Table V. Comparison of Parameters for $(en)_2CoC_2O_4^+$, $(en)_2CoCO_3^+$, and $(en)_2CoPO_4$ at 22.5°

Complex	$k_1 \times 10^4$, M^{-1} sec^{-1}	$k_{-1} \times 10^3$, sec^{-1}	$k_2(H_2O) \times 10^3$, sec^{-1}	$k_{-2} \times 10^2$, sec^{-1}	K_1, M^{-1}	Co–O cleavage in base hydrolysis, %
$(en)_2CoC_2O_4^+$	0.056[a]	...	...	...	...	0[b]
$(en)_2CoCO_3^+$	2.2	0.0042	0.034	7.1	52.8	100
$(en)_2CoPO_4$	17.5	2.4	0.025	0.083	764	65[c]

[a] Calculated from the measured value at 71° and the activation energy of 34 kcal mole^{-1} reported by S. Sheel, *et al.*, *Inorg. Chem.*, **1**, 170 (1962). [b] C. A. Andrade and H. Taube, *J. Am. Chem. Soc.*, **86**, 1328 (1964). [c] S. F. Lincoln and D. R. Stranks, *Aust. J. Chem.*, **21**, 1745 (1968).

It is also noted in Table V that the position of bond cleavage is different for the phosphate, carbonate, and oxalate complexes. The relative importance of cobalt–oxygen or oxygen–ligand central atom bond breaking will depend on the relative strengths of these two bonds and also on the susceptibility of the ligand atom to nucleophilic attack by hydroxide ion. It is not possible as yet to anticipate the bond-breaking pattern with different oxyanion ligands. It is unfortunate that in the phosphate system, where both bond-breaking paths are contributing, no kinetic parameters for the two paths are available.

It is generally observed that the ratio of the rate constants for hydroxide-catalyzed and uncatalyzed hydrolysis for cobalt(III) ammine complexes is of the order of 10^5 to 10^8 M^{-1}. The ratio $k_1/k_2[H_2O]$ for $(en)_2CoPO_4$ is 7×10^4 and seems reasonably normal; however, for $(en)_2CoCO_3^+$ the ratio is only 6.5. This strongly suggests a change of mechanism in the carbonate system and it seems likely that the $k_2[H_2O]$ path proceeds with C–O bond breaking.

It is also interesting to compare the rate constants for the ring-closing reaction (k_{-1}) in Table V for the phosphato and carbonato complexes. If this reaction is analogous to an anation reaction, then the rate would be controlled by the rate of hydroxide ion exchange from the ring-opened complex for an SN1 mechanism. The fact that k_{-1} for $(en)_2CoPO_4OH^-$ is 500 times faster than for $(en)_2CoCO_3OH$ may be due to the charge difference but is also in the direction expected for an SN2 mechanism for chelate ring closure. Studies of the $^{18}OH^-$ exchange with the ring-opened species and rate of ring closure for other ligands would be most helpful in determining the mechanism for the chelation reaction.

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Synthesis and Characterization of Some Cobalt(III) Complexes of Ethylenediaminetriacetic Acid

Gary L. Blackmer, Randall E. Hamm, and J. Ivan Legg

Contribution from the Department of Chemistry, Washington State University, Pullman, Washington 99163. *Received April 24, 1969*

Abstract: A series of complex compounds of cobalt(III) involving pentadentate ethylenediaminetriacetic acid, ED3A, as the chelating agent have been prepared. These compounds have the general formula K[Co(ED3A)X] where X^- is Cl^-, NO_2^-, or ONO^-. The structures of these complexes are inferred from their chemistries and spectral data. The infrared spectra of the compounds have been measured and interpreted. The absorption spectra of the complexes are compared with those for the related series of complexes $Co(EDTA)X^{2-}$, $Co(HEDTA)X^-$, and $Co(MEDTA)X^-$. The proton nmr spectra indicate that ED3A acts as a pentadentate ligand exhibiting three different AB acetate patterns occurring in the region 4.3 to 3.2 ppm (*vs.* sodium 3-(trimethylsilyl)-1-propanesulfonate). The spectrum in acid solution confirms the existence of the ED3A ligand by the amine proton absorption and its coupling with the low-field acetate protons. Partial resolution was achieved by use of a cellulose ion-exchange column.

Numerous examples of cobalt(III) complexes that employ pentadentate chelating agents of the aminopolycarboxylic acid variety have been prepared and are rather well characterized. Schwarzenbach[1] prepared the first pentadentate cobalt(III) complexes using ethylenediaminetetraacetic acid. He reported compounds of the general formula $Co(HY)X^-$ where HY is the singly protonated form of ethylenediaminetetraacetic acid and X^- is Br^- and NO_2^-. Recently Van Saun and Douglas[2] have prepared and resolved a series of cobalt(III) complexes of MEDTA, $Co(MEDTA)X^-$, where MEDTA is the anion of N-methylethylenedi-

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(1) G. Schwarzenbach, *Helv. Chim. Acta*, **32**, 839 (1949).

(2) C. W. Van Saun and B. E. Douglas, *Inorg. Chem.*, **7**, 1393 (1968).

amine-N,N′,N′-triacetic acid and X^- is Cl^-, Br^-, or NO_2^-.

Morris and Busch[3] carried out a rather extensive infrared investigation of pentadentate ethylenediaminetetraacetic acid and N-hydroxyethylethylenediaminetriacetic acid, HEDTA, complexes of cobalt(III) with the respective general formulation $Co(HY)X^-$ and $Co(HEDTA)X^-$ where X^- is Cl^-, Br^-, or NO_2^-. They have shown the applicability of infrared spectroscopy for distinguishing between complexed carboxyl groups and free or uncomplexed carboxylic acid groups in the presence of each other. Infrared spectroscopy was also used successfully to study cobalt(III) complexes which have the NO_2 ligand present in the coordination sphere of the metal ion.[4] Such complexes are capable of exhibiting coordination isomerism as the nitro form ($Co-NO_2$) or the less stable nitrito form (Co-ONO). The infrared correlations reported in the previous investigations were applied to the compounds under consideration in this study.

Day and Reilley[5] and Legg and Cooke[6] have reported the proton nmr spectra of the cobalt(III) complexes of EDTA and EDDA, respectively. They have shown that two types of acetate rings exist in these complexes. We have made similar observations for the ED3A ligand when coordinated with cobalt(III).

The most significant contribution to report here is that we have synthesized cobalt(III) complexes containing the ligand ethylenediamine-N,N,N′-triacetic acid (ED3A). The uniqueness of this ligand renders it essential to cobalt(III) chemistry. First, it completes the series of cobalt(III) complexes of N-substituted ethylenediamine polycarboxylic acids from EDTA through EDDA. Second, the cobalt(III) complexes of ED3A act as models for the other cobalt(III) complexes containing EDTA type pentadentate ligands, namely EDTA, HEDTA, and MEDTA.

Experimental Section

Preparation of Ethylenediaminetriacetic Acid (ED3A). The method used to prepare the acid ED3A was similar to that of Dwyer and Garvan[7] in their preparation of 1,2-propylenediaminetetraacetic acid. To 0.3 mol (28.2 g) of monochloroacetic acid, dissolved in a small amount of cold water (25 ml), maintained at 10° in an ice bath, was added a cold solution of potassium hydroxide (16.8 g, 0.3 mol) in water (33 ml). The KOH solution was added dropwise with constant stirring to keep the temperature of the reacting solution below 15°. One-tenth mole (6.68 ml, 6.0 g) of ethylenediamine was then added followed by an additional quantity of potassium hydroxide solution (0.3 mol, 16.8 g). The resulting solution was removed from the ice bath and gradually allowed to come to room temperature over a 24-hr period. The resulting solution was thought to contain ethylenediaminetetraacetic acid (EDTA), the desired product (ED3A), ethylenediaminediacetic acid (EDDA), and other possible fragmentary products. Therefore, no attempt was made at this point to isolate the free acid. Instead, the acid was separated from the other acid products of the reaction in complexed form with cobalt(III).

Preparation of Aquo(ethylenediaminetriacetato)cobalt(III) 1.5-Hydrate. The aquo complex of Co^{III}ED3A, $Co(ED3A)(H_2O)$, was prepared by dissolving cobaltous nitrate hexahydrate (0.1 mol, 29.1 g) in a small amount of water and adding it to the previously prepared ED3A solution which had been diluted to 1 l. and acidified to pH 6 with concentrated hydrochloric acid. Oxidation of the cobalt(II) to cobalt(III) was accomplished by the addition of 30% hydrogen peroxide (6 ml) and activated charcoal (4 g) to the reaction mixture. Air was drawn through the solution for 3 days to ensure complete oxidation of the cobalt. Following the removal of the charcoal, the solution was further diluted to give a 5 m*M* concentration in cobalt and the pH adjusted to 5.0.

The method used to separate the desired product, $Co(ED3A)(H_2O)$, from the other possible cobalt(III) species takes advantage of the different charges associated with the cobalt(III) complexes: $Co(EDTA)^-$, $Co(ED3A)(H_2O)^0$, and $Co(EDDA)(H_2O)_2^+$.

On passing the solution containing the cobalt(III) complexes through 700 ml of a Dowex 1-X8 anion-exchange resin column (100–200 mesh, Cl^- form), all negatively charged species, such as $Co(EDTA)^-$, were retained by the resin. The remaining solution, after passage through the anion column, was allowed to pass through 700 ml of a Dowex 50W-X8 cation-exchange resin column (100–200 mesh, K^+ form) which retained all cationic species. The blue-violet cobalt(III) solution which was obtained was evaporated to near dryness and cooled. Potassium chloride was then filtered off, and the cobalt(III) complex was precipitated as an oil with acetone and ethanol. The tarlike precipitate was dissolved in 100 ml of water, silver acetate (0.1 mol, 16.6 g) was added, and the mixture was warmed for 0.5 hr. The silver chloride was filtered off and a saturated sodium chloride solution was added dropwise to remove the excess silver. After filtration, the cobalt complex was again precipitated with acetone. Successive purifications from aqueous solution with acetone resulted in the desired cobalt(III) complex. The yield, before final purification, was 36% based on the cobalt(II) added. *Anal.* Calcd for $[Co(ED3A)(H_2O)]\cdot 1.5H_2O$: C, 28.67; H, 4.81; N, 8.37. Found: C, 28.61; H, 4.70; N, 8.64.

Preparation of Potassium Nitro(ethylenediaminetriacetato)cobaltate(III) 1-Hydrate and Potassium Nitrito(ethylenediaminetriacetato)cobaltate(III) 1-Hydrate. The nitrito and nitro complexes were prepared from the aquo complex. Aquo complex (6.7 g, 2.0×10^{-2} mol) was dissolved in water (40 ml), and sodium nitrite (2.0 g, 3.0×10^{-2} mol) was added. When dissolution was complete the solution was cooled to 0°. Glacial acetic acid (14 ml) was added and the solution allowed to stand overnight. The resulting deep red solution was diluted to 4 l. and allowed to pass through 700 ml of a Dowex 1-X8 anion-exchange resin column (100–200 mesh, Cl^- form) at a rate of 10 drops/min. The deep red band retained by the resin was eluted with 2.5×10^{-2} *M* potassium chloride at a 10-drop/min rate. The red band separated into two distinct bands, an intense red lower band and a less intense blue-purple upper band. The bands were collected separately and reduced in volume by drawing air over them in a suction flask. The concentrated solutions were treated with absolute methanol and placed in the refrigerator overnight. Both solutions yielded crystalline products on filtration which were washed with methanol and then acetone and dried in a vacuum desiccator over P_2O_5. The first eluted band, the nitro complex, gave needlelike, brick red crystals. The second band, the nitrito species, crystallized as deep purple crystals. Total yield based on cobalt(III) complex added was 40%. The solid nitrito complex was found to undergo rearrangement to yield the nitro species. *Anal.* Calcd for $K[Co(ED3A)NO_2]\cdot H_2O$; C, 24.43; H, 3.33; K, 9.94; N, 10.68. Found: C, 24.48; H, 3.35; K, 9.94; N, 10.57.

Partial resolution of the $K[Co(ED3A)NO_2]$ and K[Co(ED3A)ONO] complexes was accomplished by the cellulose ion-exchange method of Legg and Douglas.[8] A complete resolution using $(+)_{546}$-$Co(en)_2(ox)^+$ as resolving agent is being done and will be published in a future paper.

Preparation of Potassium Chloro(ethylenediaminetriacetato)cobaltate(III) 0.5-Hydrate. $Co(ED3A)(H_2O)\cdot 1.5H_2O$ (3.35 g, 0.01 mol) was dissolved in a saturated solution of sodium chloride (25 ml, room temperature), concentrated hydrochloric acid (2 ml) was added, and the entire mixture was evaporated to dryness on a steam bath. The blue mass that resulted was cooled and dissolved in cold water (2 l.) and allowed to pass through 700 ml of a Dowex 1-X8 (100–200 mesh) anion-exchange resin column. The blue band that was retained by the resin was eluted with 0.025 *M* KCl at a rapid rate. The complex was collected and its solution reduced in volume to 25 ml by drawing air over it in a suction flask. The blue solid which formed, on addition of methanol (200 ml) and cooling in the refrigerator, was collected, washed with methanol and then

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[3] M. L. Morris and D. H. Busch, *J. Amer. Chem. Soc.*, **78**, 5178 (1956).

[4] R. B. Penland, T. J. Lane, and J. V. Quagliano, *ibid.*, **78**, 887 (1956).

[5] R. J. Day and C. N. Reilley, *Anal. Chem.*, **36**, 1070 (1964).

[6] J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **4**, 1576 (1965).

[7] F. P. Dwyer and F. L. Garvan, *J. Amer. Chem. Soc.*, **81**, 2955 (1959).

[8] J. I. Legg and B. E. Douglas, *Inorg. Chem.*, **7**, 1452 (1968).

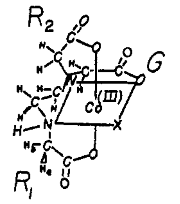

Figure 1. The structure of the ethylenediaminetriacetato complexes of cobalt(III).

acetone, and dried in a vacuum desiccator over P_2O_5. The yield was 18% based on the cobalt(III) complex added. *Anal.* Calcd for K[Co(ED3A)Cl]·$0.5H_2O$: C, 23.69; H, 2.98; Cl, 8.74; K, 9.64; N, 6.91. Found: C, 23.66; H, 3.15; Cl, 8.92; K, 10.04; N, 6.98.

The partial resolution of this complex was conducted in a manner identical with that of K[Co(ED3A)NO_2].

Spectra. The infrared spectra were obtained on a Beckman IR-8 recording spectrophotometer on samples of the compounds in Nujol mulls and potassium bromide pellets.[9] The absorption spectra were measured on a Cary Model 14 recording spectrophotometer and the circular dichroism curves were recorded with a Jasco Model ORD/UV-5 recording spectrophotometer.

All proton magnetic resonance spectra were recorded on a Varian A-60 nmr spectrophotometer at about 35°, the internal temperature of the probe. All resonances occurred on the low-field side of *t*-butyl alcohol which was used as an internal reference. Chemical shifts are referred to 3-(trimethylsilyl)-1-propanesulfonic acid, sodium salt as zero; *t*-butyl alcohol is shifted 1.233 ppm downfield from the silylsulfonate. Deuterium oxide solutions were prepared by dissolving as much of the finely powdered sample at 60° as needed to obtain a good spectrum (1.0-ml sample). Acidic solutions of the complexes were prepared by the addition of concentrated aqueous HNO_3 to the D_2O. Dissolution of the acid salt of the complex in D_2O was used as an alternate method. All spectra were recorded less than 3 min after mixing.

Results and Discussion

The colors of the complex salts in this investigation were found to be identical with those of the related series[2,3] of cobalt(III) complexes containing similar complexing agents acting as pentadentate ligands: ethylenediaminetetraacetic acid (EDTA), N-hydroxyethylethylenediaminetriacetic acid (HEDTA), and N-methylethylenediaminetriacetic acid (MEDTA). The nitrito complex, Co(ED3A)ONO^-, which was easily separated from the nitro species, Co(ED3A)NO_2^-, by use of the anion-exchange resin, was found to be bluish purple in color. This color slowly changed to the brick red color of the nitro complex if the complex was allowed to remain on the resin for several days. This observation reflects the possibility of linkage isomerization of the NO_2 ligand. A study has been done on the formation of the nitrito complex of cobalt(III) from the aquo complex $Co(NH_3)_5H_2O^{3+}$.[10] This nitrito complex was shown to rearrange to give the more stable nitro complex.

The mechanism proposed for the formation of nitrito and nitro complexes of cobalt(III) suggests that analogous cobalt(III) systems, such as the one used in this study, should yield similar products upon nitrosation of the aquo complex. Since the rearrangement of the nitrito complex, Co(ED3A)ONO^-, to its more stable nitro isomer is relatively slow, it was possible to isolate and characterize the nitrito species.

Previous studies[2,11,12] as well as this investigation have shown no evidence for geometrical isomerism with respect to the ligand even though the possibility of such isomerism exists. Chromatography revealed the presence of only one isomer in all cases. No complexity in the infrared spectral bands was noted and this also suggests the presence of only one isomer. Models show that the isomer with the X ligand *trans* to a nitrogen should be the one with the least strain. The other isomer in which the two amine nitrogens and two acetates are contained in the same plane is expected to be sterically strained as was found for the analogous planar arrangement in $Co(EDTA)^-$.[13] The proton nmr spectra not only strongly support the presence of one isomer but give good evidence that the isomer is the least strained form as shown in Figure 1.

Infrared Spectral Studies. Table I contains a summary of the infrared absorption bands for the compounds under current investigation and for similar compounds reported previously.[3,14]

The absence of the three absorptions typically associated with a free (uncoordinated) carboxylic acid group, namely the O—H stretching frequency in the 2600–2800-cm^{-1} region, the C=O stretch which commonly occurs in the 1700–1750-cm^{-1} region, and the band unambiguously associated with the carboxylic acid group occurring at 1228 cm^{-1}, rules out the possibility of an uncoordinated carboxylic acid group in the ED3A complex. The absorption at 1648–1658 cm^{-1} arising from the complexed carboxyl group appears throughout the series of cobalt(III) complexes.

The nitro complex shows the characteristic bands associated with the coordinated nitro ligand, namely 1408, 1342, and 830 cm^{-1}. The nitrito complex gives two additional absorptions occurring at 1460 and 1065 cm^{-1} which have been assigned to the two ONO stretching vibrations.[4] The presence of the three absorptions associated with the nitro ligand, in the spectrum of the nitrito complex, indicates that a trace of the nitro isomer is present in the sample. On standing for several days the nitrito sample gives a spectrum nearly identical with that of the nitro species indicating that conversion takes place in the solid state. This gives further evidence for the conversion between the isomeric Co–ONO and Co–NO_2 forms.

Adell[15] was able to obtain $[Co(NH_3)_5ONO]Cl_2$ by irradiating solid $[Co(NH_3)_5NO_2]Cl_2$ with sunlight. A recent study[16] has shown that irradiation of Nujol mulls of the solid nitro complex, $[Co(NH_3)_5NO_2](NO_3)_2$, resulted in nearly complete conversion of the nitro species into the nitrito form. Irradiation of the same complex in aqueous solution, however, produced only small amounts of the nitrito species, the major portion of the complex undergoing photodecomposition.

When solid K[Co(ED3A)NO_2], in a Nujol mull, was irradiated for 9 hr with light from an unfiltered Hg lamp (above 2900 Å), no appreciable change occurred. However, upon irradiation of an aqueous solution of the nitro species for 3 hr, with the above light source, re-

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(9) M. M. Stimson and M. J. O'Donnell, *J. Amer. Chem. Soc.*, 74, 1805 (1952).

(10) R. G. Pearson, P. M. Henry, J. G. Bergman, and F. Basolo, *ibid.*, 76, 5920 (1954).

(11) R. A. Haines and B. E. Douglas, *Inorg. Chem.*, 4, 452 (1965).

(12) F. P. Dwyer and F. L. Garvan, *J. Amer. Chem. Soc.*, 80, 4480 (1958).

(13) H. A. Weakliem and J. L. Hoard, *ibid.*, **81**, 549 (1959).

(14) K. Nakamoto, J. Fujita, and H. Murata, *ibid.*, 80, 4817 (1958).

(15) B. Adell, *Z. Anorg. Allg. Chem.*, **279**, 219 (1955).

(16) V. Balzani, R. Ballardini, N. Sabbatini, and L. Moggi, *Inorg. Chem.*, 7, 1398 (1968).

Table I. Infrared Absorptions of Cobalt(III) Complexes

			Carboxyl group										
Compound	H_2O	CH	OH	COOH	CO-OM	COO	COOH	NO_2			ONO		CH_2OH
$Na_2[Co(EDTA)NO_2]$[a]	3580	3040			1650	1604		1408	1343	833			
$Na[Co(EDTA)NO_2]$[a]	3540	3040	2600–2800	1745	1650		1228	1415	1343	833			
$Na[Co(HEDTA)NO_2]$[a]	3561	3040			1652			1408	1342	833			1080
$[Co(NH_3)_5NO_2]Cl_2$[b]								1428	1310	824			
$[Co(NH_3)_5ONO]Cl_2$[b]										825	1468	1065	
$Na[Co(ED3A)NO_2]$	3540	3040			1640			1408	1342	830			
Na[Co(ED3A)ONO]	3540	3040			1640			1408[c]	1342[c]	830[c]	1460	1065	
$Na_2[Co(EDTA)Cl]$[a]	3580	3040			1648	1600							
Na[Co(EDTA)Cl][a]	3540	3080	2500–2700	1750	1650		1228						
Na[Co(HEDTA)Cl][a]	3580	3080			1658								1080
Na[Co(ED3A)Cl]	3540	3040			1640								

[a] Reference 3. [b] Reference 14. [c] Absorptions in nitrito complex are due to a small amount of nitro species.

arrangement to the nitrito species did occur. Photodecomposition of the nitro species accompanied the rearrangement reaction. The newly formed nitrito species was isolated from the reaction products and the unreacted nitro complex by the ion-exchange technique outlined earlier.

The chloro complex of Co(III)-ED3A is seen to have infrared absorptions nearly identical with those of the analogous EDTA and HEDTA compounds.

Figure 1 shows the proposed structure for the Co(III)-ED3A complexes. The two nitrogens and the three carboxyl groups of the ligand are coordinated to the cobalt ion as is the monodentate ligand X. The hydrogen, bound to the nitrogen atom of the ED3A ligand, gives rise to an N–H stretching frequency at 3150 cm^{-1}. This absorption was observed in all of the ED3A complexes. The occurrence of this absorption further substantiates the existence of the ED3A ligand.

Visible Spectra. Table II lists the absorption data for the related complexes of cobalt(III) previously reported[2,11,17] together with those obtained in this study. The absorption spectra of the nitrito and nitro complexes of Co(III)–ED3A are given in Figure 2. The nitrito species has two low-energy maxima of nearly equal intensity occurring at 17,800 and 21,000 cm^{-1}. Upon rearrangement of the nitrito species the corresponding spectrum of the nitro complex is obtained. The absorption curves for the nitro and chloro complexes of Co(III)-EDTA, -HEDTA, and -MEDTA are all seen to be very similar to that of their model Co(ED3A)NO_2^- and Co(ED3A)Cl^-.

Table II. Absorption Data for Cobalt(III) Complexes Containing EDTA Type Pentadentate Ligands

$K_2[Co(EDTA)Cl]\cdot 3H_2O$[a]	17,100[c] (250[d]), 24,750 (221)
$K[Co(HEDTA)Cl]\cdot 1.5H_2O$[b]	17,100 (278), 24,800 (251)
$K[Co(MEDTA)Cl]\cdot H_2O$[b]	17,300 (210), 24,800 (188)
$K[Co(ED3A)Cl]\cdot 0.5H_2O$	17,450 (226), 25,130 (213)
$Na_2[Co(EDTA)NO_2]\cdot 3H_2O$[a]	17,100 sh (116), 20,050 (326)
$Na[Co(HEDTA)NO_2]\cdot H_2O$[b]	17,100 sh (110), 20,200 (232)
$Na[Co(MEDTA)NO_2]$[b]	17,100 sh (90), 20,300 (182)
$Na[Co(ED3A)NO_2]$	17,100 sh (88), 20,300 (192)
Na[Co(ED3A)ONO]	17,800 (186), 21,000 (180)

[a] Reference 11. [b] Reference 2. [c] Wave numbers given in units of cm^{-1}. [d] Units of M^{-1} cm^{-1}.

Although complete resolution has not yet been obtained, the CD spectra recorded for the complexes partially resolved by the cellulose ion-exchange technique[8] show a marked similarity to those of the corresponding EDTA, HEDTA, and MEDTA complexes.[2]

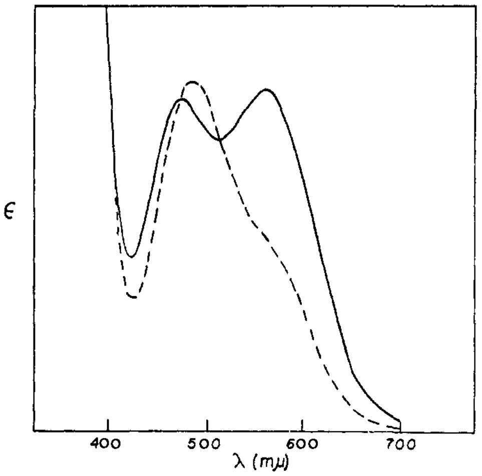

Figure 2. Absorption spectra of nitro- (------) and nitrito- (———) (ethylenediaminetriacetato)cobaltate(III) complexes.

Proton Nmr. Typical pmr spectra of the Co(ED3A)NO_2^- complex are illustrated in Figures 3 and 4. With the exception of the broad N–H resonance in acidic solution (Figure 4), the spectra are observed to be quite sharp due to the fixed conformation of the acetate rings in these inert complexes.

The spectrum of the ED3A complex appears to consist of an acetate singlet at 4.04 ppm and two acetate AB patterns (4.3–3.2 ppm) plus several ethylenic resonances at higher fields (3.5–2.5 ppm). Some of these ethylenic resonances (a complex ABCD pattern) are superimposed on the AB acetate proton resonances causing some uncertainty in assignment and area measurements. The tentative assignment of the low-field portion of the AB pattern is further complicated by the superposition of the singlet obscuring one of the resonances (Figure 3). This low-field AB assignment seems justified however in light of the observed splitting pattern of vicinal α hydrogen atoms due to the N–H proton, Figure 4 (*vide infra*). Thus the R_1 ring (Figure 1) can be distinguished

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(17) B. E. Douglas, R. A. Haines, and J. G. Brushmiller, *Inorg. Chem.*, 2, 1194 (1963).

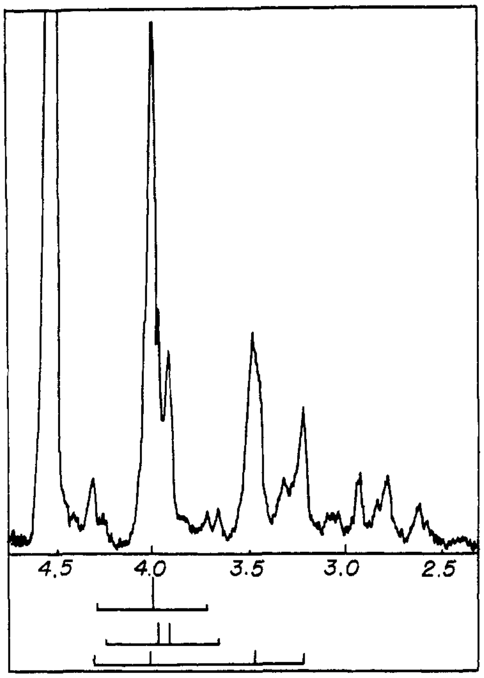

Figure 3. Nmr spectrum of a neutral solution of nitro(ethylenediaminetriacetato)cobaltate(III) in D_2O.

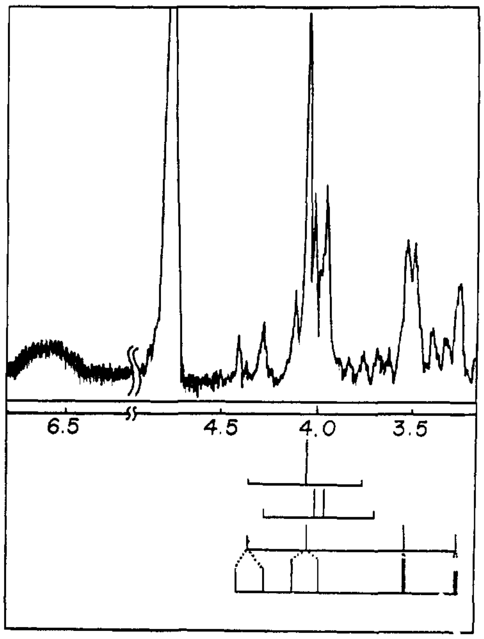

Figure 4. Nmr spectrum of an acid solution of nitro(ethylenediaminetriacetato)cobaltate(III) in D_2O.

from the R_2 and G rings since there is no amine proton associated with either of the latter.

The symmetry of the molecule, assuming the *trans* configuration (Figure 1), containing two acetate R rings[13] (oxygens above and below the Co–ED3A nitrogen plane) and one G ring (oxygen in the Co–ED3A nitrogen plane), should result in three different AB acetate ring patterns. If, however, the chemical shifts of two acetate protons on one of the rings are not too different, as might be expected for R_2, the AB pattern will collapse into a strong center peak with very weak side peaks.[18] A molecular model of the compound reveals that the two acetate protons on R_2 (Figure 1) are symmetric with respect to the C–N bond in this ring and experience nearly equal shielding by the C–N bonds of the G and E rings. Thus, the splitting of these two protons should be minimal. The collapsed AB pattern appearing as a single absorption, occurring at 4.04 ppm in the ED3A complex, is attributed to this effect and the weak side peaks can in fact be observed.

The model indicates that the protons on the G ring are in different environments due to the C–N magnetic anisotropy effects from the R_2 and E rings. The AB pattern resulting from this acetate ring (G) appears to have the J value of 16 cps and calculated[18] chemical shifts δ_A 4.08 and δ_B 3.88 ppm (the low-field proton will be designated A in each case).

On the R_1 acetate ring, H_A (the proton on the same side of the R_1 ring as the amine proton) is situated in the deshielding portion of the C–N axis of the E ring whereas H_B is situated directly over this C–N bond. This implies that H_B should be considerably shielded with respect to H_A.[6] The chemical shifts assigned from this splitting pattern are δ_A 4.16 and δ_B 3.42 ppm with J = 17 cps. The AB pattern experiences further splitting in acid solution before the amine proton undergoes deuterium exchange (Figure 4). A coupling constant of 8 cps for the low-field proton was observed. Splitting for the high-field proton could not be clearly distinguished indicating a coupling constant of less than 1 cps. Splittings of this order of magnitude are expected when a dihedral angle measurement is invoked and the Karplus[19] relationship applied. This is also in agreement with similar H–N–C–H coupling assignments reported earlier.[20,21] Due to the complex ABCD pattern resulting from the lack of symmetry of the E ring we are unable to assign chemical shifts to these protons.

Finally, if one compares the geometries of the cobalt(III) complexes of EDTA, ED3A, and EDDA, the following observations may be noted. First, the R_2 and G acetate rings of the ED3A complex (Figure 1) are essentially identical with the acetate rings of the EDTA complex.[5] Second, the R_1 acetate ring in ED3A is very much like the acetate rings found in the *trans*-EDDA complex.[6] Thus, it may be convenient to think of the ED3A complex as being composed of half of an EDTA and half of an EDDA molecule. The chemical shifts associated with the R_1 ring of the ED3A complex (δ_A 4.16, δ_B 3.42 ppm) and those of the corresponding EDDA complex (δ_A 4.22, δ_B 3.38 ppm) are nearly identical. This indicates that the protons associated with these acetate rings experience equal shielding and are in similar environments. However, even though the chemical shifts of the ED3A R_2 and G rings (4.04 center; δ_A 4.08, δ_B 3.88 ppm) show splittings similar to those of the corresponding EDTA acetate rings (3.92 center; δ_A 3.91, δ_B 3.59 ppm) the positioning of these chemical shifts is moved to lower field. This effect may be explained in terms of ring strain associated with coordination of the acetate groups. The loss of an acetate ring in going from the EDTA to the ED3A complex should

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result in a loss of ring strain in the chelate complex. This relaxation of ring strain could in turn lead to a general shift of absorbances to lower fields.

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Stepwise Aquation of 1,2,3- and 1,2,6-Triaquodiethylenetriaminechromium(III) Cations to Hexaaquochromium(III) Cation. Reaction Kinetics and Isolation of the Bidentate and Unidentate Diethylenetriamine Intermediates[1a-c]

Doris K. Lin and Clifford S. Garner

Contribution No. 2409 from the Department of Chemistry, University of California, Los Angeles, California 90024. *Received April 25, 1969*

Abstract: Aquation of 1,2,3-$Cr(dien)(OH_2)_3^{3+}$ was studied spectrophotometrically in 1–2 *F* $HClO_4$ ($\mu = 1–2\ M$, $NaClO_4$) at 50–70°. At $\mu = 2\ M$, the first-order rate constant, k_{1c}, is the same in 1 and 2 *F* $HClO_4$. At 59.80°, $k_{1c} = (5.89 \pm 0.09) \times 10^{-5}$ sec^{-1} in 1 *F* $HClO_4$ ($\mu = 1\ M$); $E_a = 24.3 \pm 0.7$ kcal mol^{-1}, log *PZ* (sec^{-1}) = 11.72 ± 0.51. By extrapolation, $k_{1c} = (8.1 \pm 0.8) \times 10^{-7}$ sec^{-1} at 25°. The product is the new complex $Cr(dienH)(OH_2)_4^{4+}$, with a singly protonated bidentate dien ligand. Aquation of this isolated pink intermediate was investigated in 0.1–2 *F* $HClO_4$ ($\mu = 1–2\ M$) at 60–80°. At 59.80°, the first-order rate constant is $k_2 = (2.16 \pm 0.03) \times 10^{-5}$ sec^{-1} in 1 *F* $HClO_4$ ($\mu = 1\ M$); $E_a = 24.0 \pm 0.6$ kcal mol^{-1}, log *PZ* (sec^{-1}) = 11.09 ± 0.40, and $k_2 = (3.1 \pm 0.3) \times 10^{-7}$ sec^{-1} at 25° by extrapolation. At 70 and 80°, k_2 is the same in 0.1 and 1 *F* $HClO_4$ ($\mu = 1\ M$). The product is purple $Cr(dienH_2)(OH_2)_5^{5+}$, a new complex with a doubly protonated unidentate dien ligand. Hydrolysis of this isolated second intermediate was studied in 0.1–2 *F* $HClO_4$ ($\mu = 1–2\ M$) at 60–80°. In 0.1–1 *F* $HClO_4$ ($\mu = 1\ M$), $k_{3\,\mathrm{obsd}} = k_3 + (k_3'/[H^+])$, where k_3 is the first-order rate constant for aquation of $Cr(dienH_2)(OH_2)_5^{5+}$ to $Cr(OH_2)_6^{3+}$ and k_3' has been interpreted as $k_{3h}K_a$, k_{3h} being the first-order aquation rate constant of $Cr(dienH_2)(OH_2)_4OH^{4+}$ and K_a being the first acid dissociation constant of $Cr(dienH_2)(OH_2)_5^{5+}$. At 59.80°, $k_3 = (2.59 \pm 0.13) \times 10^{-6}$ sec^{-1} and $k_{3h} \sim 2 \times 10^{-3}$ sec^{-1}; for the k_3 path, $E_a = 26.5 \pm 0.8$ kcal mol^{-1}, log *PZ* (sec^{-1}) = 11.81 ± 0.52, and by extrapolation $k_3 = (2 \pm 1) \times 10^{-8}$ sec^{-1} at 25°. Aquation of 1,2,6-$Cr(dien)(OH_2)_3^{3+}$ was studied in 0.01–1 *F* $HClO_4$ ($\mu = 0.15–1.1\ M$) at 15–30°. At 25.00°, the first-order rate constant is $k_{1t} = (5.34 \pm 0.05) \times 10^{-4}$ sec^{-1} in 0.1–1 *F* $HClO_4$ ($\mu = 1.1\ M$); $E_a = 19.2 \pm 0.6$ kcal mol^{-1}, log *PZ* (sec^{-1}) = 10.80 ± 0.20. Ionic strength dependences of k_{1c}, k_{1t}, k_2, and k_3 are small over the ranges involved. The same intermediates appear to be produced in aquation of 1,2,3- and 1,2,6-$Cr(dien)(OH_2)_3^{3+}$. Visible absorption spectra of the complexes are presented.

Recently the aquation of tetraaquoethylenediaminechromium(III) cation, $Cr(en)(OH_2)_4^{3+}$, and of its isolated product, $Cr(enH)(OH_2)_5^{4+}$ with a singly protonated unidentate en ligand, has been studied kinetically.[2] As part of a continuing program of investigating the "unwrapping" of multidentate amine ligands from chromium(III) centers, this paper reports the related isolation and characterization of the intermediates, namely, the new complexes $Cr(dienH)(OH_2)_4^{4+}$ and $Cr(dienH_2)(OH_2)_5^{5+}$ with "partially unwrapped" bidentate and unidentate diethylenetriamine ligands,[3] which form in the stepwise aquation of 1,2,3- and 1,2,6-triaquodiethylenetriaminechromium(III) cations, 1,2,3- and 1,2,6-$Cr(dien)(OH_2)_3^{3+}$, to the hexaaquochromium(III) cation. These intermediates appear to be the first metal complexes isolated in which the normally tridentate diethylenetriamine ligand has a denticity of less than three. We report also the kinetics of the stepwise aquation reactions. The possible structures and reaction schemes for these complexes are shown in Figure 1.

Experimental Section

1,2,3-Triaquodiethylenetriaminechromium(III) Cation. This complex was first reportedly prepared by reaction of $[Cr(dien)(O_2)_2] \cdot H_2O$[4] with warm 1 *F* $HClO_4$.[5,6] Subsequently we found that the complex prepared in this way is contaminated with large amounts of its tetraaquo aquation product, and that pure 1,2,3-$Cr(dien)(OH_2)_3^{3+}$ can be chromatographed out of this mixture, as described in the section on synthesis of the tetraaquo aquation product. Usually, however, we prepared 1,2,3-$Cr(dien)(OH_2)_3^{3+}$ from green 1,2,3-$Cr(dien)Cl_3$[7,8] by the method of Caldwell and House,[8] modified by

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