even in a distorted molecule, the Re–F bonds could retain C_{3v} symmetry. Hence, the two clearly defined absorptions in the metal–fluoride region are consistent with the fac structure and the more complex spectrum in the carbonyl region is probably the result of distortions due to crystal effects.

In the fac structure, each fluoride is opposite a carbonyl ligand and the electron withdrawing nature of these π-acceptor ligands could account for the comparatively high wave numbers observed for the rhenium(III)–fluoride stretching frequencies, as was pointed out above.

The solubility in polar solvents, the molecular weight of about 300, and the molar conductivity of only 6 cm^2 ohm^{-1} mol^{-1} in acetone, compared to values of 110–175 cm^2 ohm^{-1} mol^{-1} for 1:1 electrolytes,[15] indicate that trifluorotricarbonylrhenium(III) is a molecular monomer.

The room temperature paramagnetic moment of 1.0 BM is not easily interpreted, but this is also the case in the simple octahedral rhenium hexafluoride molecule which has a moment of only 0.25 BM, although the moment of the hexachloride is 2.07 BM.[16] The comparatively low result with fluoride ligands may be due to strong spin–orbit coupling.

Thus we postulate that trifluorotricarbonylrhenium(III) is a molecular monomer and that this preparation results in formation of the fac isomer. Reaction between decacarbonyldirhenium(0) and rhenium hexafluoride involves breaking the metal–metal bond and replacement of carbonyl ligands by fluoride ligands until no two carbonyls are axial to each other. This should proceed fairly rapidly because axial carbonyl ligands are more substitution labile than carbonyls trans to ligands which are relatively poor π acceptors.[17] The fac isomer is isolated because the remaining carbonyl ligands are less labile. Only the addition of excess rhenium hexafluoride or heating the compound with iodine displaces the remaining three carbonyl ligands.

Acknowledgment.—Financial support from the Australian Atomic Energy Commission is gratefully acknowledged. K. A. P. thanks the Council of the Royal Melbourne Institute of Technology for granting study leave.

(15) J. A. Bowden and R. Colton, *Aust. J. Chem.*, **21**, 2657 (1968).
(16) J. H. Canterford and R. Colton, ref 12, p 285.
(17) F. Basolo, *Chem. Brit.*, **5**, 505 (1969).

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Hydroxo-Bridge Cleavage in Dicobalt(III) Complexes

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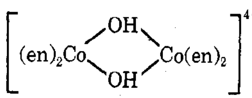
Two kinetic studies have recently been published on the hydroxo-bridge cleavage reactions of the di-μ-hydroxo-bis[bis(ethylenediamine)cobalt(III)] complex (I) in acidic solutions.[1,2] The corresponding reaction

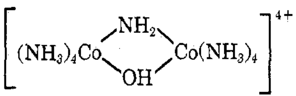


I

of the di-μ-hydroxo-bis[tetraamminecobalt(III)] complex has also been investigated.[3] We wish to comment on the mechanisms which have been proposed in the light of our studies on hydroxo-bridge cleavage of the complexes μ-hydroxo-bis[pentaamminecobalt(III)] (II),[4] and μ-amido-μ-hydroxo-bis[tetraamminecobalt(III)] (III).[5] A mechanism which has not been mentioned previously is suggested, and would seem to merit serious consideration.

$[(NH_3)_5Co{\cdot}OH{\cdot}Co(NH_3)_5]^{5+}$

II



III

Pseudo-first-order rate constants, k_{obsd}, for the formation of aquopentaamminecobalt(III) from II, $\mu = 2.0\ M$ (LiClO$_4$) and $[H^+] = 0.0001$–$2.0\ M$, conform to the rate law

$$k_{obsd} = k_a + k_b[H^+] \qquad (1)$$

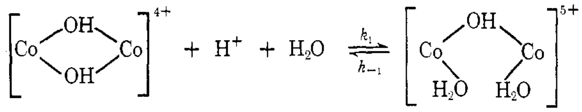
At 25° $k_a = 7.58 \times 10^{-3}$ sec^{-1} and $k_b = 5.37 \times 10^{-3}$ l. mol^{-1} sec^{-1}. Hydroxo-bridge cleavage of III gives stable μ-amido products. In the presence of chloride[5] and bromide,[6] and with $[H^+] = 0.1$–$2.0\ M$, $\mu = 2.0\ M$ (Na–Li–HClO$_4$), (2) applies

$$k_{obsd}/[X^-] = k_a + k_b[H^+] \qquad (2)$$

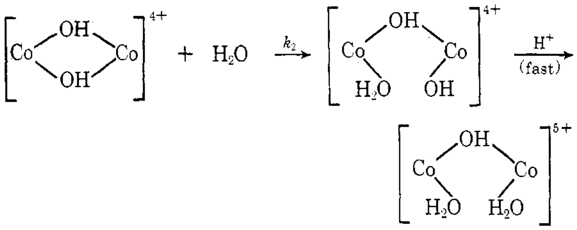
Values obtained at 25° are $k_a = 1.2 \times 10^{-4}$ l. mol^{-1} sec^{-1} (Cl$^-$) and 1.4×10^{-4} l. mol^{-1} sec^{-1} (Br$^-$), $k_b = 9.6 \times 10^{-4}$ mol^{-2} sec^{-1} (Cl$^-$) and 4.33×10^{-4} l.^{2} mol^{-2} sec^{-1} (Br$^-$). The formation of the bis-aquo complex in aqueous perchloric acid solutions, $\mu = 2.0\ M$, has also been studied,[7] and at 35° $k_b = 1.6 \times 10^{-4}$ l. mol^{-1} sec^{-1}; the path $k_a \ll 4.5 \times 10^{-5}$ sec^{-1} may also contribute but in this case cannot be distinguished from another path.[8]

A variety of mechanisms can be invoked to explain the hydrogen ion dependence observed for bridge cleavage of di-μ-hydroxo complexes. However, since complexes with only a single hydroxo bridge yield a hydrogen ion dependence of the form (1), it seems reasonable to us that any deviation from such a dependence for complexes with two hydroxo bridges is a function of the second hydroxo bridge. We propose therefore that a combination of the two hydroxo-bridge cleavage processes, which independently exhibit rate laws of the

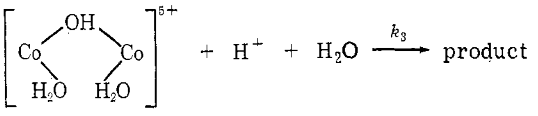
(1) A. A. El-Awady and Z Z. Hugus, *Inorg. Chem.*, **10**, 1415 (1971).
(2) M. M. DeMaine and J. B. Hunt, *ibid.*, **10**, 2106 (1971).
(3) A. B. Hoffman and H. Taube, *ibid.*, **7**, 903 (1968).
(4) R. K. Wharton and A. G. Sykes, full details to be published elsewhere. The preparation of $[(NH_3)_5Co{\cdot}OH{\cdot}Co(NH_3)_5](NO_3)_5$ and $[(NH_3)_5Co{\cdot}OH{\cdot}Co(NH_3)_5]Br_5{\cdot}H_2O$ used in this work has been described by H. Siebert and H. Feuerhake, *Chem. Ber.*, **102**, 2951 (1969). We are most grateful to Professor Siebert for providing a sample of the nitrate salt.
(5) See for example S. W. Foong, R. D. Mast, M. B. Stevenson, and A. G. Sykes, *J. Chem. Soc. A*, 1266 (1971).
(6) For details see S. W. Foong, Ph.D. Thesis, University of Leeds, 1971; S. W. Foong and A. G. Sykes, to be published.
(7) R. S. Taylor and A. G. Sykes, *J. Chem. Soc. A*, 1991 (1970).
(8) R. S. Taylor and A. G. Sykes, *ibid.*, 1426 (1971).



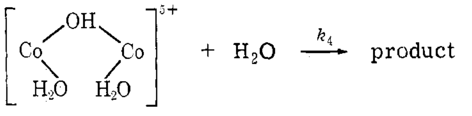
(3)



(4)



(5)

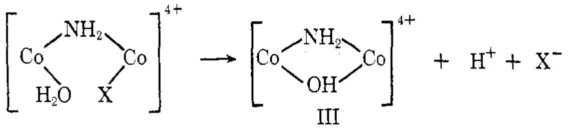


(6)

form (1), is responsible for the more complex $[H^+]$ dependence which is observed, and we suggest that the mechanism 3–6 provides an adequate framework within which to consider these reactions. Equation 3 may itself be written as two equilibria, the first step giving the μ-hydroxo-μ-aquo complex. Assuming stationary-state kinetics for the bis-aquo intermediate,[8a] pseudo-first-order rate constants k_{obsd} can be expressed as in

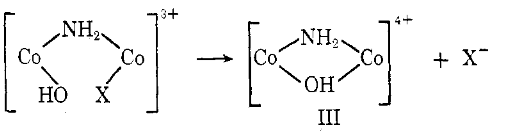
$$k_{\text{obsd}} = \frac{k_2k_4}{k_{-1} + k_4 + k_3[\text{H}^+]} + \frac{(k_2k_3 + k_1k_4)[\text{H}^+]}{k_{-1} + k_4 + k_3[\text{H}^+]} + \frac{k_1k_3[\text{H}^+]^2}{k_{-1} + k_4 + k_3[\text{H}^+]} \quad (7)$$

We have purposely ignored a pathway k_{-2} in (4), because studies on (8) ($X^- = Cl^-$ and Br^-)[9]



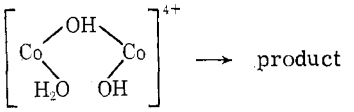
III (8)

have indicated that reaction 9



III (9)

is *ca.* 30-fold suppressed from values predicted from a consideration of microscopic reversibility.[5,6] This effect may be due to hydrogen bonding between ligands in the two coordination spheres, and involving in particular OH^-, following partial rotation of the two coordination spheres.[5] We do not expect k_{-2} to make a significant contribution except at very small $[H^+]$ values. Also we do not expect a labilization of the hydroxo bridge by a terminal hydroxide (10) which has



(10)

featured prominently in other mechanisms,[2,3] to make a significant contribution. Rather with III it is the hydroxo bridge which labilizes the ammonia ligands.[8] Furthermore present information suggests that acid dissociation constants for terminal aquo ligands in binuclear cobalt(III)-ammine complexes are *ca.* 10^{-6} mol l.$^{-1}$ [10] and very little of the aquohydroxo complex in (10) will be present for the range of hydrogen ion

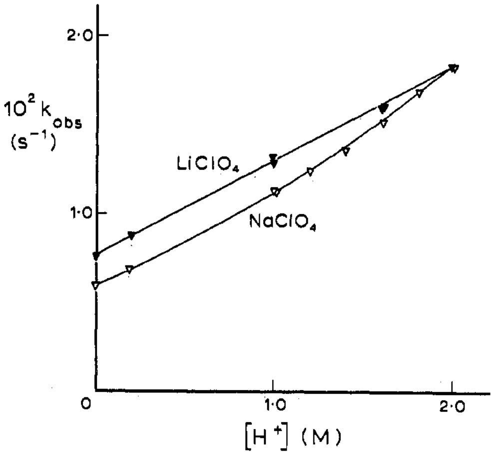


Figure 1.—The hydrogen ion dependence of rate constants, k_{obsd}, for the hydroxo-bridge cleavage of II at 25°. The ionic strength was adjusted to μ = 2.0 *M* with $LiClO_4$ (▼) and $NaClO_4$ (▽).

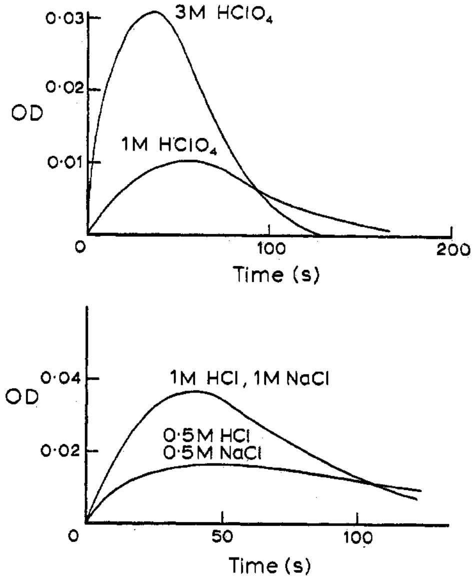


Figure 2.—Absorbance (OD) changes with time at 635 nm on mixing acid and water at room temperature using a Durrum–Gibson stopped-flow apparatus.

[8a] NOTE ADDED IN PROOF.—It is not at present clear that the stationary-state assumption is valid in the case of the hydroxo-bridge cleaxage reactions of the complexes $(en)_2Co\cdot\mu(OH,OH)\cdot Co(en)_2{}^{4+}$ and $(NH_3)_4Co\cdot\mu(OH,OH)\cdot Co(NH_3)_4{}^{4+}$. A consecutive reaction treatment similar to that used in ref 1 may be necessary, in which case the rate constant for the first stage of such a treatment corresponds to reaction by eq 3 and 4, and for second stage to reaction by eq 5 and 6.

[9] M. B. Stevenson, R. D. Mast and A. G. Sykes, *J. Chem. Soc. A*, 937 (1969).

concentrations pH <4 under consideration. It is unlikely therefore that for the conditions investigated a nonbridging hydroxo group will be effective in labilizing a hydroxo bridge and certainly not to the exclusion of k_3 and k_4. The conjugate-base mechanism does not seem to be relevant either in the first hydroxo-bridge cleavage of the dimer $[(H_2O)_4Fe(OH)_2Fe(H_2O)_4]^{4+}$, $[H^+] = 0.2\text{–}1.5\ M$, and the hydrogen ion dependence observed is of the form (1).[11]

The study by DeMaine and Hunt[2] on I includes data at pH's 2.2–4.0, and identification of a term k_0 which is independent of $[H^+]$. No attempt was made to explain this term. According to the mechanism (3)-(6) the behavior could be adequately represented by the first term in (7) with $(k_4 + k_{-1}) \gg k_3[H^+]$. For this condition k_2, k_4, and k_{-1} are the only effective paths. With $[H^+]$ in the range 0.05–0.50 M, the second term in (7), which is of the form $a[H^+]/(1 + b[H^+])$ appears to be dominant. It is possible from the appearance of Figure 2 in the DeMaine and Hunt paper that the third term with an $[H^+]^2$ dependence in the numerator may be effective over the range $[H^+] = 0.5$ to $1.0\ M$. We also note that El-Awady and Hugus[1] in their study of I require an $[H^+]^2$ dependent term in the rate law. Data obtained by Rasmussen and Bjerrum[12] for acid cleavage of I at $[H^+] < 0.05\ M$ fit a dependence of the form (1), which is again consistent with (7) providing $(k_4 + k_{-1}) \gg k_3[H^+]$. Hoffmann and Taube[3] have studied the hydroxo bridge cleavage of the complex $(NH_3)_4Co\cdot\mu(OH,OH)\cdot Co(NH_3)_4^{4+}$, and for the range of $[H^+]$ investigated find their data give an adequate fit to a rate law of the form $a[H^+]/(1 + b[H^+])$. Also Lee Hin-Fat and Higginson[13] have reported data for the hydroxo-bridge cleavage of $(C_2O_4)_2Co\cdot\mu(OH,OH)\cdot Co(C_2O_4)_2^{4-}$ at pH 3.5–4.5, and find a first-order $[H^+]$ dependence.

We wish to make two further points with regard to experimental procedures. Firstly for the reaction of II, a single-bridged 5+ species, it is necessary to adjust the ionic strength with $LiClO_4$ and not $NaClO_4$. Thus data obtained at 25° with $NaClO_4$, Figure 1, can be fitted to an $[H^+]$ dependence as in (11), where the term

$$10^3k_{\text{obsd}} = 5.95 + 4.32[H^+] + 0.99[H^+]^2 \qquad (11)$$

in $[H^+]^2$ has no mechanistic significance. For the reactions of III, a double-bridged 4+ species, it is generally found that $LiClO_4$ and $NaClO_4$ are equally acceptable for the adjustment of ionic strength.[5] El-Awady and Hugus[1] used $NaClO_4$ to adjust the ionic strength in their studies on I which involve a single-bridged 5+ species. Secondly we wish to question the evidence for single-bridged intermediates as presented in Figure 5 of reference 2. We have obtained similar curves, Figure 2, by mixing acid and water with no complex at all, using Durrum–Gibson stopped-flow apparatus. We are concerned as to whether due allowance has been made for such mixing effects.

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(10) See ref 9. As previously explained, R. S. Taylor and A. G. Sykes, *Chem. Commun.*, 1137 (1969), data for the bis-aquo complex $(NH_3)_4(H_2O)Co\cdot NH_2\cdot Co(H_2O)(NH_3)_5{}^{5+}$ should be ignored.

(11) H. N. Po and N. Sutin, *Inorg. Chem.*, **10**, 428, (1971), and references therein.

(12) S. E. Rasmussen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 735 (1955).

(13) Lee Hin-Fat and W. C. E. Higginson, *J. Chem. Soc. A*, 2589 (1971).

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Are There Heptaboranes?

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Five B_7 hydrides have been reported on the basis of mass spectrometric evidence.[1,2] The highest masses observed correspond to the formulas B_7H_{11}, B_7H_{12}, B_7H_{13}, B_7H_{14}, and B_7H_{15}. Ditter, Spielman, and Williams have shown that at least one of the "heptaboranes," B_7H_{15}, is actually a mixture of ethylpentaborane and one or more compounds containing other elements in addition to boron and hydrogen.[1] Partial mass spectra for the three lower heptaboranes have been published.[3,4] We have been able to evaluate the evidence for the existence of these three heptaboranes using a computer method which determines the elemental formulas of ions found in low-resolution mass spectra. This technique was first applied to the boranes,[5] and then to borane derivatives which contain one other element with a pair of isotopes.[6] Finally, the procedure was generalized to include all the elements and all their isotopes.[7]

The automatic computer technique for determining the formulas of ions is based upon the cluster of isotope intensities due to each formula. This procedure is especially powerful for the boranes because of the significant percentage of the second isotope, ^{10}B (20%). The computer program employs a matrix method which solves for all the formulas simultaneously. A least-squares-fit monoisotopic spectrum, restricted to positive solutions, is calculated. One, several, or all of the formulas present in the experimental spectrum may be handled exactly. A measure of the fit of the set of formulas is generated. This is used to choose between alternate sets of formulas. The limitations and sources of error of the procedure have been explored extensively.[5–7]

Results

The three published mass spectra fall into two groups. The first contains B_7H_{11} only.[4] The measure of the fit of the appropriate formulas, the root-mean deviation (rmd), for this compound is 1.0. This is within the range found for other boranes, 0.01–1.8.[5] The isotopic distribution found in B_7H_{11} therefore corroborates the existence of heptaborane(11).

The second class of spectra contains both the spectrum of B_7H_{12},[3] and the composite spectrum, B_7H_{11} with B_7H_{13}.[4] The fragmentation patterns in those two spectra are so similar that we shall treat them as one. The major difference is the lack of a peak at mass 90 in the B_7H_{12} spectrum. The rmd for the composite

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(1) J. F. Ditter, J. R. Spielman, and R. E. Williams, *Inorg. Chem.*, **5**, 118 (1966).

(2) R. T. Holzmann, Ed., "Production of the Boranes," Academic Press, New York, N. Y., 1967, p 75.

(3) R. W. Schaefer, K. H. Ludlum, and S. E. Wiberley, *J. Amer. Chem. Soc.*, **81**, 3157 (1959).

(4) T. P. Fehlner and W. S. Koski, *ibid.*, **86**, 1012 (1964).

(5) E. McLaughlin, T. E. Ong, and R. W. Rozett, *J. Phys. Chem.*, **75**, 3106 (1971).

(6) E. McLaughlin and R. W. Rozett, *ibid.*, **76**, 1860 (1972).

(7) E. McLaughlin and R. W. Rozett, *J. Organometal. Chem.*, in press.