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Structure of (+)589-cis-α-[(2S,7S)-2,7-Di(2-pyridyl)-3,6-diazaoctane]oxalatocobalt(III) Perchlorate Monohydrate

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Abstract. $[Co(C_{16}H_{22}N_4)(C_2O_4)].ClO_4.H_2O$, $C_{18}H_{22}CoN_4O_4^+.ClO_4^-.H_2O$, (+)589-cis-α-[Co(ox)(S,S-peaen)]ClO$_4$.H$_2$O, $M_r = 534.8$, monoclinic, $P2_1$, $a = 10.807$ (1), $b = 12.353$ (2), $c = 8.512$ (1) Å, $\beta = 91.20$ (1)°, $V = 1136.0$ (3) Å^3, $Z = 2$, $D_m = 1.57$, $D_x = 1.56$ Mg m^{-3}, $\lambda(Mo\ K\alpha) = 0.7107$ Å, $\mu(Mo\ K\alpha) = 0.963$ mm^{-1}. The structure was solved by Patterson–Fourier methods and refined to a final $R(F)$ value of 0.029 for 1662 observed reflections. The quadridentate ligand S,S-peaen is linked to the Co atom in Λ-cis-α-($\delta\delta\delta$) coordination.

Introduction. A new type of optically active tetramine, NC$_5$H$_4$–*CH(CH$_3$)–NH–(CH$_2$)$_n$–NH–*CH(CH$_3$)–C$_5$H$_4$N (abbreviations for $n = 2$ and 3 being peaen and peatn, respectively) was derived from 1-(2-pyridyl)-ethylamine (pea) in order to investigate the stereospecificity caused by terminal aromatic rings (Suzuki, Kimura & Fujita, 1980). The crystal structure of (−)589-Λ-cis-β-[Co(ox)(R,R-peatn)]ClO$_4$ has already been reported (Ohba, Sato & Saito, 1981). The title compound involving the related quadridentate ligand, S,S-peaen, has been examined to obtain its conformational details and to establish the absolute

configuration of the complex ion. Crystals were kindly supplied by Dr T. M. Suzuki of Government Industrial Research Institute, Tohoku. A spherical crystal *ca* 0.4 mm in diameter was mounted on a Rigaku AFC-5 four-circle diffractometer equipped with a graphite monochromator. The cell parameters were refined by least squares on the basis of 26 2θ values ($21 < 2\theta < 30°$) measured with Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å). 2142 reflections were measured by the θ–2θ scan technique up to a 2θ value of 55°; 1662 with $|F_o| > 3\sigma(|F_o|)$ were considered observed and used in the analysis. Correction for absorption was ignored ($\mu r = 0.19$).

The structure was solved by Patterson–Fourier methods and refined by block-diagonal least squares with anisotropic thermal parameters for all non-H atoms. With $R(F)$ ($= \sum ||F_o| - |F_c||/\sum |F_o|) = 0.042$, all the H atoms were located from a difference synthesis except those of the water molecule. The final $R(F)$ was 0.029 and $R_w(F)$ $|= (\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}| = 0.036$ for 1662 reflections. The weights were assigned as $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$. Complex neutral-atom scattering factors were taken from *International Tables for X-ray*

Crystallography (1974). The calculations were carried out on a HITAC M-200H computer at the Institute for Molecular Science with the *Universal Crystallographic Computation Program System UNICS* III

Table 1. *Atomic coordinates* $(\times 10^4, \times 10^3$ *for* H) *and isotropic thermal parameters*

The equivalent isotropic temperature factor B_{eq} for non-H atoms is that defined by Hamilton (1959).

	x	y	z	B_{eq}/B (Å²)
Co	777 (1)	0	2224 (1)	1·9 (0·1)
O(1)	672 (3)	−414 (2)	46 (3)	2·5 (0·1)
O(2)	8 (3)	−1368 (2)	2632 (3)	2·4 (0·1)
O(3)	−96 (3)	−1733 (3)	−1438 (3)	3·6 (0·1)
O(4)	−920 (3)	−2705 (3)	1299 (4)	3·7 (0·1)
N(1)	−846 (3)	667 (3)	2149 (4)	2·3 (0·1)
N(2)	693 (3)	449 (3)	4391 (4)	2·3 (0·1)
N(3)	1691 (3)	1315 (3)	1810 (4)	2·3 (0·1)
N(4)	2432 (3)	−586 (3)	2342 (4)	2·4 (0·1)
C(1)	−1417 (4)	1057 (4)	847 (5)	3·2 (0·1)
C(2)	−2577 (5)	1534 (5)	916 (7)	4·5 (0·1)
C(3)	−3142 (5)	1595 (5)	2371 (7)	4·7 (0·1)
C(4)	−2564 (4)	1176 (5)	3701 (6)	4·0 (0·1)
C(5)	−1405 (4)	725 (3)	3544 (5)	2·6 (0·1)
C(6)	−609 (4)	270 (3)	4872 (5)	2·6 (0·1)
C(7)	−900 (5)	722 (4)	6496 (5)	3·7 (0·1)
C(8)	1089 (4)	1607 (3)	4505 (5)	2·9 (0·1)
C(9)	2109 (4)	1783 (3)	3360 (5)	2·8 (0·1)
C(10)	3667 (5)	1908 (4)	523 (7)	4·1 (0·1)
C(11)	2731 (4)	997 (4)	778 (5)	2·7 (0·1)
C(12)	3273 (3)	−22 (5)	1535 (4)	2·7 (0·1)
C(13)	4470 (4)	−360 (4)	1438 (6)	3·5 (0·1)
C(14)	4843 (5)	−1296 (5)	2232 (6)	4·2 (0·1)
C(15)	3985 (5)	−1863 (4)	3083 (6)	3·7 (0·1)
C(16)	2792 (4)	−1505 (3)	3098 (5)	3·0 (0·1)
C(17)	96 (4)	−1304 (3)	−160 (5)	2·5 (0·1)
C(18)	−339 (4)	−1862 (3)	1365 (5)	2·4 (0·1)
Cl	5187 (2)	−213 (1)	6796 (2)	5·8 (0·1)
O(11)	5921 (5)	400 (5)	7852 (7)	9·3 (0·2)
O(12)	4647 (6)	459 (5)	5609 (7)	9·3 (0·2)
O(13)	4331 (6)	−851 (8)	7517 (7)	13·4 (0·3)
O(14)	6036 (7)	−932 (6)	5985 (8)	13·3 (0·3)
O(w)	1799 (4)	−1029 (4)	6493 (4)	5·6 (0·1)
H(N2)	117 (4)	5 (5)	501 (5)	3·7 (1·0)
H(N3)	115 (4)	168 (4)	138 (6)	4·5 (1·2)
H(C1)	−95 (4)	102 (5)	−33 (6)	4·7 (1·2)
H(C2)	−279 (5)	159 (4)	−15 (7)	5·3 (1·3)
H(C3)	−382 (5)	210 (5)	240 (6)	4·9 (1·3)
H(C4)	−281 (4)	112 (4)	483 (6)	3·8 (1·0)
H(C6)	−77 (4)	−67 (5)	499 (6)	5·3 (1·3)
H(C7)1	−161 (4)	47 (4)	686 (6)	4·4 (1·3)
H(C7)2	−93 (5)	152 (5)	635 (6)	4·9 (1·3)
H(C7)3	−30 (4)	44 (4)	726 (6)	4·8 (1·3)
H(C8)1	139 (5)	178 (5)	555 (6)	5·4 (1·4)
H(C8)2	40 (5)	196 (4)	424 (6)	5·7 (1·4)
H(C9)1	236 (4)	258 (4)	317 (6)	4·3 (1·2)
H(C9)2	286 (4)	140 (4)	371 (6)	3·9 (1·1)
H(C10)1	319 (5)	262 (5)	12 (6)	5·5 (1·4)
H(C10)2	404 (5)	204 (4)	143 (6)	4·9 (1·3)
H(C10)3	437 (5)	184 (5)	−1 (7)	5·6 (1·4)
H(C11)	232 (4)	77 (4)	−14 (5)	3·2 (1·0)
H(C13)	504 (5)	−3 (6)	81 (6)	6·7 (1·5)
H(C14)	564 (5)	−144 (5)	208 (6)	5·2 (1·4)
H(C15)	423 (4)	−259 (4)	377 (6)	4·3 (1·2)
H(C16)	235 (5)	−206 (5)	372 (7)	6·2 (1·5)

Table 2. *Determination of the absolute configuration*

$h\,k\,l$	$|F(hkl)| - |F(h\bar{k}l)|$ Obs.	Calc.
$\bar{1}\,3\,2$	1·8	1·8
$\bar{1}\,5\,2$	−2·2	−2·2
$1\,5\,4$	0·9	0·9
$\bar{3}\,7\,4$	1·3	1·0

(Sakurai & Kobayashi, 1979). The final atomic parameters are listed in Table 1.*

The absolute structure was determined by an anomalous-scattering technique. Equi-inclination Weissenberg photographs were taken around a with Cu $K\alpha$ radiation and some Bijvoet pairs having an apparent difference in intensity were selected. These reflections were measured on the four-circle diffractometer with Mo $K\alpha$ radiation. The observed and calculated intensity differences, $|F(hkl)| - |F(h\bar{k}l)|$, are compared in Table 2. The concordance in this table established the absolute crystal structure listed in Table 1. The Hamilton (1965) test supports this result, the final $R(F)$ and $R_w(F)$ factors for the enantiomeric structure being 0·034 and 0·044 respectively.

Discussion. Fig. 1 shows a perspective drawing of the complex cation. The Co atom is surrounded octahedrally by six ligating atoms. The complex cation has a pseudo twofold axis through the Co atom and the midpoint of the C(17)—C(18) bond of the oxalate ligand. The quadridentate ligand S,S-peaen is linked to the Co atom in Λ-*cis*-α coordination in agreement with the assignment based on the sign of the CD spectrum in
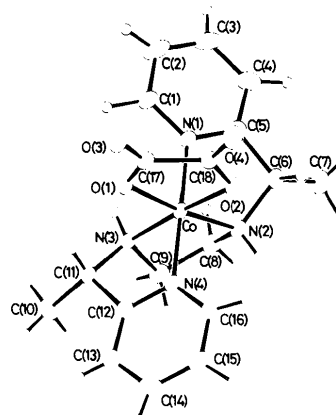
Fig. 1. An *ORTEP* drawing (Johnson, 1965) of the complex cation with thermal ellipsoids scaled at the 50% probability level. H atoms are represented by circles of radius 0·08 Å.

the first absorption region as well as on the visible absorption and PMR spectral data (Suzuki, Kimura & Fujita, 1980). The conformation of the five-membered chelate ring formed by the pea moiety is depicted in Fig. 2. It takes an envelope conformation as was found in (+)$_{589}$-Λ-[Co(ox)(S-pea)$_2$]ClO$_4$ (Ito, Ohba, Sato & Saito, 1981). The Co, N(1), C(5) and C(6) atoms lie on a plane and the secondary N atom N(2) and the methyl C(7) atom are on the same side of the plane. Dihedral angles for Co—N(1)—C(5)—C(6) and Co—N(4)—C(12)—C(11) are 1·3 (4) and 3·2 (4)° respectively. Other torsion angles in the pea chelate rings are in the range 25 to 46°. The methyl group lies in an equatorial position, the C—CH$_3$ bond axis inclining by 0·8 (5) and 1·3 (5)° with respect to the coordination plane formed by the Co and the two N atoms. The pyridine rings make angles of 23·3 (5) and 24·5 (5)° with the coordination plane. The central five-membered chelate ring takes a symmetrical skew conformation. Dihedral angles for N(3)—Co—N(2)—C(8) and N(2)—Co—N(3)—C(9) are 12·3 (3) and 14·3 (3)° respectively. Interatomic distances and bond angles are listed in Tables 3 and 4. The N—Co—N angles in the central and pea chelate rings are 88·1 (1) and 81·3 (1)° respectively. Regarding the quadridentate ligand as triethylenetetramine (trien), the absolute configuration of the coordinated secondary N atoms, N(2) and N(3), is assigned to be (R_N,R_N). The preferred conformation of three five-membered chelate rings of trien taking Λ-cis-α-(R_N,R_N) configuration is known to be $\delta\lambda\delta$ (Goto, Saburi & Yoshikawa, 1969). S,S-peaen in the present complex takes the $\delta\delta\delta$ conformation. This shows the effect of terminal pea moieties on the conformation of the central chelate ring. Molecular-model studies indicate that if the central chelate ring of the present complex took the λ conformation, the pea chelate rings would be flattened with much strain and with the methyl group not taking the preferred (equatorial) orientation. Such a planar trend of the pea chelate ring was observed in (−)$_{589}$-cis-β-[Co(ox)(R,R-peatn)]ClO$_4$ (Ohba et al., 1981).

The crystal structure can be described in terms of successive layers of ClO$_4^-$ ions and Co^{III} complexes

Table 3. *Bond lengths* (Å)

Co—O(1)	1·924 (3)	C(1)—C(2)	1·388 (7)
Co—O(2)	1·918 (3)	C(2)—C(3)	1·394 (8)
Co—N(1)	1·937 (3)	C(3)—C(4)	1·383 (8)
Co—N(2)	1·930 (3)	C(4)—C(5)	1·380 (6)
Co—N(3)	1·938 (3)	C(5)—C(6)	1·515 (6)
Co—N(4)	1·930 (3)	C(6)—C(7)	1·530 (6)
O(1)—C(17)	1·274 (5)	C(8)—C(9)	1·502 (6)
O(2)—C(18)	1·288 (5)	C(10)—C(11)	1·531 (7)
O(3)—C(17)	1·224 (5)	C(11)—C(12)	1·526 (7)
O(4)—C(18)	1·216 (5)	C(12)—C(13)	1·364 (6)
N(1)—C(1)	1·346 (6)	C(13)—C(14)	1·395 (7)
N(1)—C(5)	1·346 (5)	C(14)—C(15)	1·379 (7)
N(2)—C(6)	1·490 (5)	C(15)—C(16)	1·364 (7)
N(2)—C(8)	1·496 (5)	C(17)—C(18)	1·551 (6)
N(3)—C(9)	1·501 (3)	Cl—O(11)	1·408 (6)
N(3)—C(11)	1·493 (5)	Cl—O(12)	1·423 (6)
N(4)- C(12)	1·345 (5)	Cl—O(13)	1·370 (8)
N(4)—C(16)	1·358 (5)	Cl—O(14)	1·461 (8)

Table 4. *Bond angles* (°)

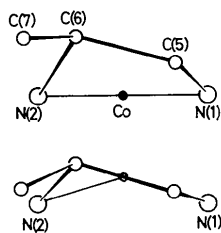| O(1)—Co—O(2)	85·6 (1)	C(3)—C(4)—C(5)	117·9 (5)
O(1)—Co—N(1)	92·7 (1)	N(1)—C(5)—C(4)	122·2 (4)
O(1)—Co—N(2)	173·8 (1)	N(1)—C(5)—C(6)	112·3 (4)
O(1)—Co—N(3)	93·9 (1)	C(4)—C(5)—C(6)	125·5 (4)
O(1)—Co—N(4)	89·2 (1)	N(2)—C(6)—C(5)	105·4 (3)
O(2)—Co—N(1)	89·2 (1)	N(2)—C(6)—C(7)	114·0 (3)
O(2)—Co—N(2)	92·9 (1)	C(5)—C(6)—C(7)	114·5 (4)
O(2)—Co—N(3)	175·0 (1)	N(2)—C(8)—C(9)	108·0 (3)
O(2)—Co—N(4)	93·7 (1)	N(3)—C(9)—C(8)	107·6 (3)
N(1)—Co—N(2)	81·3 (1)	N(3)—C(11)—C(10)	113·4 (4)
N(1)—Co—N(3)	95·9 (1)	N(3)—C(11)—C(12)	104·8 (3)
N(1)—Co—N(4)	176·7 (1)	C(10)—C(11)—C(12)	114·7 (4)
N(2)—Co—N(3)	88·1 (1)	N(4)—C(12)—C(11)	112·7 (3)
N(2)—Co—N(4)	96·9 (1)	N(4)—C(12)—C(13)	121·7 (5)
N(3)—Co—N(4)	81·3 (1)	C(11)—C(12)—C(13)	125·7 (4)
Co—O(1)—C(17)	112·4 (2)	C(12)—C(13)—C(14)	119·3 (4)
Co—O(2)—C(18)	112·7 (2)	C(13)—C(14)—C(15)	119·0 (5)
Co—N(1)—C(1)	125·3 (3)	C(14)—C(15)—C(16)	119·2 (5)
Co—N(1)—C(5)	114·6 (3)	N(4)—C(16)—C(15)	121·9 (4)
C(1)—N(1)—C(5)	120·0 (4)	O(1)—C(17)—O(3)	124·7 (4)
Co—N(2)—C(6)	106·4 (2)	O(1)—C(17)—C(18)	115·1 (4)
Co—N(2)—C(8)	108·5 (2)	O(3)—C(17)—C(18)	120·2 (4)
C(6)—N(2)—C(8)	113·3 (3)	O(2)—C(18)—O(4)	125·9 (4)
Co—N(3)—C(9)	108·0 (2)	O(2)—C(18)—C(17)	113·7 (3)
Co—N(3)—C(11)	106·2 (2)	O(4)—C(18)—C(17)	120·4 (4)
C(9)—N(3)—C(11)	113·7 (3)	O(11)—Cl—O(12)	110·9 (4)
Co—N(4)—C(12)	114·5 (3)	O(11)—Cl—O(13)	113·6 (4)
Co—N(4)—C(16)	126·5 (3)	O(11)—Cl—O(14)	106·1 (4)
C(12)—N(4)—C(16)	119·0 (4)	O(12)—Cl—O(13)	112·6 (4)
N(1)—C(1)—C(2)	121·1 (4)	O(12)—Cl—O(14)	105·8 (4)
C(1)—C(2)—C(3)	118·3 (5)	O(13)—Cl—O(14)	107·4 (4)
C(2)—C(3)—C(4)	120·5 (5)		

Fig. 2. Projection of the pea chelate ring along lines through the Co atom and the midpoint of the N(1)—N(2) or C(5)—C(6) bond axis.
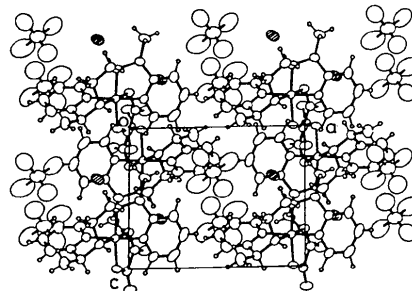

Fig. 3. A projection of the crystal structure along **b**. The hatched ellipsoids denote the water molecules.

approximately parallel to (100) as shown in Fig. 3. Two complex cations related by a twofold screw axis parallel to b are linked by weak hydrogen bonds: $N(3)\cdots O(3)$ = 2·98 (1), $H(N3)\cdots O(3)$ = 2·26 (5) Å; $N(3)\cdots O(4)$ = 3·01 (1), $H(N3)\cdots O(4)$ = 2·41 (5) Å.

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Bis(1,5-cyclooctadiene)platinum(0); X-ray Structure at 200 K

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Abstract. $C_{16}H_{24}Pt$, triclinic, $P\bar{1}$, a = 10·605 (10), b = 9·370 (12), c = 7·382 (6) Å, α = 110·33 (8), β = 89·43 (7), γ = 107·72 (9)° (200 K), Z = 2, D_m = 1·98, D_x = 2·03 g cm⁻³. 3128 corrected intensities used in the final refinement of the structure, R (R') 0·031 (0·036), showed that the Pt atom is approximately tetrahedrally coordinated to two tub-shaped cyclo-octadiene ligands. Mean Pt–C and C=C are 2·211 (7) and 1·398 (9) Å respectively.

Introduction. The title compound, $[Pt(cod)_2]$, was first prepared by Müller & Göser (1967) but their two-stage synthesis via $[Pt\{Pr^i_2(cod)\}]$ gave relatively low yields. A new synthesis was developed by Spencer (1979) in which the treatment of $[PtCl_2(cod)]$ with $Li_2(C_8H_8)$ in diethyl ether in the presence of cod gives substantially higher yields of $[Pt(cod)_2]$.

$[Pt(cod)_2]$ has since become a most useful and important entry point into zero-valent Pt chemistry (Stone, 1975, 1981; Green, Howard, Spencer & Stone, 1975), and in particular to the simple binary olefin complexes $[Pt(olefin)_3]$ (Green, Howard, Spencer & Stone, 1977; Howard, 1978). The ease of displacement of cod from $[Pt(cod)_2]$ by unstrained olefins,

isocyanides and phosphines, for example (Green *et al.*, 1975; Green, Howard, Murray, Spencer & Stone, 1977), led us to investigate the exact geometry of this interesting molecule.

The crystals are not indefinitely stable and discolour quite rapidly in air. That chosen for data collection, of approximate dimensions 0·15 × 0·16 × 0·17 mm, was sealed in a Lindemann-glass capillary and cooled to 200 K [Syntex $P2_1$ four-circle automated diffractometer, λ(Mo $K\alpha$) = 0·71069 Å]. 3128 diffracted intensities (from a total of 3439) which satisfied the criterion $I > 2\sigma(I)$ were corrected for absorption (μ = 109·6 cm⁻¹) and used in the solution and refinement of the structure. All non-hydrogen atoms were refined with anisotropic thermal parameters, while the H atoms were refined isotropically. No phase change was observed nor any significant crystal degradation on cooling to 200 K. Scattering factors and corrections for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974) and all computations were carried out using the XRAY system of programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) at the University of London Computer Centre.