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Contribution from the Department of Chemistry,
Washington State University, Pullman, Washington 99163

Crystal and Molecular Structure of ΔΔΔΛ-*cis,trans*(*N–O*)-*uns-cis*-Ethylenediamine-*N,N'*-diacetato((*R*)-1,2-diaminopropane)cobalt(III) Chloride Monohydrate. Effect of Denticity on Chelate Ring Strain

LEON J. HALLORAN, RUTH E. CAPUTO, ROGER D. WILLETT,* and J. IVAN LEGG*

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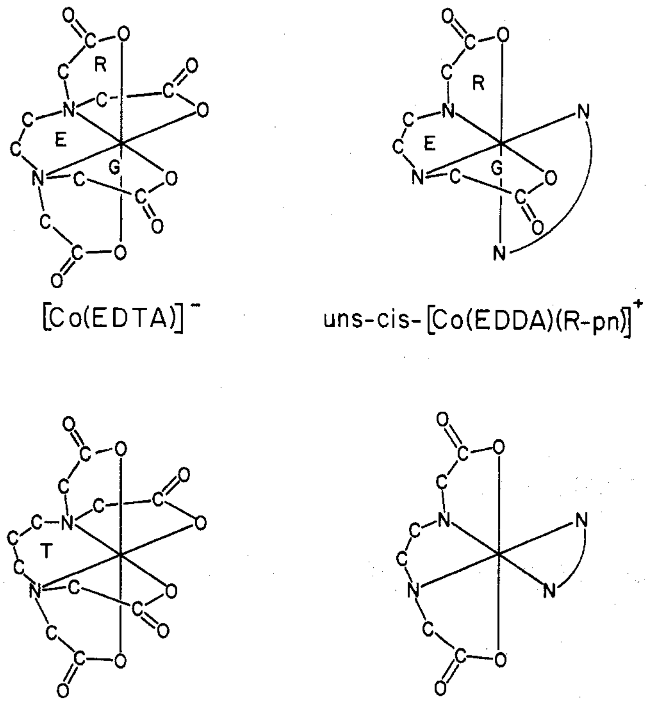
The crystal and molecular structure of ΔΔΔΛ-*cis,trans*(*N–O*)-*uns-cis*-ethylenediamine-*N,N'*-diacetato((*R*)-1,2-diaminopropane)cobalt(III) chloride monohydrate (ΔΔΔΛ-*cis,trans*(*N–O*)-*uns-cis*-[Co(EDDA)(*R*-pn)]Cl·H_2O) has been determined from three-dimensional X-ray counter data. The complex crystallizes in the monoclinic system, space group $P2_1$ with $a = 9.260$ (8) Å, $b = 7.255$ (9) Å, $c = 12.253$ (13) Å, and $\beta = 111.05$ (6)°. With $Z = 2$, the observed and calculated densities are 1.56 and 1.559 g cm^{-3}, respectively. The structure was refined by full-matrix least-squares methods to a final value of $R_1 = 0.055$ for 1305 independent reflections with $F_o > 3\sigma(F_o)$. The geometry about the cobalt atom is distorted octahedral with the tetradentate EDDA assuming the unsymmetrical-cis configuration in which the secondary nitrogen configurations are found to be *R,S* rather than the *S,S* configurations originally predicted. The *R*-pn ring conformation is λ with the methyl group in the stable equatorial position. The optically active carbon of *R*-pn is adjacent to the nitrogen trans to the nonplanar acetate oxygen (O_R) of EDDA. This isomer is similar to chelated EDTA, possessing an in-plane girdling glycinate ring (G ring), the backbone ethylenediamine ring (E ring), and an out-of-plane glycinate ring (R ring). A structural study of [Co(EDTA)]$^-$ has shown that the G rings are quite strained compared to the E and R rings,[1] but for tetradentate uns-cis coordinated EDDA, the ring strain is found to be partially averaged over all three rings with the G ring exhibiting the most distortion. ΔΔΔΛ-*cis,trans*(*N–O*)-*uns-cis*-[Co(EDDA)(*R*-pn)]$^+$ is one of the four possible isomers of this compound which have been isolated and whose absolute configurations have been tentatively assigned by spectroscopic means. The crystal and molecular structure determination confirms these assignments and this structure serves as a reference by which the absolute configuration of other uns-cis EDDA complexes can be assigned by correlation of circular dichroism spectra.

Introduction

X-Ray crystal structure investigations of transition metal–amino acid chelates have played an important role in elucidating the relationship between structure and observed properties of these compounds. Of these studies, the crystal and molecular structure of ammonium ethylenediaminetetraacetatocobaltate(III), NH_4[Co(EDTA)], determined by Weakliem and Hoard[1] and a later study of the closely related compound potassium trimethylenediaminetetraacetatocobaltate(III), K[Co(TRDTA)], by Saito and coworkers,[2] have served as an important source of structural information in studies involving polyaminepolycarboxylic acid chelates. Comparisons between [Co(EDTA)]$^-$ and cobalt(III) complexes of the linear tetradentate ethylenediamine-*N,N'*-diacetate (EDDA)[3–5] have proved to be of particular interest because of the structural similarity between the chelate systems, Figure 1.

For complexes of the type [Co(EDDA)(L)]^n where L represents a bidentate ligand, two geometric isomers are possible, Figure 1, symmetrical-cis (s-cis) and



$[Co(EDTA)]^-$

uns-cis-$[Co(EDDA)(R\text{-}pn)]^+$

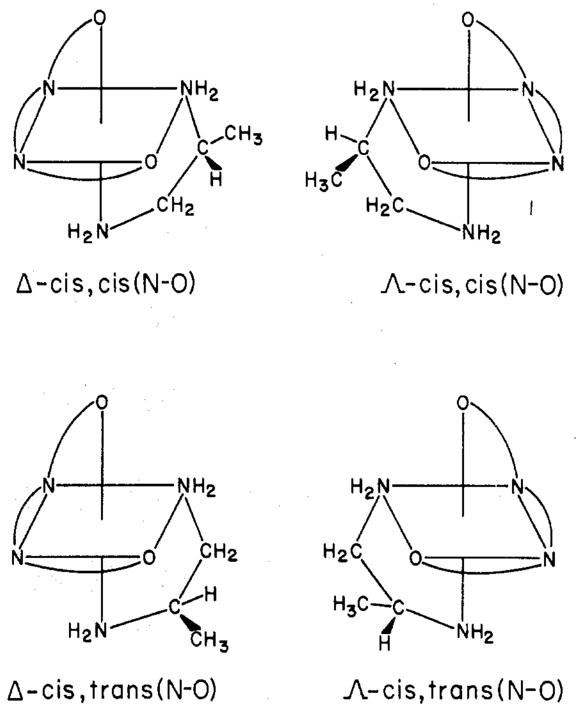
$[Co(TRDTA)]^-$

s-cis-$[Co(EDDA)(R\text{-}pn)]^+$

Figure 1. Comparison of the structures of $[Co(EDTA)]^-$ and related chelates.

unsymmetrical-cis (uns-cis). The latter isomer is most similar to chelated EDTA, possessing both an in-plane girdling ring (G ring) and an out-of-plane ring (R ring).[1] Weakliem and Hoard found that for $[Co(EDTA)]^-$, the in-plane G rings are in a strained environment relative to the out-of-plane R rings.[1] Similar strain was also found for the G rings of $[Co(TRDTA)]^-$ even though TRDTA incorporates a larger and more flexible trimethylenediamine chelate ring.[2] That this strain can influence chemical behavior has been demonstrated in a structural study of the pentacoordinate EDTA complex of the larger cation, Ni(II), in which one of the in-plane acetate arms fails to coordinate.[6] Also, the α-carbon protons of the R rings of $[Co(EDTA)]^-$ and similar metal chelates exhibit a much more rapid rate of exchange in comparison to the corresponding G ring protons.[5,7-9] The fact that no appreciable exchange of the G ring methylene protons is detected is attributed to the strained nature of the rings which prevents attainment of an enolate intermediate.[7] In addition, studies of the EDTA analogs EDDS (ethylenediamine-*N*,*N*'-disuccinate),[10,11] EDDDA (ethylenediamine-*N*,*N*'-diacetate-*N*,*N*'-dipropionate),[12] and EDDAMS (ethylenediamine-*N*,*N*-diacetate-*N*'-monosuccinate)[13] have shown that although these ligands can form five- and six-membered rings on chelation to Co(III), only isomers with the larger six-membered rings in the equatorial plane have been found.

Until recently complexes with EDDA in the uns-cis configuration have been obtained in trace quantities only. Various explanations based on steric arguments have been advanced to account for this selectivity. However, the possibility of ring strain in the uns-cis configuration has not been considered. In order to compare the ring strain in $[Co(EDTA)]^-$ and the similar $[Co(TRDTA)]^-$ with that in EDDA chelated in the uns-cis configuration, a crystal and molecular structure determination of ΔΔΔΛ-*cis*,*trans*(*N*–*O*)-*uns*-*cis*-ethylenediamine-*N*,*N*'-diacetato((*R*)-1,2-diaminopropane)cobalt(III) chloride monohydrate, Figure 2, was undertaken. This particular uns-cis EDDA complex was selected because of our interest in the additional isomerism generated by the presence of the unsymmetrical bidentate (*R*)-1,2-diaminopropane.[14] In a previous paper[15] we reported the synthesis and characterization of the two closely related sets of diastereoisomers which arise from the two possible modes of coordination of *R*-pn, Figure 2. The results of this crystallographic study confirm the absolute configuration assignments made on the basis of chemical and spectroscopic studies.[15]



Δ-cis,cis(N-O)

Λ-cis,cis(N-O)

Δ-cis,trans(N-O)

Λ-cis,trans(N-O)

Figure 2. Isomers of *uns-cis*-$[Co(EDDA)(R\text{-}pn)]^+$.

Experimental Section

Crystal Growth. Preparation, characterization, and separation of the isomers of *uns-cis*-$[Co(EDDA)(R\text{-}pn)]^+$ have been previously reported.[15] Crystals of ΔΔΔΛ-*cis*,*trans*(*N*–*O*)-*uns*-*cis*-$[Co(EDDA)(R\text{-}pn)]Cl\cdot H_2O$ were grown from ethanol–water solution by slow cooling. The crystals were in the form of red prismatic needles.

Crystal Data. Weissenberg and precession photographs indicated a monoclinic unit cell with systematic extinctions for $0k0$, $k = 2n + 1$. Of the two possible space groups, $P2_1$ or $P2_1/m$, the latter was eliminated because of the optical activity of the compound. The needle axis was found to be parallel to b^*. The unit cell dimensions were obtained by least squares refinement[16] of 12 high-angle reflections centered on a Picker four-circle automated diffractometer using Mo Kα radiation (λ 0.7107 Å) and are $a = 9.260$ (8) Å, $b = 7.255$ (9) Å, $c = 12.253$ (13) Å, $\beta = 111.05$ (6)°. With $Z = 2$ and a molecular weight of 360.69 amu, the calculated density is 1.559 g cm^{-3} compared with a measured density of 1.56 g cm^{-3} obtained by flotation in a benzene–carbon tetrachloride mixture.

Intensity Data Collection. Diffraction data were collected from a fragment of a much longer needle crystal with dimensions of 0.05 × 0.09 × 0.45 mm oriented about the b^* axis. The data were collected on a Picker four-circle diffractometer automated with a PDP-8/L computer using programs of Busing et al.[16] The θ–2θ scan method was employed with a scanning rate of 1°/min. Stationary-crystal, stationary-counter background counts of 30 sec were taken on each side of the reflection. All possible reflections with indices hkl and $\bar{h}kl$ with 2θ values between 5 and 50° were collected in two parts; 5–20° reflections were collected with a 2.0° scan and Zr-filtered Mo Kα radiation and 20–50° reflections were collected with a 2.5° scan using unfiltered radiation. One standard reflection was monitored every 20 reflections and exhibited no systematic decrease in intensity. A total of 1524 reflections were measured and the standard Lorentz and polarization corrections applied. The standard error in the intensity of each measurement was calculated from the relationship $\sigma(I)^2 = \sigma_{stat}^2 + C^2I^2$ where I and σ_{stat} are the integrated intensity and the standard deviation calculated by the diffractometer programs[16] and $C = 0.05$. Of the 1524 reflections collected, 1305 had $F_o > 3\sigma(F_o)$ and were considered observed. Absorption corrections (μ = 13.75

Table I

a. Atomic Positions[a]

Atom	x	y	z	Atom	x	y	z
Co	0.0743 (1)	0.7500	0.3078 (1)	C(8)	−0.2100 (12)	0.8282 (16)	0.1222 (10)
Cl	0.0175 (3)	0.7226 (5)	0.9392 (2)	C(9)	−0.3645 (11)	0.9410 (22)	0.0839 (11)
O(1)	0.2276 (9)	0.5691 (11)	0.3793 (6)	N1H	0.129 (14)	0.796 (20)	0.130 (11)
O(2)	0.4078 (8)	0.3961 (12)	0.3495 (6)	N2H	0.141 (15)	1.038 (22)	0.399 (13)
O(3)	−0.0143 (7)	0.7117 (11)	0.4251 (5)	N3H1[b]	−0.050	0.430	0.270
O(4)	0.0436 (7)	0.7395 (17)	0.6181 (5)	N3H2[b]	−0.020	0.530	0.167
N(1)	0.1943 (9)	0.7978 (11)	0.2091 (6)	N4H1[b]	−0.130	0.950	0.295
N(2)	0.1987 (10)	0.9361 (11)	0.4143 (7)	N4H2[b]	−0.050	1.050	0.185
N(3)	−0.0571 (11)	0.5575 (14)	0.2132 (9)	C3H1	0.394 (16)	0.965 (22)	0.244 (12)
N(4)	−0.0914 (9)	0.9205 (13)	0.2236 (8)	C3H2	0.256 (15)	1.096 (19)	0.229 (12)
H_2O	0.3072 (8)	0.3719 (15)	0.5995 (7)	C4H1	0.423 (15)	0.889 (21)	0.398 (12)
C(1)	0.3148 (11)	0.5199 (15)	0.3223 (10)	C4H2	0.371 (16)	1.069 (22)	0.424 (12)
C(2)	0.2836 (14)	0.6276 (18)	0.2079 (9)	C5H1	0.288 (12)	0.801 (18)	0.555 (10)
C(3)	0.2938 (12)	0.9644 (18)	0.2587 (10)	C5H2	0.236 (16)	1.005 (21)	0.593 (12)
C(4)	0.3444 (11)	0.9628 (14)	0.3914 (9)	C7H1	−0.311 (15)	0.599 (21)	0.209 (13)
C(5)	0.2188 (10)	0.8743 (15)	0.5359 (8)	C7H2	−0.268 (16)	0.559 (21)	0.093 (13)
C(6)	0.0760 (9)	0.7718 (17)	0.5288 (7)	C8H	−0.141 (13)	0.812 (19)	0.065 (10)
C(7)	−0.2229 (15)	0.6277 (18)	0.1604 (11)				

b. Anisotropic Thermal Parameters for Nonhydrogen Atoms[c]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	0.0064 (2)	0.0093 (2)	0.0029 (1)	0.0004 (2)	0.0016 (1)	−0.0001 (2)
Cl	0.0201 (5)	0.0112 (8)	0.0039 (2)	0.0002 (5)	0.0039 (2)	−0.0010 (3)
O(1)	0.0096 (12)	0.0147 (17)	0.0039 (6)	0.0016 (12)	0.0024 (7)	0.0004 (9)
O(2)	0.0115 (12)	0.0182 (19)	0.0084 (8)	0.0069 (14)	0.0012 (8)	−0.0006 (11)
O(3)	0.0088 (9)	0.0160 (22)	0.0032 (4)	−0.0026 (11)	0.0025 (5)	0.0004 (8)
O(4)	0.0134 (9)	0.0157 (14)	0.0038 (4)	0.0004 (15)	0.0035 (5)	−0.0013 (11)
N(1)	0.0110 (12)	0.0137 (24)	0.0033 (6)	0.0005 (12)	0.0021 (7)	0.0000 (9)
N(2)	0.0087 (12)	0.0089 (18)	0.0027 (6)	−0.0014 (13)	0.0024 (7)	0.0000 (9)
N(3)	0.0108 (15)	0.0127 (21)	0.0046 (8)	0.0031 (15)	0.0019 (9)	−0.0015 (11)
N(4)	0.0055 (12)	0.0118 (20)	0.0032 (7)	0.0002 (13)	0.0009 (7)	−0.0008 (10)
H_2O	0.0097 (11)	0.0387 (28)	0.0087 (8)	0.0004 (16)	0.0030 (7)	0.0047 (13)
C(1)	0.0073 (15)	0.0136 (24)	0.0036 (9)	0.0008 (16)	−0.0005 (10)	−0.0025 (13)
C(2)	0.0181 (22)	0.0288 (38)	0.0032 (9)	0.0130 (24)	0.0045 (12)	0.0018 (15)
C(3)	0.0095 (17)	0.0271 (36)	0.0040 (10)	−0.0003 (20)	0.0033 (11)	0.0052 (16)
C(4)	0.0095 (15)	0.0097 (21)	0.0047 (9)	0.0001 (15)	0.0025 (10)	0.0015 (12)
C(5)	0.0087 (14)	0.0147 (24)	0.0043 (8)	−0.0013 (15)	0.0030 (9)	−0.0010 (12)
C(6)	0.0083 (11)	0.0096 (22)	0.0033 (6)	0.0031 (17)	0.0017 (7)	−0.0012 (13)
C(7)	0.0126 (20)	0.0172 (30)	0.0076 (13)	−0.0065 (20)	0.0040 (13)	−0.0023 (16)
C(8)	0.0067 (14)	0.0150 (26)	0.0049 (9)	0.0006 (15)	0.0000 (9)	0.0014 (12)
C(9)	0.0072 (15)	0.0359 (43)	0.0107 (13)	0.0069 (22)	0.0005 (12)	0.0022 (21)

[a] Esd's in parentheses. [b] Calculated positions, not refined. [c] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

cm^{-1}) were applied by a modified version of ORABS.[17] The maximum and minimum transmission factors were 0.96 and 0.83.

Solution and Refinement of the Structure. A three-dimensional Patterson map[18] was calculated and the positions of the Co, Cl, and six ligating atoms were determined. Least-squares refinement[19] of these positions resulted in an R_1 value of 43.5%. The cobalt y coordinate was arbitrarily assigned as 0.25 because $P2_1$ does not have a unique origin on the b axis. Since the y coordinate of the Co and Cl atoms had essentially the same value, the resultant electron density maps[18] contained spurious mirror planes at $y = 0.25$ and $y = 0.75$ which interfered with the location of further atoms. Careful peak selection coupled with bond length calculations allowed the remaining nonhydrogen atoms to be located.

The absolute configuration of the complex was determined by reference to the known absolute configuration of the *R*-pn[20,21] used in the synthesis of the complex. It was found that the complex structure as originally solved contained *S*-pn so the sign of the y coordinate of all atoms was reversed to create the correct mirror image.[22]

Several cycles of full-matrix least-squares refinement with anisotropic thermal parameters for all nonhydrogen atoms converged on $R_1 = 0.081$ and $R_2 = 0.074$ where

$$R_1 = \frac{\Sigma\,||F_o| - |F_c||}{\Sigma\,|F_o|}$$

$$R_2 = \frac{\Sigma w\,||F_o| - |F_c||}{\Sigma w\,|F_o|}$$

The least-squares refinement minimized the function $\sum w||F_o| - |F_c||$. A difference electron density map calculated at this point revealed the positions of most of the hydrogen atoms. Hydrogen coordinates were refined with thermal parameters fixed at 4.0 Å^2. Final refinement converged at $R_1 = 0.074$ and $R_2 = 0.064$ with all reflections included. Residuals calculated omitting the unobserved reflections were $R_1 = 0.055$ and $R_2 = 0.058$. Scattering factors and anomalous dispersion corrections were taken from ref 23. A final difference Fourier map had no peaks above 0.3 e/Å^3. Final nonhydrogen parameter shifts were all below 0.22σ.

The final positional and thermal parameters along with their standard deviations are listed in Table I. A compilation of observed and calculated structure factors is available.[24]

Results and Discussion

Description of the Complex Cation. The geometry of the complex cation, tentatively assigned as ΔΔΔΛ-*cis,trans*(*N*–*O*)-*uns-cis*-[Co(EDDA)(*R*-pn)]$^+$, Figure 2, by previous chemical and spectroscopic studies,[15] is confirmed by the structure determined, Figure 3.[25] The EDDA carboxylate oxygens are cis to one another giving rise to the uns-cis configuration; the *R*-pn nitrogen next to the optically active carbon is trans to the R ring EDDA oxygen; and the absolute configuration of the complex, assigned by the known absolute configuration of *R*-pn[20,21] as an internal reference, is ΔΔΔΛ[26] (net Δ)[27] in agreement with the assignment made by analysis of the circular dichroism spectrum of the complex.[15]

A detailed view of the complex cation is given in Figure 3,

Table II. Intramolecular Bond Distances (Å)

Atoms	Distance	Atoms	Distance
Co-O(1)	1.900 (8)	N(1)-C(2)	1.49 (1)
Co-O(3)	1.914 (6)	N(2)-C(5)	1.50 (1)
Co-N(1)	1.945 (8)	N(1)-C(3)	1.51 (1)
Co-N(2)	1.943 (8)	N(2)-C(4)	1.49 (1)
Co-N(3)	1.940 (10)	N(3)-C(7)	1.52 (2)
Co-N(4)	1.952 (9)	N(4)-C(8)	1.49 (1)
O(1)-C(1)	1.29 (1)	C(1)-C(2)	1.54 (1)
O(3)-C(6)	1.32 (1)	C(5)-C(6)	1.49 (1)
O(2)-C(1)	1.21 (1)	C(3)-C(4)	1.52 (1)
O(4)-C(6)	1.26 (1)	C(7)-C(8)	1.55 (1)
		C(8)-C(9)	1.57 (2)

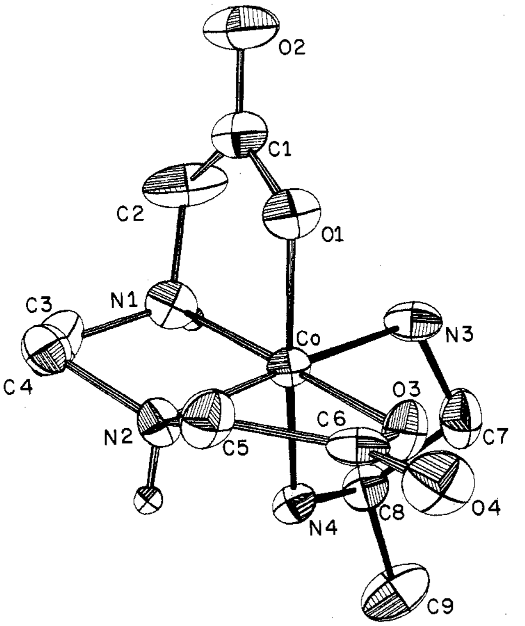


Figure 3. Molecular structure of ΔΔΔΛ-*cis,trans*(*N*-*O*)-*uns*-*cis*-[Co(EDDA)(*R*-pn)]$^+$. All hydrogen atoms except for those of the asymmetric amine nitrogens of EDDA have been omitted for clarity. Thermal ellipsoids are plotted at the 50% probability level except for the two hydrogens which are shown as spheres of arbitrary size.

Table III. Bond Angles (deg)

Atoms	Angle	Atoms	Angle
O(1)-Co-N(1)	84.9 (3)	O(1)-C(1)-O(2)	125.4 (11)
O(3)-Co-N(2)	84.7 (3)	O(3)-C(6)-O(4)	120.7 (9)
N(1)-Co-N(2)	87.7 (3)	O(1)-C(1)-C(2)	113.8 (9)
N(3)-Co-N(4)	86.3 (3)	O(3)-C(6)-C(5)	117.6 (8)
O(1)-Co-N(2)	90.3 (3)	O(2)-C(1)-C(2)	120.8 (11)
O(1)-Co-O(3)	90.2 (3)	O(4)-C(6)-C(5)	121.8 (8)
O(1)-Co-N(3)	89.0 (4)	N(1)-C(2)-C(1)	109.6 (8)
O(1)-Co-N(4)	175.0 (4)	N(2)-C(5)-C(6)	107.5 (7)
N(1)-Co-O(3)	171.0 (3)	N(1)-C(3)-C(4)	109.4 (9)
N(1)-Co-N(3)	97.6 (4)	N(2)-C(4)-C(3)	104.5 (8)
N(1)-Co-N(4)	94.3 (4)		
N(2)-Co-N(3)	174.5 (4)		
N(2)-Co-N(4)	94.5 (4)	N(3)-C(7)-C(8)	105.5 (10)
O(3)-Co-N(3)	89.9 (4)	N(4)-C(8)-C(7)	106.5 (10)
O(3)-Co-N(4)	91.2 (3)	N(4)-C(8)-C(9)	109.6 (9)
Co-O(1)-C(1)	116.7 (7)	C(2)-N(1)-C(3)	114.0 (8)
Co-O(3)-C(6)	112.4 (6)	C(4)-N(2)-C(5)	115.4 (8)
Co-N(1)-C(2)	107.6 (6)	C(7)-C(8)-C(9)	114.9 (11)
Co-N(2)-C(5)	106.9 (6)		
Co-N(1)-C(3)	107.1 (6)		
Co-N(2)-C(4)	108.9 (6)		
Co-N(3)-C(7)	109.5 (7)		
Co-N(4)-C(8)	111.1 (7)		

Table IV. Close Intermolecular Distances (Å)

Atoms	Distance	Sum of the van der Waals radii[a]
O(1)-H_2O	2.90 (1)	2.80
$O(3)_t{}^b$-$H_2O_t{}^c$	2.87 (1)	2.80
$N(1)_t{}^d$-Cl	3.17 (1)	3.30
$N(3)_t{}^e$-Cl	3.17 (2)	3.30
$N(4)_t{}^f$-Cl	3.20 (1)	3.30
$N(4)_t{}^b$-$O(4)_t{}^c$	2.95 (1)	2.90
N(2)-$O(4)_t{}^e$	3.07 (1)	2.90
$N(3)_t{}^b$-$O(4)_t{}^g$	3.07 (1)	2.90

[a] L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960, pp 257–264. [b] Transformed; related to the coordinates in Table I by the transformation $x + 1, y, z$. [c] Transformation $1 - x, y + 1/2, 1 - z$. [d] Transformation $x, y, z + 1$. [e] Transformation $-x, y + 1/2, 1 - z$. [f] Transformation $-x, y - 1/2, 1 - z$. [g] Transformation $1 - x, y - 1/2, 1 - z$.

and the intramolecular distances and bond angles are given in Tables II and III.[28] The bond length distortions are minimal except for the Co–O_G bond length of 1.914 Å which is significantly longer than the normal value of ca. 1.88 Å.[29] Similar distortions in the Co–O_G bond lengths were also observed in the [Co(EDTA)]$^-$ and [Co(TRDTA)]$^-$ structures.[1,2] The angular distortions about Co from the ideal octahedral geometry are significant, especially in the case of the five-membered glycinate rings of EDDA (average O–Co–N bond angle of 84.8°). For the two five-membered diamine rings the angles are closer to 90° with an average N–Co–N bond angle of 87.0°.

The methyl group of *R*-pn is in the less sterically crowded equatorial position producing a λ conformation for the diamine ring. This is in agreement with the previous X-ray structural studies of *R*-pn coordination compounds where pn has been found exclusively with the equatorial methyl conformation.[21,30,31]

Description of the Unit Cell. The unit cell, Figure 4, consists of two discrete complex cations, the chloride counterions, and the two waters of crystallization. The bonding in the unit cell appears to be mostly electrostatic with only weak hydrogen bonding, most distances being close to the sum of the van der Waals radii. The relevant distances are given in Table IV.

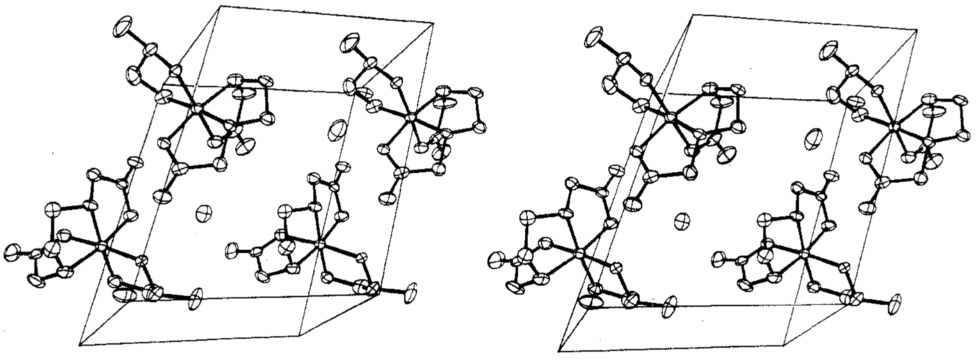


Figure 4. Stereoscopic illustration of the packing in the unit cell.

Table V. Comparison of Bond Angle Sums of [Co(EDTA)]$^-$, [Co(TRDTA)]$^-$, and *uns-cis*-[Co(EDDA)(*R*-pn)]$^+$

Ring	Ideal	EDTA[1]	TRDTA[2]	EDDA
R	538.4	537.8	539.5	532.5 (5)
G	538.4	523.5	526.5	529.0 (5)
E	527.9	520.9		517.7 (10)
T	637.3		673.8	

The interatomic contacts of the chloride ion to N(1), N(3), and N(4) are the only cases in which the bond lengths indicate significant hydrogen bonding.

Comparison of *uns-cis*-[Co(EDDA)(*R*-pn)]$^+$ with [Co(EDTA)]$^-$ and [Co(TRDTA)]$^-$. The tetradentate EDDA–Co^{III} chelate is essentially a fragment of the larger hexadentate EDTA–Co^{III} chelate, Figure 1. In the s-cis configuration, EDDA forms two out-of-plane (R) glycinate rings (the reference plane is that formed by the two E ring EDDA nitrogens and the cobalt) while, in the uns-cis configuration, EDDA forms both R and G (in-plane) rings about the cobalt (Figure 1). In the Weakliem and Hoard study of [Co(EDTA)]$^-$, it was found that the G rings are significantly more strained than the R rings.[1]

As an estimate of ring strain, Weakliem and Hoard suggested that the sum of the bond angles of the rings could be used.[1] For the five-membered glycinate rings, the ideal bond angle sum is 538.4° which would allow the rings to be nearly planar.[32] The ideal value for the sum of the bond angles belonging to the five-membered E ethylenediamine ring of EDDA or EDTA is 527.9° and that of the six-membered T trimethylenediamine ring of TRDTA is 637.3°. Table V compares the bond angle sums for the various chelate rings of [Co(EDTA)]$^-$ and [Co(TRDTA)]$^-$ and the EDDA portion of *uns-cis*-[Co(EDDA)(*R*-pn)]$^+$. The G ring strain as well as the relative lack of strain in the R rings in all three complexes is clearly demonstrated by the bond angle sums.

The primary reason for the G ring strain in [Co(EDTA)]$^-$ is thought to be the angular strain about the coordinated nitrogens, caused by the rotation of the nitrogen about the Co–N bond which is necessary for the formation of the five-membered E ring.[1] The EDTA nitrogens are the intersection points of three five-membered chelate rings with two common members, cobalt and nitrogen. Each ring attempts to impose its own stereochemical requirements on the nitrogen atom which is also constrained to approximately tetrahedral geometry. The resulting compromise structure contains not only the angle and bond length abnormalities in the G rings but also significant distortions of the nitrogen tetrahedra, specifically an opened C_G–N–C_E angle of 116.1° with the C_R–N–C_E and C_R–N–C_G angles remaining nearly tetrahedral.[1]

In contrast, [Co(TRDTA)]$^-$ with the less constricting six-membered trimethylenediamine (T ring) backbone has less strained nitrogen tetrahedra (C_G–N–C_T angle of 108.8°, C_G–N–C_R angle of 110.0°, C_R–N–C_T angle of 112.9°) but still significantly strained G rings.[2] The size and flexibility of the six-membered diamine ring serve to relieve some of the angular strain about the nitrogens but cannot completely relieve the G ring distortion produced by the nitrogen rotation. Although the G rings still remain strained, the T ring appears to compensate for the distortion induced in the cobalt coordination polyhedron. In [Co(EDTA)]$^-$ the N–Co–N angle is approximately 90° but both N–Co–O_G angles are less than 90° and, as a result, the O_G–Co–O_G angle is opened significantly to 104°.[1] However, in [Co(TRDTA)]$^-$, the T ring N–Co–N angle opens to 99° and the O_G–Co–O_G angle returns to a nearly octahedral value of 93°.[2] The bond angle sum for the T ring is also singificantly greater than the ideal value (Table V).

Table VI. Some Least-Squares Planes[a] in the *uns-cis*-[Co(EDDA)(*R*-pn)]$^+$ Molecule

Atom	Distance from Plane, Å	Atom	Distance from Plane, Å
Plane 1. R Ring			
$0.5559X + 0.6613Y + 0.5037Z - 5.1646 = 0$			
O(1)*	−0.006 (8)	C(2)*	−0.005 (13)
O(2)*	−0.007 (8)	Co	−0.164 (1)
C(1)*	0.018 (11)	N(1)	0.355 (8)
Plane 2. E Ring			
$0.5157X - 0.7030Y + 0.4898Z + 2.4445 = 0$			
N(1)*	0.0	C(3)	−0.210 (13)
N(2)*	0.0	C(4)	0.483 (10)
Co*	0.0		
Plane 3. G Ring			
$-0.4922X + 0.8577Y - 0.1486Z - 4.6960 = 0$			
O(3)*	−0.003 (8)	C(6)*	0.008 (12)
O(4)*	−0.004 (11)	Co	−0.224 (1)
C(5)*	−0.002 (11)	N(2)	0.417 (9)

[a] Atoms defining the planes are marked by an asterisk. Equations of planes in rectangular coordinates, with X parallel to the a axis, Y parallel to the b axis, and Z normal to the XY plane.

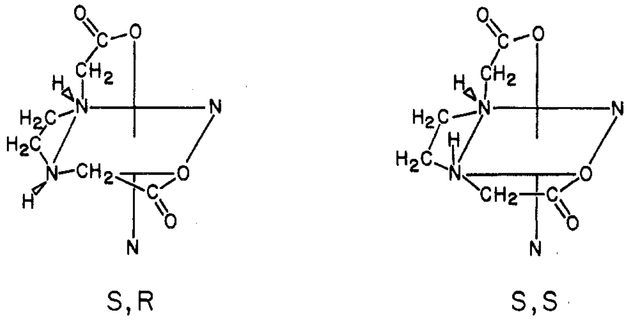
Uns-cis chelated EDDA, unlike either EDTA or TRDTA, does not possess the full ring system. This additional freedom apparently allows the chelate to average the strain over all of its parts rather than concentrating it in the G ring. Thus, as shown in Table III, the N–Co–O bond angles for the R and G rings are almost identical in *uns-cis*-Co(EDDA) while in [Co(EDTA)]$^-$ and [Co(TRDTA)]$^-$ the comparable angles differ by as much as 5°.[1,2] The bond angle sums also show this averaging. In [Co(EDTA)]$^-$ the G rings are ca. 15° below the ideal sum while the R rings are only 1° lower than ideal. [Co(TRDTA)]$^-$ has a similar pattern with the G rings 12° less and the R ring 1° larger than ideal. *uns-cis*-Co(EDDA), however, has a G ring sum that is only 9° low but both the R and E rings are more strained (6 and 10° low, respectively) than in [Co(EDTA)]$^-$.

The strain averaging is also demonstrated by the nonplanarity of the R ring. In contrast to [Co(EDTA)]$^-$ where the nitrogen and cobalt are both slightly displaced on the same side of the $CCOO_R$ reference plane, *uns-cis*-Co(EDDA) has the R ring distorted in the same manner as the G ring, with the cobalt and nitrogen lying on opposite sides of the $CCOO_R$ plane. A complete list of mean planes and deviations from these planes is given in Table VI.

The angular strain about the EDDA nitrogens also differs from the hexadentate chelates. [Co(TRDTA)]$^-$, by virtue of its six-membered diamine ring, has nearly unstrained nitrogen tetrahedra[2] while [Co(EDTA)]$^-$ has a strained C_E–N–C_G angle but a nearly tetrahedral C_E–N–C_R angle.[1] In comparison, *uns-cis*-Co(EDDA) has both angles opened to nearly the same extent; the C_E–N–C_G angle is 115.4° and the C_E–N–C_R angle is 114.0°. Again, the strain is more evenly distributed over the entire chelate rather than residing mainly in the G ring.

The difference in planarity of the R and G glycinate rings in these complexes appears to have a marked effect on the rate of exchange of the α-carbon protons with deuterium in D_2O. Previous studies of [Co(EDTA)]$^-$ and other chelates possessing R and/or G rings has demonstrated that R rings will deuterate easily in acidic or basic D_2O while G rings will not.[5,7-9] Analogous behavior for the four isomers of *uns-cis*-[Co(EDDA)(*R*-pn)]$^+$ has been demonstrated[15] even though the present structural study has shown some nonplanarity for the R ring in one of the isomers.

The observed strain in uns-cis coordinated EDDA may be a contributing factor to the generally small amounts of this isomer produced in most synthetic reactions.[8,15] From the studies of [Co(EDTA)]$^-$ and [Co(TRDTA)]$^-$, as well as the



S,R S,S

Figure 5. The two possible asymmetric nitrogen configurations in *uns-cis*-Co(EDDA).

cobalt complexes of the similar hexadentates EDDS,[10,11] EDDDA,[12] and EDDAMS,[13] the formation of the Co(EDDA) isomer with two five-membered R rings (s-cis), Figure 1, would be expected to be highly favored over formation of the isomer with both R and G rings. Certainly the trans isomer, with two G rings, is highly unlikely for $[\mathrm{Co(EDDA)(monodentate)_2}]^n$ complexes. The only known trans EDDA isomer is *trans*-$[\mathrm{Pt(EDDA)Cl_2}]$, formed by oxidation of square-planar [Pt(EDDA)] by $\mathrm{Cl_2}$.[33]

It is only in a few cases, such as the $[\mathrm{Co(EDDA)(dicarboxylate)}]^-$ complexes with carbonate and oxalate, that the *uns-cis*-EDDA confirugation appears to be the slightly favored product.[8,34,35] It has been postulated that the presence of large amounts of uns-cis isomers in these complexes is caused by the relief of the nonbonding proton–proton interactions thought to occur in the *uns-cis*-$[\mathrm{Co(EDDA)(diamine)}]^+$ complexes.[8] In any case, it appears that ring strain is only one of the factors in determining the most stable EDDA configuration.

Asymmetric Nitrogen Configurations. The configurations of the asymmetric secondary nitrgoens of EDDA in Co(III) complexes have been of interest to a number of investigators because of the influence this source of asymmetry may have on circular dichroism spectra.[36,37] The absolute configuration of the R ring nitrogen is determined by the absolute configuration of the complex but the configuration of the G ring nitrogen can be either *R* or *S* for a particular chelate geometry, Figure 5. A previous study in this laboratory of the isomerization of *uns-cis*-$[\mathrm{Co(EDDA)(ox)}]^-$ and *uns-cis*-$[\mathrm{Co(EDDA)(mal)}]^-$, where ox = oxalate and mal = malonate, to the corresponding s-cis isomers under acidic conditions indicated that the nitrogen configurations were *R,R* and *S,S* in the racemic complex (Figure 5).[8] The *R,S–S,R* racemates would require inversion at the "planar" nitrogen, N(2) (the nitrogen of the G glycinate ring), on going from uns-cis to s-cis, and it was assumed that the rate of N–H dissociation in acidic solution would be much slower than the rate of isomerization of the chelate. Similar studies with *uns-cis*-$[\mathrm{Co(EDDA)}(R\text{-pn})]^+$ isomers have been inconclusive due to the extremely slow rate of isomerization.

In the crystalline state the configurations of the EDDA nitrogens were found, by this study, to be *S,R* for the Δ isomer as shown in Figure 3. *uns-cis*-$[\mathrm{Co(EDDA)}(R\text{-pn})]^+$ was synthesized from *uns-cis*-$[\mathrm{Co(EDDA)(CO_3)}]^-$ under acidic conditions but chromatographed and recrystallized under neutral conditions[15] which would allow rapid exchange of the amine protons and which should then give the most stable nitrogen configurations. It is unlikely that the *R* configuration of N(2) is due to interactions in the crystal because the closest intermolecular approach is 3.07 Å to O(4), nearly 0.2 Å longer than the sum of the van der Waals radii, which is too long for significant hydrogen bonding. It is therefore probable that the *S,R* configuration represents the thermodynamically stable isomer in solution as well as in the solid state. It is interesting to note that an X-ray study of *uns-cis*-$[\mathrm{Co(EDDA)(H_2O)_2}]^+$, formed by acid hydrolysis of *uns-cis*-$[\mathrm{Co(EDDA)(CO_3)}]^-$, showed the product to be the *R,S–S,R* racemate and it was concluded that the nitrogen configurations in the starting material were also the *R,S–S,R* racemates.[38] In a recent paper dealing with the circular dichroism spectra of *uns-cis*-$[\mathrm{Co(EDDA)(CO_3)}]^-$ and related compounds, analysis of the various structural factors contributing to the rotational strength also supported the *R,S–S,R* configuration for the carbonato complex.[37]

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Registry No. ΔΔΔΛ-*cis,trans(N–O)-uns-cis*-$[\mathrm{Co(EDDA)}(R\text{-pn})]\mathrm{Cl{\cdot}H_2O}$, 55028-61-0.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC40821R.

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Contribution from the Department of Chemistry,
The University of Texas at Austin, Austin, Texas 78712

Crystal and Molecular Structure of Bis[(+)-N,α-dimethylphenethylammonium] Tetrachlorocuprate(II). Relationship between the Electronic Spectrum and the Distortion of the $CuCl_4$ Chromophore from Tetrahedral Symmetry

R. L. HARLOW, WILLIAM J. WELLS, III, GEORGE W. WATT, and S. H. SIMONSEN*

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Investigation of the crystal structure of bis[(+)-N,α-dimethylphenethylammonium] tetrachlorocuprate(II), $[C_6H_5CH_2CH(CH_3)NH_2CH_3]_2CuCl_4$, was prompted when its maximum d–d transition, 10,200 cm^{-1}, was noted as being considerably greater in energy than that reported for other D_{2d} tetrachlorocuprate(II) complexes. Crystals of the compound are triclinic, space group $P1$, with $a = 12.115$ (3) Å, $b = 12.968$ (2) Å, $c = 8.741$ (2) Å, $\alpha = 106.64$ (1)°, $\beta = 100.25$ (2)°, $\gamma = 98.88$ (2)°, $Z = 2$ (two crystallographically independent $CuCl_4^{2-}$ anions per asymmetric unit), $d_x = 1.329$ g cm^{-3}, and $d_m = 1.330$ g cm^{-3}. Intensities were obtained from θ–2θ scans with a four-circle automatic diffractometer using graphite-monochromatized Mo Kα radiation. A total of 3190 reflections [$I > 3\sigma(I)$] were used in the full-matrix least-squares refinement; the phenyl groups were refined as rigid bodies. The positions of the hydrogen atoms could not be located unambiguously and were not included in the refinement. The conventional and weighted agreement indices are $R = 0.074$ and $R_w = 0.053$. The $CuCl_4^{2-}$ anions are found to be highly distorted from T_d symmetry in agreement with the spectral results; the average of the two large Cl–Cu–Cl angles is 138.3°. The average Cu–Cl bond distance is 2.238 Å. The $CuCl_4^{2-}$ anions are bridged by a network of hydrogen bonds involving the $-NH_2-$ groups of the cations. A study of the maximum d–d transition vs. the distortion of the $CuCl_4$ chromophore from T_d symmetry is also reported. The transition energy appears to be a smooth function of the distortion but more data points are needed to complete the curve.

Introduction

Recent investigations of the chemistry of methamphetamine (N,α-dimethylphenethylamine) and derived salts produced two compounds with novel chlorocuprate(II) coordination geometries as determined by single-crystal X-ray analysis.[1,2] Unusual spectral properties initiated the structure determinations of these compounds and prompted a more careful examination of the d–d electronic spectra of a number of tetrachlorocuprates(II).

One of the most common geometries found for the $CuCl_4^{2-}$ anion is that often referred to as the "flattened" tetrahedron with nearly or exactly D_{2d} symmetry. That it is intrinsically more stable than a complex with either T_d (regular tetrahedron) or D_{4h} (square plane) symmetry has been shown by various theoretical calculations.[3-5] Of the discrete (purely four-coordinate) $CuCl_4^{2-}$ anions studied by X-ray crystallographic methods, only one with nearly T_d symmetry[6] and one square-planar complex have been reported,[1] while at least 12 structural studies,[1,7-16] including the present work, have revealed anions with nearly D_{2d} symmetry (deviations from precise D_{2d} symmetry are quite small).

It has been predicted theoretically that the electronic absorption spectrum of any D_{2d} $CuCl_4^{2-}$ complex should be sensitive to the amount of "flattening", or distortion, that has occurred. In particular, the maximum d–d transition should increase in energy as the geometry distorts from a regular tetrahedron toward a square plane.[4] This was shown to be the case in two recent studies of several $CuCl_4^{2-}$ salts in which the maximum d–d absorption was correlated with a distortion parameter based on X-ray results.[17,18]

We report here the crystal structure of bis[(+)-N,α-dimethylphenethylammonium] tetrachlorocuprate(II), hereafter abbreviated (d-mampH)$_2$CuCl$_4$, which was undertaken because its maximum d–d transition was found to be greater than that for other D_{2d} tetrachlorocuprate(II) complexes that have been studied. In addition, the relationship between the distortion of the tetrahedral geometry and the electronic spectra for eight compounds containing the $CuCl_4$ chromophore is discussed.

Experimental Section

Electronic Spectra. The electronic spectra were measured as described previously.[1]

Crystallographic Data Collection. The bright yellow crystal selected for the measurement of lattice parameters and intensity data had dimensions of 0.24 × 0.24 × 0.32 × 0.29 mm perpendicular to (100), $(11\bar{1})$, (010), and (110), respectively. A preliminary study of the crystal was carried out on a Syntex $P2_1$ diffractometer and showed the crystal to be triclinic. Because the cation was present only as the (+) enantiomer, the space group was unambiguously assigned as $P1$. The least-squares refinement of the Bragg angles (Cu Kα_1, λ 1.54050 Å) for 18 high-angle reflections (85° $< 2\theta <$ 104°) produced the following unit cell parameters: $a = 12.115$ (3) Å, $b = 12.968$ (2) Å, $c = 8.741$ (2) Å, $\alpha = 106.64$ (1)°, $\beta = 100.25$ (2)°, $\gamma = 98.88$ (2)°, and $V = 1263.8$ Å^3. With a formula weight of 505.85 and $Z = 2$, the calculated density is 1.329 g cm^{-3} which agrees well with the measured value of 1.330 g cm^{-3}. With $Z = 2$, of course, each unit cell must contain two crystallographically independent $CuCl_4^{2-}$ ions and four d-mampH$^+$ cations.

Intensity data were collected on the Syntex diffractometer with Mo Kα radiation monochromatized by a graphite crystal. The θ–2θ scan technique was employed with each scan ranging 1.0° in 2θ below and beyond the Kα_1 and Kα_2 peaks, respectively. The scan rate varied from 2.0 to 5.0° min^{-1} depending in a direct manner on the number of counts obtained in a rapid preliminary scan of the peak. Background counts were taken at both ends of the scan range, each for a time equal to half the scan time. A total of 4436 unique reflections