

Structure of $(-)$ ₅₈₉-*cis*- β -[(2*R*,8*R*)-2,8-Di(2-pyridyl)-3,7-diazanonane]oxalatocobalt(III) Perchlorate

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Abstract

[Co(C₁₇H₂₄N₄)(C₂O₄)]·ClO₄, C₁₉H₂₄CoN₄O₄⁺·ClO₄⁻, $M_r = 530.8$, crystallizes in space group $P2_1$, with $a = 14.700$ (4), $b = 19.928$ (6), $c = 7.783$ (2) Å, $\beta = 90.88$ (2)°, $U = 2280$ (1) Å³, $Z = 4$, $D_m = 1.56$, $D_x = 1.55$ Mg m⁻³ and $\mu(\text{Mo } K\alpha) = 0.956$ mm⁻¹. The final R is 0.061 for 3742 unique reflections. The central Co atom is octahedrally coordinated. The 2,3,2-tet-type quadridentate ligand is linked to the central Co atom in Δ -*cis*- β -(S_N, S_N) coordination, and the central six-membered chelate ring has a chair conformation.

Introduction

Quadridentate normal-chain ligands and their methyl-substituted derivatives are important tools in the study of the stereochemistry of octahedral Co^{III} complexes because of their stereospecificity in the coordination or fixation of the chirality around the central metal atom (Saburi & Yoshikawa, 1976). Recently, a new type of quadridentate ligand has been derived from 1-(2-pyridyl)ethylamine to investigate the characteristic features in coordination caused by the terminal aromatic rings (Suzuki, Kimura & Fujita, 1980). Crystals of the title compound which involves NC₅H₄-*CH(CH₃)-NH(CH₂)₃NH-*CH(CH₃)-C₅H₄N (*R,R*-peatn) have been subjected to X-ray crystal structure analysis in order to obtain conformational details of the quadridentate ligand and to establish the absolute configuration of the complex ion.

Experimental

Crystals were kindly supplied by Dr T. M. Suzuki of Government Industrial Research Institute, Tohoku. They are cherry-red hexagonal prisms elongated along c . A crystal approximately $0.5 \times 0.5 \times 0.4$ mm was mounted on a Rigaku automated four-circle diffractometer equipped with a pulse-height analyser and graphite monochromator. The cell parameters were

obtained by least-squares methods from the 2θ values of 17 independent reflections measured with Mo $K\alpha$ radiation ($23 < 2\theta < 30^\circ$, $\lambda = 0.7107$ Å). 5394 reflections were measured by the θ - 2θ scan mode ($2\theta_{\text{max}} = 55^\circ$) at a speed of 2° min^{-1} in θ and with a scan width of $(1.3 + 0.5 \tan \theta)^\circ$. 3747 independent intensities with $|F_o| > 3\sigma(|F_o|)$ were considered as observed. Corrections were applied for Lorentz and polarization effects but not for absorption.

Structure determination

The structure was solved by Patterson–Fourier methods and refined by block-diagonal least squares with anisotropic thermal parameters for all non-hydrogen atoms. The H atoms which could be located theoretically and those of the methyl groups found on a difference map were introduced in the refinement. Five low-angle reflection data affected by secondary extinction were removed from the refinement. The function minimized was $(\sum w||F_o| - |F_c||^2)$; weights $w = [\sigma^2(|F_o|) + (0.015|F_o|)^2]^{-1}$ were assigned. The final R ($= \sum ||F_o| - |F_c|| / \sum |F_o|$) was 0.061 and R_w [$= (\sum w||F_o| - |F_c||^2 / \sum w|F_o|^2)^{1/2}$] = 0.065 for 3742 reflections. Complex neutral-atom scattering factors were used (*International Tables for X-ray Crystallography*, 1974). The calculations were carried out on a FACOM 230-48 computer at this Institute with a local version of UNICS (Ashida, 1967). 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 and 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

* Lists of structure factors, anisotropic thermal parameters and relevant interatomic distances outside the complex ions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35661 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* ($\times 10^4$; for Co $\times 10^5$; for H $\times 10^3$)

The equivalent isotropic temperature factors, B_{eq} , have been calculated by $B_{\text{eq}} = \frac{1}{3}(a^2\beta_{11} + 2ab \cos \gamma\beta_{12} + \dots)$.

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} (\AA^2) $\times 10$
Co(1)	85826 (7)	58912 (7)	46252 (13)	30 (1)
Co(2)	33033 (8)	50000	40621 (13)	33 (1)
Cl(1)	4298 (3)	2910 (2)	7772 (4)	79 (1)
Cl(2)	8674 (3)	3658 (2)	946 (4)	98 (1)
N(1)	7459 (4)	5915 (4)	5844 (7)	31 (2)
N(2)	8510 (5)	4920 (4)	5022 (8)	41 (2)
N(3)	9356 (4)	6068 (4)	6612 (8)	35 (2)
N(4)	8647 (4)	6852 (4)	4208 (8)	33 (2)
O(1)	9631 (4)	5799 (4)	3263 (6)	41 (2)
O(2)	10014 (4)	5751 (5)	570 (7)	66 (3)
O(3)	8168 (4)	5769 (4)	-280 (7)	45 (2)
O(4)	7923 (3)	5753 (3)	2525 (6)	38 (2)
N(01)	4404 (4)	5173 (3)	2829 (8)	33 (2)
N(02)	3594 (5)	4063 (4)	3670 (9)	41 (2)
N(03)	2522 (4)	5062 (4)	2014 (8)	37 (2)
N(04)	2979 (5)	5927 (4)	4433 (8)	42 (2)
O(01)	2310 (4)	4754 (3)	5461 (7)	42 (2)
O(02)	2013 (5)	4517 (4)	8136 (8)	61 (2)
O(03)	3787 (4)	4912 (4)	8998 (7)	55 (2)
O(04)	3996 (4)	4971 (3)	6158 (7)	42 (2)
C(1)	6938 (7)	6466 (5)	6063 (13)	52 (3)
C(2)	6098 (7)	6417 (6)	6794 (14)	60 (3)
C(3)	5770 (6)	5809 (6)	7261 (13)	54 (3)
C(4)	6260 (7)	5268 (5)	7005 (13)	52 (3)
C(5)	7119 (6)	5323 (4)	6340 (10)	34 (2)
C(6)	7768 (7)	4735 (5)	6155 (12)	47 (3)
C(7)	7305 (10)	4088 (6)	5607 (19)	84 (5)
C(8)	9382 (8)	4572 (6)	5567 (13)	56 (3)
C(9)	9838 (6)	4901 (6)	7089 (12)	52 (3)
C(10)	10149 (6)	5615 (5)	6810 (11)	42 (3)
C(11)	9687 (7)	6795 (5)	6715 (12)	48 (3)
C(12)	9457 (12)	7131 (7)	8379 (14)	86 (5)
C(13)	9265 (6)	7160 (4)	5214 (11)	37 (2)
C(14)	9472 (8)	7850 (6)	4943 (15)	61 (3)
C(15)	9040 (8)	8174 (6)	3583 (17)	71 (4)
C(16)	8415 (7)	7840 (6)	2600 (14)	56 (3)
C(17)	8229 (6)	7190 (5)	2936 (11)	42 (3)
C(18)	9441 (6)	5759 (5)	1667 (10)	41 (3)
C(19)	8429 (6)	5751 (4)	1190 (9)	35 (2)
C(01)	4774 (7)	5779 (5)	2671 (12)	50 (3)
C(02)	5630 (7)	5848 (7)	1875 (12)	60 (3)
C(03)	6060 (7)	5307 (7)	1304 (13)	61 (4)
C(04)	5685 (7)	4678 (7)	1510 (13)	61 (4)
C(05)	4842 (6)	4607 (5)	2265 (11)	42 (3)
C(06)	4359 (7)	3983 (5)	2458 (12)	48 (3)
C(07)	4995 (10)	3403 (7)	3082 (21)	90 (5)
C(08)	2824 (7)	3599 (5)	3293 (13)	53 (3)
C(09)	2274 (7)	3839 (6)	1755 (12)	56 (3)
C(010)	1837 (7)	4495 (6)	1946 (11)	49 (3)
C(011)	2085 (7)	5721 (6)	1874 (13)	57 (3)
C(012)	2276 (9)	6075 (7)	165 (14)	75 (4)
C(013)	2332 (7)	6174 (5)	3371 (11)	43 (3)
C(014)	1920 (10)	6777 (7)	3622 (17)	79 (5)
C(015)	2236 (12)	7173 (7)	5064 (17)	90 (5)
C(016)	2871 (10)	6930 (6)	6079 (14)	73 (4)
C(017)	3235 (8)	6320 (6)	5746 (12)	55 (3)
C(018)	2526 (6)	4697 (5)	7043 (10)	38 (2)
C(019)	3516 (6)	4887 (4)	7466 (11)	38 (2)
O(11)	3877 (11)	2667 (7)	9264 (13)	137 (6)
O(12)	3695 (11)	3319 (10)	6896 (21)	199 (8)

Table 1 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} (\AA^2) $\times 10$
O(13)	4430 (20)	2439 (7)	6714 (19)	252 (12)
O(14)	4981 (12)	3273 (15)	7959 (24)	256 (12)
O(21)	8280 (13)	4256 (7)	1291 (20)	176 (7)
O(22)	8662 (10)	3196 (7)	2092 (17)	146 (6)
O(23)	8601 (13)	3499 (8)	-558 (16)	176 (8)
O(24)	9538 (18)	3771 (14)	1389 (34)	307 (15)
H(C7)1	682 (7)	385 (6)	644 (14)	92 (32)
H(C7)2	712 (8)	411 (7)	422 (15)	107 (37)
H(C7)3	762 (8)	374 (7)	567 (15)	105 (36)
H(C12)1	895 (9)	713 (7)	849 (16)	115 (40)
H(C12)2	932 (8)	682 (7)	960 (16)	115 (39)
H(C12)3	983 (7)	750 (6)	803 (12)	71 (26)
H(C07)1	469 (7)	304 (6)	345 (13)	85 (30)
H(C07)2	557 (9)	350 (7)	384 (17)	119 (40)
H(C07)3	516 (8)	330 (6)	197 (15)	102 (36)
H(C012)1	196 (7)	567 (6)	-66 (14)	93 (34)
H(C012)2	177 (9)	636 (7)	-25 (16)	123 (42)
H(C012)3	288 (8)	593 (7)	8 (15)	109 (36)
H(C1)	713 (4)	697 (4)	546 (8)	26 (15)
H(C2)	569 (6)	670 (5)	677 (11)	58 (23)
H(C3)	525 (5)	576 (4)	766 (9)	37 (18)
H(C4)	611 (5)	488 (4)	740 (9)	36 (17)
H(C6)	791 (5)	473 (4)	714 (10)	48 (20)
H(N2)	826 (5)	469 (4)	393 (10)	42 (19)
H(C8)1	975 (6)	457 (4)	476 (11)	49 (21)
H(C8)2	925 (6)	412 (5)	592 (11)	60 (24)
H(C9)1	1040 (5)	466 (4)	736 (9)	30 (16)
H(C9)2	956 (5)	486 (5)	820 (10)	49 (20)
H(C10)1	1046 (5)	586 (4)	787 (10)	46 (19)
H(C10)2	1059 (4)	566 (3)	603 (8)	27 (16)
H(N3)	914 (4)	592 (4)	735 (7)	18 (13)
H(C11)	1041 (5)	678 (4)	747 (9)	39 (18)
H(C14)	975 (7)	810 (5)	579 (12)	75 (28)
H(C15)	919 (5)	866 (4)	319 (10)	48 (20)
H(C16)	806 (5)	804 (4)	198 (10)	44 (19)
H(C17)	773 (4)	700 (4)	250 (8)	25 (15)
H(C01)	458 (5)	626 (4)	329 (9)	42 (19)
H(C02)	595 (5)	626 (4)	175 (8)	30 (16)
H(C03)	650 (5)	534 (4)	81 (11)	49 (21)
H(C04)	596 (4)	427 (3)	129 (8)	22 (15)
H(C06)	411 (6)	391 (5)	159 (11)	56 (22)
H(N02)	382 (6)	390 (5)	469 (11)	56 (22)
H(C08)1	235 (6)	363 (5)	452 (11)	53 (22)
H(C08)2	302 (5)	312 (4)	302 (9)	31 (17)
H(C09)1	185 (5)	353 (4)	145 (10)	37 (18)
H(C09)2	278 (5)	391 (4)	58 (9)	34 (17)
H(C010)1	149 (5)	460 (4)	79 (10)	46 (20)
H(C010)2	148 (7)	460 (6)	309 (13)	80 (28)
H(N03)	277 (5)	496 (4)	118 (9)	34 (16)
H(C011)	156 (9)	568 (7)	194 (17)	131 (44)
H(C014)	161 (5)	690 (5)	309 (10)	48 (20)
H(C015)	194 (7)	766 (6)	538 (14)	90 (32)
H(C016)	307 (5)	714 (4)	694 (9)	33 (17)
H(C017)	360 (6)	599 (5)	651 (11)	61 (23)

measured on the four-circle diffractometer with Mo $K\alpha$ radiation. The observed and calculated intensity ratios of seven hkl and $\bar{h}\bar{k}l$ pairs, for which $|F_o(hkl)|$ and $|F_o(\bar{h}\bar{k}l)|$ differed by more than 15%, are compared in Table 2. The observed $|F_o|$'s were averaged for some equivalent reflections. The concordance in this table indicated that $(-)\text{Co(ox)(R,R-peatn)}^+$ has the

Table 2. Determination of the absolute configuration

<i>hkl</i>	$ F_o $	$ F_c $	$ F_o(hkl) $	$ F_c(hkl) $
			$ F_o(h\bar{k}l) $	$ F_c(h\bar{k}l) $
$\bar{2}30$	20.6	25.3		
$2\bar{3}0$	16.4	21.3	1.26	1.19
630	14.6	14.3		
$6\bar{3}0$	12.4	12.2	1.18	1.17
431	22.6	25.5		
$4\bar{3}1$	19.7	21.9	1.15	1.16
621	22.9	26.3		
$6\bar{2}1$	19.6	22.8	1.17	1.15
$\bar{1}23$	18.1	17.9		
$1\bar{2}3$	13.6	14.9	1.33	1.20
$\bar{1}43$	18.7	20.0		
$1\bar{4}3$	11.3	14.6	1.65	1.37
$\bar{2}13$	13.2	13.6		
$2\bar{1}3$	11.5	11.3	1.15	1.20

absolute configuration Δ (IUPAC, 1970) in agreement with the assignment based on the sign of the circular dichroism spectrum in the first absorption region (Suzuki, Kimura & Fujita, 1980). The absolute configuration of *R,R*-peatn was confirmed to be the same as that of the starting material, (+)₅₈₉-*R*-pea.

Discussion

Fig. 1 shows a projection of the structure along *c*. There are two crystallographically independent complex ions in the unit cell. They are chemically equivalent and the geometries are quite similar: when one complex ion is superposed over the other the r.m.s. deviation of each atomic position is 0.13 Å. A perspective drawing of the complex cation is given in Fig. 2. The Co atom is surrounded octahedrally by the six ligating atoms. The quadridentate ligand *R,R*-peatn is linked to the central Co atom with its four N atoms in *cis-β*-(*S_N*, *S_N*) coordination in agreement with the assignment based on the absorption and PMR spectra (Suzuki, Kimura & Fujita, 1980). Coordination of 3,7-diazanonane-1,9-diamine (2,3,2-tet) to the Co^{III} tends to take the *trans* form (Bosnich, Gillard, McKenzie & Webb, 1966; Hamilton & Alexander, 1966). However, 1,6-di(2-pyridyl)-2,5-diazahexane (bispicen), with pyridyl groups on the terminal arms, cannot take the *trans* geometry presumably because of steric repulsion between the two pyridine rings (Gibson & McKenzie, 1971; Utsuno, Hayashi, Kondo & Utsumi, 1979). The *peatn* ligand does not take the *trans* form for the same reason. All the *cis* isomers of the 2,3,2-tet-type complex so far known are exclusively Δ -*cis-β*-(*S_N*, *S_N*) or its antipode (Brubaker & Schaefer, 1971*a,b*). One of the reasons may be that the chair conformation for the central six-membered chelate ring is preferable in energy to the skew-boat form. As shown in Fig. 2, the

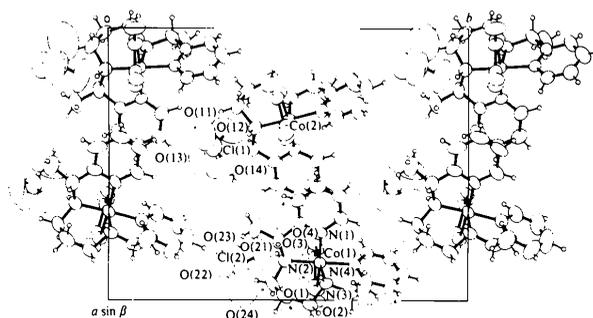


Fig. 1. A projection of the crystal structure along *c*. The pyridine rings are numbered N(1), C(1)–C(5) and N(4), C(13)–C(17). The diazanonane ring is numbered C(7), C(6), N(2), C(8), C(9), C(10), N(3), C(11), C(12). The oxalate carbons are C(18) and C(19).

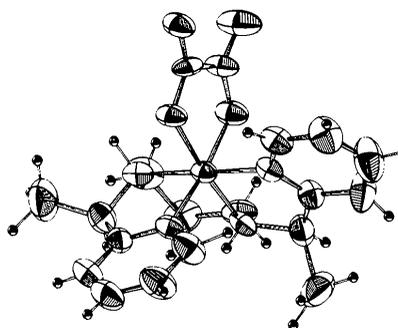


Fig. 2. An ORTEP drawing of the complex cation with thermal ellipsoids scaled at the 50% probability level (Johnson, 1965). Hydrogen atoms are represented by circles of radius 0.08 Å.

six-membered chelate ring formed by the central 1,3-pentanediamine moiety in *peatn* adopts a chair conformation as well. This was also expected from a molecular model (Suzuki, Kimura & Fujita, 1980). The dihedral angles between the NCoN and NCCN and between the NCCN and CCC planes are 136–141° and 121–122°, respectively.

The five-membered chelate rings are formed by the terminal *pea* moieties. The pyridine rings are essentially planar (the deviations of the atoms from the best plane do not exceed 0.03 Å) and make angles ranging from 6 to 10° with the coordination plane formed by the Co and the two N atoms. The dihedral angles are less than 3° for N(2)–Co(1)–N(1)–C(5) and Co(1)–N(3)–C(11)–C(13). Other torsion angles in the chelate rings formed by *pea* are less than 16°, indicating that the five-membered chelate rings in this complex cation are more flattened than those in (+)₅₈₉-[Co(*S-pea*)₃]³⁺ (the torsion angles are 20–30°; Bang, 1977). In the *pea* chelate rings the two C atoms are on the same side of the coordination plane (see Fig. 3). The apical chelate ring has the envelope conformation and the C–C bond in the ring is inclined with respect to the coordination plane. On the other hand, the C–C bond in the in-plane chelate ring is nearly parallel with the NCoN plane.

In crystals of (+)₅₈₉-[Co(*S*-pea)₃](ClO₄)₃·2H₂O, the inclination angles of the C—C bond to the methyl group with respect to the cobalt–nitrogen plane are in the range 12–23°, indicating that the most stable arrangement for the pea chelate ring is a skew conformation with the methyl group in an equatorial position. In this complex, however, the secondary N atoms are fixed because of the chair form of the central chelate ring. Thus, the methyl groups cannot take the preferred (equatorial) orientation. The C—CH₃ bonds in the apical and in-plane chelate rings make angles of 48 (1) and 35 (1)°, respectively, with respect to the NCoN plane.

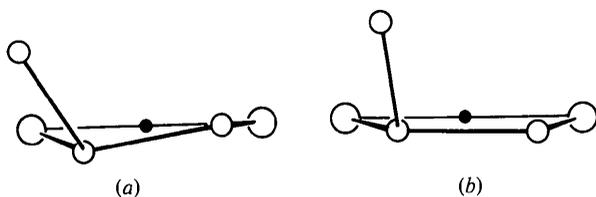


Fig. 3. Conformations of the pea chelate rings of complex 1; (a) apical, (b) in-plane chelate rings.

The values of the interatomic distances and bond angles within the complex ion are listed in Tables 3 and 4. The average octahedral angle in the six-membered ring is 94.3 (3)°. Those angles in the five-membered ring formed by pea and oxalate are 84.9 (3) and 84.9 (2)°, respectively.

Molecular packing

Approximately parallel to (010), the layers of ClO₄⁻ ions and Co^{III} complexes are stacked alternately (see Fig. 1). There is no hydrogen bonding between the layers so that the thermal motion of ClO₄⁻ is very large. The surroundings of the two independent complex cations are quite similar.*

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* See deposition footnote.

Table 3. Bond lengths (Å)

	Complex 1	Complex 2		Complex 1	Complex 2		Complex 1	Complex 2
Co(1)—N(1)	1.918 (6)	1.925 (7)	N(3)—C(11)	1.529 (13)	1.465 (14)	C(5)—C(6)	1.518 (13)	1.441 (15)
Co(1)—N(2)	1.964 (8)	1.941 (8)	N(4)—C(13)	1.338 (11)	1.344 (12)	C(6)—C(7)	1.517 (16)	1.560 (18)
Co(1)—N(3)	1.937 (6)	1.954 (6)	N(4)—C(17)	1.339 (11)	1.338 (13)	C(8)—C(9)	1.503 (14)	1.512 (14)
Co(1)—N(4)	1.945 (7)	1.930 (9)	O(1)—C(18)	1.272 (9)	1.272 (10)	C(9)—C(10)	1.511 (15)	1.464 (16)
Co(1)—O(1)	1.893 (5)	1.899 (6)	O(2)—C(18)	1.209 (10)	1.200 (11)	C(11)—C(12)	1.502 (15)	1.536 (16)
Co(1)—O(4)	1.908 (5)	1.910 (5)	O(3)—C(19)	1.202 (9)	1.252 (10)	C(11)—C(13)	1.503 (13)	1.514 (14)
N(1)—C(1)	1.351 (13)	1.332 (12)	O(4)—C(19)	1.287 (9)	1.258 (10)	C(13)—C(14)	1.423 (14)	1.361 (17)
N(1)—C(5)	1.341 (11)	1.373 (12)	C(1)—C(2)	1.370 (15)	1.418 (14)	C(14)—C(15)	1.386 (17)	1.443 (19)
N(2)—C(6)	1.461 (12)	1.488 (12)	C(2)—C(3)	1.356 (17)	1.329 (18)	C(15)—C(16)	1.359 (17)	1.307 (20)
N(2)—C(8)	1.512 (13)	1.487 (13)	C(3)—C(4)	1.313 (16)	1.379 (19)	C(16)—C(17)	1.350 (15)	1.354 (17)
N(3)—C(10)	1.482 (11)	1.515 (13)	C(4)—C(5)	1.377 (13)	1.388 (13)	C(18)—C(19)	1.527 (12)	1.535 (12)

Table 4. Bond angles (°)

	Complex 1	Complex 2		Complex 1	Complex 2		Complex 1	Complex 2
N(1)—Co(1)—N(2)	84.1 (3)	84.5 (3)	C(6)—N(2)—C(8)	110.7 (7)	112.9 (7)	N(2)—C(8)—C(9)	112.7 (8)	110.8 (8)
N(1)—Co(1)—N(3)	95.7 (3)	94.0 (3)	Co(1)—N(3)—C(10)	115.0 (5)	111.3 (6)	C(8)—C(9)—C(10)	115.5 (8)	115.7 (9)
N(1)—Co(1)—N(4)	95.9 (3)	96.6 (3)	Co(1)—N(3)—C(11)	113.4 (5)	111.7 (6)	N(3)—C(10)—C(9)	110.5 (7)	112.1 (8)
N(1)—Co(1)—O(1)	173.8 (2)	172.6 (3)	C(10)—N(3)—C(11)	108.8 (7)	112.1 (7)	N(3)—C(11)—C(12)	113.1 (8)	113.0 (9)
N(1)—Co(1)—O(4)	89.9 (2)	89.4 (3)	Co(1)—N(4)—C(13)	112.9 (5)	115.7 (6)	N(3)—C(11)—C(13)	106.9 (7)	112.2 (8)
N(2)—Co(1)—N(3)	95.0 (3)	93.5 (3)	Co(1)—N(4)—C(17)	126.6 (6)	127.4 (7)	C(12)—C(11)—C(13)	111.0 (9)	110.3 (9)
N(2)—Co(1)—N(4)	179.4 (3)	178.4 (3)	C(13)—N(4)—C(17)	120.1 (7)	116.3 (8)	N(4)—C(13)—C(11)	120.0 (8)	114.4 (8)
N(2)—Co(1)—O(1)	92.2 (3)	90.9 (3)	Co(1)—O(1)—C(18)	112.6 (5)	113.3 (5)	N(4)—C(13)—C(14)	120.1 (8)	123.2 (10)
N(2)—Co(1)—O(4)	88.0 (3)	89.4 (3)	Co(1)—O(4)—C(19)	113.6 (5)	113.4 (5)	C(11)—C(13)—C(14)	119.7 (8)	122.4 (10)
N(3)—Co(1)—N(4)	85.7 (3)	85.3 (3)	N(1)—C(1)—C(2)	120.7 (9)	119.6 (9)	C(13)—C(14)—C(15)	117.7 (10)	117.2 (12)
N(3)—Co(1)—O(1)	89.5 (2)	92.1 (3)	C(1)—C(2)—C(3)	120.1 (11)	119.9 (11)	C(14)—C(15)—C(16)	120.0 (11)	119.0 (13)
N(3)—Co(1)—O(4)	173.9 (2)	175.7 (2)	C(2)—C(3)—C(4)	119.7 (10)	120.4 (11)	C(15)—C(16)—C(17)	119.8 (10)	119.9 (12)
N(4)—Co(1)—O(1)	87.7 (3)	88.1 (3)	C(3)—C(4)—C(5)	120.0 (10)	120.2 (11)	N(4)—C(17)—C(16)	122.2 (9)	124.4 (10)
N(4)—Co(1)—O(4)	91.4 (3)	91.8 (3)	N(1)—C(5)—C(4)	121.8 (8)	118.5 (9)	O(1)—C(18)—O(2)	123.0 (8)	124.2 (8)
O(1)—Co(1)—O(4)	85.0 (2)	84.7 (2)	N(1)—C(5)—C(6)	114.5 (7)	116.2 (8)	O(1)—C(18)—C(19)	115.9 (7)	114.0 (7)
Co(1)—N(1)—C(1)	125.3 (6)	123.8 (6)	C(4)—C(5)—C(6)	123.7 (8)	125.3 (9)	O(2)—C(18)—C(19)	121.0 (7)	121.8 (8)
Co(1)—N(1)—C(5)	116.6 (6)	114.5 (6)	N(2)—C(6)—C(5)	109.8 (7)	110.6 (8)	O(3)—C(19)—O(4)	126.0 (8)	126.3 (8)
C(1)—N(1)—C(5)	117.7 (7)	121.4 (8)	N(2)—C(6)—C(7)	112.4 (8)	109.7 (8)	O(3)—C(19)—C(18)	121.8 (7)	120.0 (7)
Co(1)—N(2)—C(6)	112.7 (6)	111.9 (6)	C(5)—C(6)—C(7)	113.7 (9)	112.3 (9)	O(4)—C(19)—C(18)	112.1 (6)	113.6 (7)
Co(1)—N(2)—C(8)	116.7 (6)	117.5 (6)						

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The Structure of *N,N'*-Ethylenebis[(2-hydroxy-1-naphthyl)methaniminato]nickel(II)

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Abstract

$C_{24}H_{18}N_2NiO_2$ is monoclinic, space group $P2_1/a$, with $a = 12.982$ (2), $b = 8.197$ (1), $c = 17.721$ (2) Å, $\beta = 79.93$ (1)°, $V = 1857.1$ Å³, $d_c = 1.455$ Mg m⁻³, $Z = 4$; $\lambda(Mo K\alpha) = 0.71069$ Å. The final $R = 0.033$ for 2601 counter reflexions. The structure is made up of centrosymmetric dimers with Ni–Ni = 3.3244 (4) Å. The Ni atom is situated in a nearly square-planar environment with Ni–O = 1.849, Ni–N = 1.840 Å. One of the six-membered rings is folded by $\sim 13^\circ$, while the other is folded by $\sim 15^\circ$ about the N···O line, presumably owing to steric interaction. The ethylenediamine group has an unsymmetrical *gauche* form, the C atoms deviating from the NNiN plane by +0.118 and –0.416 Å.

Introduction

Metal complexes of the quadridentate *N,N'*-ethylenebis(salicylideneimine) ligand have been investigated fairly well and the crystal structures of the Cu^{II} (Shkol'nikova, 1967) and Ni^{II} (Shkol'nikova, Yumal, Shugam & Voblikova, 1970) complexes have been reported. However, relatively little attention has been paid to the complexes of *N,N'*-ethylenebis[(2-hydroxy-1-naphthyl)methanimine], and several metal com-

plexes of this ligand have been prepared to study their characteristics compared with the corresponding salicylideneimine complexes. The title compound is a representative of this series and in the present paper the crystal structure is discussed.

Experimental

The title compound was prepared (Ahmed, 1977) by refluxing an equimolar mixture of Ni(NO₃)₂ and *N,N'*-ethylenebis[(2-hydroxy-1-naphthyl)methanimine] (prepared from 2-hydroxynaphthaldehyde and ethylenediamine). Single crystals were grown from dimethylformamide as wine-red prisms. A crystal was placed in an argon-filled glass capillary. The crystalline quality was checked and preliminary cell constants and the space group were obtained from rotation and Weissenberg photographs. The crystal was transferred to an automated CAD-4 diffractometer equipped with a Mo source and a graphite monochromator. An orientation matrix was calculated before data collection from the setting angles of 25 centred reflections. At the end of data collection, precise cell constants were obtained by least squares from the Bragg angles of 74 reflections in the range $6 \leq \theta \leq 20^\circ$. Intensities were collected within the range $0.5 \leq \theta \leq 25^\circ$ with the $\theta/2\theta$ scan technique. Before each measurement a fast