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MECHANISMS OF THE Cr^{2+} REDUCTION OF BINUCLEAR (AND TETRANUCLEAR) COBALT(III) COMPLEXES AND THE FORMATION OF COBALT(III)–CHROMIUM(III) INTERMEDIATES

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A INTRODUCTION

Reactions of Cr^{2+} with mononuclear cobalt(III) ammine complexes have been studied extensively by Taube and colleagues[1] It has been possible to determine the mechanism of such reactions by identification of the chromium(III) product, the inner-coordination sphere of which is inert to substitution. Thus the product of the reaction

$$Cr^{2+} + Co(NH_3)_5Cl^{2+} \xrightarrow{H^+} CrCl^{2+} + Co^{2+} + 5\ NH_4^+ \qquad (1)$$

is monochloropenta-aquochromium(III), $CrCl^{2+}$, and the mechanism is unambiguously of the inner-sphere type[2] The product of (2), however, is the hexa-aquochromium(III) ion, Cr^{3+}, and the mechanism is outer-sphere[3].

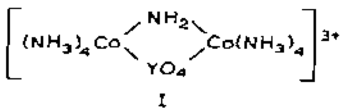
$$Cr^{2+} + Co(NH_3)_6{}^{3+} \xrightarrow{H^+} Cr^{3+} + Co^{2+} + 6\ NH_4^+ \qquad (2)$$

This review summarizes recent studies on the reactions of Cr^{2+} with binuclear cobalt(III) complexes. Stepwise reduction of the cobalt(III) centres occurs with the consumption of two Cr^{2+} ions, and the chromium(III) product from each reduction is once again diagnostic of the mechanism.

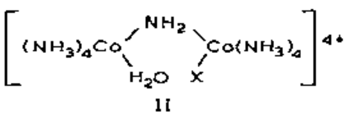
We consider, first, possible combinations of inner- and outer-sphere mechanisms, and the form of the chromium(III) product to be expected from each.

B POSSIBLE REACTION SCHEMES

With a complex of type I, it is possible for the Cr^{2+} to make use of the oxyanion, $YO_4{}^{2-}$,



I



II

as a bridging ligand for electron transfer. Such a mechanism will give a cobalt(III)–chromium(III) intermediate. If the intermediate is stable, then inner-sphere reduction by a second Cr^{2+} will give a binuclear chromium(III) product, and the reaction scheme (3)–(4) will be effective.

$$Cr^{2+} + (Co^{III})_2 \rightarrow Co^{III}\cdot Cr^{III} + Co^{2+} \tag{3}$$

$$Cr^{2+} + Co^{III}\cdot Cr^{III} \rightarrow (Cr^{III})_2 + Co^{2+} \tag{4}$$

If the $Co^{III}\cdot Cr^{III}$ intermediate decomposes before attack by the second Cr^{2+} occurs, or if the second stage is outer-sphere★, then the final product will be monomeric chromium(III) The Cr^{2+} reduction of II may also be inner-sphere with X or possibly OH^- as bridging ligand, but in this case formation of a cobalt(III)–chromium(III) intermediate would require electron exchange between the cobalt(III) and cobalt(II) centres, which in this case seems unlikely. The product is therefore monomeric chromium(III), at least 50% being hexa-aquochromium(III)

If both steps are outer-sphere then the reaction sequence is (5)–(6)

$$Cr^{2+} + (Co^{III})_2 \rightarrow Co^{III} + Cr^{III} + Co^{2+} \tag{5}$$

$$Cr^{2+} + Co^{III} \rightarrow Cr^{III} + Co^{2+} \tag{6}$$

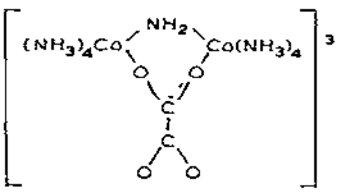
and the product will be 100% hexa-aquochromium(III) An outer-sphere followed by inner-sphere reaction sequence will give 50% hexa-aquochromium(III), and 50% substituted chromium(III).

More elaborate mechanisms are necessary when the Cr^{2+} also reduces the bridging ligand present in the dicobalt reactant. Examples of such reactions are with μ-superoxo[4] and μ-peroxo[5] dicobalt complexes.

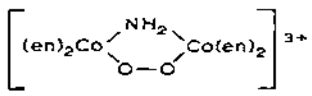
Reductions of two tetrameric cobalt(III) complexes have also been studied and will be considered briefly in a later section.

C. REACTIONS IN WHICH THE FIRST STEP IS INNER-SPHERE

In this category are complexes of type I, where $YO_4^{2-} \equiv SO_4^{2-}$ (ref. 6), SeO_4^{2-} (ref. 6) and HPO_4^{2-} (ref. 7), the μ-amido-μ-oxalato complex III (ref 8), and the μ-amido-μ-peroxo complex IV (ref. 5).



III



IV

★This possibility seems extremely unlikely, since for the second stage just as many sites are available on the oxidant for inner-sphere attack by the Cr^{2+}.

The formation of cobalt(III)–chromium(III) intermediates is apparent in all cases, and spectra of these intermediates have been obtained except in the case of the selenato complex[6]. A more detailed study of the latter is difficult because further reduction of selenate occurs during the second or subsequent stages of the reaction, with the formation of colloidal selenium. Kinetic data for the first stages of the Cr^{2+} reductions are given in Table 1. The intermediate with, for example, the μ-amido-μ-sulphato reactant is believed[6] to be the complex $(NH_3)_5Co\,SO_4.Cr(H_2O)_5{}^{4+}$. Aquation to mononuclear complexes has been shown to be slow (10^{-4}–10^{-5} sec^{-1} at 25°). Present indications are that decomposition of the intermediate is in all cases slower than the second stage of the Cr^{2+} reduction.

Final spectra are consistent with the formation of dichromium(III) species when the reactant is the μ-sulphato, μ-phosphato or μ-oxalato complex. The precise structure of the products is at present uncertain. Hydrogen-ion dependence in kinetic studies with the sulphato and phosphato complexes (Table 2) indicates involvement of

TABLE 1

The Cr^{2+} reduction of binuclear cobalt(III) complexes. Reactions in which cobalt(III)–chromium(III) intermediates are formed. Kinetic data for the first stage of reduction at 25°, $\mu = 2.0\,M$ ($LiClO_4$).

Reactant	Rate constant ($l\ mole^{-1}\ sec^{-1}$)	$\Delta H^{\ddagger}$ ($kcal.mole^{-1}$)	$\Delta S^{\ddagger}$ (e.u.)
$(NH_3)_4Co.\mu(NH_2,SO_4).Co(NH_3)_4{}^{3+}$	7.4	8.7	−25.3
$(NH_3)_4Co.\mu(NH_2,SeO_4).Co(NH_3)_4{}^{3+}$	372	7.2	−22.6
$(NH_3)_4Co.\mu(NH_2,HPO_4).Co(NH_3)_4{}^{3+}$	31.6	9.15	−21.0
$(NH_3)_4Co.\mu(NH_2,C_2O_4H).Co(NH_3)_4{}^{4+}$	1.45	8.7	−28.6
$(NH_3)_4Co.\mu(NH_2,C_2O_4).Co(NH_3)_4{}^{3+}$	35.2	9.8	−18.6
$(en)_2Co.\mu(NH_2,O_2).Co(en)_2{}^{3+}$	2040	8.03	−16.5

TABLE 2

The Cr^{2+} reduction of binuclear cobalt(III) complexes. Reactions in which cobalt(III)–chromium(III) intermediates are formed. Kinetic data for the second stage of reduction at 25° (except where stated), $\mu = 2.0\,M$ ($LiClO_4$).

Reactant	Rate constant ($l\ mole^{-1}\ sec^{-1}$)	$\Delta H^{\ddagger}$ ($kcal\ mole^{-1}$)	$\Delta S^{\ddagger}$ (e.u.)
$(NH_3)_5Co.\mu(SO_4).Cr(H_2O)_5{}^{4+}$	0.256	14.6	−12.2
$(NH_3)_5Co.\mu(SO_4).CrOH(H_2O)_4{}^{3+}$	0.192	13.9	−15.3
$(NH_3)_5Co.\mu(H_2PO_4).Cr(H_2O)_5{}^{5+}$ [a]	0.098 (30°)		
$(NH_3)_5Co.\mu(H_2PO_4).Cr(OH)(H_2O)_4{}^{4+}$	0.043 [b] (30°)		
$(NH_3)_5Co.\mu(HPO_4).Cr(OH)(H_2O)_4{}^{3+}$	0.035 [c] (30°)		
$(NH_3)_5Co.\mu(C_2O_4).Cr(H_2O)_5{}^{4+}$	1.88	5.9	−37.6

[a] Possibly outer-sphere giving 2 Cr^{3+} + Co^{2+} as products. [b] Units sec^{-1}. [c] Units $l^{-1}\ mole\ sec^{-1}$

conjugate base forms★ and hydroxo bridging to the Cr^{2+}. Some hydroxo bridging is therefore to be expected in the chromium(III) dimer from this path.

The reaction of the μ-amido-μ-peroxo complex IV (ref. 5) gives an intermediate which is tentatively assigned the formula $(en)_2(NH_3)Co\,O_2.Cr(H_2O)_5{}^{4+}$. Ion-exchange separation of the products has been carried out and no mononuclear chromium(III) ions were detected in experiments with one equivalent of Cr^{2+}. The system is complicated by the further consumption of two equivalents of Cr^{2+} and reduction of the peroxo bridge ($O_2{}^{2-} \rightarrow 2\ H_2O$), before the final stage in which the second cobalt(III) is reduced. A cobalt(III) chromophore is retained until the final stage is imminent. Other mechanisms would almost certainly give more rapid reduction of the second cobalt(III).

D. REACTIONS IN WHICH NO INTERMEDIATE IS DETECTED

Kinetic data for the first stage of reactions in this category are listed in Table 3. The first of these reactions[9] may be summarized

$$Cr^{2+} + (NH_3)_5Co.NH_2.Co(NH_3)_5{}^{5+} \xrightarrow{H^+} Co(NH_3)_6{}^{3+} + Cr^{3+} + Co^{2+} + 5\ NH_4{}^+ \quad (7)$$

$$Cr^{2+} + Co(NH_3)_6{}^{3+} \xrightarrow{H^+} Cr^{3+} + Co^{2+} + 6\ NH_4{}^+ \quad (8)$$

and, since the kinetics give no hydrogen-ion dependence, and there is no available site for bridging, both steps must clearly be outer-sphere. The first stage of the reaction of the μ-amido-μ-hydroxo complex (protonated form[10]) is also outer-sphere. No intermediates were detected in the reactions of the other complexes listed in Table 3 and

TABLE 3

The Cr^{2+} reductions of binuclear cobalt(III) complexes. Rate constants (25°) for reactions in which no cobalt(III)–chromium(III) intermediates detected

Reactant	μ (*M*)	10^3k (l mole^{-1} sec^{-1})	$\Delta H^{\ddagger}$ (kcal.mole^{-1})	$\Delta S^{\ddagger}$ (e u.)	Ref.
$(NH_3)_5Co.\,\mu(NH_2)\,Co(NH_3)_5{}^{5+}$	0.4	3.1 [a]			9
$(NH_3)_4Co.\,\mu(NH_2,\,OH)\,Co(NH_3)_4{}^{4+}$ ([H^+]-dependent)	2.0	1.12 [b] (35°)	19.9	−7.5	10
$(NH_3)_4Co.\,\mu(OH,OH).Co(NH_3)_4{}^{4+}$	1.0	1.73 [b]	8.3	−43	11
$(NH_3)_4Co.\,\mu(NH_2,HCO_2).Co(NH_3)_4{}^{4+}$	1.0	1.68 [b]	13.9	−25	12
$(NH_3)_4Co.\,\mu(NH_2,CH_3CO_2).Co(NH_3)_4{}^{4+}$	1.0	0.48 [b]	12.0	−34	12

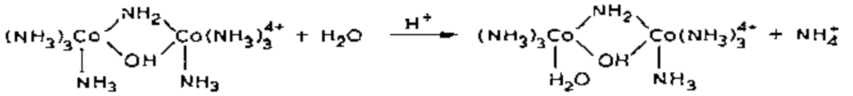
[a] Intermediate formation of $Co(NH_3)_6{}^{3+}$. Rate constant corresponds to first stage of reduction. Both steps outer-sphere. [b] No intermediate detected. Rate constant corresponds to first stage of reduction. Outer-sphere followed by inner-sphere reaction sequence is most probable.

★The pK_a for the acid dissociation of water ligands in cobalt(III)–chromium(III) intermediates, e.g. $(NH_3)_5Co\,SO_4\,Cr(H_2O)_5{}^{4+}$, is presumably in the 3–6 region.

the relative rates for the two stages of the Cr^{2+} reduction are therefore slow and then fast. A slower second stage is required for the detection of intermediates. It is concluded that formation of a cobalt(III)–chromium(III) intermediate is unlikely for these reactions since the reducibility of a complex is unlikely to be increased on replacing one of the cobalt(III) metal ions by a chromium(III). Although special considerations may prevail for some systems, the reactions in Table 3 are probably all outer-sphere The first stage of the reduction of the μ-formato complex[12] gives $Co(NH_3)_5(HCO_2)^{2+}$, similarly the μ-acetato complex gives[12] $Co(NH_3)_5(CH_3CO_2)^{2+}$ The final products will be $Cr(H_2O)_5(HCO_2)^{2+}$ and $Cr(H_2O)_5(CH_3CO_2)^{2+}$ respectively. Ion-exchange separation of the final products in the formato reaction has indicated $Cr(H_2O)_6{}^{3+}$ and small amounts of $Cr(H_2O)_5(HCO_2)^{2+}$ as products However, the separation is not quantitative, owing to the slowness of the reactions and the Cr^{2+}-catalyzed aquation of $Cr(H_2O)_5(HCO_2)^{2+}$

The reactions in Table 3 are all appreciably slower than those listed in Table 1 As a consequence of this, bridge cleavage followed by rapid Cr^{2+} reduction at ligand sites which then become available, becomes a possibility Such paths have been detected in kinetic studies of the complexes $(NH_3)_4Co\,\mu(NH_2,OH)\,Co(NH_3)_4{}^{4+}$ (ref.10), $(NH_3)_4Co\,\mu(OH,OH)\,Co(NH_3)_4{}^{4+}$ (ref 11) and $(NH_3)_4Co\,\mu(NH_2,HCO_2)\,Co(NH_3)_4{}^{4+}$ (ref. 12)

Additional steps which are observed in the Cr^{2+} reduction of the μ-amido-μ-hydroxo complex, correspond to the loss of terminal ammonia ligands[10], viz



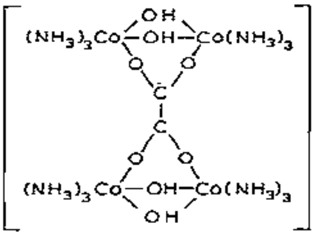
$$(NH_3)_3Co(NH_3)(\mu\text{-}NH_2)(\mu\text{-}OH)Co(NH_3)(NH_3)_3^{4+} + H_2O \xrightarrow{H^+} (NH_3)_3Co(H_2O)(\mu\text{-}NH_2)(\mu\text{-}OH)Co(NH_3)(NH_3)_3^{4+} + NH_4^+ \qquad (9)$$

The aquo product reacts rapidly with Cr^{2+} A study has been made of the Cr^{2+} reduction of the diaquo product which is obtained following replacement of a second ammonia[13] The rate law is predominantly of the form $k_{obs}\,(sec^{-1}) = a\,[H^+]^{-1}$

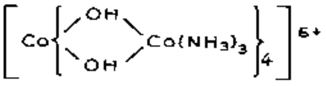
An interesting observation is that with the μ-amido-μ-superoxo complex as oxidant (the 4+ analogue of IV) the first stage of reduction is outer-sphere, and hexa-aquo-chromium(III) can be separated quantitatively by ion-exchange procedures[5] The reaction is too fast to study by the stopped-flow method ($k > 5 \times 10^5$ l mole^{-1} sec^{-1} at 4°C), and electron transfer may occur rapidly before the inner-coordination sphere of the Cr^{2+} can lose a water molecule and form an inner-sphere activated complex. The product is the μ-amido-μ-peroxo complex, and as already indicated (Table 1) this now reacts with Cr^{2+} at a somewhat slower rate by an inner-sphere mechanism Hoffman and Taube[4] have studied the Cr^{2+} reduction of the μ-superoxo complex $(NH_3)_5Co.O_2.Co(NH_3)_5{}^{5+}$ and find $k = 2.3 \times 10^3$ l mole^{-1} sec^{-1} (25°), $\Delta H^{\ddagger} = 0.5 \pm 0.5$ kcal mole^{-1} and $\Delta S^{\ddagger} = -41 \pm 1.0$ e.u. The peroxo complex, $(NH_3)_5Co.O_2.Co(NH_3)_5{}^{4+}$, decomposes rapidly in acidic solutions, and the oxygen released is presumed to react with additional Cr^{2+}.

E. REACTION OF TETRAMERS

The reactions of complexes V (ref 12) and VI (ref 11) have been studied They constitute a novel type of reaction in view of the bulkiness of the reactant and the overall charge. The reactions have been studied in the presence of excess Cr^{2+}, and good second-order kinetics are observed. A slow first step (which is outer-sphere) followed by faster subsequent steps (probably inner-sphere) seem likely. Kinetic data are listed in Table 4. The nature of the chromium(III) product has not yet been determined.



V



VI

TABLE 4

The Cr^{2+} reduction of tetrameric cobalt(III) complexes. Kinetic data for first stage of reduction at 25°.

Reactant	μ (*M*)	$10^3 k$ (mole^{-1}.sec^{-1})	$\Delta H^\ddagger$ (kcal.mole^{-1})	$\Delta S^\ddagger$ (e.u.)	Ref.
$[((NH_3)_6Co_2(OH)_2C_2O_4]^{6+}$	0.2	3.8	7.3	−45	12
$[((NH_3)_4Co(OH)_2)_3Co]^{6+}$	1.0	3.2	9.1	−39	11

F. ISOLATION OF PRODUCTS

The first stage of work on Cr^{2+} reductions of binuclear cobalt(III) complexes may be said to be complete. Kinetic and mechanistic studies have clearly indicated which systems give a build-up of cobalt(III)–chromium(III) complexes, and binuclear chromium(III) complexes as final products. Stage two calls for the isolation of the products Clearly it is possible to retain significant amounts of the cobalt(III)–chromium(III) complexes by using one equivalent only of Cr^{2+} reactant Subsequently, the study of the products of the reaction of higher polymeric cobalt(III) complexes may prove worthwhile.

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