(16) CySOH + CyS^- → CySSCy + OH^- is very rapid in aqueous solution. We have shown that reaction of $(en)_2CoCyS^+$ with $(en)_2CoCySO^+$ does not occur at a significant rate under the reaction conditions.
(17) In contrast, it has been shown that steric effects dominate in the reaction of penicillaminethiolate ion (0.0065 M^{-1} s^{-1}) and cysteinethiolate ion (0.134 M^{-1} s^{-1}) with acrylonitrile: M. Friedman, "The Chemistry and Biochemistry of the Sulfhydryl Group in Amino Acids, Peptides and Proteins", Pergamon Press, New York, N.Y., 1973, pp 107–111.
(18) However, it is possible that conformational differences in the complexes may account for a part of the difference in rates.
(19) Reference 11, p 79.
(20) For example, absorption within the 371-nm LMCT band could give rise to a $(en)_2Co^{II}\overline{NH_2,\cdot SO}$ radical pair.
(21) (a) V. Balzani, R. Ballardini, N. Sabbatini, and L. Moggi, *Inorg. Chem.*, 7, 1398 (1968); (b) F. Scandola, C. Bartocci, and M. A Scandola, *J. Am. Chem. Soc.*, **95**, 7898 (1973).
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Mechanism of the Cr^{2+}, V^{2+}, and $Ru(NH_3)_6^{2+}$ Reduction of N-Bonded Glycinato- and β-Alaninatopentaamminecobalt(III) Complexes. Evidence for Paths Involving Precursor Complex Formation with Outer-Sphere Electron Transfer

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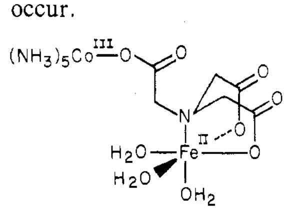
Rate constants ($[H^+]$ = 0.07–1.00 M, 25 °C, I = 1.00 M ($LiClO_4$)) for the Cr^{2+} reduction of (glycinato-*N*)pentaamminecobalt(III), $Co(NH_3)_5(NH_2CH_2CO_2H)^{3+}$, give an $[H^+]$ dependence, k_{obsd} (M^{-1} s^{-1}) = $k_1 + k_2[H^+]^{-1}$ (k_1 small). With V^{2+} as reductant the dependence is of the same form, $k_{obsd} = k_3 + k_4[H^+]^{-1}$, while with $Ru(NH_3)_6^{2+}$ no $[H^+]$ dependence is observed, $k_{obsd} = k_5$, I = 1.00 M(LiCl). Ratios of rate constants k_1, k_3, and k_5 are consistent with a mechanism of outer-sphere electron transfer. The O-bonded complex $Cr(H_2O)_5(O_2CCH_2NH_3)^{3+}$ was identified as product of the Cr^{2+} reduction, and k_2 is believed to proceed with attachment of the reductant at the remote carboxylate. Corresponding reactions of (β-alaninato-*N*)pentaamminecobalt(III), $Co(NH_3)_5(NH_2CH_2CH_2CO_2H)^{3+}$, give rate dependences of the same form, and the product $Cr(H_3O)_5(O_2CCH_2CH_2NH_3)^{3+}$ was identified. The carboxylic acid group has dissociation pK_a values of 2.43 and 2.22 for the glycinato-*N* and β-alaninato-*N* complexes, respectively, and with the labile Cr^{2+} and V^{2+} reductants the remote (unprotonated) carboxylate serves to hold the reductant in the vicinity of the oxidant (paths k_2 and k_4). Since the metal atoms are linked by a flexible but saturated chain of atoms, electron transfer occurs as in an outer-sphere process. These studies provide the simplest and most clearly established case yet of reactions involving precursor complex formation but with outer-sphere electron transfer.

The possibility that precursor complex formation may not always be diagnostic of inner-sphere electron transfer has been recognized for some time. Cannon and Gardiner[1] in their study of the Fe^{2+} reduction of O-bonded (nitrilotriacetato)pentaamminecobalt(III) obtained kinetic evidence for the formation of a precursor complex (I) but were unable to rule out formation of a second intermediate (II), in which inner-sphere electron transfer via the bridging carboxylate could occur.



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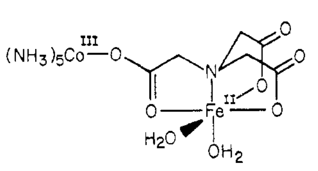
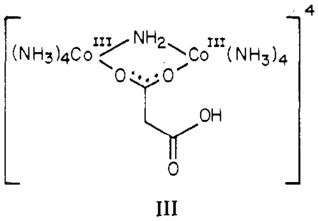
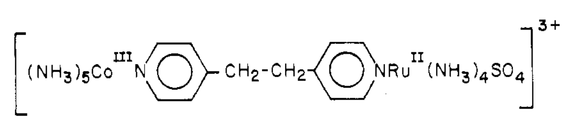


II

Substantial contributions from $[H^+]^{-1}$-dependent paths have been observed in the Cr^{2+} reduction of μ-malonato- and μ-dimethylmalonato-dicobalt(III) complexes of type III and are believed to correspond to acid dissociation with reductant attachment at the remote carboxylate.[2] Furthermore, outer-sphere electron transfer occurring independently of a connecting chain of atoms has been proposed by Taube and colleagues in studies on intramolecular electron transfer in the binuclear complex IV.[3]

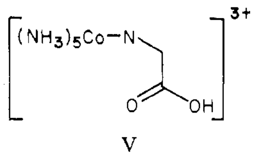


III



IV

This paper reports investigations into the mechanism of reduction of (glycinato-*N*)pentaamminecobalt(III), V, and (β-alaninato-*N*)pentaamminecobalt(III), VI, with Cr^{2+}, V^{2+}, and $Ru(NH_3)_6^{2+}$. The possibility that precursor complex formation occurs with Cr^{2+} and V^{2+} reductant at the remote carboxylate position is investigated.



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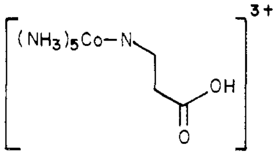

VI

Experimental Section

Reactants. The (glycinato-*N*)pentaamminecobalt(III) complex, $Co(NH_3)_5(NH_2CH_2CO_2H)^{3+}$, was prepared by the literature method previously described.[4] This involved conversion of the azido complex $Co(NH_3)_5N_3^{2+}$ to the tri-*n*-butyl phosphato complex $Co(NH_3)_5(TBP)^{3+}$ and then to the glycine ethyl ester. The latter was hydrolyzed in 2 M HCl and the chloride salt converted to the perchlorate, $[Co(NH_3)_5(NH_2CH_2CO_2H)](ClO_4)_3$. No loss in weight was observed when the sample was left over P_2O_5 in vacuo for 4 days. An identical procedure was used for the preparation of the β-alaninato-*N* analogue, $Co(NH_3)_5(NH_2CH_2CH_2CO_2H)^{3+}$. Completion of the ester hydrolysis

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step in 3 M HCl (~12 h at 20 °C) was confirmed by loss of C_2H_5 ^{1}H NMR peaks. Anal. Calcd for $[Co(NH_3)_5(NH_2CH_2CH_2CO_2H)](ClO_4)_3{\cdot}H_2O$: C, 6.8; H, 4.1; N, 15.8; Cl, 20.0. Found: C, 6.8; H, 4.2; N, 15.5; Cl, 20.0. Dehydration over P_2O_5 in vacuo gave a loss in weight corresponding to a single H_2O. Peak positions λ, nm (ε, M^{-1} cm^{-1}), for the glycinato complex of 340 (54) and 478 (60) were in satisfactory agreement with literature values 342 (54) and 480 (64).[4] Corresponding values for the β-alaninato-*N* complex were 340 (48) and 475 (56). Spectra were identical in 1 M $HClO_4$ and H_2O and are unaffected by deprotonation of the remote carboxylate. Spectra of both the glycinato-*N* and the β-alaninato-*N* complex resemble closely that of $Co(NH_3)_6^{3+}$ with peaks at 339 (47) and 473 (58).[5]

Solutions of the hexaaquo ions Cr^{2+} (ca. 0.5 M) and V^{2+} (ca. 0.2 M) were prepared by electrolytic reduction under N_2 of Cr^{3+} and VO^{2+} perchlorate–perchloric acid solutions at a mercury-pool cathode. Hexaammineruthenium(II) was prepared by reduction of hexaammineruthenium(III) on an amalgamated zinc-shot column. The chloride salt of $Ru(NH_3)_6^{3+}$ (Johnson and Matthey) was purified by recrystallization.[6] Solutions of $Ru(NH_3)_6^{2+}$ in 0.01 M HCl were prepared under argon gas and were used within 1 h. Spectra of $Ru(NH_3)_6^{2+}$, peak 275 nm (ε 624 M^{-1} cm^{-1}), and $Ru(NH_3)_6^{3+}$, peak 275 nm (ε 475 M^{-1} cm^{-1}), are not sufficiently different to provide an accurate means of estimation. Instead $Ru(NH_3)_6^{2+}$ was determined by addition of an aliquot to a solution of μ-superoxo-bis(pentaamminecobalt(III)) in 0.10 M $HClO_4$ and by measuring the change in absorbance at 670 nm (ε 890 M^{-1} cm^{-1}) following 1:1 reaction.[7] Standard air-free techniques involving the use of nylon syringes, stainless steel needles, and rubber seals were used in the transference of reductant solutions.

Lithium perchlorate was prepared by addition of $HClO_4$ (AnalaR) to Li_2CO_3 followed by recrystallization. Lithium chloride (BDH, reagent grade) was recrystallized.

Acid Dissociation Constants. A value $pK_a = 2.43$ (25 °C) has already been reported for the glycinato-*N* complex $Co(NH_3)_5(NH_2CH_2CO_2H)^{3+}$.[4] The pK_a of the β-alaninato-*N* complex $Co(NH_3)_5(NH_2CH_2CH_2CO_2H)^{3+}$ (0.012 g in 10 mL, $[HClO_4] = 0.010$ M, $I = 0.10$ M ($LiClO_4$)) was determined by potentiometric titration at 25 °C using 0.10 M NaOH which gave a value $pK_a = 2.22 \pm 0.04$.

Product Analyses. A full analysis was carried out for the Cr^{2+} reduction of $Co(NH_3)_5(NH_2CH_2CO_2H)^{3+}$. A reactant solution (12 mL; $[HClO_4] = 0.10$ M, $I = 1.00$ M ($LiClO_4$)) with $[Cr^{2+}] = 0.012$ M, $[Co^{III}] = 0.003\,45$ M, was allowed to react at 25 °C for ca. 50 min (4–5 half-lives). After exposure to air the solution was diluted with H_2O (ca. 110 mL) at 0 °C. It was then loaded onto a 50W-X2 Dowex ion-exchange column (5 cm long, 1 cm diameter) at 0 °C. A pink Co^{2+} band was eluted with 0.10 M $HClO_4$ (ca. 250 mL). A second purple band of Cr(III) was eluted with 0.5 M $HClO_4$ (ca. 300 mL) followed by 1.0 M $HClO_4$ (ca. 250 mL). This band became more diffuse as it moved down the column but further separation was not observed. Seven different fractions were collected and analyzed for Cr and N. A third dark green band of Cr(III) dimer, which is formed on air oxidation of excess Cr^{2+}, remained at the top of the column.

To determine the Co^{2+}, 2.5 mL was diluted to 25 mL with concentrated HCl and the absorbance measured at 692 nm (ε 411 M^{-1} cm^{-1}. The Cr was determined by addition of sodium hydroxide to a 10-mL portion to give 1 M NaOH, together with 2–3 drops of H_2O_2 (100 vol). This was then heated to remove excess peroxide (i.e., no effervescence observed on shaking) and made up to standard volume. The chromate was determined spectrophotometrically at 372 nm (ε 4.82×10^3 M^{-1} cm^{-1}). The nitrogen content of Cr solutions was determined by the micro-Kjeldahl method.[8] To 5- or 10-mL aliquots of $CuSO_4$ (0.1 g), K_2SO_4 (0.5 g) and concentrated H_2SO_4 (3–5 mL) were added. Solutions were heated vigorously in a long-necked (Kjeldahl) flask, loosely fitted with a small conical funnel, until they became colorless or pale green (ca. 3 h). The solution was transferred to a steam distillation apparatus and neutralized with the calculated amount (or slight excess) of NaOH, and NH_3 was removed by a flow of steam. The latter was collected in ca. 2% boric acid (25 mL) containing a few drops of screened methyl red indicator. When no further color change was apparent, the solution was titrated against 0.01 M HCl.

Table I. Rate Constants (25 °C) for the Cr^{2+} Reduction of $Co(NH_3)_5(NH_2CH_2CO_2H)^{3+}$, $I = 1.00$ M ($LiClO_4$)

$[H^+]$, M	$10^2[Cr^{2+}]$, M	$10^3[Co^{III}]$, M	10^2k_{obsd}, M^{-1} s^{-1}
0.065	0.6	0.51	15.2
0.08	2.4	1.02	10.8
0.11	2.9	1.29	7.5
0.13	4.5	1.25	7.3
0.13	2.4	1.02	6.9
0.13	0.45	0.51	7.4
0.15	1.1	1.02	6.8
0.25	3.5	3.02	3.7
0.37	5.0	4.53	2.52
0.60	5.3	1.29	1.99
0.82	5.0	4.53	1.23

The above procedure gave 44 μmol of Co^{2+} (calcd 41) and 40 μmol of Cr(III) (corrected for Cr initially present), consistent with a 1:1 stoichiometry. Analyses for N indicated a 1:1 ratio (8% accuracy) of Cr:N, where for the two largest fractions containing 75% of the product agreement was to <4%. The spectrum of the Cr(III) product, peaks at 402 nm (ε 20.4 M^{-1} cm^{-1}) and 560 nm (ε 19.0 M^{-1} cm^{-1}), is similar to that of other O-bonded carboxylatopentaaquochromium(III) species[9] and different from that of $Cr(H_2O)_5NH_3^{3+}$, peaks at 397 nm (ε 19.0 M^{-1} cm^{-1}) and 547 nm (ε 20.5).[10] It is therefore concluded that the product of the Cr^{2+} reduction of $Co(NH_3)_5(NH_2CH_2CO_2H)^{3+}$ at $[H^+] = 0.10$ M is $Cr(H_2O)_5(O_2CCH_2NH_3)^{3+}$. No evidence was obtained for significant amounts of $Cr(H_2O)_6^{3+}$.

Similar product analyses were carried out for the Cr^{2+} reduction of $Co(NH_3)_5(NH_2CH_2CH_2CO_2H)^{3+}$. Reactant conditions were $[Cr^{2+}] = 0.012$ M, $[Co^{III}] = 0.0085$ M, $[HClO_4] = 0.10$ M, and $I = 1.00$ M ($LiClO_4$). The reaction was left for 2 h at 25.0 °C. The slowness of the reaction and likely incidence of Cr^{2+}-catalyzed aquation of the primary Cr(III) products precluded accurate product determination. Substantial formation of $Cr(H_2O)_5(O_2CCH_2CH_2NH_3)^{3+}$ was indicated. Ion-exchange separation of $Cr(H_2O)_5(O_2CCH_2CH_2NH_3)^{3+}$ and $Cr(H_2O)_6^{3+}$ into separate bands was not achieved,[11] but one of the seven fractions, containing ca. 13% of the Cr(III) recovered, gave a 1:1 ratio of Cr:N (5% error), indicating at least partial separation. The spectrum of this fraction gave peaks at 400 nm (ε 23.7 M^{-1} cm^{-1}) and 560 nm (ε 17.6 M^{-1} cm^{-1}). The fractions determined contained 85% of the Cr(III) of which 34% was present as $Cr(H_2O)_5(O_2CCH_2CH_2NH_3)^{3+}$ (based on N determinations) and contained the rest as $Cr(H_2O)_6^{3+}$.

Kinetic Studies. Reactions (all at 25 °C) were monitored at the Co(III) peak at 475 nm. The stopped-flow technique was used for the V^{2+} and $Ru(NH_3)_6^{2+}$ reductions of $Co(NH_3)_5(NH_2CH_2CO_2H)^{3+}$, and conventional spectrophotometry was used in all other cases. The reductant was in large (≥8-fold) excess. First-order plots of absorbance (*A*) changes log Δ*A* against time were linear for at least 2 half-lives with Cr^{2+} and V^{2+} as reductants, $I = 1.00$ M ($LiClO_4$). Rate constants were obtained from slopes (×2.303). A linear dependence on reductant was observed, and hence second-order rate constants were obtained. Because of solubility problems we chose to use Cl^- rather than ClO_4^- salts for making up $Ru(NH_3)_6^{2+}$ reaction solutions. Rate constants for the β-alaninato-*N* complex gave little variation with increasing amounts of chloride, $I = 0.10$–1.00 M, and we have no reason to believe that there is a significant Cl^- catalysis. For the slower reactions (particularly with β-alaninato-*N*) at $[H^+] \geq 0.25$ M and with $I \geq 0.5$ M (LiCl) blue colors formed after a 30-min reaction. To minimize these side effects, a lower range of $[H^+]$ and $I = 0.10$ M was adopted for most of the β-alaninato-*N* study. Acceptable runs gave plots linear to >60% completion using calculated A_∞ values.

Treatment of Data. For stopped-flow runs rate constants from three traces were averaged. An unweighted standard least-squares fit of data was used in all cases.

Results

Reduction of the Glycinato-*N* Complex. Rate constants k_{obsd} (Table I) for the Cr^{2+} reduction of $Co(NH_3)_5(NH_2CH_2CO_2H)^{3+}$ give a fit to eq 1, where $k_1 = (1.23 \pm 3.6)$

$$k_{obsd} = k_1 + k_2[H^+]^{-1} \qquad (1)$$

$\times 10^{-3}$ M^{-1} s^{-1} is small and uncertain in magnitude (Figure 1) and $k_2 = (9.25 \pm 0.45) \times 10^{-3}$ s^{-1}. For the V^{2+} reduction (Table II), the same dependence applies, eq 2, with $k_3 = 0.41$

$$k_{obsd} = k_3 + k_4[H^+]^{-1} \qquad (2)$$

Table II. Rate Constants (25 °C) for the V^{2+} Reduction of $Co(NH_3)_5(NH_2CH_2CO_2H)^{3+}$, $I = 1.00$ M ($LiClO_4$)

$[H^+]$, M	$10^2[V^{2+}]$, M	$10^3[Co^{III}]$, M	k_{obsd}, $M^{-1}\ s^{-1}$
0.073	0.70	0.30	1.83
0.080	0.70	0.30	1.80
0.080	1.99	0.78	1.56
0.100	1.60	0.78	1.62
0.100	2.50	0.78	1.48
0.125	2.50	0.78	1.28
0.200	1.66	0.78	0.93
0.200	0.50	0.99	0.85
0.200	1.40	0.78	0.98
0.500	1.66	0.70	0.66
0.660	1.66	0.78	0.64
0.950	1.66	0.82	0.43

Table III. Rate Constants (25 °C) for the $Ru(NH_3)_6^{2+}$ Reduction of $Co(NH_3)_5(NH_2CH_2CO_2H)^{3+}$, $I = 1.00$ M (LiCl)

$[H^+]$, M	$10^3[Ru(NH_3)_6^{2+}]$, M	$10^4[Co^{III}]$, M	k_{obsd}, $M^{-1}\ s^{-1}$
0.03	5.7	3.8	1.34
0.05	4.0	3.4	1.32
0.05	3.3	3.8	1.25
0.10	3.5	3.4	1.41

Table IV. Rate Constants (25 °C) for the Cr^{2+} Reduction of $Co(NH_3)_5(NH_2CH_2CH_2CO_2H)^{3+}$, $I = 1.00$ M ($LiClO_4$)

$[H^+]$, M	$10^2[Cr^{2+}]$, M	$10^3[Co^{III}]$, M	10^4k_{obsd}, $M^{-1}\ s^{-1}$
0.12	4.7	4.0	12.4
0.16	9.4	2.1	11.4
0.20	1.3	1.1	10.3
0.37	2.4	2.6	9.5
0.37	5.3	2.2	9.0
0.83	4.7	4.0	8.6
0.86	3.9	3.1	8.8

Table V. Rate Constants (25 °C) for the V^{2+} Reduction of $Co(NH_3)_5(NH_2CH_2CH_2CO_2H)^{3+}$, $I = 1.00$ M ($LiClO_4$)

$[H^+]$, M	$10^2[V^{2+}]$, M	$10^3[Co^{III}]$, M	10^2k_{obsd}, $M^{-1}\ s^{-1}$
0.098	2.03	2.16	8.4
0.150	2.03	2.16	5.5
0.200	0.50	0.35	5.4
0.40	3.78	3.14	3.9
0.93	2.03	2.16	3.0

Table VI. Rate Constants (25 °C) for the $Ru(NH_3)_6^{2+}$ Reduction of $Co(NH_3)_5(NH_2CH_2CH_2CO_2H)^{3+}$, $I = 0.10$–1.00 M (LiCl)

$[H^+]$, M	I, M	$10^3[Ru(NH_3)_6^{2+}]$, M	$10^4[Co^{III}]$, M	$10^2 \times k_{obsd}$, $M^{-1}\ s^{-1}$
0.0075	0.10	2.14	3.52	5.2
0.0075	0.10	0.78	3.52	5.8
0.01	0.10	2.40	3.52	4.8
0.01	0.10	4.05	4.05	6.3
0.05	0.10	5.64	3.40	5.3
0.01	0.50	5.44	3.41	5.3
0.01	1.00	5.70	8.35	6.4

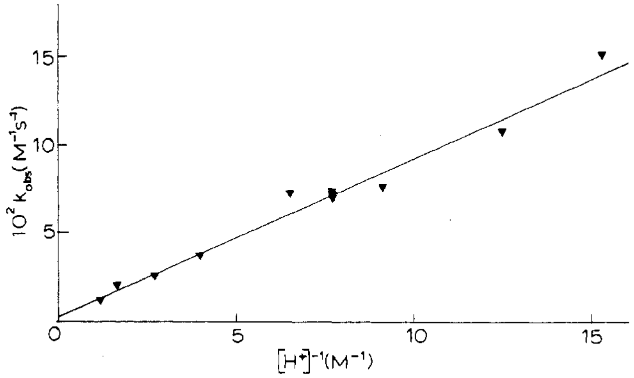


Figure 1. Dependence of rate constants k_{obsd} on $[H^+]^{-1}$ for the Cr^{2+} reduction of (glycinato-*N*)pentaamminecobalt(III) at 25 °C, $I = 1.00$ M ($LiClO_4$).

± 0.06 $M^{-1}\ s^{-1}$ and $k_4 = 0.106 \pm 0.008\ s^{-1}$. No $[H^+]$ dependence was observed in the reaction with $Ru(NH_3)_6^{2+}$, Table III, and $k_5 = 1.33 \pm 0.06\ M^{-1}\ s^{-1}$.

Reduction of the β-Alaninato-*N* Complex. Although appreciably slower, similar $[H^+]$ dependences were observed. Thus, the Cr^{2+} reduction (Table IV) conforms to (1) with $k_1' = (7.9 \pm 0.2) \times 10^{-4}\ M^{-1}\ s^{-1}$ (an appreciable intercept) and $k_2' = (5.2 \pm 0.5) \times 10^{-5}\ s^{-1}$. With V^{2+} (Table V), eq 2 applies, and $k_3' = (2.36 \pm 0.03) \times 10^{-2}\ M^{-1}\ s^{-1}$ and $k_4' = (5.6 \pm 0.6) \times 10^{-3}\ s^{-1}$. Most of the $Ru(NH_3)_6^{2+}$ runs were at $I = 0.10$ M (LiCl) and gave $k_5' = (5.5 \pm 0.6) \times 10^{-2}\ M^{-1}\ s^{-1}$. The rate constant at $I = 1.00$ M (LiCl) is of similar magnitude where k_5 = ca. $6.5 \times 10^{-2}\ M^{-1}\ s^{-1}$, Table VI.

Discussion

Quantitative formation of a Cr(III) complex, which gives a 1:1 ratio of Cr:N, is observed in the Cr^{2+} reduction of $Co(NH_3)_5(NH_2CH_2CO_2H)^{3+}$. Visible absorption spectra are in accordance with formation of the pentaaquo O-bonded glycinato complex $Cr(H_2O)_5(O_2CCH_2NH_3)^{3+}$. If the ammine group were coordinated, peaks in the spectrum would be shifted to lower wavelengths. At $[H^+] = 0.10$ M the kinetics (k_1 and k_2) indicate >98% of the reaction proceeds by k_2. Consistent with this, no $Cr(H_2O)_6^{3+}$ product was detected. Product separation at higher $[H^+]$, when formation of as much as 10% $Cr(H_2O)_6^{3+}$ is predicted, presents difficulties owing to the increasing slowness of the reaction and likely incidence of Cr^{2+}-catalyzed aquation of the primary Cr(III) product.[12] The same is true of the Cr^{2+} reduction of $Co(NH_3)_5(NH_2CH_2CH_2CO_2H)^{3+}$, where, although k_1' makes a larger relative contribution, the overall rates are ca. 10^2 slower than for the glycinato complex at $[H^+] = 0.10$ M. The O-bonded β-alaninato product $Cr(H_2O)_5(O_2CCH_2CH_2NH_3)^{3+}$ was identified and constitutes at least 34% of the product under the conditions investigated. The expected yield based on rate constants k_1' and k_2' is 40% at $[H^+] = 0.10$ M.

Formation of O-bonded products clearly implicates binding of the Cr^{2+} reductant at the remote carboxylate group. Although weak interaction with the carbonyl group is possible when the carboxylate is protonated, we have no reason to

Table VII. Summary of Kinetic Data, 25 °C, $I = 1.00$ M ($LiClO_4$)

Oxidant	Reductant	Rate constants: $M^{-1}\ s^{-1}$ [a]	Rate constants: s^{-1} [b]
$Co(NH_3)_5(NH_2CH_2CO_2H)^{3+}$	Cr^{2+}	Ca. 1.23×10^{-3} (k_1)	9.3×10^{-3} (k_2)
	V^{2+}	0.41 (k_3)	0.106 (k_4)
	$Ru(NH_3)_6^{2+}$	1.33 (k_5)	
$Co(NH_3)_5(NH_2CH_2CH_2CO_2H)^{3+}$	Cr^{2+}	7.9×10^{-4} (k_1')	5.2×10^{-5} (k_2')
	V^{2+}	2.36×10^{-2} (k_3')	5.6×10^{-3} (k_4')
	$Ru(NH_3)_6^{2+}$	5.5×10^{-2} (k_5')[c]	

[a] $[H^+]$-independent path. [b] $[H^+]^{-1}$-dependent path. [c] $I = 0.10$ M (LiCl).

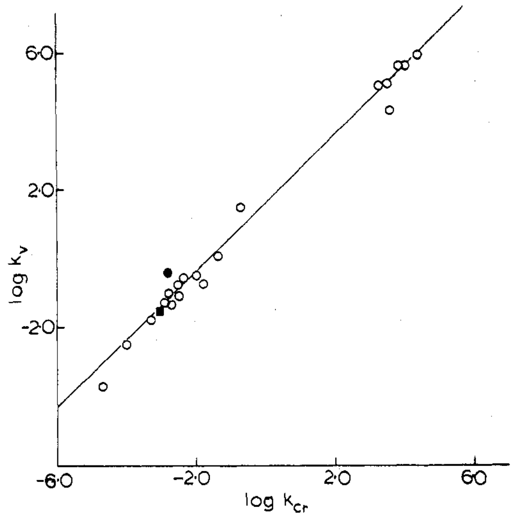


Figure 2. Correlation of existing literature rate constants (○) for Cr^{2+} (k_{Cr}) and V^{2+} (k_V) reduction of a common oxidant (mononuclear or binuclear Co(III) complexes); see ref 13. The point ● is with $Co(NH_3)_5(NH_2CH_2CO_2H)^{3+}$ as oxidant (k_1 and k_3, where k_1 carries a large error), and the point ■ with $Co(NH_3)_5(NH_2CH_2CH_2CO_2H)^{3+}$ (k_1' and k_3') as oxidant.

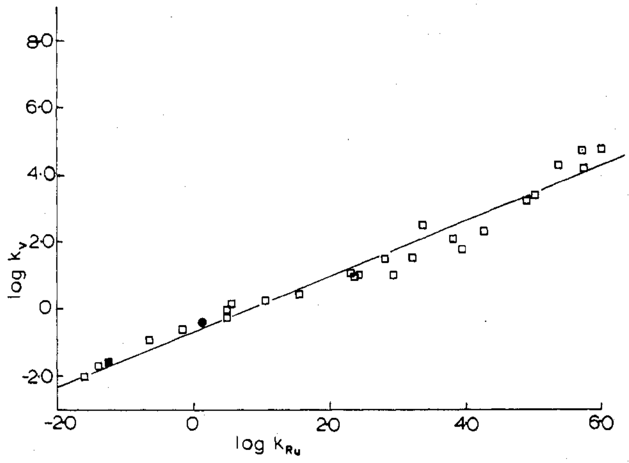
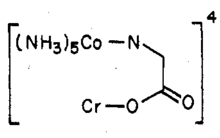


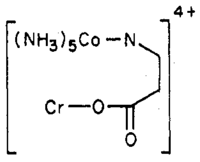
Figure 3. Correlation of existing literature rate constants (□) for V^{2+} (k_V) and $Ru(NH_3)_6^{2+}$ (k_{Ru}) reduction of a common oxidant (Co(III) complexes); see ref 15. The point ● is with $Co(NH_3)_5(NH_2CH_2CO_2H)^{3+}$ as oxidant (k_3 and k_5), and the point ■ with $Co(NH_3)_5(NH_2CH_2CH_2CO_2H)^{3+}$ (k_3' and k_5') as oxidant.

believe that such a path makes a significant contribution. The rate constants k_1' and k_3' (Table VII) for the β-alaninato complex give a ratio 0.034 which is consistent with values previously reported for outer-sphere electron transfer (ca. 0.020). Satisfactory agreement with the existing correlation of rate constants for outer-sphere Cr^{2+} and V^{2+} reactions is also observed with k_1 and k_3 (ratio ca. 0.022), Figure 2. Since $Ru(NH_3)_6^{2+}$ is substitution inert it is assumed to react by an outer-sphere mechanism.[14] Rate constants k_3 and k_5 (ratio 0.31) and k_3' and k_5' (ratio 0.43) are also in close agreement with the existing correlation of data for outer-sphere V^{2+} and $Ru(NH_3)_6^{2+}$ reactions, Figure 3.[15]

The $Ru(NH_3)_6^{2+}$ reactant cannot benefit by attachment at the remote carboxylate, and it is of interest that rate constants remain unchanged even at $[H^+] = 0.0075$ M when ca. 70% of the β-alaninato-*N* complex is unprotonated. It follows that outer-sphere rate constants for the reaction of protonated and unprotonated species are of similar magnitude. It is concluded that attachment of the labile Cr^{2+} and V^{2+} reductants at the unprotonated carboxylate is responsible for the $[H^+]^{-1}$-dependent pathway, and this is confirmed in the Cr^{2+} case by product analyses. The chain of atoms linking the reductant and oxidant is saturated however and is unable to assist in electron transfer, which must therefore occur over intervening space as in an outer-sphere reaction. Since the chain of atoms linking the two metals is flexible, the distance of separation is variable. Close approach is possible as illustrated for glycinato-*N* (VII) and β-alaninato-*N* (VIII) ligands.



VII



VIII

The greater number of unfavorable positions the chain can adopt in the case of β-alaninato-*N* is expected to contribute to the slower rate constant ($k_2/k_2' = 180$). Interestingly, k_2 and k_4 (as well as k_2' and k_4') also conform reasonably well to the correlations in Figure 2. This may not be meaningful, however. Thus, the full mechanism may be written as in eq 3–5 where M^{2+} is the reductant Cr^{2+} or V^{2+}. If the acid

$$\text{CoN}\!\sim\!\sim\!\text{H} \overset{K_a}{\rightleftharpoons} \text{CoN}\!\sim\!\sim + \text{H}^+ \tag{3}$$

$$\text{CoN}\!\sim\!\sim + \text{M}^{2+} \overset{K}{\rightleftharpoons} \text{CoN}\!\sim\!\sim\!\text{M} \tag{4}$$

$$\text{CoN}\!\sim\!\sim\!\text{M} \xrightarrow{k_{et}} \tag{5}$$

dissociation constant (K_a) for the glycinato-*N* complex is taken into account, rate constants (25 °C) of 2.5 $M^{-1}\ s^{-1}$ (for Cr^{2+}, k_2/K_a) and 28 $M^{-1}\ s^{-1}$ (for V^{2+}, k_4/K_a) are obtained. It can be assumed in the case of Cr^{2+} that (4) is rapid; hence, $k_{et}K = 2.5\ M^{-1}\ s^{-1}$. For V^{2+} the same assumption does not hold since V^{2+} is much less labile,[16] and a rate constant of 28 $M^{-1}\ s^{-1}$ is perfectly acceptable for a V^{2+} substitution-controlled process; i.e., the forward reaction in (4) may be rate determining. Similar discussion holds for the β-alaninato-*N* complex, $k_4'/K_a = 1.1\ M^{-1}\ s^{-1}$, although here the case for a substitution-controlled process is less strong.

Knowledge of K for (4) with Cr^{2+} as reductant allows the intramolecular electron-transfer rate constant k_{et} to be determined. An estimate only, K = ca. 10 M^{-1}, is available for the complexing of Cr^{2+} with carboxylates.[17] This gives $k_{et} = 0.25\ s^{-1}$ for glycinato, and by a similar procedure $k_{et} = 0.001\ s^{-1}$ for the β-alaninato complex. We further note that the ratios k_2/k_5 and k_2'/k_5' do not conform to a log k_{Cr} against log k_{Ru} outer-sphere correlation. Although reactions with both reductants fall within the outer-sphere definition, with $Ru(NH_3)_6^{2+}$ the reaction does not benefit from coordination at the remote carboxylate.

Finally, this study would seem to add weight to the interpretation given for the Cr^{2+} reduction of μ-amido-μ-malonato-bis(tetraamminecobalt(III)). It is noted that the $[H^+]^{-1}$ contribution makes a much larger contribution in the latter than for the di-μ-hydroxo-μ-malonato-bis(triamminecobalt(III)) complex. Closer approach of the pendant carboxylate of the malonate to the Co(III)'s is possible in the former case.

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Registry No. $Co(NH_3)_5(NH_2CH_2CO_2H)^{3+}$, 66183-84-4; $Co(NH_3)_5(NH_2CH_2CH_2CO_2H)^{3+}$, 66183-83-3; $Co(NH_3)_5(NH_2CH_2CH_2CO_2H)](ClO_4)_3$, 14974-22-2; $Cr(H_2O)_5(O_2CCH_2NH_3)^{3+}$, 60745-67-7; $Cr(H_2O)_5(O_2CCH_2CH_2NH_3)^{3+}$, 66183-82-2; Cr^{2+}, 22541-79-3; V^{2+}, 15121-26-3; $Ru(NH_3)_6^{2+}$, 19052-44-9.

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Structures of Metallocarboranes. 8. Crystal and Molecular Structure of the 11-Vertex Heterobimetallocarborane 1,8-Di-η-cyclopentadienyl-1-ferra-8-cobalta-2,3-dicarbaundecaborane(9), 1,8-(η-C_5H_5)$_2$-1-Fe-8-Co-2,3-$C_2B_7H_9$[1]

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The crystal and molecular structure of 1,8-(η-C_5H_5)$_2$-1-Fe-8-Co-2,3-$C_2B_7H_9$ has been determined by three-dimensional x-ray diffraction techniques. The compound crystallizes in the monoclinic space group $P2_1/c$ with a = 7.923 (1) Å, b = 13.474 (3) Å, c = 14.707 (4) Å, β = 107.10 (3)°, and Z = 4. Observed and calculated densities are 1.58 (2) and 1.57 g cm^{-3}, respectively. Diffraction data to $2\theta_{\max}$ = 45° (Mo Kα radiation) were collected on a Syntex $P\bar{1}$ automated diffractometer, and the structure was solved by conventional Patterson, Fourier, and full-matrix least-squares techniques to a final discrepancy index of R = 0.04 for the 1346 independent nonzero reflections. All atoms, including hydrogens, were located, and the iron and cobalt atoms were unambiguously differentiated. Although it is one electron short of the ideal $2n + 2$ electrons for closo polyhedral bonding, the molecule has the closo 11-vertex octadecahedral geometry with the iron atom in the six-coordinate vertex, the two carbon atoms located at the four-coordinate vertices, and the cobalt atom situated in a five-coordinate position, adjacent to a carbon atom and nonadjacent to the iron vertex. The molecule exhibits some unusual bond length asymmetries.

Introduction

Polyhedral metallocarboranes containing two different transition-metal vertices can be prepared by use of either polyhedral expansion[2] or polyhedral subrogation[3] reactions on previously prepared metallocarboranes.[4] When the 10-vertex compound 2-(η-C_5H_5)-2-Co-1,6-$C_2B_7H_9$[5] was subjected to polyhedral expansion conditions with $FeCl_2$ and $C_5H_5^-$, the 11-vertex complex $(C_5H_5)_2CoFeC_2B_7H_9$ was isolated.[4] According to commonly accepted electron-counting rules,[6,7] this complex has one electron less than required for idealized closo octadecahedral geometry. In $(C_5H_5)_2Fe_2C_2B_6H_8$, which is two electrons short of the required $2n + 2$ (where n is the number of vertices in the polyhedron), a large distortion from the usual 10-vertex bicapped square antiprism geometry was observed.[8] To assess the effect of a one-electron deficiency, the x-ray structural determination of $(C_5H_5)_2FeCoC_2B_7H_9$ was undertaken.

Experimental Section

Crystals of the title compound were kindly provided by Dr. W. J. Evans, who prepared them by the polyhedral expansion of 2-(η-C_5H_5)-2-Co-1,6-$C_2B_7H_9$ with $FeCl_2$ and $C_5H_5^-$.[4] Spectroscopic studies (^{1}H and ^{11}B NMR) on this compound and on the reduced diamagnetic Fe(II) species were consistent with the proposed octadecahedral geometry, but the precise locations of the two metal atoms could not be determined by these methods.

A single crystal of dimensions 0.1 × 0.2 × 0.3 mm was selected for crystallographic investigation and mounted on a glass fiber enclosed in a thin-walled glass capillary. Preliminary oscillation and Weissenberg photographs indicated that the compound crystallized in space group $P2_1/c$ with systematic absences of the type $h0l$, $l \neq 2n$, and $0k0$, $k \neq 2n$.

The crystal was transferred to a Syntex $P\bar{1}$ automated diffractometer, and 12 automatically centered reflections were used to accurately determine the unit cell parameters as a = 7.923 (1) Å, b = 13.474 (3) Å, c = 14.707 (4) Å, and β = 107.10 (3)°. A graphite crystal was used to provide monochromatic Mo Kα radiation (0.71069 Å). The sample density was found to be 1.58 (2) g cm^{-3} by flotation, while the calculated density was 1.57 g cm^{-3} (Z = 4).

Intensity data were collected with a θ–2θ scan technique to a limit of 2θ = 45° and with a takeoff angle of 4°. Reflections were scanned at a constant rate of 2.4°/min from 1.0° below the Kα_1 reflection to 1.0° above the Kα_2 reflection. Backgrounds were measured at each end of the scan. The total time spent counting background radiation was equal to the scan time for each reflection. The intensities of three standard reflections were measured every 97 reflections to monitor the tube efficiency and possible crystal deterioration. No significant deviations were observed.

The data were corrected for Lorentz and polarization effects and for absorption (T = 0.76–0.85).[9] The intensity of a reflection, $I(hkl)$, and $\sigma[I(hkl)]$, its estimated standard deviation, were calculated according to the equations $I = CT - (t_c/t_b)(B_1 + B_2)/2$ and $\sigma(I) =$

0020-1669/78/1317-1658$01.00/0