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X-ray Crystal Structures of the *trans*-Dichloro- and Λ-*cis*-β-Oxalatocobalt(III) Complexes of 1,7-Bis(2(*S*)-pyrrolidyl)-2,6-diazaheptane. Reasons for Stereospecific Coordination of the Tetraamine Ligand

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The crystal structures of the perchlorates of the two title ions have been determined by counter methods. The *trans*-dichloro forms hexagonal crystals with $a = b = 10.846$ (4) Å and $c = 29.529$ (8) Å in space group $P6_5$. The Λ-*cis*-β gives monoclinic crystals with $a = 10.533(3)$ Å, $b = 12.068$ (4), Å $c = 7.858(2)$ Å, and $\beta = 100.75$ (4) Å in space group $P2_1$. The structures were solved by the heavy-atom method and refined by least-squares methods to give conventional R factors of 0.039 and 0.035 for 1390 and 2248 data, respectively. Both structures have the chair conformation in the six-membered "backbone" chelate ring. The absolute configurations of the four coordinated amines are *S*,*R*,*S*,*S* in the *trans*-dichloro and *S*,*R*,*R*,*S* in the Λ-*cis*-β. The five-membered chelate rings are both δ in conformation in the Λ-*cis*-β but λ and δ in the *trans*-dichloro. The absolute configurations at the inner amines in the *trans*-dichloro complex differ from those previously suggested on the basis of circular dichroism studies.

Introduction

The tetradentate ligand 1,7-bis(2(*S*)-pyrrolidyl)-2,6-diazaheptane) or *SS*-phyt was designed with the possibility of stereoselectivity in mind,[1,2] in terms of both its own coordination and its probable effects upon other ligands coordinated in the remaining two positions of an octahedral coordination sphere. Like other 2,3,2-type tetramines (ligands with the four nitrogen atoms spaced by two, three, and two carbon atoms along a straight chain), this chelating agent favors the trans geometry when coordinated with cobalt(III).[3] Thus only the *trans*-(diacido)(*SS*-pyht)Co^{III} ions could be isolated from the standard air-oxidation preparation of the cobalt(III) complexes. When, however, *trans*-[Co(*SS*-phyt)Cl$_2$]$^+$ was reacted with potassium oxalate, the ligand was forced to adopt a less favored geometry: the [Co(*SS*-pyht)(C$_2$O$_4$)]$^+$ complex ion has the cis-β (or uns-cis) geometry.[4]

In this paper the results of X-ray diffraction studies to determine the structures of *trans*-[Co-(*SS*-phyt)Cl$_2$]ClO$_4$ and *cis*-β-[Co(*SS*-phyt)C$_2$O$_4$]ClO$_4$ are reported. The observed structure of the first of the ions differs from that proposed previously on the basis of solution circular dichroism data.

Insight into the nature of this ligand's coordination, the reasons for the stereospecificity of its coordination, and, by extension, the selectivity of coordination of other similar tetramines is provided by comparison of the details of these structures.

Experimental Section

Preparation of Complexes. The ligand and the complexes were prepared according to the method given in ref 4.

Collection of Diffraction Data and Solution of Structures. Methods of data collection and reduction were the same in the determination of both of the structures. They have been published previously.[5,6] Specific experimental details are summarized in Table I.

***trans*-[Co(*SS*-pyht)Cl$_2$]ClO$_4$.** Crystals were prepared by the published procedure, including recrystallization from dilute HClO$_4$ solution. The green crystals were regular hexagonal prisms. Preliminary photographic data on several crystals included precession and cone axis photographs. These indicated Laue symmetry $6/m$ and the systematic absence $00l$ for $l \neq 6n$. These observations meant the space group was hexagonal and one of the enantiomorphic pair: $P6_1$ and $P6_5$. Refinement succeeded in the latter space group.

The data crystal was an approximately regular hexagonal prism about 0.22 mm across its base and 0.48 mm in height. It was mounted on the automatic diffractometer with the [100] coincident with the instrument's ϕ axis. To determine the severity of the absorption problem, the 600 reflection was measured (by repeated θ–2θ scans) at $\chi = 90°$ and at $\phi = 0°$ to $\phi = 350°$. The variation in intensity as a function of ϕ [defined as (maximum − minimum)/average] was 17%. This variation represented the maximum effect of absorption in the crystals since the maximum variation in the thickness of the crystal lay perpendicular to [100]. The data were not corrected for absorption.

The structure was solved without special complication by the heavy-atom method, using computer programs described previously.[5] All calculations were performed on an IBM 370/158 computer.

Scattering factors for neutral cobalt, oxygen, nitrogen, carbon, and chlorine were taken from the compilation of Cromer and Waber;[7] for hydrogen, the "best floated spherical H atom" values of Stewart et al.[8] were used. Both the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion were included for all nonhydrogen atoms, using the values of Cromer and Liberman.[9]

The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(|F_o|)$. Discrepancy indices used below are as defined previously.[10]

Refinement with all 25 nonhydrogen atoms included (with isotropic temperature factors) gave $R_F = 0.076$ and $R_{wF} = 0.079$ using the space group $P6_5$. Use of the space group $P6_1$ failed to lead to convergence. The complex ion is dissymmetric, and refinement with all coordinates reversed in sign gave at this stage $R_F = 0.081$ and $R_{wF} = 0.085$ These significantly higher values showed that the correct handedness corresponds to the two optically active C atoms having the *S* absolute configuration. This confirmed the previously determined absolute configuration.[4]

Next, thermal parameters for all nonhydrogen atoms were made anisotropic, and 28 hydrogen atoms were inserted in idealized positions based on d(C–H) = 0.95 Å and d(N–H) = 0.87 Å.[11] These steps led to further reduction of the discrepancy indices. The hydrogen atoms were "riding" hydrogen atoms—their shifts were set equal to the shifts of their attached atoms. Their thermal parameters were set equal to 1.1 times the isotropic-equivalent value of the attached nonhydrogen atom.

In the final stages of refinement it was noted that the F_c values of low-angle reflections were systematically too small. An empirical correction for absorption by the β filter was applied to 13 high-intensity low-angle reflections as described previously.[5] The correction resulted in slight but significant improvement in R factors.

The final R_F was 0.0390; R_{wF} was 0.0422. The largest shift during the last cycle of refinement was 0.008σ. The "goodness of fit" defined by $[\sum w(|F_o| - |F_c|)^2 \ (m - n)]^{1/2}$ was 2.33 where m (the number of observations) was 1390, n (the number of variables) was 225, and $m{:}n = 6.178{:}1$. Final positional and thermal parameters are given in Tables II and III.

***cis*-β-[Co(*SS*-phyt)(C$_2$O$_4$)]ClO$_4$.** Red crystals of this substance were recrystallized from dilute HClO$_4$ solution. Preliminary photographs showed Laue symmetry $2/m$ and the systematic absence $0k0$ for $k = 2n + 1$. The monoclinic space groups $P2_1$ and $P2_1/m$ were thus indicated. Because of the optical activity of the crystals, the former was chosen.

A ϕ scan, as described previously, was carried out on the $0\bar{6}0$ reflection. The variation in intensity was 28%. An absorption correction, using the program DRABZ,[5] was applied to the data. After this correction, the variation in the ϕ scan was reduced to 7.0%. The crystal was an irregular heptagonal prism of approximate dimensions 0.25 mm maximum across the base and 0.50 mm in length.

Table I. Experimental Data for X-ray Diffraction Studies

(A) Crystal Parameters (at 21 °C)[a]

$[Co(SS\text{-pyht})Cl_2]ClO_4$		$[Co(SS\text{-pyht})(C_2O_4)]ClO_4$	
$a = 10.8458\ (42)$ Å	space group $P6_5$ [C_6^3; No. 170]	$a = 10.5332\ (35)$ Å	space group $P2_1$ [C_2^2; No. 4]
$b = 10.8458\ (42)$ Å	$Z = 6$	$b = 12.0678\ (35)$ Å	$Z = 2$
$c = 29.5295\ (76)$ Å	mol wt 469.685	$c = 7.8583\ (22)$ Å	mol wt 486.80
$V = 3008.22$ Å^3	ρ(calcd) = 1.555 g cm^{-3}	$\cos\beta = -0.1866\ (4)$	ρ(calcd) = 1.647 g cm^{-3}
	ρ(obsd) = 1.55 (2) g cm^{-3} [b]	$V = 981.34$ Å^3	ρ(obsd) = 1.65 (2) g cm^{-3} [b]

(B) Measurement of Intensity Data

	$[Co(SS\text{-pyht})Cl_2]ClO_4$	$[Co(SS\text{-pyht})(C_2O_4)]ClO_4$
radiation	Mo Kα	Mo Kα
filter(s)	Nb foil at counter aperture (~47% transmission of Mo Kα)	Nb foil at counter aperture (~47% transmission of Mo Kα)
attenuators	Cu foil, inserted if $I > 10^4$ count/s	Cu foil inserted if $I > 10^4$ count/s
takeoff angle	3.0°	3.0°
detector aperture	5 mm × 5 mm	5 mm × 5 mm
crystal-detector dist	330 mm	330 mm
crystal orientation	mounted on [100]	mounted on [010]
reflections measd	$h,k,\pm l$	$h,\pm k,\pm l$
maximum 2θ	36.0°	42.0°
scan type	coupled θ(crystal)–2θ(counter)	coupled θ(crystal)–2θ(counter)
scan speed	1.0°/min	1.0°/min
scan length	$\Delta(2\theta) = (1.30 + 0.692 \tan\theta)°$, starting 0.65° below the Mo Kα_1 peak	$\Delta(2\theta) = (1.30 + 0.692 \tan\theta)$, starting 0.65° below the Mo Kα_1 peak
background measurement	stationary crystal, stationary counter; 20 s each at beginning and end of 2θ scan	stationary crystal, stationary counter; 20 s each at beginning and end of 2θ scan
standard reflections	three remeasured after every 48 reflections; rms deviations (after application of anisotropic linear decay correction) were 2.07% for 300, 1.45% for 230, 1.80% for 0,0,12	three remeasured after every 48 reflections; rms deviations (after application of anisotropic linear decay correction) were 0.95% for 500, 2.59% for 003, and 0.97% for 040
reflections collected	1390 independent measurements, 98 duplicate or equivalent measurements (averaged into primary data set)	2248 independent measurements, 1187 duplicate or equivalent measurements (averaged into primary data set) and 24 systematic absences

(C) Treatment of Intensity Data[c]

	$[Co(SS\text{-pyht})Cl_2]ClO_4$	$[Co(SS\text{-pyht})(C_2O_4)]ClO_4$
conversion to $\lvert F_o\rvert$ and $\sigma(\lvert F_o\rvert)$	as in ref 5, using an "ignorance factor" of $p = 0.030$	as in ref 5, using an "ignorance factor" of $p = 0.030$
absorption coefficient	$\mu = 12.96$ cm^{-1}; data were not corrected for absorption	$\mu = 10.92$ cm^{-1}; maximum and minimum transmission factors were 0.849 and 0.654 at $1\bar{9}\bar{4}$ and 100, respectively[d]

(D) Details of Refinement

	$[Co(SS\text{-pyht})Cl_2]ClO_4$	$[Co(SS\text{-pyht})(C_2O_4)]ClO_4$
unique data used	1390	2248
final no. of variables	225 independent, 84 dependent (for "riding" hydrogens)	274 independent, 99 dependent (for "riding" hydrogens)
final error in observation of unit weight	2.33	2.21
final R_F	0.0390	0.0346
final R_{wF}	0.0422	0.0456
Function minimized		

[a] Based on λ(Mo Kα_1) 0.709 300 Å: J. A. Bearden, *Rev. Mod. Phys.*, 39, 78 (1967). [b] By neutral buoyancy in 1,1,2,2-tetrachloroethane–$CHCl_3$. [c] Data reduction (including averaging, linear decay correction, etc.) was performed using the Fortran IV program RDUS, by B.G. DeBoer. [d] Absorption correction was carried out using the Fortran IV program DRABZ, by B. G. DeBoer.

Again the structure was solved without difficulty by the heavy-atom method. All 29 nonhydrogen atoms were located in three stages from a difference Fourier synthesis phased by the Co atom and four of its donors. Refinement with the model including these 29 atoms and with anisotropic thermal parameters for all but the carbon atoms led to $R_F = 0.056$ and $R_{wF} = 0.080$. At this point refinement using enantiomorphous coordinates gave $R_F = 0.066$ and $R_{wF} = 0.095$. These significantly higher discrepancy indices confirmed that the original model, which was chosen so that the optically active carbon atoms were both *S*, indeed was of the correct handedness.

The final stages of solution included the conversion of all nonhydrogen thermal parameters to anisotropic and the insertion of the 28 hydrogen atoms in idealized positions. These again were treated as "riding" hydrogens, using the same scheme as described above. This time, however, overall isotropic thermal parameters were varied—parameters were grouped (constrained to equal each other) for all hydrogen atoms bonded to a given carbon atom and for the four nitrogen-bonded hydrogen atoms. Again an empirical correction for β-filter absorption[5] was applied in the late stages; this time 27 reflections were affected. The final R_F was 0.0346; R_{wF} was 0.0456. The largest shift during the last cycle of refinement was 0.035σ. The "goodness of fit" was 2.21 with $m = 2248$, $n = 274$, and $m{:}n = 8.204{:}1$. Final positional and thermal parameters are given in Tables IV and V.

Results and Discussion

Nature of the Ligand. The tetradentate ligand *SS*-pyht is a symmetrically substituted heptane. The two ends may in certain conformations be related by a twofold axis passing through the central carbon atom (but never by a mirror plane). Although this ligand is not easy to synthesize, it is of considerable interest in its stereochemical possibilities. The *S* absolute configurations at the carbons in the two pyrrolidine rings specify the absolute configurations adopted by the two terminal nitrogen donors upon coordination. This specificity

Table II. Final Parameters for Nonhydrogen Atoms in *trans*-$\mathrm{Cl_2}$(*SS*-pyht)$\mathrm{Co^{III}ClO_4}$[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	0.32907 (11)	0.50765 (11)	0	4.67 (6)	5.09 (6)	2.28 (5)	2.47 (5)	−0.36 (4)	−0.20 (4)
Cl1	0.20703 (25)	0.41422 (25)	−0.06425 (8)	6.44 (12)	7.28 (13)	3.05 (11)	3.13 (11)	−1.32 (9)	−0.70 (10)
Cl2	0.44692 (22)	0.59470 (23)	0.06593 (7)	5.47 (12)	6.03 (12)	2.95 (10)	2.69 (10)	−0.82 (9)	−0.66 (9)
N1	0.5073 (7)	0.5818 (8)	−0.0362 (2)	5.2 (4)	6.4 (4)	2.5 (3)	3.6 (4)	0.1 (3)	0.6 (3)
C1	0.6324 (11)	0.7222 (11)	−0.0273 (4)	5.2 (6)	6.9 (7)	5.4 (5)	2.3 (6)	1.3 (4)	1.4 (5)
C2	0.7512 (12)	0.6968 (14)	−0.0118 (5)	5.8 (6)	9.5 (9)	8.9 (8)	3.7 (6)	−0.9 (5)	1.7 (6)
C3	0.6823 (11)	0.5428 (12)	−0.0013 (4)	7.2 (6)	10.6 (9)	5.0 (5)	6.4 (6)	1.3 (6)	1.4 (7)
C4	0.5604 (11)	0.4767 (12)	−0.0340 (3)	6.2 (6)	8.5 (7)	4.2 (5)	5.2 (6)	−0.2 (5)	−1.2 (5)
C5	0.4370 (13)	0.3320 (11)	−0.0241 (4)	9.3 (7)	6.1 (7)	6.1 (7)	4.7 (7)	−1.5 (6)	−0.0 (5)
N2	0.3415 (8)	0.3367 (8)	0.0089 (2)	4.9 (4)	3.1 (4)	0.4 (3)	1.9 (4)	0.1 (3)	−0.4 (3)
C6	0.2138 (13)	0.1978 (11)	0.0125 (4)	10.6 (8)	5.9 (6)	4.9 (6)	4.6 (7)	−2.6 (6)	−0.0 (5)
C7	0.1071 (12)	0.1941 (10)	0.0468 (4)	7.7 (7)	5.7 (6)	5.3 (7)	1.6 (5)	−0.8 (6)	0.6 (4)
C8	0.0458 (10)	0.2851 (13)	0.0333 (3)	5.2 (6)	8.8 (8)	3.2 (5)	1.9 (7)	−0.2 (4)	0.9 (5)
N3	0.1500 (7)	0.4365 (9)	0.0345 (2)	4.2 (4)	6.1 (5)	3.2 (4)	1.7 (4)	−0.6 (3)	0.8 (3)
C9	0.0874 (10)	0.5239 (13)	0.0219 (3)	4.3 (5)	9.5 (8)	4.1 (5)	3.7 (6)	0.7 (4)	0.9 (5)
C10	0.2010 (11)	0.6740 (11)	0.0220 (3)	6.4 (6)	7.7 (7)	3.3 (5)	4.2 (6)	1.0 (4)	−0.3 (4)
C11	0.1600 (14)	0.7768 (13)	0.0009 (5)	11.8 (8)	10.8 (8)	9.3 (9)	9.3 (7)	1.3 (7)	1.1 (7)
C12	0.2199 (15)	0.8094 (15)	−0.0447 (4)	11.6 (8)	13.6 (1.9)	5.7 (7)	8.9 (9)	−0.7 (6)	0.6 (7)
C13	0.3132 (11)	0.7471 (11)	−0.0500 (3)	8.1 (6)	6.8 (6)	4.8 (6)	4.8 (5)	0.4 (5)	−0.1 (4)
N4	0.3225 (8)	0.6850 (8)	−0.0060 (2)	6.0 (4)	7.1 (4)	2.9 (3)	3.8 (3)	0.4 (3)	1.3 (3)
Cl3	0.6460 (3)	0.0981 (3)	0.0013 (11)	5.9 (1)	6.1 (2)	4.5 (1)	2.5 (1)	0.2 (1)	−0.7 (1)
O1	0.7470 (9)	0.0726 (10)	−0.0182 (4)	8.8 (5)	10.7 (6)	16.4 (8)	4.3 (5)	2.3 (5)	−5.7 (5)
O2	0.7056 (8)	0.2233 (7)	0.0275 (3)	8.2 (4)	6.3 (4)	7.9 (4)	2.7 (3)	−0.7 (3)	−3.4 (4)
O3	0.5467 (9)	−0.0208 (8)	0.0270 (2)	11.9 (5)	7.1 (4)	4.6 (4)	1.8 (4)	1.7 (4)	0.4 (3)
O4	0.5659 (11)	0.1110 (9)	−0.0359 (3)	14.3 (7)	10.6 (6)	7.2 (5)	5.6 (5)	−3.0 (5)	−0.0 (4)

[a] Estimated standard deviations, shown in parentheses, are right adjusted to the last digit of the preceding number and were derived from the inverse of the final least-squares matrix. [b] Anisotropic thermal parameters are in units of Å^2 and enter the structure factor equation in the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table III. Final Positional Parameters for "Riding" Hydrogen Atoms in *trans*-$\mathrm{Cl_2}$(*SS*-pyht)$\mathrm{Co^{III}ClO_4}$[a]

	x	y	z
H1C1	0.6097	0.7695	−0.0045
H2C1	0.6610	0.7783	−0.0541
H1C2	0.7932	0.7493	0.0151
H2C2	0.8221	0.7239	−0.0345
H1C3	0.6494	0.5222	0.0291
H2C3	0.7475	0.5101	−0.0067
HC4	0.5966	0.4575	−0.0607
H1C5	0.4705	0.2714	−0.0134
H2C5	0.3845	0.2937	−0.0512
H1C6	0.2384	0.1280	0.0207
H2C6	0.1682	0.1747	−0.0162
H1C7	0.1577	0.2319	0.0743
H2C7	0.0321	0.0994	0.0517
H1C8	−0.0328	0.2657	0.0522
H2C8	0.0144	0.2622	0.0029
H1C9	0.0128	0.5074	0.0422
H2C9	0.0502	0.4987	−0.0080
HC10	0.2188	0.6959	0.0533
H1C11	0.1981	0.8603	0.0190
H2C11	0.0594	0.7348	−0.0007
H1C12	0.2761	0.9098	−0.0478
H2C12	0.1461	0.7731	−0.0667
H1C13	0.4052	0.8166	−0.0602
H2C13	0.2707	0.6722	−0.0715
HN1	0.4785	0.5939	−0.0624
HN2	0.3748	0.3514	0.0364
HN3	0.1769	0.4460	0.0627
HN4	0.4092	0.7453	0.0029

[a] Thermal parameters equal 1.1 times isotropic equivalent of bonded atom.

can be understood by considering a model $\mathrm{Co(NH_2CH_2CH_2NH_2)}$ ring in the usual gauche conformation. Conversion to the system studied here corresponds formally to the insertion of a three-carbon chain to link a C and its neighboring N. This insertion can occur only at N-axial and C-equatorial or N-equatorial and C-axial positions—the chain cannot span N equatorial to C equatorial or N axial to C axial. Therefore the handedness at the N and the handedness at the C, both of which are made optically active by the insertion, are linked. In this case, *S* absolute configuration at the C requires *S* absolute configuration at the coordinated N. This is a simplification from the complexities of coordination of such ligands as 2,5,9,12-tetraazatridecane.[12] However, the two inner nitrogen donors may still adopt upon coordination either *S* or *R* absolute configurations.

This tetramine ligand when coordinated presents a system of five fused rings—two pyrrolidine rings, two five-membered chelate rings, and a single six-membered chelate ring—of variable stereochemistry. Such a description emphasizes another factor which operates to reduce the number of possible diastereomers of this ligand when coordinated—inter-ring nonbonded interactions. The pyrrolidine rings' hydrogens would undergo, in some otherwise conceivable stereochemical dispositions, heavy steric interactions with other ligand hydrogens because the rings are fairly rigidly held in a complex system.

Structure of *trans*-[Co(*SS*-pyht)$\mathbf{Cl_2}$]$\mathbf{ClO_4}$. In the *trans*-$\mathrm{Cl_2}$(*SS*-pyht)$\mathrm{Co^{III}}$ ion the following list of possible absolute configurations at the four amines can be written: *SSSS*, *SRRS*, *SSRS*, and *SRSS*. The third and fourth of these are superimposable upon each other. The first and second designate diastereomers in which the molecule–ion has a twofold axis. In these two diastereoisomers, the central six-membered chelate rings have skew boat conformations which are enantiomers of each other. In contradistinction, in the isomer in which the central amines are of opposite absolute configuration, the six-membered chelate ring must have a chair conformation. Conversion among the chair conformation and boat conformations would entail inversions of configuration at the two inner nitrogen donors.

The observed structure of the *trans*-$\mathrm{Cl_2}$(*SS*-pyht)$\mathrm{CO^{III}}$ ion is represented in Figure 1 (left) and Table II. It has near-regular octahedral coordination. A designation for the stereochemistry of this ion would be *trans*-(*SSRS*)-($\lambda\delta$) where the *SSRS* refers to the absolute configurations of the nitrogen donors and the $\lambda\delta$ refers to the chirality of the two five-membered chelate rings. This structure has the central six-membered ring in the chair conformation. It has the inner two nitrogen atoms of different absolute configuration, and

Table IV. Final Parameters for Nonhydrogen Atoms in Λ-*cis*-β-(oxalato)(*SS*-pyht)$Co^{III}ClO_4$[a]

atom	*x*	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	0.08758 (5)	$^1/_4$	0.30045 (6)	2.31 (3)	1.61 (3)	1.62 (3)	−0.07 (3)	0.44 (2)	−0.00 (2)
O1	0.1009 (3)	0.1918 (3)	0.0770 (3)	3.9 (2)	2.3 (1)	1.7 (1)	0.0 (1)	0.7 (1)	−0.1 (1)
O2	0.0173 (3)	0.1075 (2)	0.3394 (4)	3.6 (2)	2.0 (1)	2.3 (1)	−0.5 (1)	0.6 (1)	−0.1 (1)
C1′	0.0558 (5)	0.0923 (4)	0.0523 (6)	3.0 (2)	1.7 (2)	3.2 (2)	−0.0 (2)	0.0 (2)	−0.3 (2)
C2′	−0.0011 (5)	0.0452 (5)	0.2026 (6)	2.8 (2)	1.7 (2)	3.4 (3)	−0.1 (2)	0.2 (2)	0.6 (2)
O3	0.0546 (4)	0.0387 (3)	−0.0796 (4)	5.5 (2)	2.5 (2)	2.4 (2)	−0.2 (2)	0.7 (1)	−0.9 (1)
O4	−0.0590 (4)	−0.0411 (3)	0.1880 (5)	4.8 (2)	2.4 (2)	4.1 (2)	−0.8 (2)	0.4 (2)	0.3 (1)
N1	0.1681 (4)	0.3867 (3)	0.2416 (5)	2.2 (2)	1.6 (2)	2.6 (2)	−0.4 (1)	0.2 (1)	0.3 (1)
C1	0.1908 (5)	0.4854 (4)	0.3586 (7)	3.2 (2)	2.8 (2)	3.3 (2)	0.1 (2)	0.1 (2)	−0.5 (2)
C2	0.2862 (6)	0.5531 (7)	0.2854 (7)	3.6 (3)	2.3 (2)	4.1 (3)	−0.6 (2)	0.2 (2)	0.6 (2)
C3	0.3664 (7)	0.4739 (5)	0.2058 (9)	5.2 (4)	4.1 (3)	6.6 (4)	−1.8 (3)	3.0 (3)	0.4 (3)
C4	0.3002 (5)	0.3612 (4)	0.2072 (6)	3.0 (2)	3.9 (2)	3.6 (2)	−0.3 (2)	1.8 (2)	0.0 (2)
C5	0.3607 (5)	0.2859 (4)	0.3532 (7)	2.1 (2)	3.8 (3)	4.6 (3)	−0.1 (2)	0.7 (2)	0.3 (2)
N2	0.2662 (4)	0.1986 (3)	0.3814 (5)	2.5 (2)	2.3 (2)	3.1 (2)	0.3 (2)	−0.0 (2)	0.1 (2)
C6	0.3051 (6)	0.1473 (5)	0.5559 (6)	3.4 (3)	3.5 (2)	4.0 (3)	0.8 (2)	−0.7 (2)	1.2 (2)
C7	0.2590 (5)	0.2157 (5)	0.6972 (6)	5.3 (3)	4.3 (3)	2.3 (2)	0.1 (2)	−0.5 (2)	0.4 (2)
C8	0.1171 (5)	0.2243 (4)	0.6770 (5)	5.0 (3)	3.0 (3)	1.8 (2)	−0.5 (2)	0.7 (2)	0.3 (2)
N3	0.0575 (4)	0.2944 (3)	0.5291 (5)	3.3 (2)	2.3 (2)	2.1 (2)	−0.5 (1)	0.7 (1)	0.0 (1)
C9	−0.0842 (5)	0.2964 (5)	0.5161 (6)	3.3 (2)	3.9 (3)	2.7 (2)	−0.7 (2)	1.5 (2)	−1.5 (2)
C10	−0.1432 (5)	0.3607 (5)	0.3557 (6)	3.4 (3)	3.0 (2)	3.2 (2)	0.4 (2)	0.8 (2)	−0.9 (2)
C11	−0.2868 (5)	0.3438 (6)	0.3034 (8)	3.0 (3)	6.3 (4)	5.2 (3)	0.2 (3)	1.1 (2)	−1.2 (3)
C12	−0.2992 (5)	0.2391 (7)	0.1998 (7)	3.6 (3)	6.4 (4)	5.6 (3)	−0.6 (4)	−0.2 (2)	1.1 (4)
C13	−0.1926 (4)	0.2502 (6)	0.0981 (6)	3.0 (2)	3.3 (2)	3.9 (2)	0.2 (3)	−0.2 (2)	−0.6 (3)
N4	−0.0873 (3)	0.3149 (3)	0.2095 (4)	2.5 (2)	2.7 (2)	2.3 (2)	0.2 (1)	0.5 (2)	−0.2 (1)
Cl	0.4250 (2)	−0.0397 (2)	0.2159 (2)	4.7 (1)	6.4 (1)	4.0 (1)	1.0 (1)	0.1 (1)	−1.2 (1)
O5	0.3044 (7)	−0.0463 (8)	0.2591 (11)	9.4 (5)	14.7 (6)	11.8 (6)	−2.7 (4)	5.2 (4)	−4.3 (4)
O6	0.4661 (7)	−0.1237 (7)	0.1342 (13)	7.9 (4)	12.9 (5)	21.0 (7)	4.5 (4)	−3.0 (4)	−11.1 (6)
O7	0.5134 (6)	0.0055 (5)	0.3522 (8)	10.0 (4)	9.3 (4)	8.5 (4)	−0.7 (3)	−4.1 (3)	−2.1 (3)
O8	0.4014 (9)	0.0485 (10)	0.0871 (10)	14.5 (6)	16.3 (7)	10.2 (5)	3.6 (6)	−0.4 (4)	4.8 (5)

[a] See notes to Table II.

Table V. Final Parameters for "Riding" Hydrogen Atoms in Λ-*cis*-β-(oxalato)(*SS*-pyht)$Co^{III}ClO_4$[a]

atom	*x*	*y*	*z*	*B*,[b] Å²
H1C1	0.1127	0.5255	0.3546	2.8
H2C1	0.2239	0.4636	0.4745	
H1C2	0.3398	0.5929	0.3756	7.2 (1.6)
H2C2	0.2437	0.6037	0.2009	
H1C3	0.4516	0.4699	0.2715	7.8 (1.6)
H2C3	0.3696	0.4960	0.0907	
HC4	0.3037	0.3252	0.1007	4.1 (9)
H1C5	0.3846	0.3284	0.4560	4.7 (9)
H2C5	0.4354	0.2518	0.3248	
H1C6	0.3963	0.1388	0.5814	2.3 (6)
H2C6	0.2652	0.0767	0.5546	
H1C7	0.2917	0.2886	0.6903	5.0 (1.0)
H2C7	0.2942	0.1847	0.8070	
H1C8	0.0965	0.2540	0.7805	2.7 (7)
H2C8	0.0822	0.1517	0.6587	
H1C9	−0.1066	0.3270	0.6179	3.3 (8)
H2C9	−0.1147	0.2222	0.5021	
HC10	−0.1267	0.4367	0.3825	4.1 (9)
H1C11	−0.3263	0.3881	0.4022	3.6 (8)
H2C11	−0.3257	0.4026	0.2317	
H1C12	−0.2837	0.1772	0.2755	2.7 (7)
H2C12	−0.3818	0.2318	0.1274	
H1C13	−0.2245	0.2879	0.0072	8.4 (1.5)
H2C13	−0.1600	0.1798	0.0733	
HN1	−0.0675	0.3631	0.1363	4.0 (7)
HN2	0.0937	0.3589	0.5516	
HN3	0.2686	0.1409	0.3156	
HN4	0.1078	0.4075	0.1562	

[a] See notes to Table III. [b] Isotropic thermal parameters were grouped and constrained to vary together as indicated.

it has the two five-membered chelate rings of opposite chirality. Indeed the wrapping of the ligand is such as to give the complex a mirror plane were it not for the fact that C4 and C10, the optically active carbon atoms, have the same absolute configurations (and the associated fact that N1 and N4 also have the same absolute configurations).

An *RS*, or meso, arrangement at the inner amines has been reported to be thermodynamically more stable than either the *SS* or *RR* isomers in the *trans*-diacido complexes of 2,3,2-tet with cobalt(III), where 2,3,2-tet is 3,7-diaza-1,9-nonanediamine, a closely related tetramine ligand. Nevertheless the observation is unexpected. The observed absolute configuration at the inner nitrogen atoms and conformation of the ligand are contrary to the conclusion of Jun and Liu,[4] which was based upon correlation of configuration using solution circular dichroism spectra. They concluded this substance had the central six-membered ring in the skew–boat conformation, that it had the two inner nitrogen atoms both *R*, and that it had the two five-membered chelate rings both δ in chirality. The discrepancy must follow from at least one of the following factors: (a) the method of CD correlation failed; (b) the stereochemistry of the complexes to which correlation was made was incorrectly identified; (c) the stereochemistry of this ion is different in the crystalline state (this result) and in solution (the CD-based result).

Taking the last factor first, we note that the crystals used in this study were prepared as given by Jun and Liu; the method includes air oxidation of Co(II) complexes in basic solution for 36 h followed by acidification with first HCl and then $HClO_4$. Crystals were recrystallized from dilute HCl.

This preparation would favor the attainment of conformational equilibrium before crystal formation.[3] Since the chair conformation of the backbone ring is thermodynamically more stable,[13–15] the isolation of the *trans*-(*SSRS*)-(δλ) isomer is on this ground alone not unexpected. Jun and Liu's circular dichroism spectra were observed on aqueous solutions from just such crystalline material. Under the conditions of their experiment, it seems quite unlikely that inversion at the inner nitrogens occurred very fast[13] or[16] even if it were fast that more than small equilibrium concentrations of skew–boat conformers that are *RR* and *SS* at these nitrogens could have resulted. However, the possibility of the presence of at least some *trans*-(*SRRS*)-(δδ) isomer in solution cannot absolutely be ruled out.

The second factor given above was that the conformation of the comparison complexes was incorrect. These include

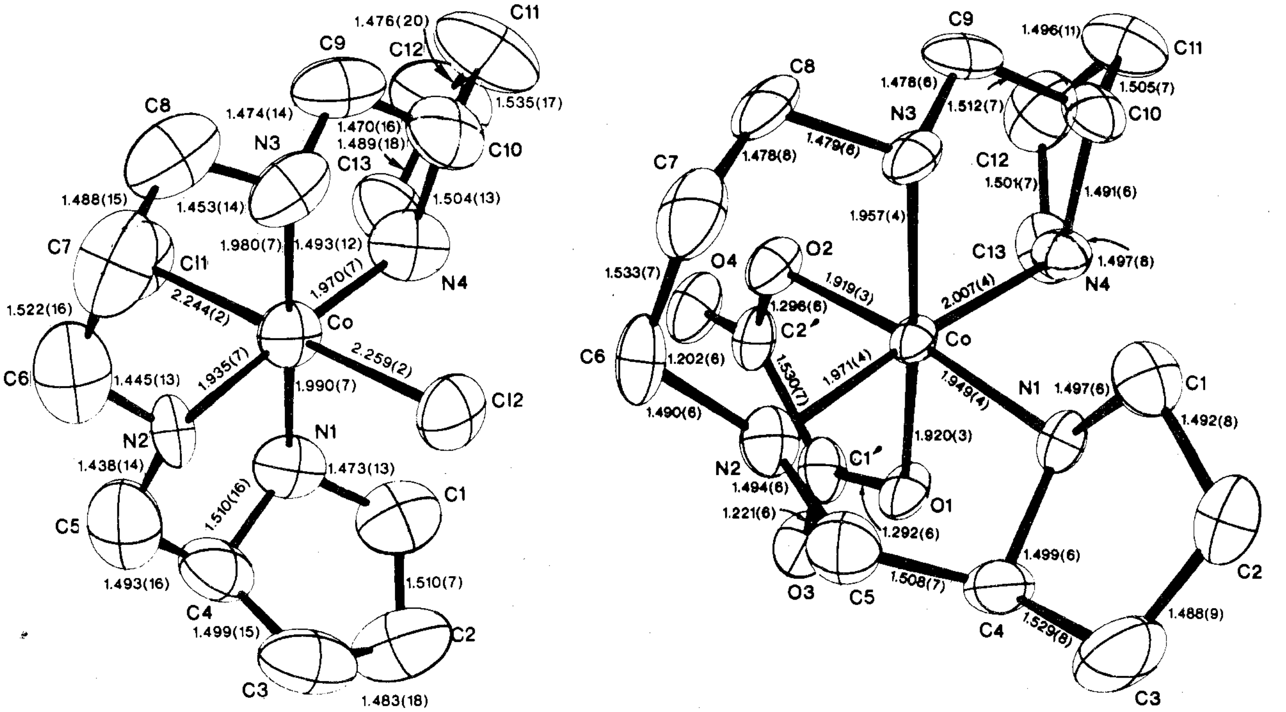

Figure 1. ORTEP drawings of the structure of (left) the *trans*-(Co[*SS*-pyht]Cl_2)$^+$ and Λ-*cis*-β-(Co[*SS*-phyt]C_2O_4)$^+$ ions. The dispositions of the tetramine ligands in the two ions are related formally by the motion of N1 chelate arm and inversion at the N2 asymmetric center. Bond distances are in angstroms. Esd's are shown in parentheses and are right adjusted to the last digit of the preceding number. Their calculation includes the effects of all elements of the positional covariance matrix as well as the uncertainties in unit-cell dimensions. No corrections for the effects of thermal motion have been applied. Hydrogen atoms are omitted for clarity.

trans-[Co(*SS*-Me_2-2,3,2-tet)Cl_2]$^+$[12] and *trans*-[Co(2,3,2-tet)Cl_2]$^+$.[3] The latter complex is not optically active unless its inner nitrogens are *RR* or *SS*. Therefore the CD of this complex at least is the CD of a complex with a skew-boat conformation in the six-membered backbone ring. The possibility that incorrect comparison stereochemistries cause the discrepancy is therefore ruled out.

The first factor now bears consideration. The CD correlation used by Jun and Liu was based on the similarities of the CD spectrum of *trans*-(*SRSS*)-[Co(pyht)Cl_2]$^+$ to the spectra of the comparison ions named above. All three spectra are quite similar in the long-wavelength region: negative extrema are found at 660 nm and smaller positive Cotton effects occur at 590 nm. The two comparison complexes continue their similarity to shorter wavelengths, having negative extrema at 450 nm; this complex ion has a positive Cotton effect at 450 nm. But the assignment of configuration by Jun and Liu follows with the general principle for such correlations—it is based on comparison of the signs of Cotton effects in the absorption wavelength region of electronic transitions common to all the ions under discussion.[17] The different Cotton effect at 450 nm is ascribed by Jun and Liu to the vicinal effect of the terminal nitrogen atoms.

The most compelling conclusion then of this discussion is that the method of correlation of configuration has broken down in this case, a case where the pyrrolidine rings perhaps exert influences on the CD not accountable by simple qualitative comparisons.

Inspection of the Co–N bond distances (Figure 1) in this complex shows that Co–N2 (1.935 (7) Å) is significantly shorter than any of the other Co–N bonds. In similar complexes it has been suggested[17] that the inner nitrogen–cobalt bonds are slightly but distinctly shorter than the terminal. Possible reasons for much greater shortening of the Co–N2 bond in this case are discussed below.

Another noteworthy factor in this structure is the quite substantial increase from the nominal value at the C3–C4–C5 angle. The observed value of 119.3 (9)° is 9.8 (9)° larger than the tetrahedral value (see Table VI). It is also 4.6 (1.3)° larger than the similar bond angle C9–C10–C11 on the "other side" of the complex ion. Yet another major deviation from the nominal bond angle values is the Co–N2–C6 angle which at 120.9 (6)° is 11.4 (6)° larger than the tetrahedral value. The Co–N3–C8 angle, on the "other side" of the ligand, is 119.0 (6)°, also signficantly expanded from the tetrahedral. Finally, the C2–C3–C4 angle is compressed significantly from the tetrahedral value to 103.4 (1.0)° and is possibly also significantly different from the similar bond on the "other side" of the complex ion (angle C12–C11–C10 = 107.3 (1.1)°; Δ/σ = 2.8). As might be expected, the angle at the cobalt to the six-membered central ring donors is in this complex (N2–Co–N3 = 94.7 (3)°) distinctly larger than the values in the terminal rings (N1–Co–N2 = 86.7 (3)°; N4–Co–N3 = 85.2 (3)°).

In the perchlorate counterion the Cl–O distances are 1.387 (10), 1.406 (8), 1.415 (8), and 1.446 (10) Å for Cl3 to O1 through O4, respectively. The large anisotropic parameters for the oxygen atoms and the differences among the Cl–O bond distances suggest the possibility of disorder in the location of the ClO_4^-.

Structure of *cis*-β-[Co(*SS*-pyht)(C_2O_4)]ClO_4. In the *trans*-(*SSRS*)-($\lambda\delta$) complex ion there were no elements of symmetry and the two ends of the coordinated ligand were therefore obviously distinguishable. The two ends of the ligands are also distinguishable in the cis-β geometry. When the *trans*-Cl_2(*SS*-pyht)Co^{III} complex is treated with potassium oxalate solution, a *cis*-β-(oxalato)(*SS*-pyht)Co^{III} ion can be isolated. The observed X-ray structure of this ion is depicted in Figure 1 (right). It can be designated Λ-*cis*-β-(*SRRS*)-($\delta\delta$) where the Λ refers to the chirality of the wrapping of the ligand around the cobalt(III)[18] and the other designations have the meanings given above. This complex also has a chair conformation for the six-membered chelate ring. It can be viewed as deriving formally from the *trans*-Cl_2(*SS*-pyht)Co^{III} ion by

Table VI. Bond Angles[a] in *trans*-Cl_2(*SS*-pyht)$Co^{III}ClO_4$ and Λ-*cis*-β-(oxalato)(*SS*-pyht)$Co^{III}ClO_4$

trans				Λ-cis-β			
			Pyrrolidine Ring Angles				
C4-N1-C1	105.6 (7)	C10-N4-C13	105.1 (7)	C4-N1-C1	103.1 (3)	C10-N4-C13	106.8 (3)
N1-C1-C2	107.0 (8)	N4-C13-C12	109.4 (9)	N1-C1-C2	104.0 (4)	N4-C13-C12	106.3 (4)
C1-C2-C3	105.8 (9)	C13-C12-C11	108.0 (1.1)	C1-C2-C3	106.6 (5)	C13-C12-C11	102.5 (6)
C2-C3-C4	103.4 (1.0)	C12-C11-C10	107.3 (1.0)	C2-C3-C4	105.9 (5)	C12-C11-C10	104.1 (5)
C3-C4-N1	104.1 (8)	C11-C10-N4	106.3 (8)	C3-C4-N1	105.0 (4)	C11-C10-N4	105.1 (4)
			Five-Member Chelate Ring Angles				
N1-C1-N2	86.7 (3)	N4-Co-N3	85.3 (3)	N1-Co-N2	84.9 (2)	N4-Co-N3	85.7 (1)
C4-N1-Co	109.3 (6)	C10-N4-Co	109.3 (6)	C4-N1-Co	109.2 (3)	C10-N4-Co	109.7 (3)
C5-C4-N1	108.7 (8)	C9-C10-N4	107.5 (8)	C5-C4-N1	105.1 (4)	C9-C10-N4	107.0 (4)
N2-C5-C4	112.1 (8)	N3-C9-C10	108.2 (8)	N2-C5-C4	109.9 (4)	N3-C9-C10	108.6 (4)
Co-N2-C5	109.7 (6)	Co-N3-C9	107.4 (6)	Co-N2-C5	110.6 (3)	Co-N3-C9	106.0 (3)
			Six-Member Chelate Ring Angles				
N2-Co-N3	94.7 (3)	C6-C7-C8	112.9 (8)	N2-Co-N3	95.6 (2)	C6-C7-C8	114.2 (4)
Co-N2-C6	120.9 (6)	C7-C8-N3	112.8 (8)	Co-N2-C6	120.6 (3)	C7-C8-N3	113.4 (4)
N2-C6-C7	113.2 (8)	Co-N3-C8	119.0 (6)	N2-C6-C7	111.9 (4)	Co-N3-C8	116.6 (3)
			Inter-Ring Bond Angles				
C5-N2-C6	110.0 (8)	C9-N3-C8	111.9 (7)	C5-N2-C6	110.7 (4)	C9-N3-C8	109.8 (4)
C3-C4-C5	119.3 (9)	C9-C10-C11	114.7 (9)	C3-C4-C5	114.4 (5)	C9-C10-C11	113.2 (4)
			Angles at Cobalt Atom				
Cl1-Co-N1	87.8 (2)	Cl2-Co-N4	87.6 (2)	O1-Co-N1	89.1 (1)	O2-Co-N4	92.9 (1)
Cl1-Co-N2	89.4 (2)	Cl2-Co-N3	87.6 (2)	O1-Co-N2	87.3 (1)	O2-Co-N3	88.0 (1)
Cl1-Co-N3	91.0 (2)	Cl2-Co-N2	89.3 (2)	O1-Co-N3	172.6 (1)	O2-Co-N2	92.3 (1)
Cl1-Co-N4	93.7 (2)	Cl2-Co-N1	93.5 (2)	O1-Co-N4	92.1 (1)	O2-Co-N1	173.6 (1)
N1-Co-N3	178.2 (3)	N4-Co-N2	176.9 (3)	N1-Co-N3	97.9 (2)	N4-Co-N2	174.8 (2)
N1-Co-N2	86.7 (3)	N4-Co-N3	85.3 (3)	N1-Co-N2	84.9 (2)	N4-Co-N3	85.7 (1)
N1-Co-N4	93.4 (3)	Cl1-Co-Cl2	178.1 (1)	N1-Co-N4	89.8 (2)	O1-Co-O2	85.0 (1)
N2-Co-N3	94.7 (3)			N2-Co-N3	95.6 (2)		

[a] In degrees.

the displacement of N1 donor out of the plane of the amine ligands. This is accompanied by inversion of configuration at N2 and followed by recoordination of N1 at the out-of-plane position. This relationship is represented by a comparison of Figure 1 (left) and (right). (The numbering of the atom has been chosen to facilitate this comparison.)

The same formal operation at the other end of the ligand coordinated in the trans complex would give a Δ-*cis*-β diastereomer. But good arguments can be made that the observed diastereomer is the only one which has any likelihood at all of forming. The argument works this way. A list of five independent factors affecting the stereochemistry is composed: First, as pointed out previously, the terminal nitrogen atoms, N1 and N4, must each have the *S* absolute configuration. Second, in all Δ-*cis*-β isomers there are serious nonbonded interactions involving the pyrrolidine rings—between hydrogen atoms on C1 and C13 or between hydrogens on C1 and N4. These interactions tend to rule out the Δ-*cis*-β diastereomers. Third, with this ligand the inner two nitrogens must have the same absolute configuration rather than opposite, or else, as molecular models show, severe steric hindrance between the hydrogens of the six-membered chelate ring and those of the out-of-plane pyrrolidine ring occurs. Fourth, the *cis*-β isomers with opposite absolute configurations at the inner two nitrogen donors tend not to occur; they have been shown to be less stable in other systems previously. For example for *cis*-β-(diacido)(trien)Co^{III} ions and for *cis*-Λ-(diacido)(2,3,2-tet)Co^{III} ions the isomers where the inner amines have the same absolute configuration are more stable.[3,19] Fifth, the inner nitrogen bridging to the out-of-plane chelate ring must have the *R* absolute configuration in the Λ wrapping of the ligand. Each of these five sources of specificity reduces by a factor of 2 the possible number of diastereomers. With five distinct centers of asymmetry formed upon coordination $2^5 = 32$ diastereomers were conceivable. But only one is, by the above arguments, expected to form. It is the Λ-*cis*-β-(*SRRS*). This diastereomer was the only one isolated by Jun and Liu. Its structure is of course confirmed by this X-ray study (Figure 1 and Tables IV and V).

In the Λ-*cis*-β structure there are, naturally, changes from the *trans*-dichloro. The notably short Co–N2 length found in the *trans*-dichloro disappears (see Figure 1). Now the shortest Co–N bond is Co–N1 (1.949 (4) Å) whereas in the *trans*-dichloro structure the Co–N1 bond was the longest such bond in the structure.

The C3–C4–C5 bond angle in the Λ-*cis*-β structure contracts to 114.4 (5)°—the similar angle in the *trans*-dichloro was 119.3 (9)°—and is no longer significantly larger than its "other side" analogue (angle C9–C10–C11). The abnormally large Co–N2–C6 angle remains essentially unchanged between the two structures although the Co–N3–C8 becomes significantly smaller in the Λ-*cis*-β structure (Table VI).

In the perchlorate ion in this structure the range of Cl–O bond distances is 0.147 (14) Å, larger than in the perchlorate in the *trans*-dichloro structure. Again this, together with the anisotropic thermal parameters, suggests the possibility of disorder in this portion of the structure.

The side-question of the *cis*-α geometry can be approached by the kind of arguments of stereospecificity used previously. Only the Δ-*cis*-α-(*SRRS*) and Λ-*cis*-α-(*SSSS*) diastereomers would be at all likely since the *cis*-α geometry also requires the central nitrogen atoms of any tetradentate ligand to have the same absolute configuration—*R* in the Δ configuration and *S* in the Λ configuration. But, as has been stated,[3] any *cis*-α geometry with even the simple 2,3,2-tet ligand leads to highly unfavorable steric interactions among ligand hydrogens. Such interactions would be even worse in the case of *SS*-pyht and no *cis*-α isomers would therefore be expected in the formation of the oxalate complex. None was found.

Crystal Packing and Hydrogen Bonds

The overall packing arrangements in the crystals involve of course hydrogen bonding. Table VII gives all intermolecular

Table VII. Intermolecular Contacts (to 3.40 Å)

atoms A···B	d(A···B), Å	symmetry operation[a]
	trans-Cl_2(*SS*-pyht)$Co^{III}ClO_4$	
N2···Cl1	3.368 (8)	$y, y-x, \frac{1}{6}+z$
N1···O3	3.188 (10)	$x-y, x, z-\frac{1}{6}$
N3···O4	3.184 (11)	$y, 1+y-x, \frac{1}{6}+z$
N4···O3	3.052 (11)	$x, 1+y, z$
N1···O2	3.395 (10)	$x-y, x, z-\frac{1}{6}$
C1···O1	3.365 (15)	$x, 1+y, z$
C4···O3	3.207 (12)	$x-y, x, z-\frac{1}{6}$
C6···Cl1	3.398 (12)	$y, y-x, \frac{1}{6}+z$
C8···O1	3.264 (14)	$x-1, y, z$
C9···O4	3.230 (13)	$y, 1+y-x, \frac{1}{6}+z$
C13···O2	3.366 (13)	$x-y, x, z-\frac{1}{6}$
	Λ-*cis*-β-(C_2O_4)(*SS*-pyht)$Co^{III}ClO_4$	
N4···O3	2.927 (6)	$-x, y+\frac{1}{2}, -z$
N3···O4	2.972 (6)	$-x, y+\frac{1}{2}, 1-z$
N2···O5	3.162 (11)	x, y, z
N1···O3	3.064 (6)	$-x, y+\frac{1}{2}, -z$
C1′···O5	3.273 (10)	x, y, z
C2′···O5	3.357 (10)	x, y, z
O4···C8	3.128 (7)	$-x, y-\frac{1}{2}, 1-z$
O4···C9	3.197 (7)	$-x, y-\frac{1}{2}, 1-z$

[a] To move atom B into region of atom A.

Table VIII. Torsional Angles (deg) in Chelate Rings

trans-[Co(*SS*-pyht)Cl_2]$^+$				Λ-*cis*-β-[Co(*SS*-pyht)Cl_2]$^+$			
			Five-Membered Rings				
Co-N1	4.8	Co-N4	6.5	Co-N1	26.6	Co-N4	0.3
N1-C4	24.5	N4-C10	34.0	N1-C4	45.3	N4-C10	26.7
C4-C5	40.4	C10-C9	49.2	C4-C5	44.8	C10-C9	50.2
C5-N2	37.2	C9-N3	45.1	C5-N2	24.6	C9-N3	49.3
N2-Co	16.9	N3-Co	21.5	N2-Co	1.0	N3-Co	26.9
			Six-Membered Rings				
Co-N2	31.9			Co-N2	33.4		
N2-C6	50.9			N2-C6	48.0		
C6-C7	66.7			C6-C7	64.1		
C7-C8	67.6			C7-C8	70.4		
C8-N3	54.5			C8-N3	59.2		
N3-Co	34.2			N3-Co	37.0		

contacts of $d < 3.40$ Å. The structure of the *trans*-dichloro consists of positive ions weakly hydrogen bonded (N2···Cl1) in a spiral along the sixfold axis. This is the closest cation-to-cation approach. Other possible hydrogen bonds involve all three of the other nitrogen donors. The N1···O3 and N3···O4 interactions have the same distance. The N4···O3 is certainly a hydrogen bond. The oxygens involved in all of these belong to different symmetry-equivalent perchlorates. Thus the structure is maintained in directions perpendicular to the unique axis.

In the crystal structure of the Λ-*cis*-β material the positive ions are again hydrogen bonded together in a spiral along the unique axis (N1···O3 = 2.927 Å). Other hydrogen bonds involve all the amines and the perchlorate counterion and form a three-dimensional network.

Chelate and Pyrrolidine Rings

It is useful to discuss the various chelate and pyrrolidine rings found in these two ions more closely. In the *trans*-Cl_2(*SS*-pyht)Co^{III} ion the two five-membered chelate rings are almost enantiomorphous—they are similar in geometry and are of opposite chirality. The torsional angles cited in Table VIII help show this. In contrast, in the Λ-*cis*-β-(oxalato)-(*SS*-pyht)Co^{III} ion the two five-membered chelate rings are quite different geometrically although they have the same chirality (δ). All four of these five-membered rings are represented in Figure 2.

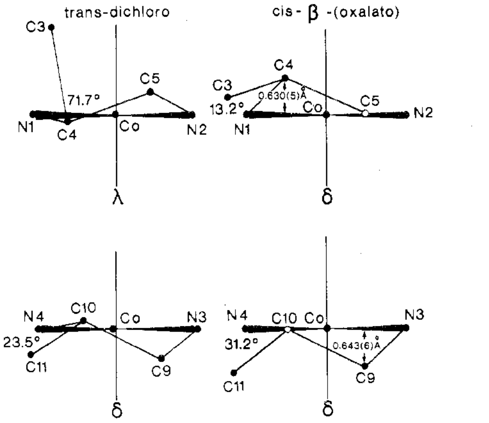

Figure 2. Comparison of the conformations of the five-membered chelate rings found in the two crystal structure determinations. The rings are viewed along an axis lying in the N–Co–N plane. Quoted angles are between this plane and the C3–C4 (or C10–C11) bond vector. Also see Table VIII.

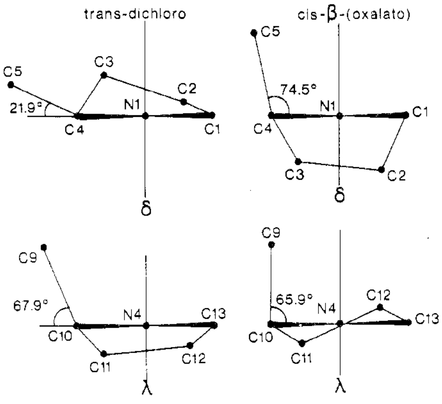

Figure 3. Comparison of the conformations of the five-membered pyrrolidine rings as found in the two crystal structure determinations. All of the conformations are dissimilar. Quoted angles are defined by the C–N–C plane and the C4–C5 (or C10–C11) bond vector in each case.

The angles quoted in Figure 2 present a rationale for the deviations from nominal bond angles in the *trans*-Cl_2(*SS*-pyht)Co^{III} structure. The λ five-membered ring includes the short Co–N2 bond and is linked via the abnormally large C3–C4–C5 angle to the rest of the ligand. This ring has its fused pyrrolidine ring "axial-like". In the Λ-*cis*-β structure the five-membered ring reverts to the δ conformation, its fused pyrrolidine ring becomes "equatorial-like" and the source of the strain vanishes, leaving no abnormal bond parameters in this portion of the ion.

In *cis*-β-(oxalato)(*SS*-pyht)Co^{III} ion the conformations of both five-membered rings are quite different from what they were in the trans complex ion and, as previously pointed out, quite different from each other (see Figure 2). In both of these rings four of the five ring atoms are essentially coplanar. In the first ring, however, it is C4 (an optically active C) that is well out of plane. In contrast, in the second ring, C9, the optically *inactive* carbon, deviates.

Among the four pyrrolidine rings in the two ions no two are particularly similar in geometry although the first ring (involving N1) has δ chirality in both ions and the second ring (involving N4) has λ chirality in both ions. All of the rings are shown in Figure 3. In the *cis*-β-(oxalato)(*SS*-pyht)Co^{III} ion the two pyrrolidine rings both have the bond that links them to the rest of the molecule axial-like to the ring. In the *trans*-Cl_2(*SS*-pyht)Co^{III} ion one of the similar bond vectors is axial-like, but the other is equatorial-like. This echoes the difference in chirality in the conjoined chelate rings.

The six-membered chelate rings in the two complex ions are surprisingly similar in conformation. In both the ions, this ring adopts a distorted chair conformation. All the bond angles in both six-membered rings are widened significantly from their nominal values (Table VI). The Co–N2–C6 and Co–N3–C8 angles are the most strained. Comparison of the torsional angles (Table VIII) shows the six-membered rings' similarity.

The distortion from the "perfect chair" conformation amounts in the six-membered rings mainly to a flattening at the amine atoms. In the *trans*-dichloro ion the N2–C6 bond vector makes an angle of 27.3° with the N2–Co–N3 plane. In the Λ-*cis*-β the comparable angle is 28.3°. The N3–C8 bond vectors make angles of 29.4 and 32.7° with the N2–Co–N3 planes in the respective ions. These values are about 9° less than similar values in comparable structures.[20]

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Registry No. *trans*-$[\mathrm{Co}(SS\text{-pyht})\mathrm{Cl_2}]\mathrm{ClO_4}$, 59202-14-1; *cis*-β-$[\mathrm{Co}(SS\text{-pyht})(\mathrm{C_2O_4})]\mathrm{ClO_4}$, 59318-03-5.

Supplementary Material Available: A listing of structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

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Structures and Circular Dichroism of Monomeric and Novel Dimeric Platinum(II) Complexes of the (*S*)-Methionine *S*-Oxides, Including the X-ray Crystal Structure of Bis[μ-[(2*S*,*SS*)-2-amino-4-(methylsulfinyl)butanoato(2–)-*S*,*O*,μ-*N*]]-diplatinum(II)

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The preparation and characterization of four complexes containing equimolar platinum(II) and (*S*)-methionine *S*-oxide are reported. The crystal and molecular structure of bis[μ-[(2*S*,*SS*)-2-amino-4-(methylsulfinyl)butanoato(2–)-*S*,*O*,μ-N]]-diplatinum(II), $[\mathrm{Pt_2}\{(2S,SS)\text{-methionine } S\text{-oxide}(2-)\}_2]$, $\mathrm{Pt_2[C_5H_9NO_3S]_2}$, is reported from single-crystal three-dimensional X-ray data collected by counter methods. The dinuclear complex crystallizes as rhombic prismatic crystals in space group $P2_1$ (C_2^2; No. 4). Cell constants are $a = 11.4826$ (15) Å, $b = 12.5007$ (19) Å, $c = 5.5839$ (9) Å, and $\beta = 96.684$ (12)°. For $Z = 2$ this gives $d_{\mathrm{calcd}} = 2.99$ g cm^{-3}; $d_{\mathrm{obsd}} = 2.97$ (2) g cm^{-3}. There were 2826 independent measurements, and the structure was refined to an R value of 0.0257. The complex has two bridging imido nitrogens (ionized α-amino groups from the amino acid) that link the platinum(II) centers in a four-membered ring. Each four-coordinate platinum atom is surrounded by nearly coplanar N, S, and O atoms from one methionine *S*-oxide ligand and the bridging imido nitrogen from the other. The two planes of coordination meet at the bridging imido groups at an angle of 129.59 (3)°. The molecule lacks C_2 symmetry in the crystal lattice because of quite dissimilar hydrogen bonding arrangements involving the two imido nitrogen atoms and different oxygen atoms of a neighboring molecule in the crystal. The (2*S*,*RS*)-diastereomeric dimer is concluded to be similar in molecular structure by comparison of analyses, circular dichroism spectra, infrared spectra, and titration data. Comparison is also made with the structure and properties of the corresponding dichloromononuclear complexes.

Introduction

The details of the interaction of platinum(II) with optically active amino acids and peptides are of interest not only as coordination phenomena but also with respect both to the known biological activity of platinum(II) complexes[1] and to the means by which stereoselectivity is exerted. Circular dichroism spectra of such complexes are easy to get experimentally but present difficulty in interpretation.[2-4] Thus, during the characterization of the newly prepared dichloroplatinum(II) complexes of the diastereomeric ligands 2*S*,*SS*-methionine *S*-oxide and 2*S*,*SR*-methionine *S*-oxide, it was observed that, whereas in acid solution the CD spectra of the two were almost mirror images, in base the CD spectra of both changed, becoming quite similar. Both the original observation and the changes were unexpected. The changes were soon in fact confirmed to be caused by further reaction—the formation of two quite novel dinuclear platinum(II) complexes. These complexes represent the first cases of a double imido bridge in coordination compounds. They hold interest both for bonding theory and for the nature of the interaction of platinum(II) in biological systems.

In this paper the syntheses of the dinuclear complexes and their precursors are given, their structures established (by means that include X-ray crystal-structure studies), and their CD spectra interpreted on the basis of these structures.

Experimental Section

Preparation of Ligands. (2*S*,*SS*)- and (2*S*,*SR*)-methionine *S*-oxide were prepared and resolved by the method of Lavine.[5] The purity of the diastereomers was checked by comparing the rotation with that

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