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The Crystal Structure and Absolute Configuration of L$(-)_{589}\beta_2$-(*RRS*)-(triethylenetetramine-(*S*)-prolinato)cobalt(III) Diiodide Dihydrate

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The crystal structure and absolute configuration of L$(-)_{589}\beta_2$-(RRS)-(triethylenetetramine-(S)-prolinato)cobalt(III) diiodide dihydrate, $[\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2)(\overline{\text{NHCH}_2\text{CH}_2\text{CH}_2\text{C}}\text{HCOO})]\text{I}_2 \cdot 2\text{H}_2\text{O}$, have been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in space group $P2_12_12_1$ (D_2^4, no. 19) of the orthorhombic system with a = 9.12 (1), b = 14.43 (2), c = 14.90 (2) Å, and Z = 4. Measured and calculated densities are, respectively, 2.03 (2) and 2.06 (1) g cm^{-3}. The structure has been refined by full-matrix least-squares techniques to a final residual R = 0.066 for 1417 independent nonzero reflections. The crystal is composed of L$(-)_{589}\beta_2$-(RRS)-Co(trien)-((S)-Pro)$^{2+}$ cations, I$^-$ anions, and H_2O molecules which are held together by hydrogen bonds and electrostatic forces. The coordination around Co is octahedral with the proline O(carboxyl) atom coordinated *trans* to the out-of-plane N atom of β-trien. Important bond distances are as follows: mean Co–N = 1.96 ± 0.01 Å, Co–O(carboxyl) = 1.88 ± 0.01 Å. The absolute configuration of the complex cation has been determined by the X-ray anomalous dispersion method. The X-ray analysis confirms the structure and absolute configuration as deduced from chemical and relative stability studies.

Introduction

Recently there have been a number of studies on cobalt(III) compounds containing coordinated asymmetric nitrogen atoms. For the complexes of Co(en)$_2$sar^{2+} [1,2] and β_2-Co(trien)sar^{2+} [3] (en = ethylenediamine, trien = triethylenetetramine, sar = N-methylglycine) it has been shown that the coordination of sarcosine is stereospecific with respect to the asymmetric N-methyl center. Thus, for a given absolute configuration about the cobalt ion, only one configuration is allowed for the N-methyl group of sarcosine. This has been established by showing that under conditions where proton exchange is very rapid at this N center, mutarotation is excluded.[1,2]

These results have led to the possibility of a completely stereospecific synthesis if the center at nitrogen can be forced to adopt a fixed configuration. This might be accomplished using (S)-proline as the ligand, where the configuration at nitrogen is determined by the configuration at the α-carbon atom by virtue of the five-membered ring which links these two atoms.

Two Co(trien)((S)-Pro)$^{2+}$ species[4] have been shown to be formed from the reaction mixture in approximately equal amounts. Optical rotatory dispersion (ORD) and circular dichroism (CD) spectra indicate that these two complexes have mirror-image configurations with respect to the cobalt ion.[5] Evidently the synthesis, which is conducted under nonequilibrium conditions, shows very little stereospecificity.

Comparisons with the L$(-)_{589}\beta_2$-(RRS)-Co(trien)-sar^{2+} [4] and D$(+)_{589}\beta_2$-(SSR)-Co(trien)sar^{2+} complexes[3] indicated that the most probable structures of the proline complexes were L$(-)_{589}\beta_2$-(RRS)-Co(trien)-((S)-Pro)$^{2+}$ and D$(+)_{589}\beta_2$-(SSS)-Co(trien)((S)-Pro)$^{2+}$. The possibility of other isomeric species, particularly with regard to the mode of chelation of the trien moiety, could not be excluded. The lack of stereospecificity in this system was not understood.

For these reasons the crystal structure analyses of the two isomeric forms of Co(trien)((S)-Pro)$^{2+}$ were undertaken. This paper describes the crystal and molecular structure of the $(-)_{589}$Co(trien)((S)-Pro)$^{2+}$ isomer. Unfortunately this complex could be obtained in a form suitable for a single-crystal study only as the diiodide salt. The large contributions by the iodine atoms to the X-ray scattering reduce the precision with which the parameters of the lighter atoms can be determined.

Experimental Section

Crystal Data.—$(-)_{589}$[Co(trien)((S)-Pro)]$I_2 \cdot 2H_2O$ forms dark orange crystals which are stable to both air and X irradiation. The unit cell is orthorhombic with a = 9.12 (1) Å, b = 14.43 (2) Å, c = 14.90 (2) Å, V = 1960.8 Å^3, D_m = 2.03 (2) g cm^{-3} (by flotation in bromoethane–methanol), Z = 4, D_x = 2.06 (1) g cm^{-3} for $C_{11}H_{30}N_5O_4I_2Co$ with FW = 609.2, and $\mu_{\text{Cu K}\alpha}$ = 318.0 cm^{-1}. The space group is $P2_12_12_1$ (D_2^4, no. 19) from systematic absences of reflections observed on precession and Weissenberg photographs (h00 absent for $h = 2n + 1$, 0k0 for $k = 2n + 1$, 00l for $l = 2n + 1$). The unit cell dimensions were calculated from the values of θ for a number of zero and upper layer reflections measured on an equiinclination diffractometer with Ni-filtered Cu Kα radiation [λ(Cu Kα_1) 1.5405 Å, λ(Cu Kα_2) 1.5443 Å].

X-Ray Data Collection and Reduction.—The use of Cu X radiation was dictated by the available experimental facilities. In order (i) to increase the proportion of observably strong reflections in the presence of high background radiation and (ii) to compensate for the high absorption coefficient by providing ac-

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[1] D. A. Buckingham, S. F. Mason, A. M. Sargeson, and K. R. Turnbull, *Inorg. Chem.*, **5**, 1649 (1966).

[2] J. F. Blount, H. C. Freeman, A. M. Sargeson, and K. R. Turnbull, *Chem. Commun.*, 324 (1967).

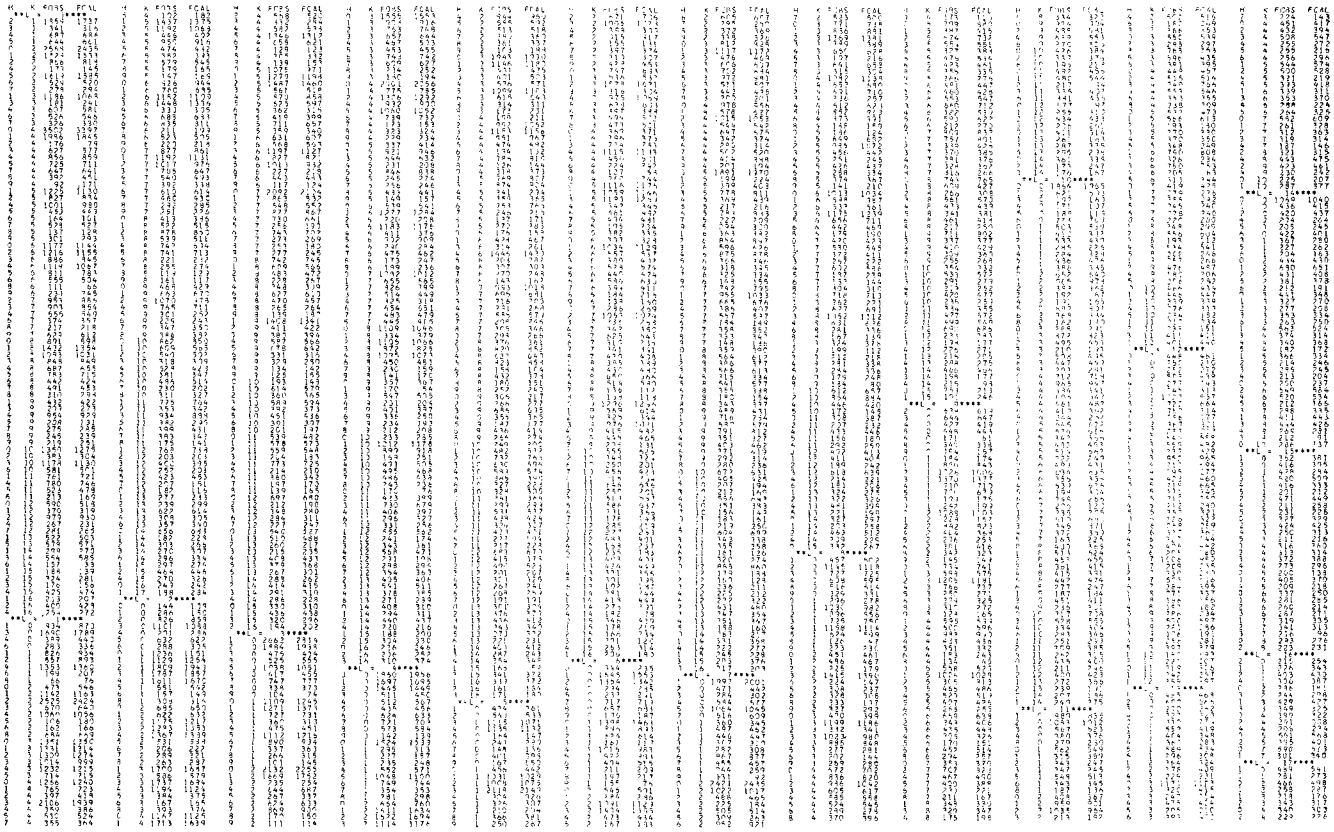
[3] L. G. Marzilli and D. A. Buckingham, *Inorg. Chem.*, **6**, 1042 (1967).

[4] Nomenclature: R and S designate the asymmetry about the "angular" and "planar" asymmetric N atoms of triethylenetetramine and the secondary N atom of the amino acid in that order and follow the rules suggested by C. K. Ingold, V. Prelog, and R. S. Cahn, *Angew. Chem. Intern. Ed. Engl.*, **5**, 385 (1966), and accepted by IUPAC. For consistency we have also used this nomenclature to specify the configuration of the α-C atom of the amino acid (*e.g.*, (S)-proline = L-proline). The use of β, β_1, and β_2 follows that used in ref 3. The absolute configuration about the cobalt center and the optical rotation are indicated by the prefix L$(-)_{589}$.[5]

[5] D. A. Buckingham, L. G. Marzilli, I. E. Maxwell, A. M. Sargeson, and H. C. Freeman, *Chem. Commun.*, 583 (1969).

Table I

Observed and Calculated Structure Amplitudes (in electrons × 10) for L$(-)_{589}\beta_2$-(*RRS*)-[Co(trien)((*S*)-Pro)]$I_2 \cdot 2H_2O$



curately measurable crystal dimensions for inclusion in precise absorption corrections, a relatively large crystal was used for data collection. The chosen crystal had well-developed (010), (0$\bar{1}$0), (110), ($\bar{1}$10), (1$\bar{1}$0), ($\bar{1}\bar{1}$0), (011), (01$\bar{1}$), and (001) faces and had dimensions 0.12 × 0.18 × 0.11 mm parallel to *a*, *b*, and *c*, respectively. It was mounted about its *a* axis. The intensity data were recorded by the ω-scan (stationary counter, moving crystal) method on an automated Buerger–Supper equi-inclination diffractometer, using an early version of the control program described by Freeman, Guss, Nockolds, Page, and Webster.[6] The reflection indices *hkl*, setting angles ϕ (crystal) and Υ (counter), and scan range ω were input from punched paper tape. The background and peak intensities—B_1, P, B_2—were recorded under computer control, using a sequence of operations analogous to that described earlier.[7]

A fully stabilized X-ray generator provided Cu Kα radiation. An Ni-foil filter, scintillation counter (Philips PW 1964/10), and pulse-height analyzer (Philips PW 4280) were used. A fixed angle of 2° 50′ was subtended at the crystal by the counter aperture. The maximum observed count rate was below the region where coincidence losses were significant and therefore no attenuation of the X-ray beam was necessary. The scan range was generally 3°, being increased for very extended reflections. A constant scan speed of 2°/min was used.

Data were collected in the range $10° \leqslant \Upsilon \leqslant 140°$ for the zones *Hkl* ($0 \leqslant H \leqslant 9$). A number of reflections of the type $hk\bar{l}$ were also collected on each layer for later use in determining the absolute configuration of the structure by the anomalous dispersion method. The net count $I(hkl)$ for each reflection was calculated as $I(hkl) = P - (B_1 + B_2)$ where P is the peak scan and B_1 and B_2 are the first and second stationary background counts. A reflection was considered unobserved if $I(hkl) < 2(B_1 + B_2)^{1/2}$. Unobserved reflections were not included in the analysis or refinement of the structure. Ten zero-layer reflections were remeasured after the completion of data collection for each reciprocal layer. Scale factors between the ten sets of standard reflections, calculated by least squares,[8] indicated that crystal decomposition and instrumental instability were negligible.

Lorentz-polarization corrections were applied and corrected relative structure factor amplitudes $|F_o(hkl)|$ were obtained. Estimated standard deviations in the relative structure factor amplitudes (observed and unobserved) were calculated using the method due to Hoard and Jacobson.[9] The values of K_T, K_B, and K_D used in this expression were 0.02, 0.05, and 0, respectively. Absorption corrections were applied using the method of Coppens, Leiserowitz, and Rabinovich,[10] with a 6 × 6 × 8 grid parallel to the *a*, *b*, and *c* axes, respectively. Transmission factors ranged from 0.03 to 0.19. A total of 1825 independent reflections of the type *hkl* were recorded, of which 408 were unobservably weak.

Solution and Refinement of the Structure.—The structure was solved by the use of a sharpened Patterson synthesis and standard Fourier syntheses. A $(F_o - F_c)$ synthesis in the later stages of the solution indicated the presence of two noncoordinated water molecules. Full-matrix least-squares refinement was carried out, minimizing the function $\Sigma w(|F_o| - s|F_c|)^2$ where weights $w = 1/\sigma^2(F)$ and s is the inverse of scale factor to be applied to $|F_o|$. The unobserved data were assigned zero weights. After three cycles in which an overall scale factor, atomic coordinates, and isotropic temperature factors were varied, the residuals $R_1 = \Sigma\Delta/\Sigma|F_o|$ and $R_2 = [\Sigma w\Delta^2/\Sigma w F_o^2]^{1/2}$ were 0.106 and 0.079, respectively ($\Delta = ||F_o| - s|F_c||$).

An analysis of $\langle 1/\Delta^2 \rangle$ in ranges of $|F_o|$ and $(\sin\theta)/\lambda$ indicated a systematic dependence on $|F_o|$. New weights were assigned by

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[6] H. C. Freeman, J. M. Guss, C. E. Nockolds, R. Page, and A. Webster, *Acta Cryst.*, in press.

[7] H. C. Freeman and I. E. Maxwell, *Inorg. Chem.*, **8**, 1293 (1969).

[8] (a) A. D. Rae, *Acta Cryst.*, **19**, 683 (1965); (b) A. D. Rae and A. B. Blake, *ibid.*, **20**, 586 (1966).

[9] L. C. Hoard and R. A. Jacobson, *J. Chem. Soc., A*, 1203 (1966).

[10] P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Cryst.*, **18**, 1035 (1965).

TABLE II

FRACTIONAL ATOMIC POSITIONAL PARAMETERS AND ANISOTROPIC TEMPERATURE FACTORS FOR $\text{L}(-)_{589}\beta_2$(*RRS*)-[Co(trien)((*S*)-Pro)]$I_2 \cdot 2H_2O$[a,b]

Atom	10^4x	10^4y	10^4z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
I(1)	5169(2)	4140(1)	1082(1)	0147(3)	0045(1)	0031(1)	0013(1)	-0001(1)	0005(1)
I(2)	1822(2)	1223(1)	-1897(1)	0127(3)	0055(1)	0057(1)	0021(1)	0002(2)	-0015(1)
Co	6366(4)	-0054(2)	1020(2)	0094(5)	0027(2)	0030(2)	0005(2)	0004(3)	-0003(2)
O(1)	8577(23)	-1618(11)	-0639(13)	0176(35)	0037(9)	0062(11)	0016(15)	0002(16)	0014(8)
O(2)	6878(18)	-0770(10)	0013(10)	0090(22)	0034(8)	0039(8)	0011(13)	0020(11)	-0004(7)
O(3)	3535(20)	2052(11)	3949(13)	0144(28)	0047(9)	0060(10)	0016(13)	-0005(16)	0006(10)
O(4)	8679(32)	1070(20)	3088(17)	0336(57)	0134(22)	0083(15)	-0092(30)	-0044(26)	-0011(16)
N(1)	5370(21)	-1124(14)	1549(13)	0080(27)	0049(11)	0049(10)	-0050(15)	-0000(13)	0005(9)
N(2)	4508(21)	0214(13)	0467(12)	0095(29)	0045(11)	0038(10)	-0005(14)	0032(14)	-0015(9)
N(3)	7059(26)	1088(12)	0441(12)	0167(36)	0030(11)	0035(10)	0024(17)	0013(16)	0006(8)
N(4)	5964(22)	0720(12)	2074(12)	0131(31)	0025(9)	0037(10)	0013(14)	0024(15)	-0010(8)
N(5)	8317(24)	-0392(13)	1490(12)	0129(32)	0033(9).	0032(9)	0015(15)	0008(15)	-0001(8)
C(1)	3768(31)	-1151(17)	1253(14)	0179(44)	0032(12)	0027(11)	0005(19)	0006(18)	0001(9)
C(2)	3671(30)	-0683(18)	0355(18)	0142(41)	0044(15)	0052(14)	0033(20)	-0043(21)	-0020(12)
C(3)	4786(34)	0651(18)	-0393(14)	0182(46)	0064(16)	0019(9)	-0004(24)	0016(20)	0025(10)
C(4)	5850(35)	1468(20)	-0176(19)	0178(51)	0056(19)	0056(16)	0002(24)	-0030(24)	0045(14)
C(5)	7393(27)	1796(15)	1157(19)	0123(37)	0027(11)	0060(14)	-0010(16)	-0032(22)	0021(12)
C(6)	6174(32)	1737(18)	1832(18)	0179(47)	0042(14)	0048(14)	0009(21)	0076(24)	0009(12)
C(7)	8506(33)	-1005(20)	2302(16)	0156(47)	0065(18)	0034(11)	-0022(24)	-0019(19)	0020(12)
C(8)	9991(30)	-1446(16)	2176(17)	0091(36)	0043(13)	0058(14)	0007(19)	0003(22)	0006(11)
C(9)	9922(29)	-1770(16)	1167(19)	0102(36)	0043(13)	0065(15)	0040(19)	0008(25)	0012(13)
C(10)	9191(26)	-0886(16)	0749(14)	0108(35)	0027(11)	0029(10)	0013(17)	-0020(15)	-0004(9)
C(11)	8119(30)	-1133(17)	-0001(17)	0102(35)	0041(13)	0047(14)	0000(21)	0024(20)	-0013(11)

[a] Numbers in parentheses are estimated standard deviations right-adjusted to the least significant digit of the preceding number.
[b] The form of the anisotropic parameter T is: $T = \exp\{-[h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2\,hk\beta_{12} + 2\,hl\beta_{13} + 2\,kl\beta_{23}]\}$.

fitting the $|F_o|$ dependence to a modified Cruickshank function[11] of the type $w = K/[1 + (F_o - P_2)/P_1)^2]$. The weighting scheme was modified after each subsequent refinement cycle. The final parameters were $K = 0.075$, $P_1 = 57.5$, and $P_2 = 75.0$.

After two cycles of anisotropic refinement, an $(F_o - F_c)$ synthesis showed no significant positive electron density in positions expected for hydrogen atoms. The inclusion of hydrogen atoms at their calculated positions caused no improvement in the residuals R_1 and R_2. Hydrogen atoms were therefore not included in the refinement or subsequent structure factor calculations. Anisotropic refinement converged with residuals $R_1 = 0.066$ and $R_2 = 0.071$ and an overall scale factor $s = 1.2019$. The maximum parameter shift was 0.47 standard deviation in the final cycle of least squares. A final difference Fourier map had no positive maxima greater than 0.7 $e^-/\text{Å}^3$ except in the vicinity of the iodine atoms (maximum 1.3 $e^-/\text{Å}^3$).

Scattering factor tables used for I^-, Co^{3+}, O, N, and C were those of Cromer and Waber[12] and the anomalous scattering terms, $\Delta f'$ and $\Delta f''$, for I and Co were those listed by Cromer.[13] Observed and calculated structure amplitudes are compared in Table I. The final atomic positions and anisotropic thermal parameters are presented in Table II. As expected, the large X-ray scattering associated with the iodide and cobalt ions has reduced the precision and accuracy of the lighter atom parameters. Since data were recorded about only one crystal axis and with a fixed counter aperture, we make no deductions from the vibrational parameters. A single complex is shown in Figure 1, and a view of the unit cell down the *a* axis, in Figure 2.

Absolute Configuration.—The compound was known to contain a dissymmetric complex.[5] Cobalt and iodine have relatively large $\Delta f''$ terms for Cu Kα radiation ($\Delta f''_I = 6.68$, $\Delta f''_{Co} = 3.95$[13]), leading to the possibility of determining the absolute configuration of the complex cation by the anomalous dispersion method.

TABLE III

BIJVOET PAIRS FOR ABSOLUTE CONFIGURATION OF $\text{L}(-)_{589}\beta_2$-(*RRS*)-[Co(trien)((*S*)-Pro)]$I_2 \cdot 2H_2O$ (STRUCTURE AMPLITUDES IN ELECTRONS × 10)

$\|h\|$	$\|k\|$	$\|l\|$	$\|F_o(hkl)\|$	$\|F_c(hkl)\|$	$\|F_o(hk\bar{l})\|$	$\|F_c(hk\bar{l})\|$
1	1	1	827	934	1053	999
2	1	1	858	894	987	947
4	1	1	1354	1361	1280	1232
1	2	1	1143	1164	1202	1211
2	2	1	2525	2425	2716	2622
1	3	1	1332	1315	1469	1385
2	4	1	398	419	510	489
5	5	1	474	433	566	486
6	9	1	229	244	321	327
1	2	2	622	633	784	737
2	1	3	727	731	863	836
3	2	3	236	255	156	180
4	2	3	645	687	820	833
2	3	3	763	748	976	876
1	5	3	921	947	1095	1083
6	8	3	450	481	388	386
4	5	4	341	294	200	194
1	6	5	1034	1129	1239	1204
5	7	5	625	643	771	734
2	4	6	1016	1053	1237	1162

The fully refined atomic parameters were used to calculate structure amplitudes for reflections of the type $hk\bar{l}$. Table III compares values of $|F_o|$ and $|F_c|$ for the Bijvoet pairs which gave the most significant differences between $|F_c(hkl)|$ and $|F_c(hk\bar{l})|$.

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(11) J. S. Rollett and O. S. Mills in "Computing Methods and the Phase Problem in X-Ray Crystal Analysis," R. Pepinsky, Ed., Pergamon Press, New York, N. Y., 1961, p 117.

(12) D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).

(13) D. T. Cromer, *ibid.*, **18**, 17 (1965).

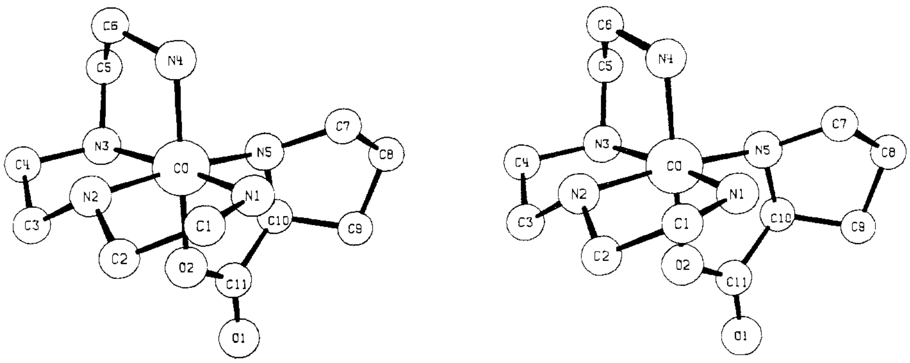

Figure 1.—Perspective view and absolute configuration of the L($-$)$_{589}\beta_2$-(*RRS*)-Co(trien)((*S*)-Pro)$^{2+}$ cation.

TABLE IV

INTRAMOLECULAR DISTANCES FOR

L($-$)$_{589}\beta_2$-(*RRS*)-[Co(trien)((*S*)-Pro)]$I_2 \cdot 2H_2O$[a]

(DISTANCES WITHIN

L($-$)$_{589}\beta_2$-(*RRS*)-Co(trien)((*S*)-Pro)$^{2+}$ CATION)

Atoms	Distance, Å	Atoms	Distance, Å
Co–N(1)	1.957 (18)	N(3)–C(4)	1.54 (3)
Co–N(2)	1.924 (21)	N(3)–C(5)	1.51 (3)
Co–N(3)	1.965 (19)	C(5)–C(6)	1.50 (4)
Co–N(4)	1.963 (17)	N(4)–C(6)	1.52 (3)
Co–N(5)	1.973 (21)	N(5)–C(7)	1.51 (3)
Co–O(2)	1.880 (14)	N(5)–C(10)	1.54 (3)
N(1)–C(1)	1.53 (3)	C(7)–C(8)	1.51 (4)
C(1)–C(2)	1.50 (3)	C(8)–C(9)	1.58 (4)
N(2)–C(2)	1.51 (3)	C(9)–C(10)	1.57 (3)
N(2)–C(3)	1.45 (3)	C(10)–C(11)	1.53 (3)
C(3)–C(4)	1.56 (4)	O(1)–C(11)	1.25 (3)
		O(2)–C(11)	1.25 (3)

[a] Numbers in parentheses are estimated standard deviations right-adjusted to the least significant digit of the preceding number.

TABLE V

INTRAMOLECULAR BOND ANGLES FOR

L($-$)$_{589}\beta_2$-(*RRS*)-[Co(trien)((*S*)-Pro)]$I_2 \cdot 2H_2O$[a]

(ANGLES WITHIN L($-$)$_{589}\beta_2$-(*RRS*)-Co(trien)((*S*)-Pro)$^{2+}$ CATION)

Atoms	Angle, deg	Atoms	Angle, deg
N(1)–Co–N(2)	85.5 (9)	C(3)–C(4)–N(3)	107.5 (1.9)
N(2)–Co–N(3)	85.8 (9)	C(4)–N(3)–Co	109.4 (1.7)
N(3)–Co–N(4)	86.2 (8)	Co–N(3)–C(5)	108.8 (1.3)
O(2)–Co–N(5)	85.7 (7)	N(3)–C(5)–C(6)	106.6 (1.9)
N(1)–Co–N(4)	92.2 (8)	C(5)–C(6)–N(4)	107.9 (1.9)
N(2)–Co–N(4)	93.6 (8)	C(6)–N(4)–Co	109.6 (1.4)
N(1)–Co–N(5)	94.6 (9)	Co–N(5)–C(10)	109.1 (1.3)
N(5)–Co–N(4)	91.4 (8)	N(5)–C(7)–C(8)	104.5 (2.0)
N(1)–Co–O(2)	90.2 (8)	C(7)–C(8)–C(9)	102.0 (2.0)
N(2)–Co–O(2)	89.3 (7)	C(8)–C(9)–C(10)	98.9 (1.7)
N(3)–Co–O(2)	91.8 (7)	C(9)–C(10)–N(5)	108.2 (1.8)
N(3)–Co–N(5)	94.2 (9)	C(10)–N(5)–C(7)	104.2 (1.7)
Co–N(1)–C(1)	110.4 (1.6)	Co–N(5)–C(7)	122.2 (1.7)
N(1)–C(1)–C(2)	107.6 (2.1)	C(9)–C(10)–C(11)	111.9 (2.0)
C(1)–C(2)–N(2)	104.9 (1.9)	N(5)–C(10)–C(11)	107.6 (1.8)
C(2)–N(2)–Co	108.6 (1.4)	C(10)–C(11)–O(1)	118.2 (2.3)
C(2)–N(2)–C(3)	111.3 (1.9)	C(10)–C(11)–O(2)	118.1 (2.0)
Co–N(2)–C(3)	108.2 (1.6)	O(1)–C(11)–O(2)	123.4 (2.5)
N(2)–C(3)–C(4)	104.7 (1.9)	Co–O(2)–C(11)	118.0 (1.6)

[a] Numbers in parentheses are estimated standard deviations right-adjusted to the least significant digit of the preceding number.

For each pair the present parameters give the best agreement between observed and calculated structure factor amplitudes. The parameters listed in Table II and the structure as drawn in Figure 1 therefore represent the true absolute configuration of the L($-$)$_{589}$Co(trien)((*S*)-Pro)$^{2+}$ cation.

Computer Programs.—Data reduction, Fourier syntheses, and subsidiary calculations were carried out on a CDC 3600 computer using programs written by Dr. J. F. Blount. Full-matrix least-squares refinement was performed on an IBM 360/50 computer, using a modified version of program ORFLS.[14] The major modification[15] was the inclusion of a rigorous anomalous dispersion option. Estimated standard deviations (including correlation terms) were calculated using program ORFFE,[16] adapted for use on an IBM 360/50 computer. Figures 1 and 2 were produced using program ORTEP.[17]

Description of the Structure

Description of the L($-$)$_{589}\beta_2$-(*RRS*)-Co(trien)((*S*)-Pro^{2+}) Cation.—Intramolecular bond distances and angles with their estimated standard deviations are given in Tables IV and V. The Co^{III}–N bond distances, although not chemically equivalent, differ by less than three standard deviations from their mean (1.96 (1) Å). Comparable values are 1.93 (1) Å in β-[Co(trien)ClOH$_2$](ClO$_4$)$_2$,[7] 1.96 (2) Å in *trans*-[Co(en)$_2$Cl$_2$]S$_2$O$_6$·H$_2$O,[18] 1.92 (2) Å in D-[Co(en)$_2$(L-glutamate)]ClO$_4$,[19] 1.97 (1) Å in L-[Co(en)$_2$sar]$I_2 \cdot 2H_2O$,[2] and 1.94 (2) Å in *trans*-[Co(en)$_2$SO$_3$NCS]·2H$_2$O.[20] The average C–N (1.52 (1) Å) distance in the trien ligand is similar to those found in the above trien and en structures. The Co^{III}–O(2) bond length (1.880 (14) Å) compares with 1.91 (1) Å in L-[Co(en)$_2$sar]$I_2 \cdot 2H_2O$[2] and 1.85 (2) Å in D-[Co(en)$_2$(L-glutamate)]ClO$_4$.[19]

Geometry of Coordinated Proline.—The pyrrolidine ring is nonplanar. The deviation (0.70 Å) of the C$_\gamma$ atom C(8) from the mean plane formed by N(5), C(7), C(9), and C(10) (maximum deviation 0.10 Å) is similar to those in [Cu(DL-Pro)$_2$]·2H$_2$O (0.60 Å)[21] and in hydroxy-L-proline (0.4 Å). In all three structures the C$_\gamma$ atom is *trans* to the carboxyl C atom. Average values for angles within the pyrrolidine ring are 104 (1)° in the present structure, 104° in [Cu(DL-Pro)$_2$]·2H$_2$O,[21] and 106° in hydroxyl-L-proline,[22] indicating significant ring strain within the five-membered ring. The carboxyl group is planar within the limits of

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(14) W. R. Busing, K. O. Martin, and H. A. Levy, Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(15) Personal communication from Professor J. A. Ibers.

(16) W. R. Busing, K. O. Martin, and H. A. Levy, Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(17) C. K. Johnson, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(18) O. Foss and K. Maroy, *Acta Chem. Scand.*, **19**, 2219 (1965).

(19) J. H. Dunlop, R. D. Gillard, N. C. Payne, and G. B. Robertson, *Chem. Commun.*, 874 (1966).

(20) S. Baggio and L. N. Becka, *ibid.*, 506 (1967).

(21) A. McL. Mathieson and H. K. Welsh, *Acta Cryst.*, **5**, 599 (1952).

(22) J. Donohue and K. N. Trueblood, *ibid.*, **5**, 419 (1952).

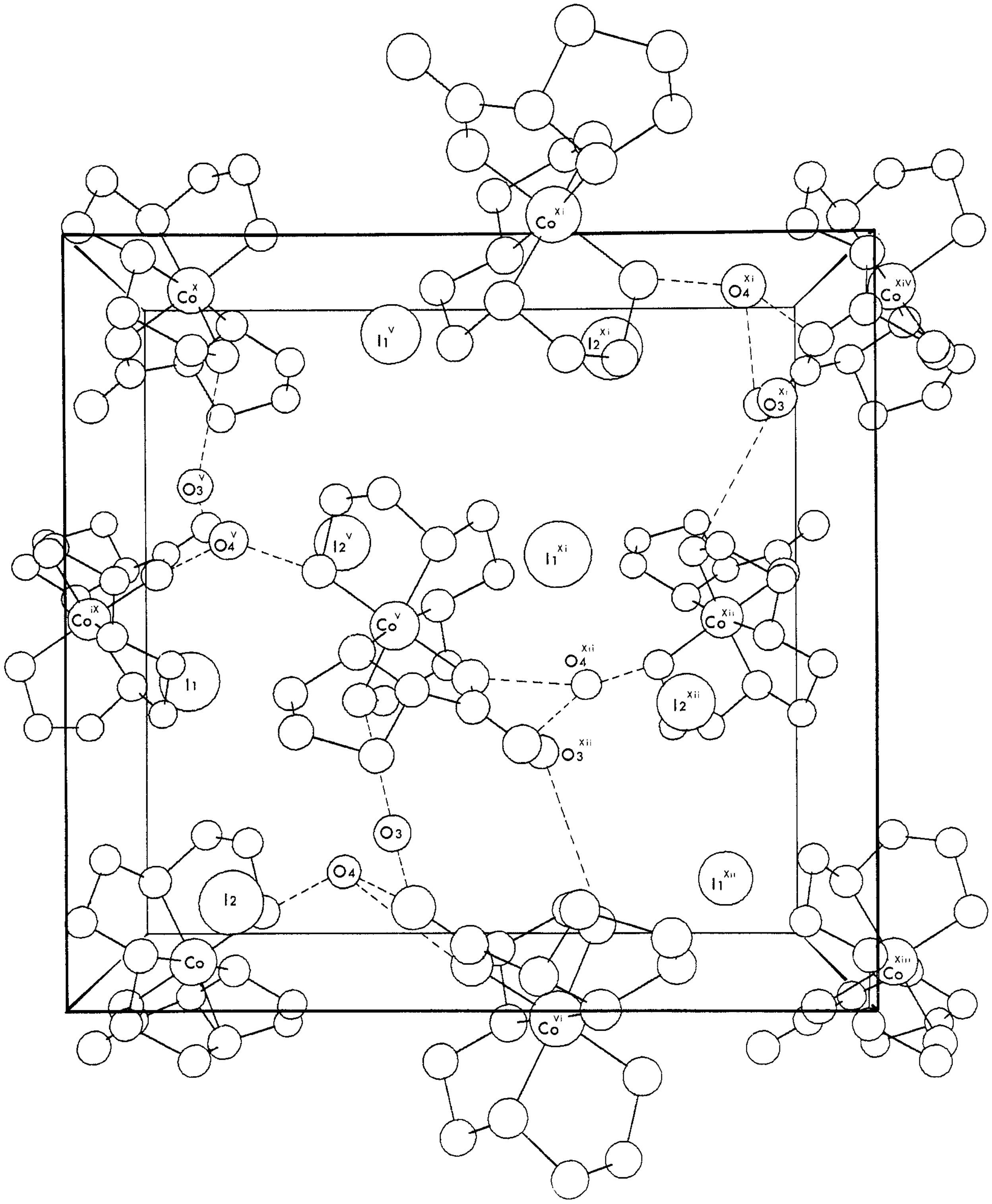

Figure 2.—Perspective view of the unit cell of L(−)$_{589}\beta_2$-(*RRS*)-[Co(trien)((*S*)-Pro)]$I_2 \cdot 2H_2O$ down the *a* axis (*c* axis is horizontal). Symmetry transformations are given in footnote *a* of Table VII.

precision. As has been found in other metal–amino acid complexes,[23] the five-membered chelate ring, formed by the coordinating amino acid, exhibits only a small degree of puckering. The maximum deviations from the mean plane are those of N(5) and C(10) (0.09 and 0.09 Å in opposite senses). From a comparison with other metal complexes of amino acids,[23] the C–O bond lengths in the carboxyl group should be unequal. The difference, if any, between them is not observable relative to their present standard deviations.

Conformations of trien Chelate Rings.—The angles subtended at the cobalt atom by the trien chelate rings are all equal to within one standard deviation (mean 85.5 (5)°), compared with a mean value of 86.4 (3)° found in β-Co(trien)(Cl)(OH_2)$^{2+}$.[6] These angles, coupled with that of the amino acid chelate ring (N-

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[23] H. C. Freeman, *Advan. Protein Chem.*, **22**, 342 (1967).

(5)–Co–O(2), 85.7 (7)°), combine to produce significant distortions from regular octahedral coordination. The bonds from Co to O(2), N(2), N(4), and N(5) are coplanar (Table VI, plane 3), but significant deviations occur from the other two coordination planes (planes 1 and 2).

TABLE VI

LEAST-SQUARES PLANES

(a) Equations of Planes: $AX + BY + CZ + D = 0$, Where $X = ax$, $Y = by$, $Z = cz$

Atoms included in plane	Plane no.	*A*	*B*	*C*	*D*
Co, N(1), N(2), N(3), N(5)	1	0.2226	−0.5306	−0.8179	−0.1138
Co, O(2), N(1), N(3), N(4)	2	−0.8894	0.2243	−0.3982	5.7466
Co, O(2), N(2), N(4), N(5)	3	0.3990	0.7982	−0.4512	−1.5848

(b) Distances of Atoms from Planes

Atoms	Dev (Å) from Plane 1	Plane 2	Plane 3
Co	−0.02	−0.04	−0.02
O(2)		−0.09	0.02
N(5)	0.06		−0.01
N(1)	−0.05	0.11	
N(2)	0.07		−0.01
N(3)	−0.05	0.11	
N(4)		−0.09	−0.02

The configuration at the asymmetric nitrogen atom N(2) of trien is the same as that found for β-Co(trien)(Cl)$(OH_2)^{2+}$.[6] As might be expected, the conformations of the chelate rings are similar in the two structures. The outer chelate rings adopt an unsymmetrical skew conformation while the inner ring has both methylene carbon atoms on the same side of the central N(2)–Co–N(3) plane in an unsymmetrical envelope conformation. The distances of the ring carbon atoms from the relevant N–Co–N planes are: C(1), −0.01, and C(2), 0.66 Å; C(3), 0.77, and C(4), 0.15 Å; C(5), −0.47, and C(6), 0.20 Å. The dihedral angles between the N–C–C planes about their common C–C bonds, progressing from N(1) to N(4), are 48.2, 46.5, and 49.0°, respectively. The comparable angles (in the same order) found in β-Co(trien)(Cl)$(OH_2)^{2+}$ [6] are 47.4, 37.0, and 51.8°, respectively. The significantly different dihedral angles about the C(3)–C(4) bonds in the two structures may be associated with differences in the hydrogen bonding by the N–H groups.

Hydrogen Bonds and Nonbonded Contacts.—Table VII lists the hydrogen bonds, identifies the proton donor and acceptor atoms, and shows the relevant bonding angles.[24] The asymmetric unit includes two molecules of water of crystallization. Each complex cation is hydrogen bonded to four H_2O molecules (Figure 2). Two hydrogen bonds are of the type N–H···O, in which the nitrogen atoms must be the donor atoms. One hydrogen bond links the uncoordinated O(carboxyl) atom of the proline residue to a water molecule O(3), which is therefore the proton donor. The fourth hydrogen bond has a geometrical configuration which can best be described by a bifurcated interaction to the two proline O atoms and a water molecule O(4). The distances from O(4) to O(1) and O(2) are 2.91 and 2.95 Å, respectively. The angle O(1)···$O(4)^{i}$···O(2) is 44°. If a proton is placed 0.94 Å from O(4) and along the bisector of O(1)···$O(4)^{i}$···O(2), then the distances H–O(1) and H–O(2) are 2.07 and 2.11 Å, respectively. This hydrogen-bonding geometry is remarkably similar to that found in crystals of perdeuterated violuric acid monohydrate.[25] The comparable distances and angle between the deuterium atom (water molecule) and oxygen atoms of the water molecule and violuric acid are: 2.79, 2.96 Å; 52°; 2.07, 2.10 Å, respectively.[25]

TABLE VII

HYDROGEN BONDS IN THE $L(-)_{589}\beta_2$-(*RRS*)-[Co(trien)((*S*)-Pro)]$I_2 \cdot 2H_2O$ CRYSTAL[a]

X–H···Y	Y···H–X	d(X···Y), Å
O(3)–H···$O(1)^{iv}$	O(1)···H–$O(3)^{i}$	2.78
N(1)–H···$O(3)^{ii}$	O(3)···H–$N(1)^{v}$	2.91
O(4)–H···$O(1)^{iv}$	O(1)···H–$O(4)^{i}$	2.91
O(4)–H···$O(2)^{iv}$	O(2)···H–$O(4)^{i}$	2.95
N(4)–H···O(4)		2.94

Atoms[a]	Angle, deg
C(11)–O(1)···$O(3)^{i}$	128
C(1)–N(1)···$O(3)^{ii}$	103
Co–N(1)···$O(3)^{ii}$	117
O(1)–$O(3)^{i}$···$N(1)^{iii}$	86
C(11)–$O(1)^{i}$···$O(4)^{i}$	96
C(11)–O(2)···$O(4)^{i}$	95
Co–O(2)···$O(4)^{i}$	145
Co–N(4)···O(4)	111
C(6)–N(4)···O(4)	81
O(1)···$O(4)^{i}$···O(2)	44
O(1)···$O(4)^{i}$···$N(4)^{i}$	78
O(2)···$O(4)^{i}$···$N(4)^{i}$	109

[a] Symmetry transformations with respect to the coordinates listed in Table II are as follows: none = x, y, z; i = $^3/_2 - x, \bar{y}, z - ^1/_2$; ii = $1 - x, y - ^1/_2, ^1/_2 - z$; iii = $^1/_2 + x, ^1/_2 + y, \bar{z}$; iv = $^3/_2 - x, \bar{y}, ^1/_2 + z$; v = $1 - x, ^1/_2 + y, ^1/_2 - z$; vi = $^1/_2 - x, \bar{y}, ^1/_2 + z$; vii = $^1/_2 + x, \bar{y} - ^1/_2, \bar{z}$; viii = $x - 1, y, z$; ix = $^1/_2 + z, ^1/_2 - y, \bar{z}$; x = $x, 1 + y, z$; xi = $^1/_2 - x, 1 - y, ^1/_2 + z$; xii = $^1/_2 + x, ^1/_2 - y, 1 - z$; xiii = $x, y, 1 + z$; xiv = $x, 1 + y, 1 + z$.

Nonbonded contacts (<3.5 Å) involving water molecules are $O(3)^{ii}$···C(11), 3.41 Å; O(4)···N(5), 3.20 Å; O(4)···C(5), 3.28 Å; O(4)···C(6), 3.11 Å; O(4)···C(7), 3.22 Å; $O(4)^{i}$···C(11), 3.29 Å. Within this range there is one intercomplex contact, O(1)···$C(1)^{vi}$ at 3.35 Å. The closest contact involving an iodide ion is I(2)···$O(4)^{vii}$ at 3.38 Å. The identification of this as a weak hydrogen bond is marginal.

Chemical Significance of this Structure.—This structure analysis has shown that the levorotatory (at λ 589 mμ) isomer isolated from the reaction of β-Co(trien)(OH)$(OH_2)^{2+}$ and (*S*)-proline[5] is in fact $L(-)_{589}\beta_2$-(*RRS*)-Co(trien)((*S*)-Pro)$^{2+}$ (Figure 1). The coordination of trien in the β configuration supports earlier evidence[3] that no β- → α-trien or β- → *trans*-trien isomerization occurs during the formation of Co(trien)((*S*)-Pro)$^{2+}$ from β-Co(trien)(OH)$(H_2O)^{2+}$. trien coordinated in the β configuration potentially exists in two diastereoisomeric forms differing in the configuration at the "planar" asymmetric nitrogen center. The present structure, in common with β_2-Co(trien)-

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[24] Symmetry transformations are given in footnote *a* to Table VII.

[25] B. M. Craven and W. J. Takei, *Acta Cryst.*, **17**, 415 (1964).

(glyglyOEt)$^{3+}$ [26] and β-Co(trien)(Cl)(OH$_2$)$^{2+}$,[6] has that configuration at N(2) in which the proton is directed toward the apical chelate ring of trien. These structures support the conclusion that in general this configuration is the more stable for β-trien.[27,28]

The coordination of (*S*)-proline, with O(2) *trans* to N(4) of trien (referred to as β_2),[3] is in agreement with the prediction that large nonbonded interactions would occur in the alternative β_1 configuration. Steric considerations further imply that for the coordination of (*S*)-proline the most stable configuration at cobalt would be L($-$)$_{589}$, which is the situation realized in this structure. As mentioned earlier, a species containing (*S*)-proline but having the opposite configuration at cobalt has been found in almost equal abundance.[5] This contradicts the stereospecificity predicted for this system. A crystal-structure analysis of the D(+)$_{589}$Co(trien)((*S*)-Pro)$^{2+}$ complex has been completed, and a detailed discussion of the relative stabilities of the two diastereoisomers will be included in a subsequent paper.

The absolute configuration as determined by the anomalous dispersion method confirms the assignment of confiurgation to (*S*)-proline.[29] More importantly, the absolute configuration of the complex confirms the assignment made by Douglas.[30] It also supports the suggestion by Sargeson and Searle[31] that in β-Co(trien)X$_2$$^{2+}$ complexes, a negative dominant circular dichroism coinciding with the first ligand field band is indicative of an L configuration about the cobalt center.

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[26] D. A. Buckingham, M. Fehlmann, H. C. Freeman, P. A. Marzilli, I. E. Maxwell, and A. M. Sargeson, *Chem. Commun.*, 488 (1968).

[27] P. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, **6**, 1032 (1967).

[28] A. M. Sargeson and G. H. Searle, *ibid.*, **6**, 2172 (1967).

[29] Z. Pravda and J. Rudinger, *Collection Czech. Chem. Commun.*, **20**, 1 (1955).

[30] C. Lin and B. E. Douglas, *Inorg. Nucl. Chem. Letters*, **4**, 15 (1968).

[31] A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **4**, 45 (1965).

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The Mechanism of Base Hydrolysis for $Co^{III}(NH_3)_5X^{2+}$ Ions. Hydrolysis and Rearrangement for the Sulfur-Bonded $Co(NH_3)_5SCN^{2+}$ Ion

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The base hydrolysis of a set of $(NH_3)_5CoX^{2+}$ ions (X = Cl, Br, I, NO$_3$) in the presence of anions such as N_3^- and NCS^- shows that the rate of entry of the extraneous anion is coincident with the rate of loss of X^-. The preparation of the S-bonded isomer $[(NH_3)_5CoSCN]Cl_2\cdot 1.5H_2O$ is also described. The base hydrolysis of this isomer follows two paths, one leading to the N-bonded isomer (24%) and the other to the hydroxo complex. The former path occurs without exchange with $N^{14}CS^-$ in solution. The latter path shows the same competition characteristics as observed for the chloro, bromo, iodo, and nitrato complexes. The results in this study complement those in support of the SN1CB mechanism for base hydrolysis in pentaamminecobalt(III) complexes. Some results for the rearrangement of CoSCN → CoNCS in dilute acid and in the solid state are also given.

Several recent publications have described competition studies[1-3] which support the proposal for an SN1CB mechanism in the base hydrolysis of acidocobalt(III)-pentaammine complexes. The present study was instituted to test this proposal further by measuring the rate of entry of competing anion.

If the following mechanism obtains

$$\begin{tikzcd}
(NH_3)_5CoX^{2+} + OH^- \arrow[r, shift left, "fast"] & (NH_3)_4NH_2CoX^+ + H_2O \arrow[l, shift left] \arrow[d, "slow"] \\
\left.\begin{matrix}(NH_3)_5CoY^{2+}\\ (NH_3)_5CoOH^{2+}\end{matrix}\right\} & (NH_3)_4NH_2Co^{2+} + X^- \arrow[l, "H_2O \text{ or } Y^-"', "fast"]
\end{tikzcd}$$

the rate of entry of the competing anion (Y^-) should coincide with the rate of loss of X^- if the intermediate is as reactive as has been suggested.[2-4] Experiments of this nature can be performed using anions such as N_3^-

[1] M. Green and H. Taube, *Inorg. Chem.*, **2**, 948 (1963).

[2] D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *J. Am. Chem. Soc.*, **88**, 5443 (1966).

[3] D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *ibid.*, **90**, 6654 (1968).

[4] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd. ed, John Wiley & Sons, Inc., New York, N. Y., p 182.