times faster than its less basic Zn–TMpyP(2) counterpart. The lack of resonance interaction between the meso nitrogens on the pyridyl rings and the porphyrin nucleus may account for the slightly faster solvolysis rate of Zn–TMpyP(3) as compared with that of Zn–TMpyP(4).

The observed ZnP kinetic solvolysis order, TpyP(3) > TpyP(4) > TpyP(2), parallels the electrochemical reduction potentials[8] of the porphyrins in 1.0 M HCl. The meso derivative is the most difficult to reduce (most basic?), while the ortho species (most acidic) is the easiest.

Acknowledgment. We thank ERDA, Contract No. At-(40-1)-4047, for generous financial support.

Registry No. TMpyP(2) tosylate, 59728-90-4; TMpyP(3) tosylate, 59728-92-6; TMpyP(3) iodide, 59728-93-7; Zn–TMpyP(3), 59729-16-7; Zn–TpyP(3), 59729-17-8; Zn–TMpyP(4), 40603-58-5; Zn–TpyP(4), 31183-11-6; Zn–TMpyP(2), 59729-18-9; Zn–TpyP(2), 59729-19-0.

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Outer-Sphere Mechanisms in the Reductions of Polynuclear μ-Terephthalato Cobalt(III) Complexes by Chromium(II) and Vanadium(II)

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Received March 8, 1976 AIC60181N

It has been suggested that the reducibility of a given uncomplexed organic ligand is a necessary prerequisite for its ability to function as an electron mediating bridge between two metal ions in an inner-sphere electron-transfer process with attack of the reductant at a remote polar group and transfer of an electron through the ligand.[1-4]

In the past it has not been possible to test this thoroughly because the reduction of mononuclear carboxylatopentaamminecobalt(III) complexes by Cr^{2+} can always proceed via an inner-sphere mechanism with attack of the reductant at the adjacent carbonyl oxygen.

It is this mechanism that has been assigned to the reduction of the terephthalatopentaamminecobalt(III) complex by Cr^{2+}.[5] Terephthalic acid represents a promising ligand in order to test the correlation concerning the reducibility of the ligand and its effectiveness in mediating electrons. Good conjugation is given as well as a suitable "lead in" functional group for precursor complex formation with Cr^{2+} and the ligand is not reducible by Cr^{2+} or V^{2+}.

We have prepared the present series of polynuclear complexes I, II, III, and IV which contain terephthalic acid as bridging ligand because it is now well established that the oxygen atoms of a μ-carboxylato bridge where both oxygens are coordinated to two Co(III) centers do not represent favorable sites of attack for Cr^{2+}.[6,7]

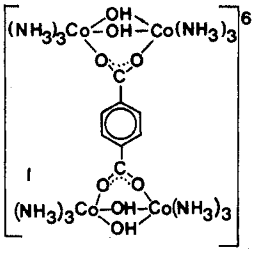
Experimental Section

Preparation of μ_4-Terephthalato-bis{di-μ-hydroxo-bis[triamminecobalt(III)]} Perchlorate (I). To a solution of 2 g of terephthalic acid in 70 ml of dioxane and 40 ml of 0.5 M perchloric acid at 70 °C 6 g of tri-μ-hydroxo-bis[triamminecobalt(III)] perchlorate dihydrate[8] (hereafter referred to as "triol") was added in small amounts with stirring. The temperature was maintained for 15 min during which time most of the dioxane was evaporated by bubbling a stream of nitrogen through the solution. The solution was cooled to 15 °C and unreacted terephthalic acid precipitated and was filtered off. Concentrated perchloric acid (2 ml) and solid $NaClO_4$ were added to the solution which was kept at 0 °C for 2 h. Red crystals were collected and washed thoroughly with ethanol and ether and recrystallized from a minimum amount of water with 2 ml of concentrated $HClO_4$.

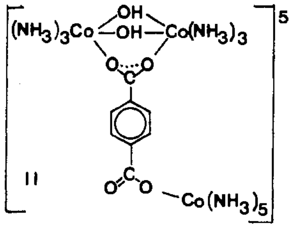
Preparation of μ_3-Terephthalato-di-μ-hydroxo-bis[triamminecobalt(III)][pentaamminecobalt(III)] Perchlorate (II). Terephthalatopentaamminecobalt(III) perchlorate was prepared as described in the literature.[9] One gram of this complex in 20 ml of 0.5 M perchloric acid was reacted at 65 °C with 2 g of triol. The temperature was maintained for 15 min. To the cooled (20 °C) and filtered solution 2 ml of concentrated $HClO_4$ and solid $NaClO_4$ were added. The solution was kept at 0 °C for a few hours. Red crystals were collected and washed with ethanol and ether.

Preparation of μ-(Terephthalato monomethyl ester)-di-μ-hydroxo-bis[triamminecobalt(III)] Perchlorate (III). The complex was prepared by the same method as described for complex I. A solution of 2 g of terephthalic monomethyl ester in a mixture of 30 ml of dioxane and 15 ml of 0.5 M perchloric acid was reacted at 60 °C with 3 g of triol.

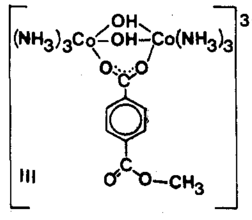
Preparation of μ-Terephthalato-di-μ-hydroxo-bis[triamminecobalt(III)] Perchlorate (IV). Complex II (1.7×10^{-3} mol; 2 g) was dissolved in 60 ml of 0.5 M perchloric acid at 40 °C. Argon was passed through the solution which was kept in a 100-ml flask fitted with a rubber serum cap until all the oxygen has been removed. Then 1.7×10^{-3} mol of $[V(H_2O)_6]^{2+}$ in perchloric acid were added using a hypodermic syringe. The mixture was allowed to react at room temperature for 1 h. A minor precipitation of uncomplexed terephthalic acid occurs. To the cooled (0 °C) and filtered solution 5 ml of concentrated $HClO_4$ was added. Red crystals of unreacted trinuclear complex II precipitated and were filtered off. The solution was then saturated with solid $NaClO_4$ and kept in the refrigerator for 2 h. Red crystals of complex II were collected and washed with ethanol and ether. Yield: 0.4 g. See Table I.



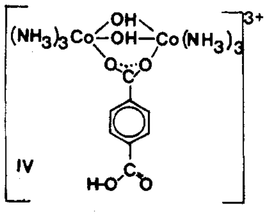
I



II



III



IV

Reagents. Solutions of $[Cr(H_2O)_6]^{2+}$ and $[V(H_2O)_6]^{2+}$ ions in perchloric acid were prepared by electrolytic reduction of chromium(III) and vanadium(IV) solutions under an argon atmosphere. The organic ligands were commercially available (Merck) and were used without further purification.

Physical Measurements. Kinetic runs were followed using a Unicam SP 1700 spectrophotometer fitted with thermostated cell housing.

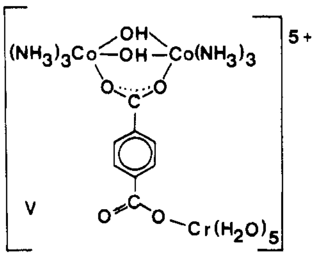
Table I. Elemental Analyses (%) for Complexes I-IV and Electronic Spectra

Complex	C[a]	H[a]	N[a]	Cl[a]	Co[a]	λ_{max}, nm	ϵ, M^{-1} cm^{-1}
(I) $[Co_4(NH_3)_{12}(OH)_4(C_8H_4O_4)](ClO_4)_6\cdot 3H_2O$	7.3	3.8	12.7	16.1	17.8	524	226
	7.6	3.8	12.4	15.7	17.8		
(II) $[Co_3(NH_3)_{11}(OH)_2(C_8H_4O_4)](ClO_4)_5\cdot 4H_2O$	8.5	4.2	13.6	15.7	15.6	513	195
	8.8	4.1	13.5	15.8	15.6		
(III) $[Co_2(NH_3)_6(OH)_2(C_9H_7O_4)](ClO_4)_3\cdot H_2O$	14.4	4.2	11.2	14.2	15.7	524	113
	13.9	4.2	11.2	14.3	15.9		
(IV) $[Co_2(NH_3)_6(OH)_2(C_8H_5O_4)](ClO_4)_3\cdot 2H_2O$	12.8	3.9	11.2	14.1		524	110
	12.8	4.0	11.1	14.0			

[a] Top values are calculated, bottom values are found.

Chromium concentrations were determined spectrophotometrically as chromate, and solutions of cobalt(II) as $CoCl_4^{2-}$ or $CoCl_3H_2O^-$ by standard procedure.[10]

Determination of Products by Ion Exchange. A product analysis of a 1:1 reaction mixture (1 mol of complex II and 1 mol of $[Cr(H_2O)_6]^{2+}$) was carried out by ion exchange chromatography in order to substantiate the proposed reaction scheme. Separation of such a reaction mixture {$[(Co^{III}_3)] = 6.3 \times 10^{-3}$ M, $[Cr^{2+}] = 6.3 \times 10^{-3}$ M, $[H^+] = 0.1$ M, 25 °C, reaction time 45 min} yielded three fractions: pink $[Co(H_2O)_6]^{2+}$ (33% of initial Co(III)), $[Cr(H_2O)_6]^{3+}$ (18% of initial Cr^{2+}), and a red Cr(III) and Co(III) containing complex which was eluted off the column (resin: Sephadex SP C-25, H^+ form) with 2.0 M perchloric acid. This fraction was analyzed for Cr and Co; a 1:2 ratio was found. Incorporation of terephthalic acid was shown by base hydrolysis of solutions containing only the red fraction; uncomplexed terephthalic acid precipitated from reacidified solutions. The uv–visible spectrum of this complex has a maximum of absorption at 524 nm (ϵ = 125 l. mol^{-1} cm^{-1}) and a very strong absorption in the 300-nm region which can be attributed to the presence of a hydroxy bridged Co^{III}–OH–Co^{III} group.[8] It is concluded that complex V is formed.



V

Results

Reductions of Complexes I, III, and IV by Cr^{2+} and V^{2+}. The rates of the reductions of the tetranuclear complex I and two binuclear complexes III and IV by Cr^{2+} have been studied by conventional spectrophotometry at the 524 nm absorption maximum of the complexes (under pseudo-first-order conditions with large excess of reductant). Spectrophotometric changes are consistent with 2:1 reactions as in eq 1 for

$$Co^{III}_2 + 2Cr^{2+} \rightarrow 2Co^{2+} + 2Cr^{3+} \tag{1}$$

complexes III and IV and a 4:1 for complex I as in eq 2.

$$Co^{III}_4 + 4Cr^{2+} \rightarrow 4Co^{2+} + 4Cr^{3+} \tag{2}$$

Reduction of the first Co(III) of all complexes is rate determining. A strictly first-order dependence on reductant is observed in all cases, and the rates are independent of hydrogen ion concentration. It has not been possible to follow runs at 25 °C to completion because precipitation of uncomplexed terephthalic acid occurred after 2–3 half-lives. First-order rate constants were obtained from plots of log ($A_t - A_\infty$) against time where A_t is the absorbance at time t and A_∞ that after the reaction is complete and after the uncomplexed ligand was deposited on the bottom of the cell. Such plots were linear to only 50–70% completion of the reaction. Second-order rate constants, k_{Cr} (M^{-1} s^{-1}), are listed in Table II.

Table IV. Second-Order Rate Constants for the Reductions of Complexes I–IV by Chromium(II) and Vanadium(II) at 25 °C, μ = 1.0 M ($LiClO_4$)

Complex	$10^3 \times k_{Cr}$,[c] M^{-1} s^{-1}	k_V,[c] M^{-1} s^{-1}	k_{Cr}/k_V	Mechanism[d]
I	1.16 ± 0.09	0.056 ± 0.005	0.021	o.s.
II	178 ± 4[a]	0.62 ± 0.07[a]	0.29	i.s.
	1.15 ± 0.03[b]	0.065 ± 0.005[b]	0.018	o.s.
III	1.66 ± 0.02	0.085 ± 0.003	0.020	o.s.
IV	1.89 ± 0.09	0.096 ± 0.005	0.020	o.s.

[a] First stage of the reaction. [b] Second stage of the reaction. [c] Error limits are standard deviations. [d] o.s. = outer sphere; i.s. = inner sphere.

A similar experimental procedure was adopted for the reductions by V^{2+}. The over-all stoichiometries of the reductions of complexes I, III, and IV were found to be 4:1 (4 mol of V^{2+} to 1 mol of complex), 2:1, and 2:1, respectively. This is consistent with Co^{2+} and V^{3+} being the only products. Reduction of the first Co(III) is again rate determining in all cases. Due to precipitation of uncomplexed ligand, plots of log ($A_t - A_\infty$) were only linear to 60% completion of reactions. The rates of reductions are first order in reductant and oxidant and independent of $[H^+]$ (Table III). The main purpose of the V^{2+} reductions is to help with the assignments of outer-sphere mechanisms for the Cr^{2+} reductions. If the ratio of rate constants for the reductions of a common oxidant by Cr^{2+} and V^{2+}, k_{Cr}/k_V, is ca. 0.02, this is considered to be indicative for outer-sphere mechanisms.[11-13] It follows from the data of Table IV that this is the case for the reductions of the first Co(III) centers of complexes I, III, and IV.

Reduction of the Trinuclear Complex II by Cr^{2+} and V^{2+}. The stoichiometry of the reduction of complex II by Cr^{2+} was found to be 3:1. The reaction was followed spectrophotometrically at 502 nm using pseudo-first-order conditions (excess Cr^{2+}). Two distinct stages were observed corresponding to the stepwise reduction of one Co(III) of the pentaamminecobalt(III) moiety and subsequently two Co(III) centers of the di-μ-hydroxo-bis[triamminecobalt(III)] moiety, reduction of the first of which is rate determining for the second stage. The product analysis is in support of this reaction sequence.

Pseudo-first-order rate constants for the first and second stage were evaluated from plots of log ($A_t - A_{\infty 1}$) and log ($A_{t_2} - A_{\infty 2}$) against time, where A_t and A_{t_2} correspond to the absorption at times t and t_2, and $A_{\infty 1}$ is the absorption of the reaction mixture after 4–5 half-lives of the first stage and $A_{\infty 2}$ after completion of the reaction. Such plots were linear to 90% of completion of both stages; although it is noted that at very high $[Cr^{2+}]$ uncomplexed ligand precipitated during the second stage probably due to Cr^{2+}-catalyzed decomposition of possible Cr(III) terephthalato complexes. No dependence of rates on $[H^+]$ was detected. The kinetic data are summarized in Tables II and IV.

Reduction of complex II by V^{2+} occurs also in two distinct stages, corresponding to the stepwise reduction of one Co(III) of the pentaamminecobalt(III) moiety (fast), and two remaining Co(III) ions, reduction of the first of which is rate determining (slow). This reaction sequence is substantiated by the fact that from 1:1 reaction mixtures complex IV is obtained as the major product. Since the rates of reduction of the two stages differ only by one order of magnitude a standard consecutive reaction treatment was employed to evaluate first-order rate constants.[14] No dependence of rates on $[H^+]$ was detected. The kinetic data are listed in Tables III and IV. Activation parameters for the first stage ($\Delta H^{\ddagger}_1 = 13 \pm 1$ kcal mol^{-1}, $\Delta S^{\ddagger}_1 = -15 \pm 3$ cal K^{-1} mol^{-1}) are consistent with substitution into $[V(H_2O)_6]^{2+}$ controlled inner-sphere mechanism. The values found for the second stage are quite different ($\Delta H^{\ddagger}_2 = 7 \pm 1$ kcal mol^{-1}, $\Delta S^{\ddagger}_2 = -40 \pm 2$ cal K^{-1} mol^{-1}). They are not characteristic for an inner-sphere process. They are remarkably similar to other known outer-sphere reactions of mononuclear Co(III) complexes with V^{2+}.[15]

Discussion

The important structural feature of complex I is the lack of a suitable functional group at the aromatic ring which is available for precursor complex formation with the reductants Cr^{2+} or V^{2+}. The kinetic data of the reductions of the first Co(III) center of complex I can therefore be regarded as typical for outer-sphere mechanisms.[16] This assignment is supported by a rate ratio, k_{Cr}/k_V, of 0.021.

The trinuclear complex II has one uncomplexed carboxylic oxygen adjacent to a $Co(NH_3)_5$ moiety. This Co(III) center is rapidly reduced by Cr^{2+} via an inner-sphere mechanism with attack of the reductant at the uncomplexed carbonyl oxygen; a mixed $Co(III)_2$–Cr(III) complex V is formed. Further reduction of Co(III) proceeds slowly and from the rate ratio it is concluded that an outer-sphere mechanism is operative. It is noted that the second-order rate constants for the reductions of the first Co(III) of complex II and of the mononuclear terephthalatopentaamminecobalt(III) are identical within experimental error.[5]

V^{2+} reacts with complex II in a fast–slow sequence, too. The first stage corresponds to the inner-sphere reduction of the $Co(NH_3)_5$ moiety, and due to the kinetic lability of V(III) complexes the binuclear complex IV can be isolated. This species is subsequently reduced by V^{2+} via an outer-sphere mechanism.

Complexes III and IV are slowly reduced by Cr^{2+} at rates comparable with the one observed for complex I. Although these complexes contain a bridging ligand with good conjugation and a suitable "lead in" functional group, an inner-sphere mechanism with attack of the reductant at the remote carbonyl oxygen appears not to be an energetically favorable path. From the rate ratio outer-sphere mechanisms can be assigned for the reductions of both complexes by Cr^{2+} and V^{2+}.

These results clearly demonstrate that terephthalic acid does not mediate electrons efficiently from one carboxylic group through the benzene ring to the remote Co(III) (inner-sphere: remote attack); whereas it is possible to transfer an electron across a carboxylic group if one Co(III) is coordinated to one oxygen of the carboxylic group (inner-sphere: adjacent attack).

Acknowledgment. Support of this research by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Registry No. I, 59753-09-2; II, 59780-56-2; III, 58482-23-8; IV, 59753-11-6; Cr^{2+}, 22541-79-3; V^{2+}, 15121-26-3; V, 59753-12-7; tri-μ-hydroxo-bis[triamminecobalt(III)] perchlorate, 22445-08-5; terephthalatopentaamminecobalt(III) perchlorate, 59753-14-9.

Supplementary Material Available: Table II showing kinetic data for the reductions of complexes I–IV by chromium(II) and Table III showing kinetic data for the reductions by vanadium(II) (2 pages). Ordering information is given on any current masthead page.

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The Defect Model and Oxidation State of Europium and Molybdenum in Eu_xMoO_4

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Received March 26, 1976 AIC60239Y

A new series of tetragonal scheelite-type compounds with stoichiometry Eu_xMoO_4 ($0.67 \leq x \leq 1.00$) was recently reported by Banks[2] and the scheelite solid-solution series $EuMO_4$–$Eu_2(MO_4)_3$ (M = Mo, W) have also been studied by McCarthy.[3] Unit cell parameters and density measurements suggest a cation vacancy model leading to the formulation $Eu^{II}{}_{1-3y}Eu^{III}{}_{2y}\square MoO_4$ where $y = 1 - x$ and x is the stoichiometric amount of europium in Eu_xMoO_4 (i.e., $Eu^{II}{}_{3x-2}Eu^{III}{}_{2-2x}\square_{1-x}MoO_4$). There is some uncertainty though, concerning the oxidation state of molybdenum, and the possible presence of Mo^V has been postulated.[2] We sought to remove this uncertainty by determining the area ratios of Eu^{II} and Eu^{III} Mössbauer resonance peaks as previously described by Greenwood et al.[4] for the related phases Eu_xWO_4. Our results allow us to rule out the presence of $[Mo^VO_4]^{3-}$ tetrahedra in the series Eu_xMoO_4, though when gadolinium is also present, as in the two-phase mixture of overall composition "$Gd_{0.5}Eu_{0.5}MoO_4$", then the observed Eu^{II}/Eu^{III} ratio can only be explained by the simultaneous partial reduction of molybdenum(VI) or the much less likely reduction of gadolinium(III).

Experimental Section

Samples were prepared as previously described.[2] The material listed as "$Gd_{0.5}Eu_{0.5}MoO_4$" was, in fact, an equimolar mixture of $Gd_{0.85}Eu_{0.15}MoO_4$ and $Gd_{0.15}Eu_{0.85}MoO_4$.

Mössbauer spectra were obtained using Elscint equipment as previously described,[5] with both source and absorber at 4.2 K. The source was 300 mCi $^{151}SmF_3$ and the resonance line widths were in the range 2.4–3.5 mm s^{-1} for Eu^{III} and 4.3–5.7 mm s^{-1} for Eu^{II}. Samples were mounted with a thickness of 10–20 mg of $^{151}Eu/cm^2$ except for "$Gd_{0.5}Eu_{0.5}MoO_4$" which had 6.7 mg of $^{151}Eu/cm^2$. Acceptable spectra were obtained with about 3×10^6 counts per channel.

Results and Discussion

Typical spectra are shown in Figure 1. The most obvious features are the complete lack of any magnetic hyperfine interaction at 4.2 K and the presence of substantial amounts of Eu^{II}. The relative proportions of Eu^{II} and Eu^{III} in the various samples are shown in the Table I. Experimental values were calculated from the areas of the computer-fitted reso-