The Reactions of μ-Amido-μ-hydroxodicobalt Complexes with Perchloric Acid. Evidence for the Formation of μ-Perchlorato-complexes

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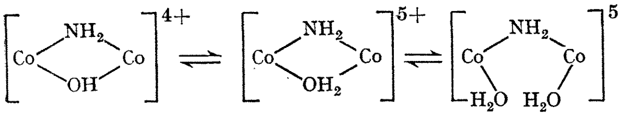
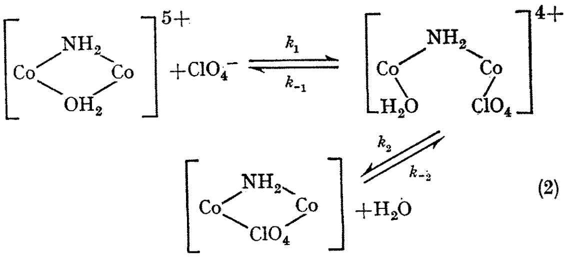
Summary Changes in visible spectra which are observed when perchloric acid is added to solutions of the complexes $(en)_2Co{\cdot}\mu(NH_2,OH){\cdot}Co(en)_2^{4+}$ and $(NH_3)_4Co{\cdot}\mu(NH_2,OH){\cdot}Co(NH_3)_4^{4+}$ have led to the identification of perchlorato-complexes.

THE perchlorate ion is a poor donor group having little tendency to complex to metal ions, and well authenticated examples of perchlorato-complexes are extremely rare. A perchloratopenta-aquochromium(III) complex has been identified,[1] but there is as yet no evidence for cobalt(III) complexes, *e.g.* perchloratopenta-amminecobalt(III).[2]


(1)

A sample of the μ-amido-μ-hydroxobis[bis(ethylenediamine)cobalt(III)] complex, ϵ_{max} 191 at 512 nm,[3] was prepared as the perchlorate salt (small samples only were prepared at any one time; these should not be washed with ether). On adding perchloric acid to an aqueous solution of the complex, the absorption coefficient increases to ϵ 210 in 8M-perchloric acid, the peak remaining at 512 nm. The changes observed are consistent with the formation of μ-amido-μ-aquo- and/or μ-amido-bisaquo-complexes as in (1). On diluting to decrease the perchloric acid concentration, changes in absorption at 512 nm can be followed using conventional techniques. Since protonation and deprotonation reactions are generally rapid the changes observed are believed to correspond to the second stage in which the bisaquo-complex is formed (k_{obs} *ca.* $1{\cdot}8 \times 10^{-2}$ sec.$^{-1}$ at 1·5°). At perchloric acid concentrations above 8M changes in spectra are more marked. The peak position shifts to 538 nm and the absorption coefficient increases to ϵ *ca.* 335 as shown in the Figure. The reactions occurring are believed to be


(2)

The fact that there is bridge cleavage in the first stage is probably important in accounting for the formation of the aquo-perchlorato-complex. The concentration of the aquo-perchlorato-complex is probably never very high. It is sufficiently high, however, for the μ-amido-μ-perchlorato-complex to form as the activity of water is reduced. There is a marked fall in the activity of water as the concentration of perchloric acid is increased and in 10·6M-acid $a(H_2O)$ is 0·015. Under these conditions k_{-2} is therefore less effective. In 12·2M-acid, formation of the μ-perchlorato-complex appears to be nearing completion (see Figure).

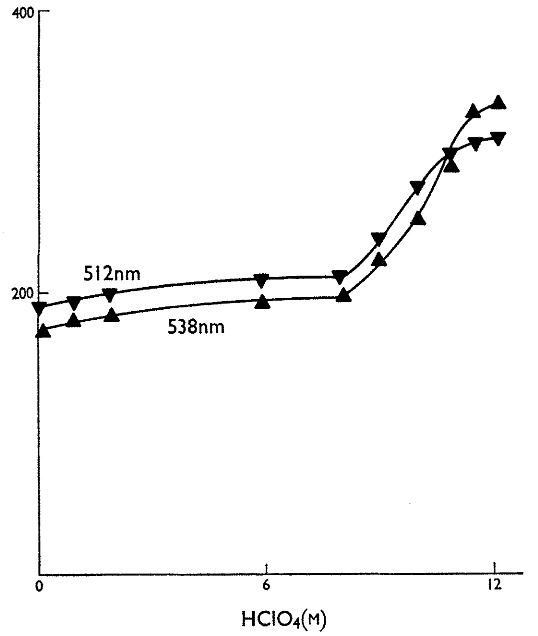


FIGURE. *Variation in absorption coefficients* (ε) *for the ethylenediamine complex,* $(en)_2{\cdot}Co{\cdot}\mu(NH_2,OH),Co(en)_2^{4+}$, *with perchloric acid concentration.*

Similar changes are observed with the μ-amido-μ-hydroxobis[tetra-amminecobalt(III)] complex. Kinetic studies are consistent with the above interpretation. Thus on dilution of 12M-perchloric acid solutions the reactions as in (2) can be studied. Two distinct stages are observed. Pseudo-first-order rate constants (k_{obs}) for the first stage give a linear dependence on the water activity $a(H_2O)$, (3)

$$k_{obs} = k_2 + k_{-2}\,a(H_2O) \qquad (3)$$

Values of $a(H_2O)$ are as reported in ref. 4. At 1·5°, $k_2 = 7{\cdot}1 \times 10^{-3}$ sec.$^{-1}$ and $k_{-2} = 0{\cdot}11$ l.mole^{-1}sec.$^{-1}$. The second stage is appreciably slower, and the change in spectrum much smaller. At $[H^+] = 6M$ and 1·5°, k_{obs} (for the equilibration) is 3×10^{-4} sec.$^{-1}$. The interpretation is more complex in that both the μ-amido-μ-hydroxy- and bisaquo-complexes may be involved.

It is important in these experiments that the perchlorate salts of the μ-amido-μ-hydroxo-complexes are used. When the iodide salt of the ethylenediamine complex is dissolved in 8M-perchloric acid an iodo-complex, probably the aquo-iodo-complex $(en)_2(H_2O)Co{\cdot}NH_2{\cdot}Co(I)(en)_2^{4+}$, is formed (peak at 565 nm, ε *ca.* 218). When the chloride salt of the ammine complex is used the aquo-chloro-complex $(NH_3)_4(H_2O)Co{\cdot}NH_2{\cdot}Co(Cl)(NH_3)_4^{4+}$ (peak at 554 nm, ε 167) is likewise formed, although there are no significant changes corresponding to the formation of the latter in 2M-$HClO_4$. It would appear therefore that solutions prepared by treating a sample of the complex $[(NH_3)_4Co{\cdot}\mu(NH_2,OH){\cdot}Co(NH_3)_4]Cl_4,4H_2O$ with 8M-$HClO_4$, which were formerly believed[5] to be the bisaquo-complex $(NH_3)_4(H_2O)Co{\cdot}NH_2{\cdot}Co(H_2O)(NH_3)_4^{5+}$ are contaminated with—and possibly predominantly consist of—the aquo-chloro-complex. In the light of these findings we are re-investigating the kinetic data reported for the conversion of the bisaquo-complex into the μ-amido-μ-hydroxo-complex.[6]

The spectrum of the μ-amido-μ-perchloratobis[tetra-amminecobalt(III)] complex resembles closely the spectra of other complexes of general formula $(NH_3)_4Co{\cdot}\mu$-$(NH_2,XO_4){\cdot}Co(NH_3)_4^{(5-n)+}$ which have a bridging oxyanion XO_4^{n-}. Thus spectra of the μ-amido-μ-sulphato- (ϵ_{max} 366 at 540 nm), μ-amido-μ-selenato- (ϵ_{max} 320 at 542 nm), and μ-amido-μ-dihydrogenphosphato- (ϵ_{max} 422 at 538 nm) complexes are in good agreement with that for the μ-perchlorato-complex (ϵ_{max} *ca.* 350 at 544 nm). All four complexes have in addition well resolved peaks in the 360—375 nm region. It is also of interest that the aquo-sulphato-, aquo-selenato-, and aquo-phosphato-complexes have not been isolated or identified with certainty (spectra), although they are presumed to be precursors of the $\mu(NH_2,XO_4)$ double-bridged complexes.

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