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Structure of $(+)_{589}$-*ab*-Oxalato-*cd*,*ef*-bis[(−)-1(*S*)-(2-pyridyl)ethylamine]-cobalt(III) Perchlorate $\{(+)_{589}$-*cis*(*O*)-*trans*(py)-*cis*(*N*)-$[Co(ox)(S\text{-pea})_2]ClO_4\}$

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Abstract. $[Co(C_2O_4)(C_7H_{10}N_2)_2]^+.ClO_4^-$, $M_r = 490{\cdot}8$, monoclinic, $C2$, $a = 16{\cdot}040$ (5), $b = 7{\cdot}770$ (1), $c = 10{\cdot}324$ (3) Å, $\beta = 128{\cdot}02$ (2)°, $V = 1013{\cdot}7$ (3) Å^3, $Z = 2$, $D_m = 1{\cdot}60$, $D_x = 1{\cdot}61$ Mg m^{-3}, μ(Mo $K\alpha$) = 1·05 mm^{-1}. The structure was solved from a Patterson synthesis and refined to a final R of 0·036 for 1898 independent reflections. The complex cation possesses a crystallographic twofold axis. The central Co atom is octahedrally coordinated, the pyridine N atoms of two (*S*)-(2-pyridyl)ethylamine (*S*-pea) being in *trans* positions with the amino N atoms in *cis* positions. The absolute configuration is Λ.

Introduction. When an oxalate ion and two molecules of *S*-pea $[NC_5H_4{-}C^*H(CH_3)NH_2]$ coordinate to the Co atom octahedrally, three geometrical ways are possible: *cis*(*O*)-*cis*(py)-*cis*(*N*), *cis*(*O*)-*trans*(py)-*cis*(*N*) and *cis*(*O*)-*cis*(py)-*trans*(*N*), where the oxalate O atoms are designated first, then the pyridine N atoms and finally the amino N atoms of *S*-pea ligands. These isomers are all optically active. Considering their enantiomeric configuration, six types of isomers of the $[Co(ox)(S\text{-pea})_2]^+$ complex are possible. In the synthesis of this substance only three species have been isolated (Suzuki, 1979). Crystals of the title complex with the largest yield among the three, being considered as the most stable isomer, were subjected to the X-ray structure analysis in order to determine the configuration of the complex cation as well as its absolute configuration.

Preliminary determination of the lattice parameters and the crystal symmetry (space group $C2$ from systematic absences hkl, $h + k = 2n$) was made using a Weissenberg goniometer. Lattice parameters were obtained by a least-squares refinement of 45 θ values ($20 < \theta < 26°$) measured with a Rigaku automated four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å). Data were collected with a crystal of dimensions 0·5 × 0·5 × 0·4 mm (approximately a cubo-octahedron). Intensities of 1957 reflections (the $\pm h$, $+k$, $-l$ set) were measured by the θ–2θ scan mode ($2\theta_{max} = 65°$) at a speed of 2° min^{-1} in θ and with a scan width of $(1{\cdot}3 + 0{\cdot}5 \tan \theta)°$. 1898 independent intensities with $|F_o| > 3\sigma(|F_o|)$ were regarded as observed. Corrections were applied for Lorentz and polarization effects but not for absorption (μr for sphere = 0·25). Co, Cl and three N atoms were located by Patterson maps. The positions of all other non-H atoms were derived by the Fourier method. They were refined by the block-diagonal least-squares program *HBLS* (Ashida, 1967) with anisotropic thermal parameters. The function minimized was $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where the weight w was defined by $w = \{[\sigma(|F_o|)]^2 + (0{\cdot}015|F_o|)^2\}^{-1}$. All the H atoms were located from a difference synthesis, and were refined isotropically. The final R ($=\sum ||F_o| - |F_c||/\sum |F_o|$) was 0·036 and $R_w = 0{\cdot}038$ for 1898 unique reflections. At the final stage of the refinement all the parameter shifts except those of the perchlorate O atoms were less than one eighth of the corresponding standard deviations. Complex neutral-atom scattering factors were taken from *International Tables*

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Table 1. *Positional coordinates* ($\times 10^4$; *for* H $\times 10^3$), *equivalent isotropic thermal parameters for non-*H *atoms* ($\times 10$) *and isotropic thermal parameters for* H *atoms* ($\times 10$) *with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}(a^2\beta_{11} + 2\,ab\cos\gamma\beta_{12} + \ldots).$$

	x	y	z	B_{eq}/B (Å^2)
Co	5000	5000	5000	19 (1)
Cl	5000	4289 (3)	0	71 (2)
O(1)	4649 (2)	6783 (3)	3474 (3)	29 (1)
O(2)	4652 (3)	9643 (3)	3386 (4)	49 (2)
O(3)	4812 (6)	3296 (13)	−1150 (8)	162 (6)
O(4)	5763 (13)	5137 (22)	217 (21)	412 (10)
N(1)	4514 (2)	3329 (3)	3281 (3)	25 (1)
N(2)	3553 (2)	4887 (6)	4208 (3)	26 (1)
C(1)	3206 (3)	5410 (5)	5043 (5)	37 (2)
C(2)	2143 (3)	5307 (7)	4362 (6)	48 (2)
C(3)	1461 (3)	4600 (8)	2821 (7)	56 (2)
C(4)	1806 (3)	4033 (7)	1975 (6)	45 (2)
C(5)	2871 (3)	4190 (4)	2697 (4)	29 (1)
C(6)	3369 (3)	3703 (4)	1911 (4)	30 (1)
C(7)	2820 (4)	2241 (6)	682 (5)	45 (2)
C(8)	4803 (3)	8299 (4)	4112 (5)	32 (1)
HN1(1)	468 (3)	220 (6)	375 (5)	34 (9)
HN1(2)	492 (3)	335 (6)	299 (5)	39 (10)
HC1(3)	366 (3)	580 (6)	599 (5)	47 (11)
HC2(4)	190 (3)	561 (5)	499 (4)	30 (8)
HC3(5)	74 (4)	450 (8)	239 (6)	76 (16)
HC4(6)	131 (3)	350 (6)	94 (5)	46 (11)
HC6(7)	339 (3)	471 (7)	134 (4)	39 (9)
HC7(8)	332 (5)	159 (9)	64 (8)	104 (21)
HC7(9)	212 (3)	263 (7)	−15 (6)	55 (13)
HC7(10)	277 (4)	125 (7)	125 (6)	51 (12)

for X-ray Crystallography (1974). The final atomic parameters are given in Table 1.*

The absolute structure was determined by the anomalous-scattering technique. Equi-inclination Weissenberg photographs were taken around **c** with Cu $K\alpha$ radiation and some Bijvoet pairs, for which $|F(hkl)|$ and $|F(h\bar{k}l)|$ differed appreciably, were selected and the ratios $|F(hkl)|/|F(h\bar{k}l)|$ were measured on the diffractometer with Mo $K\alpha$ radiation.* It is concluded that $(+)_{589}$-*cis*(*O*)-*trans*(py)-*cis*(*N*)-$[Co(ox)(S\text{-pea})_2]^+$ has the absolute configuration Λ (IUPAC, 1970). To confirm this result, the enantiomeric structure was refined separately. It converged to $R = 0{\cdot}039$ and $R_w = 0{\cdot}041$, and could be rejected at the 0·005 significance level (Hamilton, 1965).

Discussion. A perspective drawing of the complex ion is shown in Fig. 1. It has a twofold axis of symmetry and is a *cis*(*O*)-*trans*(py)-*cis*(*N*) isomer. The Co atom exhibits distorted octahedral coordination. The two *S*-pea ligands are coodinated to the Co atom with their amino N atoms in *cis* positions. The five-membered chelate ring formed by the *S*-pea takes an envelope conformation. The C atoms of the chelate ring, C(5) and C(6), are located on the same side of the N(1)—Co—N(2) plane, being shifted by 0·37 (1) and 0·75 (1) Å, respectively. Co, N(2), C(5), C(6) and the C atoms in the pyridine ring are practically planar. The deviations of the atoms from the best plane do not exceed 0·02 Å, the amino nitrogen N(1) and the methyl carbon C(7) being off the plane on the same side at distances of 0·60 (1) and 0·63 (1) Å, respectively. The methyl group lies in an equatorial position, the $C—CH_3$ bond inclining by 8·2 (5)° with respect to the coordination plane formed by the Co and the two N atoms. Interatomic distances and bond angles within the complex cation are listed in Table 2. The angles subtended at the Co atom by the five-membered chelate rings, N(1)—Co—N(2) and O(1)—Co—O(1′), are 83·1 (1) and 86·6 (1)°, respectively.

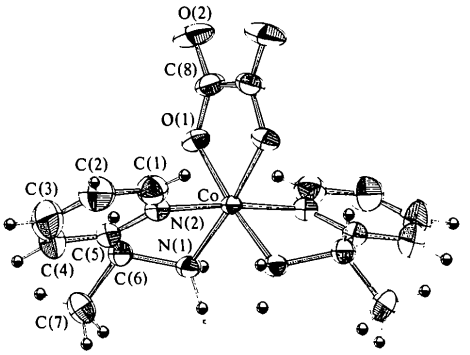

Fig. 1. An *ORTEP* drawing of the complex cation with thermal ellipsoids scaled at the 50% probability level (Johnson, 1965). H atoms are represented by circles of radius 0·08 Å.

Table 2. *Interatomic distances* (Å) *and bond angles* (°) *within the complex cation with e.s.d.'s in parentheses*

Co—O(1)	1·904 (3)	N(2)—C(5)	1·350 (4)
Co—N(1)	1·934 (3)	C(1)—C(2)	1·390 (7)
Co—N(2)	1·930 (3)	C(2)—C(3)	1·374 (7)
Cl—O(3)	1·287 (9)	C(3)—C(4)	1·363 (10)
Cl—O(4)	1·282 (21)	C(4)—C(5)	1·386 (6)
O(1)—C(8)	1·297 (4)	C(5)—C(6)	1·496 (7)
O(2)—C(8)	1·220 (5)	C(6)—C(7)	1·517 (5)
N(1)—C(6)	1·503 (4)	C(8)—C(8′)	1·528 (7)
N(2)—C(1)	1·345 (7)		
O(1)—Co—N(1)	89·0 (1)	C(2)—C(3)—C(4)	121·6 (5)
O(1)—Co—N(2)	91·0 (1)	C(3)—C(4)—C(5)	118·6 (5)
N(1)—Co—N(2)	83·1 (1)	N(2)—C(5)—C(4)	120·7 (4)
Co—O(1)—C(8)	111·9 (2)	N(2)—C(5)—C(6)	113·9 (4)
Co—N(1)—C(6)	107·6 (2)	C(4)—C(5)—C(6)	125·4 (4)
Co—N(2)—C(1)	125·4 (3)	N(1)—C(6)—C(5)	106·8 (3)
Co—N(2)—C(5)	114·5 (3)	N(1)—C(6)—C(7)	112·7 (3)
C(1)—N(2)—C(5)	120·1 (4)	C(5)—C(6)—C(7)	114·5 (4)
N(2)—C(1)—C(2)	121·4 (4)	O(1)—C(8)—O(2)	124·2 (4)
C(1)—C(2)—C(3)	117·6 (6)	O(1)—Co—O(1′)	86·6 (1)

* Lists of structure factors, anisotropic thermal parameters and observed and calculated intensity relations between some Bijvoet pairs have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35964 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

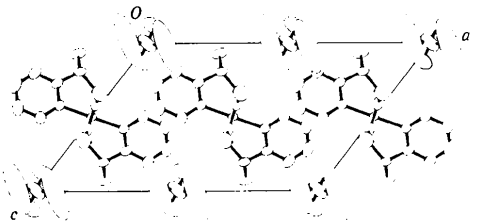

Fig. 2. A projection of the crystal structure along **b**.

The crystal structure can be described in terms of successive layers of anions and cations parallel to (001) as shown in Fig. 2. There is no close contact less than 2·9 Å. The perchlorate thermal parameters are extraordinarily large. The thermal ellipsoids do not represent the electron density of the perchlorate O atoms properly. In fact, in the final difference synthesis, diffuse residual electron densities are found around the Cl atoms, suggesting some other possible locations of the O atoms. The perchlorate ions exhibit orientational disorder as often found in the X-ray crystal structures of the perchlorate salts (*e.g.* Bang, 1977).

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Tetraaquabis(monochloroacetato)nickel(II) Dihydrate

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Abstract. $[Ni(C_2H_2ClO_2)_2(H_2O)_4].2H_2O$, $M_r = 353·78$, orthorhombic, *Fddd*, $a = 26·009$ (2), $b = 16·396$ (2), $c = 12·080$ (2) Å, $Z = 16$, $D_o = 1·82$, $D_c = 1·82$ Mg m^{-3}. The structure has been solved by direct methods, and refined by block-diagonal least squares to an R value of 0·048 for 825 independent reflections. The Ni atom displays an octahedral coordination and the structure is packed in layers with the hydrate water molecules acting as bridges between different layers.

Introduction. It was suspected that the structure of the title compound was similar to that obtained by van Niekerk & Schoening (1953) for nickel(II) acetate tetrahydrate but the study of the IR and UV spectra was inconclusive. For this reason it was decided to determine its crystal structure by X-ray diffraction.

Blue crystals suitable for X-ray studies were obtained by recrystallization from an aqueous solution. The dimensions of the crystal selected were 0·2 × 0·2 × 0·2 mm. Lattice parameters were determined by least-squares refinement of the θ values for 25 reflections measured with a Philips PW 1100 four-circle diffractometer on which all further experimental work was carried out. Monochromated Mo $K\alpha$ radiation, pulse-height discrimination and the ω-scan mode [scan width = 1·3°(θ), scan speed = 0·05°(θ) s^{-1}] were used. 838 independent reflections were collected in the range $2 \leq \theta \leq 24°$, of which 825 were considered as observed according to the criterion $I \geq 2\sigma(I)$. Only Lorentz–polarization corrections were made.

The structure was solved by direct methods with the *MULTAN* 77 system of computer programs (Main, Woolfson, Lessinger, Germain & Declercq, 1977). 120 reflections were used in the phase-determining procedure. An E map calculated with the set of signs with the highest combined figure of merit revealed peaks for all non-hydrogen atoms. Refinement was carried out by means of the program *SSFLS* (Solans & Miravitlles,

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