shown that the Co–CO and Co–PF_3 bond energies are essentially identical (56 ± 15 kcal/mol). Also, calculated heats of formation of the series of complexes imply similar bonding character for CO and PF_3 to Co.

Corresponding to these strong bonding abilities of PF_3 we find the M–PF_3 bond distance to be short compared with M–PR_3 where R is alkyl or aryl. The average Co–P distance in $CoH(PF_3)_4$ is 2.052 (5) Å. This is significantly shorter than Co–PR_3 distances that have been reported: $[Co(C_5H_5)P(C_6H_5)_2]_2$ (bridged P), 2.16 (1) Å;[28] $[Co(CO)_3P(n\text{-}C_4H_9)_3]_2$, 2.18 (2) Å;[29] $Co(C_3H_4CO_2C_6H_5)(CO)_2P(C_6H_5)_3$, 2.18 Å;[30] $CoH(N_2)\{P(C_6H_5)_3\}_3$, 2.19 (1) Å (av);[31] $Co\{P(C_6H_5)_2H\}_3Br_2$, 2.20 (2) Å (av);[32] $Co(C_9H_{11})_2\{P(C_2H_5)_2(C_6H_5)\}_2$, 2.23 (1) Å;[33] $Co_3CCH_3(CO)_8P(C_6H_5)_3$, 2.25 Å;[34] $Co(C_2HF_4)(CO)_3P(C_6H_5)_3$, 2.27 (1) Å.[35]

A similar contraction has been observed[36] for metal–fluoroalkyl bonds relative to metal–alkyl bonds. The contraction of *ca.* 0.07 Å for Co–C derivatives is considerably less than that observed above for the Co–P analogs.

The P–F bond distances in $CoH(PF_3)_4$ range from 1.52 (1) to 1.56 (1) Å, with an average of 1.55 (1) Å. These values are similar to the P–F distances (Å) obtained for the following compounds: $PF_3B_4F_6$ (1.51),[37] PF_3O (1.52),[38,39] PF_3S (1.53),[38,39] PF_5 (1.53 axial, 1.58 equatorial),[40] PF_3BH_3 (1.54),[41] PF_4CH_3 (1.54 axial, 1.61 equatorial),[42] $PF_3(CH_3)_2$ (1.55 equatorial, 1.64 axial),[42] PF_3 (1.57),[43] PF_2H (1.58),[44] PF_6^- (1.58).[45] (Structures reported before 1950 have been omitted from the tabulation.) The average F–P–F angle in $CoH(PF_3)_4$ is 97.1 (13)°, which compares favorably with 97.8 (2) for PF_3 itself.[43]

Acknowledgment.—We are indebted to Professor R. J. Clark for so generously supplying the samples and for many helpful discussions. We also wish to thank Dr. J. H. Enemark for his assistance in the collection of some of the initial data. This work was supported by the Advanced Research Projects Agency of the Department of Defense through the Northwestern University Materials Research Center.

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The Crystal Structure and Absolute Configuration of D-β_2-(*SSS*)-(Triethylenetetramine-(*S*)-prolinato)cobalt(III) Tetrachlorozincate

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The crystal structure and absolute configuration of D-β_2-(*SSS*)-(triethylenetetramine-(*S*)-prolinato)cobalt(III) tetrachlorozincate, D-β_2-(*SSS*)-[Co(trien)((*S*)-Pro)]$ZnCl_4$, has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in space group $P2_1$ (C_2^2; no. 4), with a = 7.01 (1) Å, b = 15.58 (2) Å, c = 9.66 (1) Å, β = 109.9 (3)°, and Z = 2. Measured and calculated densities are, respectively, 1.76 (2) and 1.76 (1) g cm^{-3}. The structure has been refined by full-matrix least-squares techniques to a final residual R = 0.055 for 1694 independent nonzero reflections. The crystal is composed of discrete D-β_2-(*SSS*)-Co(trien)((*S*)-Pro)$^{2+}$ cations and $ZnCl_4^{2-}$ anions held together by hydrogen bonds and electrostatic forces. The coordination around cobalt is octahedral with the quadridentate trien ligand in the β configuration and the proline residue coordinated through the amino nitrogen and a carboxyl oxygen. Large angular distortions within the D-β_2-(*SSS*)-Co(trien)((*S*)-Pro)$^{2+}$ cation are shown to relieve steric crowding within the complex. A detailed comparison is made between this structure and that of the related complex cation L-β_2-(*RRS*)-Co(trien)((*S*)-Pro)$^+$.

Introduction

It was shown that the coordination of sarcosine in $Co(en)_2sar^{2+}$ [1,2] and $Co(trien)sar^{2+}$ (en = ethylenediamine, sar = *N*-methylglycine, trien = triethylenetetramine) is stereospecific with respect to the asymmetric *N*-methyl center.[3] For a given configuration

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about the metal ion mutarotation at the *N*-methyl center was excluded.

In the related *S*-proline complexes, where the ligand has a fixed configuration at the secondary N center by virtue of the pyrrolidine ring, there exists the possibility of a stereospecific synthesis. When this was attempted, however, two Co(trien)((*S*)-Pro)$^{2+}$ complexes were formed in almost equal abundance.[4] The complexes were isolated from the reaction mixture and shown to have enantiomeric configurations with respect to the cobalt ion.

A crystal structure analysis[5] of the levorotatory (589 nm) isomer showed the complex to be L-β_2-(*RRS*)-Co(trien)((*S*)-Pro)$^{2+}$ (Figure 3(a)), as predicted.[4] The formation of a dextrorotatory isomer was difficult to understand since Dreiding models indicated that an isomer with the D configuration about the metal ion would be sterically unfavorable. The sterically least hindered and therefore the most probable dextrorotatory complex ion would be D-β_2-(*SSS*)-Co(trien)((*S*)-Pro)$^{2+}$. An examination of rigid stereomodels indicated that even in this complex ion considerable steric repulsion would occur between the hydrogen atoms on the proline pyrrolidine ring and hydrogen atoms on the apical trien ring. Even more puzzling was the fact that abundances of the two Co(trien)((*S*)-Pro)$^{2+}$ ions in the reaction mixture were almost equal. On the other hand, this lack of stereospecificity might be due to a kinetic rather than a thermodynamic effect.

It was hoped that a crystal structure analysis would provide the answers to some of these questions. The $(+)_{589}$-Co(trien)((*S*)-Pro)$^{2+}$ ion was crystallized as the tetrachlorozincate salt, in a form suitable for a single-crystal study.

Experimental Section

Crystal Data.—$(+)_{589}$-[Co(trien)((*S*)-Pro)]ZnCl$_4$ formed orange crystals which were stable to both air and X-irradiation. The unit cell was monoclinic with $a = 7.01$ (1) Å, $b = 15.58$ (2) Å, $c = 9.66$ (1) Å, $\beta = 109.9$ (3)°, $V = 992$ Å^3, $d_m = 1.76 \pm 0.02$ g cm^{-3} (by flotation in dibromopropane–toluene), $Z = 2$, $d_x = 1.76$ (1) g cm^{-3} for $C_{11}H_{26}N_5O_2Cl_4CoZn$ with formula weight 526.5, and $\mu_{\mathrm{Cu\,K}\alpha} = 130.1$ cm^{-1}. The space group was $P2_1$ ($C_2{}^2$; no. 4) or $P2_1/m$ ($C_{2h}{}^2$; no. 11) from systematic absences of reflections ($0k0$ absent for $k = 2n + 1$). Since the crystal was known to contain an optically active complex, the space group could be unambiguously identified as $P2_1$. The unit cell dimensions were calculated from values of θ for a number of high-angle zero-layer reflections measured from crystals mounted about the *a* and *b* axes. The measurements were made 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.—Two well-formed crystals of dimensions 0.24 × 0.25 × 0.15 mm and 0.11 × 0.25 × 0.14 mm (parallel to *a*, *b*, and *c* respectively) were mounted about the *a* and *c* axes, respectively. The intensity data were recorded on a fully automated Buerger-Supper equiinclination diffractometer, using the ω-scan method as previously described.[6] A fully stabilized X-ray generator provided Ni-filtered Cu Kα radiation and a scintillation counter (Philips PW 1964/10) and pulse-height analyzer (Philips PW 4280) were used. The angle subtended at the crystal by the counter aperture was increased with increasing μ (in the range 2° 50′–3° 50′). Reflections whose observed maximum count rate was outside the linear range of the counter were remeasured using an attenuator. The mosaicity factor[7] was found to be 1.0° for both crystals from measurements of peak profiles on a number of zero-layer reflections. The scan range and scan speed were calculated for each reflection individually,[6] the scan speed being such that $\sigma_s(F_o)/F_o$ was constant (where $\sigma_s(F_o)$ is the standard deviation of F_o calculated from counting statistics and the limits of scan speed were 2.4 and 15.0°/min).

Data were collected in the range $0° \leqslant \Upsilon \leqslant 140°$ for the zones Hkl, $Hk\bar{l}$ ($0 \leqslant H \leqslant 7$) and hKl, $hK\bar{l}$ ($0 \leqslant K \leqslant 3$). An examination of films showed that there were significant intensity differences between Bijvoet-related reflections. A few chosen reflections of the type $h\bar{k}l$ were measured for later confirmation of absolute configuration. For each reflection, the net count $I(hkl) = P - (B_1 + B_2)$ where P is the peak count and B_1 and B_2 are the first and second background counts. If the relationship $I(hkl) \leqslant 2(B_1 + B_2)^{1/2}$ was obeyed, a reflection was considered unobserved. Lorentz–polarization and absorption corrections were applied, the latter by the method of Coppens, *et al.*,[8] with grid sizes of 6 × 6 × 6 (parallel to *a*, *b*, and *c*) for both *a* and *b* axis crystals. Transmission factors were in the ranges 0.15–0.34 and 0.17–0.34 for the *a* and *b* axis crystals, respectively. Initially, estimated standard deviations assigned to the relative structure amplitudes were calculated from counting statistics. Least-squares[9] scale factors, calculated for different reciprocal levels by means of the reflections recorded about both axes, indicated that there was no crystal decomposition. The data were merged to a common scale and a total of 1785 independent reflections were obtained of which 91 had intensities below the observable threshold.

Solution and Refinement of the Structure.—The structure was solved using the usual sharpened Patterson and heavy-atom Fourier techniques. Full-matrix least-squares refinement was used to minimize the function $\Sigma w(|F_o| - s|F_c|)^2$ where w is the weight given to each reflection and s is the inverse of the scale factor to be applied to $|F_c|$. Unit weights were assigned to all observed reflections, and zero weights to all unobserved reflections. Three cycles were carried out varying an overall scale factor, atomic coordinates, and isotropic temperature factors. After four cycles incorporating anisotropic temperature factors the residuals $R_1 = \Sigma\Delta/\Sigma|F_o|$ and $R_2 = [\Sigma w\Delta^2/\Sigma wF_o{}^2]^{1/2}$, where $\Delta = |F_o - F_c|$, were constant at $R_1 = 0.095$ and $R_2 = 0.110$. The refined structure at this stage was, however, unsatisfactory. There were large differences between the metal–nitrogen bond lengths: Co–N(1), 2.15 Å; Co–N(2), 1.87 Å; Co–N(3), 1.78 Å; Co–N(4), 1.94 Å; Co–N(5), 2.07 Å. The differences between these bond lengths were of the order of magnitude predicted by Cruickshank and McDonald[10] for the effect of anomalous dispersion on the coordinates of Co atoms observed with Cu Kα radiation in polar space groups. Since the absolute configuration of the present structure was fixed by the known absolute configuration of (*S*)-proline, the polarity of the space group could be checked. Reexamination of the data revealed that at an early stage in the analysis a left-handed crystal system had inadvertently been incorporated. When the correct space group of reverse polarity was used, further refinement of the structure produced more reasonable values for the Co–N bond distances (Table IV). These results clearly emphasize the importance of the correct choice of polarity and the inclusion of anomalous dispersion corrections when dealing with polar space groups (see also footnote on p 1294 of ref 6).

A $(F_o - F_c)$ synthesis in one of the final stages of refinement confirmed the absence of water of crystallization and indicated

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TABLE I

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (IN ELECTRONS × 10) FOR D-β_2-(SSS)-[Co(trien)((S)-Pro)]$ZnCl_4$

H	K	FO	FC
[illegible]	[illegible]	[illegible]	[illegible]

the presence of significant electron density in the regions expected for all the hydrogen atoms of the complex cation. A structure factor calculation in which all the hydrogen atoms of the cation were included decreased the residuals from $R_1 = 0.100$ and $R_2 = 0.140$ to $R_1 = 0.097$ and $R_2 = 0.112$, respectively. The hydrogen atoms were therefore included at recalculated positions in all subsequent cycles. At no stage were the hydrogen atom coordinates or temperature factors refined.

An analysis of $\langle 1/\Delta^2 \rangle$ in ranges of $|F_o|$ was carried out after each cycle. No systematic dependence on $|F_o|$ was apparent at any stage during the refinement. Hence the original unit weights were maintained throughout the refinement. The least-squares refinement coverged to residuals $R_1 = 0.055$ and $R_2 = 0.059$. The maximum parameter shift in the final cycle was 0.4 standard deviation. A final difference Fourier map had no positive maxima greater than 0.8 e$^-$/Å^3 except in the vicinity of the metal ions

TABLE II

FRACTIONAL ATOMIC POSITIONAL PARAMETERS[a–c] AND ANISOTROPIC TEMPERATURE FACTORS[d] FOR D-β_2-(*SSS*)-[Co(trien)((*S*)-Pro)]ZnCl$_4$

Atom	10^4x	10^4y	10^4z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$	Atom	10^4x	10^4y	10^4z
Zn	-487(2)	7500 [e]	7657(2)	169(4)	25(1)	64(2)	5(1)	44(2)	2(1)	H(1)	6390	5814	8676
Co	4803(2)	4457(1)	7620(2)	121(4)	18(1)	50(2)	-3(1)	50(2)	1(1)	H(2)	4155	5822	8628
Cl(1)	241(5)	7805(3)	5624(3)	274(9)	59(2)	92(4)	31(3)	102(5)	20(2)	H(3)	6471	3627	9776
Cl(2)	1542(7)	6570(3)	9306(4)	415(13)	57(2)	96(4)	94(4)	54(6)	10(2)	H(4)	3223	3344	5923
Cl(3)	-3755(5)	7086(2)	7067(4)	202(8)	41(2)	137(5)	-40(3)	37(5)	16(2)	H(5)	7985	4679	7161
Cl(4)	-251(5)	8793(2)	8839(3)	213(8)	29(1)	89(4)	4(3)	33(4)	-12(2)	H(6)	8487	4407	8791
O(1)	-868(12)	5199(6)	5890(9)	137(21)	44(4)	115(11)	-10(8)	53(12)	13(6)	H(7)	5243	5536	6179
O(2)	1948(11)	4568(5)	7286(8)	159(19)	26(4)	77(9)	3(6)	61(11)	6(5)	H(8)	5653	5763	11062
N(1)	5357(15)	5486(6)	8862(10)	219(27)	19(4)	85(12)	8(9)	76(15)	-4(6)	H(9)	7661	5152	10844
N(2)	5204(14)	3831(6)	9437(9)	177(23)	29(4)	63(10)	9(8)	80(13)	11(6)	H(10)	5624	4172	11663
N(3)	4349(14)	3317(6)	6706(10)	188(24)	19(4)	72(11)	1(8)	76(14)	2(5)	H(11)	3359	4568	10352
N(4)	7644(13)	4295(6)	7801(9)	154(21)	27(4)	74(11)	6(8)	60(12)	-7(6)	H(12)	2224	3294	8797
N(5)	4218(13)	5170(6)	5827(9)	130(21)	23(4)	62(10)	-6(8)	59(12)	-5(5)	H(13)	4143	2635	9990
C(1)	6033(21)	5251(8)	10435(13)	284(36)	31(5)	75(15)	19(12)	85(19)	1(7)	H(14)	5410	2246	8129
C(2)	4955(19)	4442(9)	10567(13)	238(32)	38(6)	84(15)	8(13)	87(19)	6(9)	H(15)	2756	2263	7195
C(3)	3784(20)	3078(9)	9070(15)	213(33)	33(6)	122(18)	-2(12)	97(21)	28(8)	H(16)	5966	3428	5197
C(4)	4074(19)	2652(8)	7758(12)	250(33)	31(6)	84(14)	-15(11)	77(17)	14(7)	H(17)	6166	2411	6050
C(5)	6113(18)	3096(8)	6215(12)	187(29)	29(5)	79(14)	8(10)	70(17)	1(7)	H(18)	8284	2973	8363
C(6)	7990(17)	3386(8)	7408(12)	142(26)	34(5)	85(14)	19(10)	62(16)	1(7)	H(19)	9273	3362	7023
C(7)	4117(17)	4851(7)	4354(11)	190(29)	25(4)	52(12)	-9(9)	57(15)	-3(6)	H(20)	5626	4787	4290
C(8)	2925(19)	5540(8)	3319(12)	227(32)	31(5)	63(13)	-11(11)	66(17)	8(7)	H(21)	3346	4237	4115
C(9)	1248(19)	5748(8)	3893(13)	160(30)	38(6)	77(14)	16(11)	21(17)	24(8)	H(22)	3856	6098	3352
C(10)	2237(17)	5610(7)	5580(11)	167(27)	24(5)	66(13)	-18(9)	64(16)	3(6)	H(23)	2318	5299	2200
C(11)	961(16)	5098(7)	6263(11)	137(27)	23(5)	58(12)	-3(9)	42(14)	2(6)	H(24)	749	6407	3643
										H(25)	-34	5320	3432
										H(26)	2487	6225	6144

[a] Numbers in parentheses are estimated standard deviations right-adjusted to the least significant digit of the preceding number. [b] Hydrogen atom positions were calculated as follows: tetrahedral primary N, $d_{N-H} = 0.95$ Å; tetrahedral secondary N, $d_{N-H} = 0.89$ Å; methylene C, $d_{C-H} = 1.084$ Å. [c] Hydrogen atoms are numbered sequentially around the chelate rings from atom N(1) to N(4) and around the proline ring from N(5) to C(10). [d] The form of the anisotropic temperature parameter T is $T = \exp(-[h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}])$. Hydrogen atoms were all assigned fixed isotropic temperature factors $\exp(-6.0(\sin^2\theta)/\lambda^2)$. [e] The y coordinate of the Zn atom is arbitrary and was fixed at 0.7500 throughout the refinement.

(maximum 1.0 e$^-$/Å^3). The scattering factor tables used for Zn^{2+}, Co^{3+}, Cl$^-$, O, N, and C were those of Cromer and Waber[11] and the H table was that listed by Ibers.[12] Anomalous scattering terms $\Delta f'$ and $\Delta f''$ for Zn, Co, and Cl were those given by Cromer.[13]

Calculated and observed structure factor amplitudes are compared in Table I. The $|F_o|$ values for the unobserved data were shown to be insignificant. Final atomic positional and thermal parameters with estimated standard deviations are listed in Table II. The excellent diffraction properties of the crystals used in this analysis have considerably increased the precision of this structural analysis relative to that of the related L-β_2-(*RRS*)-Co(trien)((*S*)-Pro)$^{2+}$ ion.[5]

A perspective view of the complex cation showing atom numbering and ellipsoids of thermal motion is given in Figure 1. Figure 2 is a perspective diagram of the unit cell as viewed down the a axis.

Absolute Configuration.—As previously discussed, the absolute configuration of the complex cation could be assigned from the known absolute configuration of (*S*)-proline. To confirm this assignment the relative intensities of a number of Bijvoet-related reflections, which had clearly different intensities on films, were measured. Table III compares $|F_o|$ and $|F_c|$ values for reflections of the type hkl and $h\bar{k}l$. The anomalous dispersion results confirm the assignment of configuration to the D(+)$_{589}$-β_2-(*SSS*)-Co(trien)((*S*)-Pro)$^{2+}$ isomer. The parameters listed in Table II and the structure drawn in Figure 1 therefore represent the correct absolute configuration.

TABLE III

BIJVOET PAIRS FOR D-β_2-(*SSS*)-[(Co(trien)((*S*)-Pro)]ZnCl$_4$ (STRUCTURE AMPLITUDES IN ELECTRONS, × 10)

h	$\|k\|$	l	$\|F_o(hkl)\|$	$\|F_c(hkl)\|$	$\|F_o(h\bar{k}l)\|$	$\|F_c(h\bar{k}l)\|$
0	4	6	414	422	352	345
1	3	−6	234	236	170	170
1	1	−6	177	158	220	214
0	2	4	344	337	425	426
1	1	−4	456	467	506	526
2	4	−3	244	229	202	189
2	2	−3	475	453	518	499
0	2	3	265	262	301	301
3	5	−2	403	378	442	417
3	4	−1	198	176	233	221

Description of the Structure

Description of the D-β_2-(*SSS*)-Co(trien)((*S*)-Pro)$^{2+}$ Cation.—Intramolecular bond distances and angles and their estimated standard deviations are given in Tables IV and V. Four of the Co–N bond distances lie within 1σ of their mean value of 1.955 (5) Å. However,

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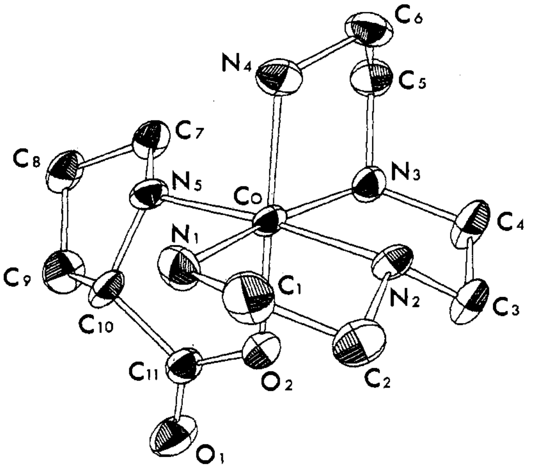

Figure 1.—Perspective view of the D-β_2-(*SSS*)-Co(trien)((*S*)-Pro)$^{2+}$ cation, showing thermal vibration ellipsoids.

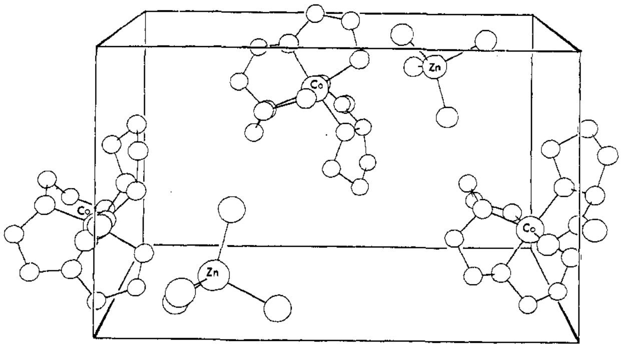

Figure 2.—Part of the unit cell contents in D-β_2-(*SSS*)-[Co(trien)((*S*)-Pro)]ZnCl$_4$. The origin is in the rear bottom, left-hand corner, and the *a*, *b*, and *c* axes run toward the reader, left to right and vertically upward, respectively. The complexes in the bottom half of the figure are at $1 - x, -{}^1/_2 + y, 1 - z$ and $1 - x, {}^1/_2 - y, 1 - z$ with respect to the central complex.

TABLE IV

INTRAMOLECULAR DISTANCES FOR D-β_2-(*SSS*)-[Co(trien)((*S*)-Pro)]ZnCl$_4$[a]

(a) Distances within D(+)$_{589}$-β_2-(*SSS*)-Co(trien)((*S*)-Pro)$^{2+}$

Co–N(1)	1.960 (9)	N(3)–C(4)	1.51 (1)
Co–N(2)	1.943 (8)	N(3)–C(5)	1.51 (1)
Co–N(3)	1.961 (9)	C(5)–C(6)	1.49 (2)
Co–N(4)	1.955 (9)	N(4)–C(6)	1.51 (1)
Co–N(5)	1.980 (9)	N(5)–C(7)	1.49 (1)
Co–O(2)	1.924 (7)	N(5)–C(10)	1.49 (1)
N(1)–C(1)	1.48 (1)	C(7)–C(8)	1.51 (2)
C(1)–C(2)	1.50 (2)	C(8)–C(9)	1.50 (2)
N(2)–C(2)	1.50 (1)	C(9)–C(10)	1.55 (2)
N(2)–C(3)	1.50 (1)	C(10)–C(11)	1.51 (1)
C(3)–C(4)	1.51 (2)	O(1)–C(11)	1.22 (1)
		O(2)–C(11)	1.29 (1)

(b) Distances within ZnCl$_4^{2-}$

Zn–Cl(1)	2.242 (3)	Zn–Cl(3)	2.259 (4)
Zn–Cl(2)	2.262 (4)	Zn–Cl(4)	2.293 (3)

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

the Co–N(5) bond distance is 3σ longer than this mean (1.980 (9) Å). The Co–O(2) bond length (1.924 (7) Å) is probably not significantly different from 1.880 (14) Å as found in L-β_2-(*RRS*)-Co(trien)((*S*)-Pro)$^{2+}$,[5] although some polarization of the coordinated amino acid carboxyl group is now evident.

The O(1)–C(11) and O(2)–C(11) bond lengths are 1.22 (1) and 1.29 (1) Å, respectively. This difference was not significant in the L-β_2-(*RRS*)-Co(trien)((*S*)-Pro)$^{2+}$ structure due to the larger standard deviations in the bond lengths.

Some interesting angular distortions occur in the complex ion. These distortions will be pointed out now and their significance will be discussed in some detail later. The most marked angular distortion occurs in the Co–N(5)–C(7) bond angle of 125.3 (7)°, an increase of almost 16° from the unstrained tetrahedral value. A similar distortion occurs in the L-β_2-(*RRS*)-Co(trien)((*S*)-Pro)$^{2+}$ ion,[5] where the Co–N(5)–C(7) bond angle is 122.2 (1.7)°. Further angular expansion occurs at the N(3)–Co–N(5) bond angle (99.2 (4)°), which is accompanied by a contraction of the N(1)–Co–N(5) angle to 90.9 (4)°. The comparable angles in the L-β_2-(*RRS*)-Co(trien)((*S*)-Pro)$^{2+}$ ion are equal (94.2 (9) and 94.6 (9)°).[5]

Geometry of Coordinated Proline.—As in the L-β_2-(*RRS*)-Co(trien)((*S*)-Pro)$^{2+}$ ion,[5] the five-membered pyrrolidine ring of proline is puckered. The puckering is such that the C_γ atom, C(8), lies 0.57 Å from a mean plane from which N(5), C(7), C(9), and C(10) all deviate by less than 0.09 Å. The position of the C_γ atom with respect to the plane of the other ring atoms is similar to that in previously reported structures containing proline residues,[5,14,15] *i.e.*, *trans* to the carboxyl C atom. Some ring strain within the pyrrolidine ring is shown by a mean internal angle of 104.5°. The geometry of the five-membered chelate ring formed by the amino acid and the metal ion is very similar to that in L-β_2-(*RRS*)-Co(trien)((*S*)-Pro)$^{2+}$ [5] and in complexes of α-amino acids in general.[16] The carboxyl group (C(10), C(11), O(1), O(2)) is strictly planar and the five-membered chelate ring is only slightly puckered (maximum deviations from the plane of best fit: N(5), 0.18 Å; C(10), −0.19 Å).

Conformations of the trien Chelate Rings.—The angles subtended at the metal by the puckered five-membered chelate rings (N(1)–Co–N(2), 85.5 (4)°; N(2)–Co–N(3), 84.5 (3)°; N(3)–Co–N(4), 85.8 (4)°) are comparable with those (85.5 (9), 85.8 (9), and 86.2 (8)°, respectively) found in L-β_2-(*RRS*)-Co(trien)((*S*)-Pro)$^{2+}$.[5] Deviations of ligating atoms from their mean coordination planes are given in Table VI. The atom deviations from both planes 1 and 2 in the D- and L-Co(trien)((*S*)-Pro)$^{2+}$ isomers are similar (see also ref 5). The torsion angles about the C–C bonds and the chiralities of the chelate rings, progressing from N(1) to N(4), are 48.9° (δ), 39.0° (λ), and 48.7° (λ). Deviations of carbon atoms from their respective N–Co–N planes are as follows: C(1), −0.19 and C(2), 0.48 Å; C(3), 0.82 and C(4), 0.31 Å; C(5), −0.44 and C(6), 0.22 Å.

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(14) A. McL. Mathieson and H. K. Welsh, *Acta Crystallogr.*, **5**, 599 (1952).
(15) J. Donohue and K. N. Trueblood, *ibid.*, **5**, 419 (1952).
(16) H. C. Freeman, *Advan. Protein Chem.*, **22**, 342 (1967).

TABLE V

INTRAMOLECULAR BOND ANGLES FOR D-β_2-(*SSS*)-[Co(trien)((*S*)-Pro)]$ZnCl_4$[a]

Atoms	Angle, deg	Atoms	Angle, deg
	(a) Angles within D(+)$_{589}$-β_2-(*SSS*)-Co(trien)((*S*)-Pro)$^{2+}$		
N(1)-Co-N(2)	85.5 (4)	C(3)-C(4)-N(3)	110.5 (1.0)
N(2)-Co-N(3)	84.5 (3)	C(4)-N(3)-Co	110.9 (7)
N(3)-Co-N(4)	85.8 (4)	Co-N(3)-C(5)	109.0 (7)
O(2)-Co-N(5)	84.8 (3)	N(3)-C(5)-C(6)	106.8 (9)
N(1)-Co-N(4)	93.9 (4)	C(5)-C(6)-N(4)	107.7 (9)
N(2)-Co-N(4)	91.4 (4)	C(6)-N(4)-Co	110.2 (7)
N(1)-Co-N(5)	90.9 (4)	Co-N(5)-C(10)	107.5 (6)
N(5)-Co-N(4)	93.0 (4)	N(5)-C(7)-C(8)	103.3 (9)
N(1)-Co-O(2)	90.4 (4)	C(7)-C(8)-C(9)	103.7 (9)
N(2)-Co-O(2)	91.1 (3)	C(8)-C(9)-C(10)	103.4 (9)
N(3)-Co-O(2)	90.3 (4)	C(9)-C(10)-N(5)	106.8 (8)
N(3)-Co-N(5)	99.2 (4)	C(10)-N(5)-C(7)	105.2 (8)
Co-N(1)-C(1)	110.7 (7)	Co-N(5)-C(7)	125.3 (7)
N(1)-C(1)-C(2)	107.6 (1.0)	C(9)-C(10)-C(11)	114.4 (9)
C(1)-C(2)-N(2)	106.5 (8)	N(5)-C(10)-C(11)	110.2 (9)
C(2)-N(2)-Co	108.7 (7)	C(10)-C(11)-O(1)	121.6 (1.0)
Co-N(2)-C(3)	107.4 (7)	C(10)-C(11)-O(2)	115.5 (9)
N(2)-C(3)-C(4)	105.9 (9)	O(1)-C(11)-O(2)	123.0 (1.0)
C(2)-N(2)-C(3)	115.8 (9)	Co-O(2)-C(11)	116.2 (6)
	(b) Angles within $ZnCl_4^{2-}$		
Cl(1)-Zn-Cl(2)	118.5 (2)	Cl(2)-Zn-Cl(3)	109.6 (2)
Cl(1)-Zn-Cl(3)	110.7 (1)	Cl(2)-Zn-Cl(4)	106.9 (1)
Cl(1)-Zn-Cl(4)	104.5 (1)	Cl(3)-Zn-Cl(4)	105.7 (2)

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

TABLE VI

LEAST-SQUARES PLANES

(a) Equation 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	−0.9921	0.0617	−0.1092	−2.5680
Co, O(2), N(1), N(3), N(4)	2	0.1596	0.4966	−0.8532	2.9530
Co, O(2), N(2), N(4), N(5)	3	−0.0295	−0.8415	−0.5395	−8.5210

(b) Distances of Atoms from Planes

	Deviations (Å) from		
Atoms	Plane 1	Plane 2	Plane 3
Co	−0.03	−0.05	0.00
O(2)		−0.09	0.07
N(5)	0.04		−0.07
N(1)	−0.03	0.12	
N(2)	0.05		−0.06
N(3)	−0.03	0.12	
N(4)		0.09	0.06

Hydrogen Bonds and Nonbonded Contacts.—Compared with other complexes of this type, crystals of D-β_2-(*SSS*)-[Co(trien)((*S*)-Pro)]$ZnCl_4$ are unusual in that they are anhydrous and contain very few hydrogen bonds. There are only two distinct hydrogen bonds of the type N–H···Cl and one of the type N–H···O. Table VII lists these H bonds and identifies proton donor and acceptor atoms. There are, in addition, four N···Cl distances which may represent N–H···Cl bonds:[17] N(1)···Cl(2), 3.31 Å; N(2)···Cl(4^{iv}), 3.36 Å; N(3)···Cl(1^{v}), 3.34 Å; N(5)···Cl(3^{ii}), 3.35 Å. [The transformations represented by the superscripts are given in the footnote to Table VII.] Evidently the dominant binding forces in the lattice are electrostatic forces between anions and cations. The shortest non-

TABLE VII

HYDROGEN BONDS IN THE

D-β_2-(*SSS*)-[Co(trien)((*S*)-Pro)]$ZnCl_4$ CRYSTAL[a]

Atoms X–H···Y	Atoms Y···H–X	*d*(X···Y), Å
N(1)–H···Cl(3^{ii})	Cl(3)···H–N(1^{i})	3.22
N(4)–H···Cl(4^{iv})	Cl(4)···H–N(4^{iii})	3.23
N(4)–H···O(1^{ii})	O(1)···H–N(4^{i})	2.79

Atoms	Angle, deg	Atoms	Angle, deg
Zn–Cl(3)···N(1^{i})	116.8	C(6)–N(4)···Cl(4^{iv})	86.6
Co–N(1)···Cl(3^{ii})	109.8	C(11)–O(1)···N(4^{i})	109.4
C(1)–N(1)···Cl(3^{ii})	134.0	Co–N(4)···O(1^{ii})	118.3
Zn–Cl(4)···N(4^{iii})	129.2	C(6)–N(4)···O(1^{ii})	100.4
Co–N(4)···Cl(4^{iv})	109.3	Cl(4^{iv})···N(4)···O(1^{iv})	125.1

[a] Symmetry transformations are as follows: (i) $-1 + x, y, z$; (ii) $1 + x, y, z$; (iii) $1 - x, {}^1/_2 + y, 2 - z$; (iv) $1 - x, -{}^1/_2 + y, 2 - z$; (v) $-x, -{}^1/_2 + y, 1 - z$; (vi) $-x, {}^1/_2 + y, 1 - z$.

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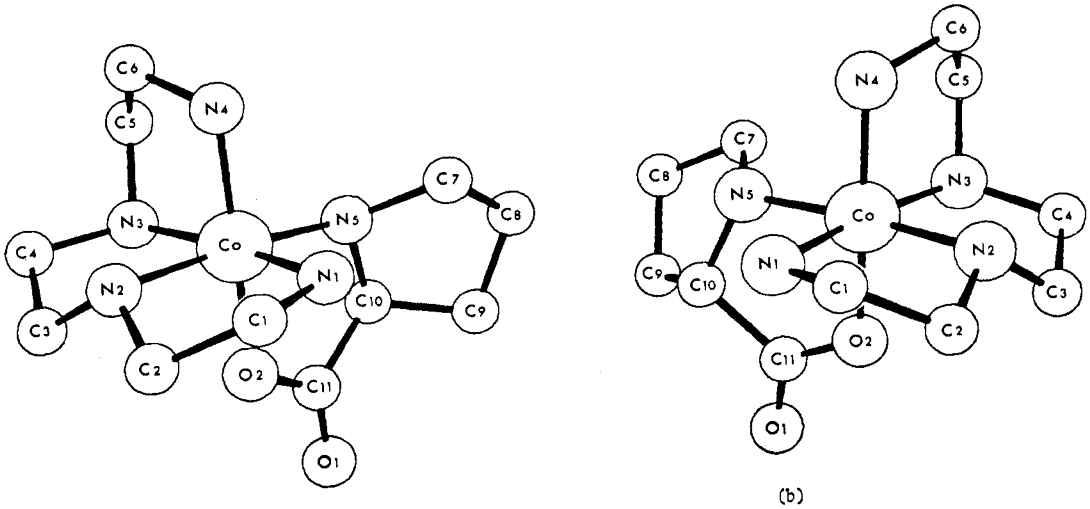
(17) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968, p 184.



(a) (b)

Figure 3.—Perspective views of (a) the L-β_2-*RRS* isomer and (b) the D-β_2-*SSS* isomer of the Co(trien)((*S*)-Pro)$^{2+}$ ion.

bonded contacts are as follows: O(2)···N(4^{i}), 3.25 Å; O(1)···C(6^{i}), 3.40 Å; Cl(3)···C(5^{vi}), 3.42 Å.

Chemical Significance of This Structure.—The structure analysis has shown that the dextrorotatory (λ 589 nm) isomer isolated as the second fraction from the reaction mixture is D-β_2-(*SSS*)-Co(trien)((*S*)-Pro)$^{2+}$ (Figure 1). (*S*)-Proline is coordinated bidentate to the metal ion in the β_2 configuration (O(2) trans to N(4)). This is consistent with the prediction[4] that the alternative β_1 configuration (N(5) trans to N(4)[3]) would be sterically less favorable. The relative configuration at N(2), the asymmetric secondary N atom of β-trien in this structure, is analogous to that found in β-Co(trien)-ClOH$_2$$^{2+}$ [14] and L-β_2-(*RRS*)-Co(trien)((*S*)-Pro)$^{2+}$.[5] In all these structures the configuration is such that the proton on this secondary N center is directed toward the apical trien chelate ring. For the L and D configurations about the metal ion the configurations at N(2) are *R* and *S*, respectively.

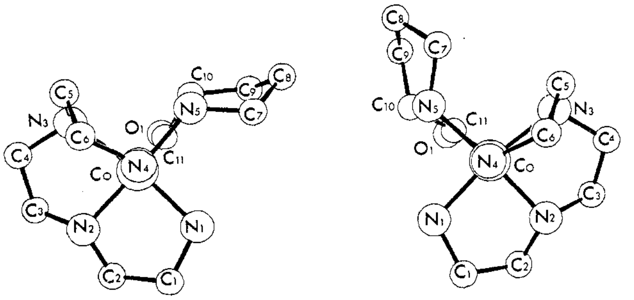


Figure 4.—Perspective views (in orientations different from those in Figure 3) of (a) the L-β_2-*RRS* isomer and (b) the D-β_2-*SSS* isomer of the Co(trien)((*S*)-Pro)$^{2+}$ ion.

The major geometrical difference between the L-β_2-(*RRS*)-Co(trien)((*S*)-Pro)$^{2+}$ and D-β_2-(*SSS*)-Co(trien)-((*S*)-Pro)$^{2+}$ isomers consists of the relative orientations of the proline moieties. Perspective views of the two isomers from two different orientations are given in Figures 3 and 4. Figure 4 shows that in the D-β_2-*SSS* isomer the pyrrolidine ring is oriented toward the apical trien chelate ring, N(3)–C(5)–C(6)–N(4). In the L-β_2-*RRS* isomer the pyrrolidine ring is remote from the apical chelate ring. Crude measurements using Dreiding stereomodels and a conservative H···H nonbonded potential function[18] indicate that nonbonded repulsions between the amino acid and the chelate ring should be prohibitive for the D-β_2-*SSS* form. In reality, when hydrogen atoms are placed at calculated positions on the fully refined crystal structure model of D-β_2-*SSS*, these interactions are relatively small. The bond angle distortions which are found from the structure analysis—*e.g.*, the expansions of the bond angles N(3)–Co–N(5) (99.2°) and Co–N(5)–C(7) (125.3°)—clearly alleviate close nonbonded interactions between the amino acid and trien moieties. Further, the angular strain energy thereby introduced into the complex is relatively small compared with the considerable reduction in nonbonded interaction energy. The actual thermodynamic stability difference between the D-β_2-*SSS* and L-β_2-*RRS* isomers is therefore smaller than that (14 kcal/mol) calculated from Dreiding models using the conservative H···H nonbonded potential function of Hill,[18] and the structure analysis shows that the formation of the D-β_2-*SSS* isomer is much more reasonable than originally expected. In the L-β_2-*RRS* complex[5] the expansion of the Co–N(5)–C(7) bond angle (122.2°) can likewise be explained in terms of relief of steric strain. These results clearly demonstrate that the relative ease of bond angle bending can be an important factor in determining isomer stabilities.

A comprehensive strain energy minimization calculation has been carried out on these complexes in an attempt to predict stability differences and reproduce the distorted geometries. The results of these calculations are described in a separate paper.[19]

As mentioned earlier, the formation of the two isomers was carried out under reaction conditions where their relative abundances might be kinetically con-

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[18] T. L. Hill, *J. Chem. Phys.*, **16**, 339 (1948).

[19] D. A. Buckingham, I. E. Maxwell, A. M. Sargeson, and M. R. Snow, *J. Amer. Chem. Soc.*, **92**, 3617 (1970).

trolled. In this case the relative abundances in the reaction mixture might not reflect the relative thermodynamic stabilities of the complexes. The stability difference between the two forms could be measured if equilibrium were established. This would require inverting the coordinated amino acid. Inversion might occur in highly basic solution where hydroxide ions would remove protons from both the secondary N and α-carbon atoms of the amino acid. Unfortunately base-catalyzed hydrolysis of the amino acid preceded inversion. Hence the amino acid moiety is cleaved from the complex before inversion occurs.[4]

Recently, however, Yoshikawa[20] was able to measure the free energy difference between these two isomers by equilibration on activated charcoal and found the L-β_2-*RRS* isomer to be more stable than the D-β_2-*SSS* isomer by only 1.3 kcal/mol. This small energy difference is consistent with the conclusions based on the isomer geometries determined by X-ray analysis.

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[20] Professor S. Yoshikawa, private communication.

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On the Structure of $Ni(CN)_5^{3-}$. Raman, Infrared, and X-Ray Crystallographic Evidence[1a]

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A single-crystal X-ray diffraction analysis has shown that in $[Cr(tn)_3][Ni(CN)_5]\cdot 2H_2O$ (tn = 1,3 propanediamine, space group *Pbca* with $a = 23.497$ (6), $b = 13.306$ (4), $c = 14.402$ (4) Å), the $Ni(CN)_5^{3-}$ anions are exclusively square pyramidal. The cyanide stretching bands of this complex have been assigned in the Raman and infrared spectra. Crystals of $[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$, which have previously been shown to contain both square-pyramidal and distorted trigonal-bipyramidal $Ni(CN)_5^{3-}$ units, give complicated spectra in the cyanide stretching region, which, however, simplify dramatically when the crystals are dehydrated: one set of bands disappears while the other set remains essentially unaltered. This latter set is attributable to square-pyramidal $Ni(CN)_5^{3-}$, while the former set is consistent with the distorted trigonal-bipyramidal units, which evidently convert to square-pyramidal geometry on dehydration of $[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$. For $Ni(CN)_5^{3-}$ in aqueous solution the Raman and infrared evidence favors a square-pyramidal structure.

Introduction

One of the intriguing structural problems in inorganic chemistry is presented by the complex anion $Ni(CN)_5^{3-}$. That $Ni(CN)_4^{2-}$ adds a fifth ligand in concentrated aqueous cyanide solutions was demonstrated by the extensive spectrophotometric studies of Coleman, Petersen, and Penneman.[2] In the context of the rapid development of the field of pentacoordination, the fact that $Ni(CN)_5^{3-}$ remains among the few known complexes with five identical nonchelated ligands[3] lends considerable significance to the question of its structure.

Coleman, Petersen, and Penneman themselves favored a square-pyramidal structure based on a count of the infrared bands in the cyanide stretching region.[2] Recently Raymond and Basolo[4] obtained the first crystalline salts of $Ni(CN)_5^{3-}$ using $Cr(NH_3)_6^{3+}$ and $Cr(en)_3^{3+}$ (en = ethylenediammine) as the counter ions. An X-ray diffraction study of $[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$ was carried out by Raymond, Corfield, and Ibers,[5] who found that the unit cell contains *both* square-pyramidal and (somewhat distorted) trigonal-bipyramidal $Ni(CN)_5^{3-}$. They concluded that the energy difference between the two geometries is exceedingly small. When $Cr(tn)_3^{3+}$ (tn = 1,3-propanediamine) is the counterion, only square-pyramidal

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