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Chromium(II) Reductions of N,O-Chelated (Amino Acidato)tetraamminecobalt(III) Ions – a reinvestigation [1]

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The rate and activation parameters for the Cr(II) reductions of N,O-chelated (glycinato)- and (D,L-alanato)tetraamminecobalt(III) ions have been redetermined and the corresponding D,L-phenylalanato complex investigated for the first time. The reactions are inner sphere and exhibit simple, mixed second order kinetics with k s, M^{-1} s^{-1} ($\Delta H^{\ddagger}$, Kcal/mol; $\Delta S^{\ddagger}$, cal/deg mol): 6.4 ± 0.24 (7.1 ± 0.58; −31 ± 2.1), 1.7 ± 0.12 (9.2 ± 0.73; −27 ± 2.4) and 2.3 ± 0.32 (10.1 ± 0.85; −23 ± 2.5), respectively. These results are discussed in relation to other amino acid bridged Co(III)–Cr(II) reactions.

Introduction

Kopple and Svatos [2] were the first investigators to report the chromium(II) reductions of amino acid complexes of cobalt(III). They reported the reductins of glycine, N-acetylglycine and γ-acetylaminobutyrate, as well complexes of pentaamminecobalt(III). Subsequently, Holwerda, Deutsch, and Taube [3] examined the kinetic effect of sequentially methylating the amine nitrogen of the glycine complex. More recently Bembi and Malik [4] reported the variations in rates among pentaammine complexes of several of the naturally occurring amino acids; and Ogino, Tsukahara, and Tanaka [5] examined the effect of moving the amino group away from the adjacent carboxylate center. Finally, the chromium(II) reductions of N-bonded blycine- and β-alaninepentaamminecobalt(III) were examined by Glennon, Edwards, and Sykes [6].

Historically, the first chromium(II) reduction of an N,O-chelated amino acid complex of cobalt(III) was that of glycinatobis(ethylenediamine)cobalt(III) studied by Gilroy, Sedor, and Bennett [7]. Several studies, one by Balahura and Lewis [8] and one by Williams and Pennington [9], were directed at examining kinetic effects of various substituents on the alpha carbon.

Prior to 1977 only one chromium(II) reduction of an amino acid tetraamminecobalt(III) complex, the *cis*-(N-acetylglycine)aquotetraamminecobalt(III) ion, had been studied [10]. Just prior to the publication of the last noted series of bis(ethylenediamine) complexes Malik, Bembi, and Sushila [11] reportedly examined the chromium(II) reductions for a series of chelated (amino acidato)tetraamminecobalt(III) species. However, two serious objections to that study are to be noted: 1) The reported rate constants were nearly 100X slower than their corresponding bis(ethylenediamine) counterparts [7, 9], whereas the chelate effect [12] in inner-sphere electron transfer reactions would have predicted them to be larger; 2) The first maxima in the visible absorption spectra for the complexes reported are not consistent with CoN_5O chromophores. Herein are reported the results of a reinvestigation of two reactions in that series of tetraammine complexes, along with that for the related D,L-phenylalanine complex.

Experimental

Materials

The glycinato- and D,L-alanatotetraamminecobalt(III) complexes were prepared by the method of Shimura [13] with some modification. A mass equal to 2.7×0^{-2} mol of the amino acid and 1.0 g (9.3×10^{-3} mol) of sodium carbonate were dissolved in approximately 6 ml of deionized water. To this solution was added 7.4 g (2.7×10^{-2} mol) of chloroaquatotetraamminecobalt(III) sulfate [14], 0.5 g of charcoal, and 0.5 ml concentrated aqueous ammonia. The resulting solution was evaporated nearly to dryness on a hot plate at 80 °C with stirring. Approximately 50 ml of deionized water was added with stirring and insoluble materials were removed by filtration through a celite filter mat.

The filtrate was charged onto an ion-exchange column (3 × 40 cm) of Dowex 50W-X1 (50–100

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mesh, H^+ form). The column was washed with water until the washings were clear of anionic and neutral species. One or more of the deep red bis(glycinato)-diamminecobalt(III) complexes were eluted with 0.55 *M* $HClO_4$. There was very little bis(alanato)-diamminecobalt(III) species observed. The desired 2+ charged complexes were eluted rapidly with 2.0 *M* $HClO_4$. The eluted solutions were concentrated at 30 °C until crystals first appeared. The solutions were then cooled in a freezer at −10 °C until crystallization was complete. The red-orange glycinate and pink alanate complexes were filtered, washed with absolute alcohol and ether, and air dried.

Visible spectra: λ_{max} nm, (ϵ M^{-1} cm^{-1}) $[Co(NH_3)_4(gly)]^{2+}$ 493 (74.8), 356 (88.8); lit. [13] 493 (72.4), 347 (85.1), $[Co(NH_3)_4(D,L\text{-ala})]^{2+}$ 493 (73.2), 348 (86.0); lit. [13] 488 (74.1), 346 (79.4). ^1H NMR (downfield DDS): $[Co(NH_3)_4gly]^{2+}$ −3.61 ppm; $[Co(NH_3)_4(D,L\text{-ala})]^{2+}$ −1.40, 1.51 ppm. Both complexes were recrystallized from water before use.

Two different literature procedures [15, 16] for preparation of the D,L-phenylalanatotetraamminecobalt(III) complex proved unsuccessful in our hands. The desired complex was prepared by the following procedure. A mixture of 6.9 g (4.2×10^{-2} mol) of D,L-phenylalanine and 11 ml of concentrated aqueous ammonia in 20 ml of deionized water was warmed with stirring on a hot plate at 35 °C until the amino acid had dissolved. A solution of 10 gm (4.2×10^{-2} mol) hexaaquocobalt(II) chloride in 10 ml of deionized water was added. Ten g of lead dioxide was added and the mixture warmed to 60 °C. After 30 min an additional 10 gm of PbO_2 was added and the mixture kept at 60 °C for an additional hour. Water was added at intervals to maintain the volume. At the end of the heating period the mixture, which had a slight benzaldehyde odor, was cooled, filtered through a Celite mat and the residue washed with water until the washings were nearly colorless. The filtrate and washings were combined and the desired pink complex isolated as above. Visible spectrum: 492 (75.8) 347 (92.4); lit. [16b] 495 (81.3), 348 (97.7). ^1H NMR: 2.18, 3.23, 7.41 ppm.

Solutions of sodium perchlorate, perchloric acid, and chromium(II) perchlorate were prepared from reagent chemicals as described previously [17]. Tap deionized water was distilled from alkaline permanganate and then from dilute sulfuric acid in an all Pyrex apparatus. This water, referred to as triply distilled water was stored in stoppered, all Pyrex bottles.

Kinetics

Kinetics experiments were performed by pipetting aliquots of a solution of cobalt(III) complex, perchloric acid, sodium perchlorate, and triply distilled water into a five centimeter cylindrical spectrophotometer cell. The cell was capped with a self-sealing rubber septum and the contents purged with water-saturated, prepurified argon (delivered through a 3″ stainless steel needle) for 15–20 minutes. Because of the cell design, in some experiments an additional quantity of deaerated, triply distilled water was added via syringe. After the cell and contents had come to reaction temperature in a thermostatted cell compartment of a Cary 14 recording spectrophotometer, a thermostatted aliquot of chromium(II) solution was injected into the cell via simple transfer syringe techniques. The cell was momentarily removed from the compartment, inverted and shaken vigorously to insure thorough mixing, and returned to the compartment for continuous absorbance measurements. This manipulation generally required less than 10 seconds.

After the absorbance had become constant, the cell cap was removed and a thermometer (±0.1 °C, very near reaction temperature) was inserted into the neck of the cell and allowed to equilibrate whereupon the temperature was recorded. The gap in the cell compartment was covered with a towel during this procedure.

Most of the kinetics runs were conducted with chromium(II) in excess. In some cases, this excess was large enough (>10×) such that pseudo-first order kinetics were obeyed. Under these conditions plots of $\ln(A_t - A_\infty)$ *vs.* time (A_t and A_∞ are the absorbances at time t and the final constant absorbance, respectively) were linear through three half-lives. The mixed second order rate constants were obtained from the pseudo-first order constant by the relationship $k^{2nd} = k^{1st}/[Cr(II)]_{avg}$, where $[Cr(II)]_{avg}$ is the average chromium concentration over the first two half-lives.

In most of the experiments where the excess of chromium(II) was low, equation 1 [18] was utilized.

$$\ln\{1 + [(A_o - A_\infty)/(A_t - A_\infty)](B_o - A_o)/A_o\} = \ln(B_o/A_o) + (B_o - A_o)k^{2nd}t \qquad (1)$$

Here A_o, A_t, and A_∞ are the respective absorbances initially, at time t, and finally. B_o and A_o are the initial concentrations with B being the excess reactant. Plots of the function of the left side of the equation *vs.* t were linear through three half-lives.

Stoichiometries

The stoichiometries of the reactions were determined by preparing solutions of the cobalt(III) complex in dilute perchloric acid in 30 ml serum bottles. These bottles were capped with self sealing rubber septa and deaerated with prepurified argon. A slight excess (approximately 10–15%) of chromium(II) was added via syringe. After the solutions were allow-

TABLE I. Stoichiometries of $[Co(NH_3)_4(AA\text{-}N,O)]^{2+}$–$Cr^{2+}$ Reactions and Spectral Maxima of Chromium(III) Products.

	Amino Acid	mmol Cr(III) reacted	mmol Co(II) recovered	mmol Cr(III) recovered
1.	glycine	0.207	0.210	0.207
		0.190	0.168	0.188
	λ_{max}, nm (ϵ, M^{-1} cm^{-1}) Cr(III) product: 572(20.8), 410(20.8)			
2.	D,L-alanine	0.200	0.201	0.175
		0.206	0.194	0.195
	λ_{max}, nm (ϵ, M^{-1} cm^{-1}) Cr(III) product: 572(22.4), 410(20.9)			
3.	D,L-phenylalanine	0.172	0.151	0.170
		0.172	0.160	0.174
	λ_{max}, nm (ϵ, M^{-1} cm^{-1}) Cr(III) product: 572(20.6), 410(20.4)			

ed to react for ten half-lives, the bottles were opened to the air to oxidize the excess chromium(II). The solutions were then diluted and charged onto an ion-exchange column (1 X 5 cm) of Sephadex C-25 (Na^+/H^+ form). The cobalt(II) was eluted with 0.1 *M* $NaClO_4$/0.1 *M* $HClO_4$ and the chromium(III) produced during the reaction eluted with 0.5 *M* $NaClO_4$/0.1 *M* $HClO_4$ [19]. The excess chromium(II) which had been air oxidized remained on the column as $[Cr(H_2O)_4OH]_2^{4+}$.

The quantity of cobalt(II) recovered was determined by diluting a small sample (<3 ml) in a 25 ml volumetric flask with concentrated hydrochloric acid. The absorbance was determined at 675 nm (ϵ = 440 M^{-1} cm^{-1}). The quantity of trivalent chromium(III) recovered was determined by oxidation to CrO_4^{2-} with alkaline peroxide ($\epsilon_{372\,nm}$ = 4815 M^{-1} cm^{-1}) [20].

^1H *NMR Spectra*

The ^1H NMR spectra of the cobalt(III) complexes were recorded on a JEOL FX-60 NMR instrument at 59.75 *M* Hz in the FT mode using an 8 K transform and 100 Hz spectral width. The pulse width was 80°. The samples consisted of 1–6 mg of complex dissolved in 1 ml D_2O with either DSS (2,2-dimethyl-2-silapentane-5-sulfonate) or tert-butyl alcohol as a standard. All of the chemical shifts reported are referenced to DSS. Signals due to the amine groups and ammonia were not observed due to their rapid exchange with solvent in neutral solution. All of the signals were rather broad and weak. No evidence of splitting was observed.

Results and Discussion

In addition to the use of known procedures for the preparations of the glycinato- and the (D,L-alanato)-tetraamminecobalt(III) complexes, ion-exchange purification of these and the corresponding D,L-phenylalanato complex, and consistent visible absorption spectra within the series and with published literature the PMR results were further used to characterize the complexes. A chemical shift of 3.61 ppm (from DSS) was observed for the methylene protons of the N,O-bonded glycinato complex in good agreement with that (3.65 ppm) observed by Buckingham, Durham and Sargeson [21] for the (glycinato)bis-(ethylenediamine)cobalt(III) complex. Extremely low solubilities of the (D,L-alanato)- and (D,L-phenylalanato)tetraamminecobalt(III) complexes in D_2O and DSS necessitated the recording of the chemical shifts of these species with tert-butyl alcohol rather than DSS as the standard. The chemical shifts were then referenced to DSS for purposes of comparison. No chemical shifts were observed for the alpha carbon hydrogen in either complex. However, for the D,L-alanine complex there were two resonances at 1.40 and 1.51 ppm which are interpreted to be a doublet arising from α-H splitting (J = 6.6 cps) of the methyl resonance by analogy to (D,L-alanato)bis-(ethylenediamine)cobalt(III) [21]. The related O-bonded (L-alanato)pentaamminecobalt(III) exhibits only one resonance with a chemical shift of 1.43 ppm due to the β-CH_3 group [22]. Sakaguchi, Morito and Yoneda [22] have reported a similar solubility difficulty for the L-phenylalanato complex in D_2O and DSS; however, they obtained a complete set of resonances with chemical shifts of 4.00 (α-H), 3.18 and 3.29 (β-Hs), and 7.493 ppm (C_6H_5-). For the D,L-phenylalanato complex in the present study a single resonance showing a chemical shift of 3.23 ppm was observed for the β-H's along with the phenyl resonance of chemical shift 7.41 ppm and an extraneous one shifted 2.18 ppm.

In Table I are shown the results of the stoichiometric studies and the visible absorption maxima of

TABLE II. Kinetics Experiments for the Reactions of N,O-Chelated (Amino Acidato)Tetraamminecobalt(III) Complexes with Chromium(II) at $\Sigma[ClO_4^-] = 1.0\,M$ and $[H^+] = 0.93\,M$.[a]

Amino Acidato	Run No.	t, °C[b]	10^3 [Co(III)]$_o$ M	10^3 [Cr(II)]$_o$ M		k[c] M^{-1} s^{-1}
Glycinate	1.	25.0	0.220	2.30		6.64[d]
	2.	24.9	1.36	18.3		6.19
	3.	25.0	1.75	8.87		6.35
	4.	25.1	1.75	8.87		6.77
	5.	25.0	1.81	9.17		6.20[e]
	6.	25.1	2.40	9.17		6.63
	7.	25.0	4.37	8.87		6.24
					avg.	6.4 ± 0.24[f]
	8.	19.0	0.807	15.3		5.54
	9.	19.1	2.42	7.67		5.29
	10.	19.0	2.42	15.3		5.43
					avg.	5.4 ± 0.10[f]
	11.	10.9	2.30	9.70		3.35
	12.	10.9	3.17	7.93		3.14
					avg.	3.2 ± 0.15[f]
D,L-Alanate	1.	25.0	1.51	17.7		1.58
	2.	25.0	1.56	18.3		1.52[e]
	3.	25.0	2.26	8.87		1.70
	4.	25.1	2.92	7.67		1.81
	5.	25.1	2.92	15.3		1.64
	6.	24.9	3.77	17.7		1.81
					avg.	1.7 ± 0.12[f]
	7.	19.1	0.217	7.67		1.24[d]
	8.	19.0	2.17	7.67		1.31
	9.	19.0	2.17	15.3		1.32
	10.	19.2	8.69	7.67		1.43
					avg.	1.3 ± 0.08[f]
	11.	10.9	1.16	15.3		0.719[d]
	12.	10.4	5.03	15.9		0.693[d]
					avg.	0.71 ± 0.018[f]
D,L-Phenylalanate	1.	25.1	1.51	3.07		2.87
	2.	25.0	1.56	3.17		2.12
	3.	25.1	0.168	3.07		2.33[d]
	4.	25.0	1.68	15.3		2.13
	5.	25.0	1.68	15.3		2.02[e]
	6.	25.1	4.20	7.67		2.53
					avg.	2.3 ± 0.32[f]
	7.	19.2	0.268	7.67		1.79[d]
	8.	19.0	0.268	15.3		1.61
	9.	19.0	0.268	30.7		1.50
					avg.	1.6 ± 0.15[f]

(continued on facing page)

TABLE II. *(continued)*

Amino Acidato	Run No.	t, °C[b]	10^3 [Co(III)]$_o$ *M*	10^3 [Cr(II)]$_o$ *M*	k[c] M^{-1} s^{-1}
	10.	10.9	1.47	20.1	0.902[d]
	11.	10.7	4.26	19.4	0.987
				avg.	0.94 ± 0.045[f]

[a]Except as noted. [b]Temperature ±0.1 °C. [c]Obtained from eqn. 1 except as noted. [d]Obtained from pseudo first order rate constant. [e][H^+] = 0.2 *M*, Σ[ClO_4^-] = 1.0 with $NaClO_4$. [f]Std. dev.

TABLE III. Comparison of the Rate Constants and Activation Parameters for the Reactions of $[Co(NH_3)_4(AA\text{-}N,O)]^{2+}$, $[Co(en)_2(AA\text{-}N,O)]^{2+}$, and $[Co(NH_3)_5(HAA\text{-}O)]^{3+}$ with Cr^{2+} for HAA = Glycine, D,L-Alanine, and D,L-Phenylalanine.

	Complex[b]	k[c], M^{-1} s^{-1}	$\Delta H^{\ddagger}$, Kcal/mol	$\Delta S^{\ddagger}$, cal/mol deg	Ref.
1.	$[Co(NH_3)_4(gly)]^{2+}$	6.4 ± 0.24	7.1 ± 0.58	−31 ± 2.1	d
2.	$[Co(NH_3)_4(D,L\text{-}ala)]^{2+}$	1.7 ± 0.12	9.2 ± 0.77	−27 ± 2.4	d
3.	$[Co(NH_3)_4(D,L\text{-}pala)]^{2+}$	2.3 ± 0.32	10.1 ± 0.85	−23 ± 2.5	d
4a.	$[Co(en)_2(gly)]^{2+}$	2.2(Li^+)	8.9 ± 0.13	−27 ± 0.4	7
4b.	$[Co(en)_2(gly)]^{2+}$	1.65 ± 0.06	9.1 ± 0.1	−25 ± 1	9
5.	$[Co(en)_2(D,L\text{-}ala)]^{2+}$	0.367 ± 0.008	10.9 ± 0.4	−24 ± 1	9
6.	$[Co(en)_2(D,L\text{-}pala)]^{2+}$	0.529 ± 0.021	11.2 ± 0.4	−22 ± 1	9
7.	$[Co(NH_3)_5(Hgly)]^{3+}$	0.064	7.7 ± 0.2	−38 ± 1	3
8.	$[Co(NH_3)_5(D,L\text{-}Hala)]^{3+}$	0.018 ± 0.001	7.4 ± 0.1	−42 ± 1	5
9.	$[Co(NH_3)_5(D,L\text{-}Hpala)]^{3+}$	0.015 ± 0.001	7.5 ± 0.2	−42 ± 1	5

[a]Ethylenediamine = en. [b]Glycinate = gly; alanate = ala; and phenylalanate = pala. [c]At 25 °C and Σ[ClO_4^-] = 1.0 (H^+/Na^+), except as noted. [d]This work.

the chromium(III) products obtained. These spectra are in agreement with those reported [9, 23] for O-bonded amino acid complexes of pentaaquochromium(III). These complexes had absorption maxima in the ranges 572–575 and 410–412 nm with molar absorptivities in the range of 22.0–25.4 M^{-1} cm^{-1}. In view of the nearly 1:1 redox stoichiometries and the nature of the chromium(III) products isolated, the reaction stoichiometries are adequately represented by equation 2.

$$[Co(NH_3)_4AA]^{2+} + Cr^{2+} + 5H^+ =$$

$$Co^{2+} + 4\,NH_4^+ + [Cr(H_2O)_5AAH]^{3+} \qquad (2)$$

In Table II are summarized the conditions and results for the individual kinetic runs. The consistency of the observed second order rate constants indicates that the reactions are first order in both cobalt(III) and chromium(II). The rate constants do not change when the acid concentration is decreased from 0.93 *M* to 0.2 *M*. (Run 5 in glycinate data, run 2 for D,L-alanate, and run 5 for D,L-phenylalanate). Thus the rate laws for these reactions are simply $-d[Co(III)]/dt = k^{2nd}[Co(III)][Cr(II)]$.

The activation parameters and associated errors [24] were computed by a linear least squares fit for the temperature data to the logarithmic form of the Eyring equation [25] assuming $\kappa = 1$. In Table III are summarized the results of the present study along with those for the bis(ethylenediamine)cobalt(III) and pentaamminecobalt(III) complexes containing glycine, D,L-alanine, and D,L-phenylalanine. In all three systems the glycine/glycinate complexes were found to react more rapidly than those with an alpha substituent other than hydrogen (*cf.* entry 1 with entries 2 and 3; entry 4 with entries 5 and 6; entry 7 with entries 8 and 9), whereas variation of the alpha substituent from $-CH_3$ to $-C_6H_5$ was found to have little effect (*cf.* entries 2 and 3; 5 and 6; 8 and 9). The enhanced rate for the glycine complexes may be due primarily to a decreased steric hindrance at the reaction center or possibly to some electronic effect. It should be noted, however, that none of the

Fig. 1. Chelated *vs.* Monodentate Amino Acid.

classical substituent parameters correlated with the rate constants for either the tetraammine or the bis(ethylenediamine) complexes [9]. When the amino acids are chelated, the alanate species are seen to react slightly faster than the phenylanate species while the converse is observed for the corresponding monodentate species.

The large (100X) enhancement in rate upon going from a pentaammine complex to a tetraammine complex most probably is due to the 'locking in' of the carboxylate group upon chelation and to the lowered charge of the activated complex. Chelation effectively opens the carboxylate out for attack as can be seen in Fig. 1. The effect of chelation, as well as the lowered charge (4+ *vs.* 5+) of the activated complexes are reflected in the much less negative activation entropies which more than compensate for the increased activation enthalpies for the alanine and phenylalanine species.

The enhanced rate for the tetraammines compared to the bis(ethylenediamine) complexes can be attributed to the 'chelate effect' of ethylenediamine. This effect is, according to Ogard and Taube [26], at least in part due to the reduced mobility of the ligand group *trans* to the bridging group. If the energy of the orbital accepting the electron (for example, the d_{z^2}) during the reduction process is lowered, the rate is increased. One way the energy could be lowered is by moving the *trans* ligand away from the metal center. When this ligand is one of the nitrogens of ethylenediamine, the stretching of this bond is hindered relative to a unidentate ligand such as ammonia. Thus, in the present case, having ammonia *trans* to the carboxylate enhances the electron transfer rate over that where an ethylenediamine nitrogen occupies that position.

At the outset the rate constants previously reported [11] for the (glycinato)- and (L-alanato)tetraamminecobalt(III)–chromium(II) reactions were questioned. The arguments are based on both characterization of the reactants and on the kinetic results. First, in spite of specific conductance, ir and visible spectra, and magnetic susceptibility data to characterize the reactants there is a substantial (27 nm) discrepancy in the first absorption maxima (520 nm) [11] with earlier literature values (493 nm) [13], indicating that some complexes other than the CoN_5O^{2+} chromophores were involved. The complexes in question did exhibit a weak paramagnetism, but their identities remain a puzzlement.

The complexes prepared in the present study confom to the earlier literature report [13]. Second, both Orgel's crystal field theory of nonbridging ligand effects [12] and the bond stretching corollary of Ogard and Taube [26] predict that the tetraammine complexes should react faster than the corresponding bis(ethylenediamine) complexes. While the present results conform to this expectation, the earlier reported rate constants were nearly 100X less for the tetraammine species (ks: 3.45×10^{-3} and 2.00×10^{-3} M^{-1} s^{-1} [11]), *cf.* the bis(ethylenediamine) species (k s: 1.65 and 0.367 M^{-1} s^{-1} [9]) for the glycinato and alanato complexes, respectively.

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