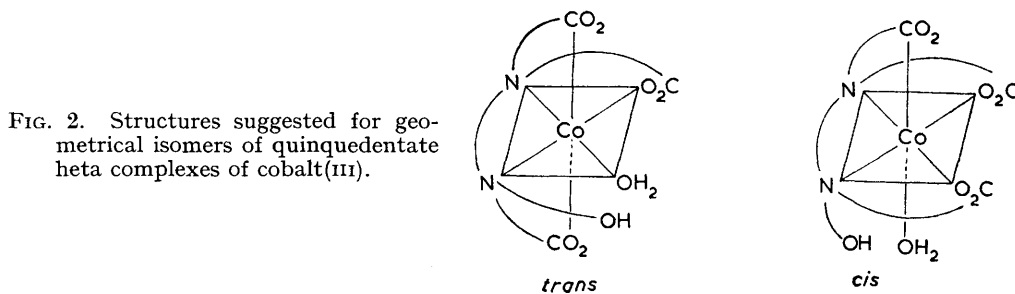
considered to be more stable than the others. We suggest that the two geometrical isomers of quinquedentate $Co(YOH)H_2O$ possess structures corresponding to those of the two most stable quinquedentate edta complexes. The structures suggested for these heta complexes are shown in Fig. 2; both complexes can undergo conversion into sexidentate forms in which the ligand water is replaced by the hydroxyethyl group without disturbing the other co-ordinated groups. Of these structures, the *trans*-form (H_2O or $CH_2 \cdot OH$ *trans* to one of the two nitrogen atoms) is probably the more stable (cf. ref. 9).

EXPERIMENTAL

Reagents were of AnalaR grade unless otherwise specified. Solutions of iron(II) perchlorate were obtained by double decomposition between iron(II) sulphate heptahydrate dissolved in dilute perchloric acid, and aqueous barium perchlorate solution.

Sodium bromo-(N'-hydroxyethylethylenediamine-NNN'-triacetato)cobaltate(III) monohydrate was prepared and purified as described previously.[10] The complexing agent was obtained as a 44% aqueous solution of its trisodium salt $Na_3(YOH)$ from L. Light Ltd. and also from Fluka A.G. No significant differences in spectra or kinetic behaviour were apparent when comparing solutions of a given heta complex prepared from different samples of the trisodium salt.

[7] Hoard, Smith, and Lind, " Advances in the Chemistry of the Co-ordination Compounds," ed. Kirschner, Macmillan, New York, 1961, p. 296.
[8] Dyke and Higginson, *J.*, 1960, 1998.
[9] Smith and Hoard, *J. Amer. Chem. Soc.*, 1959, **81**, 556.
[10] Morris and Busch, *J. Amer. Chem. Soc.*, 1956, **78**, 5178.

Potassium chloro-(N'-hydroxyethylethylenediamine-NNN'-triacetato)cobaltate(III) mono-hydrate was prepared as follows. (We abandoned the use of the corresponding sodium salt; it is difficult to purify and is hygroscopic.) The 44% solution of heta (trisodium salt) was mixed with a solution containing an equivalent amount of cobalt(II) chloride hexahydrate plus a small excess of potassium chloride dissolved in a small volume of water. The mixture was kept at 0° while a slow stream of chlorine was passed through it for *ca.* 5 hr. Cold ethanol was slowly added to the mixture with good stirring until precipitation occurred; a further 50% more ethanol was then added. [A large excess of ethanol gave a product heavily contaminated with Co(YOH) or Co(YOH)H_2O.] The impure chloro-complex was separated by filtration, washed with cold ethanol, and purified by dissolving it in a small volume of cold water followed by precipitation with cold ethanol, as described above. This procedure was repeated several times until the filtrate became deep blue with no trace of purple. The final product was washed with ethanol and acetone and dried in air to give a non-hygroscopic blue powder [Found: C, 28·3; H, 4·0; Cl, 8·15%; M, 435. Calc. for KCo($C_{10}H_{15}O_7N_2$)Cl,H_2O: C, 28·1; H, 4·0; Cl, 8·3%; M, 427]. The molecular weight was determined by allowing a weighed quantity of the complex to hydrolyse in acid solution to Co(YOH)H_2O and determining the concentration of the latter spectrophotometrically.

Solutions of oxoethylethylenediaminetriacetatocobaltate(III), Co(YO)$^-$, were prepared by shaking a 0·2M-solution of the pure bromo-complex in warm water with an excess of freshly-precipitated silver oxide for about 10 min. The solution was filtered, a part was used for experiments with Co(YO)$^-$, and the remainder was converted as required into a solution of the corresponding hydroxoethyl-complex Co(YOH) by the addition of dilute perchloric acid. A similar procedure was used for the preparation of Co(YOH) from Co(YOH)Cl$^-$. Solutions of (hydroxyethyl-ethylenediaminetriacetato)aquocobalt(III), Co(YOH)H_2O, were obtained (i) by heating an aqueous solution of Co(YOH)Br$^-$ to *ca.* 85° for several minutes, (ii) by adding a small excess of silver nitrate solution to a solution of Co(YOH)Br$^-$ in dilute perchloric acid (pH ∼2), warming it gently and shaking it for several minutes before removal of silver bromide by filtration, (iii) by adding " B.D.H. activated decolourising " charcoal as a powder to a warm aqueous solution of Co(YOH)Br$^-$ and shaking the mixture until the colour change from the blue-green bromo-complex to the purple aquo-complex was complete. We obtained solid complexes by adding cold ethanol slowly, with stirring, to aqueous solutions containing, respectively, Co(YOH) and Co(YOH)H_2O, the latter prepared by method (iii). The solid was filtered off, washed rapidly with cold ethanol, and dried *in vacuo*. Hygroscopic powders were obtained which appeared to be hydrates [Found for the solid from the Co(YOH) solution: C, 30·6; H, 4·85; N, 7·2%; M, 391. Calc. for Co($C_{10}H_{15}O_7N_2$),3H_2O: C, 30·9; H, 5·45%; N, 7·2%; M, 388. Found for the solid from the Co(YOH)H_2O solution: C, 31·6; H, 5·0%; M, 386. Calc. for Co($C_{10}H_{15}O_7N_2$)H_2O,2H_2O: C, 30·9; H, 5·45%; M, 388]. Solutions of these solids showed kinetic and spectral properties very similar to those of the corresponding aqueous solutions from which they were obtained. The molecular weight was estimated by allowing a known volume of a standard iron(II) perchlorate solution to react with a solution containing a known weight of the complex. The amount of complex was chosen so that a small excess remained when all the iron(II) had been oxidised and the fraction of the complex reduced was determined by spectrophotometric measurements which also served to indicate the completion of the oxidation–reduction. Thus the weight of complex equivalent to a given amount of iron(II) was found and hence the molecular weight of the complex. A similar procedure was used in standardising solutions of the various complexes.

Spectrophotometric measurements were made by using a Unicam S.P. 600 instrument equipped with a temperature-controlled cell compartment. Details of the kinetic measurements will be given in a separate paper; the procedure adopted was similar to that previously described.[1] Measurements of pH were made by meter.

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