

Tableau 4 (suite)

P(1)-P(2)	2,946 (2)	P(1)-P(L34)-P(4)	132,0 (3)
P(2)-P(3)	2,991 (2)	P(1)-P(L12)-P(2)	135,4 (3)
P(3)-P(4)	2,954 (2)	P(2)-O(L23)-P(3)	141,0 (3)
P(4)-P(1)	2,913 (2)	P(3)-O(L14)-P(4)	136,9 (3)
Ba-O(E11)	2,805 (4)	Ba-O(E32)	2,828 (4)
Ba-O(E42)	2,866 (4)	Ba-O(E21)	2,855 (4)
Ba-O(E41)	2,821 (4)	Ba-O(E22)	2,761 (5)
Ba-O(E31)	2,782 (4)	Ba-O(E12)	2,706 (4)
	Ba-O(E22)	3,056 (5)	
Cd-O(E11)	2,298 (4)	Cd-O(E32)	2,315 (4)
Cd-O(E42)	2,291 (4)	Cd-O(E21)	2,245 (4)
Cd-O(E41)	2,267 (4)	Cd-O(E31)	2,321 (4)

prises entre 2,671 Å et 3,056 Å. Le voisinage de l'atome de cadmium est un octaèdre pour lequel les distances Cd-O s'échelonnent entre 2,245 et 2,321 Å. Il est à noter qu'aucun des oxygènes de liaison des chaînes, dénotés O(L), ne participe aux voisinages des cations associés.

La Fig. 1 donne une projection de cet arrangement sur le plan *ac*. La Fig. 2 fournit le détail d'une chaîne (PO<sub>3</sub>)<sub>∞</sub> en projection sur le même plan.

La totalité des calculs cristallographiques a été effectuée à l'aide des programmes de Prewitt (1966).

#### Références

- AVERBUCH-POUCHOT, M. T. (1975). *J. Appl. Cryst.* **8**, 389-390.  
 PREWITT, C. T. (1966). *SFLS 5*, Oak Ridge National Laboratory Report ORNL-TM-305.

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## The Crystal Structure of (+)<sub>589</sub>-ΛΛΛΛ-Linear Pentaethylenehexaminecobalt(III) Hexacyanocobaltate(III) Trihydrate

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Crystals of the title compound, one of the seven isomers of the cobalt(III) complex incorporating sixidentate linear pentaethylenehexamine (1,14-diamino-3,6,9,12-tetraazatetradecane) as the ligand, are monoclinic *P*2<sub>1</sub> with *a* = 12·427 (1), *b* = 11·008 (1), *c* = 8·758 (1) Å, β = 100·61 (1)° and *Z* = 2. The structure has been refined to an *R* value of 0·031 on the basis of 2583 observed reflexions collected by diffractometry. The complex cations and anions are arranged like those in sodium chloride. The ligand molecule is sixidentate. The complex cation has an approximate twofold axis of rotation. The six nitrogen atoms of the ligand are coordinated to the central cobalt atom at an average distance of 1·977 (4) Å, exhibiting a distorted octahedral coordination. All the bond distances and angles are normal. The conformations of the five consecutive chelate rings are δλδλδ. The absolute configuration of the complex cation can be designated as ΛΛΛΛ.

### Introduction

Seven isomers of the cobalt(III) complex involving linear pentaethylenehexamine (1,14-diamino-3,6,9,12-tetraazatetradecane, linpen) were prepared and separated by means of column chromatography on an ion-exchange Sephadex (Yoshikawa & Yamasaki, 1973). All seven isomers were characterized by their absorption, circular dichroism and p.m.r. spectra. One isomer that forms stable crystals suitable for X-ray work was selected and subjected to X-ray crystal-structure anal-

ysis, in order to verify the characterization and to gain conformational details of the complex ion.

### Experimental

Crystals of (+)<sub>589</sub>-[Co(linpen)] [Co(CN)<sub>6</sub>]. 3H<sub>2</sub>O [(+)-I]\* were supplied by Professor Yamasaki of Nagoya University. The orange-red tabular crystals

\* Designation given in the paper of Yoshikawa & Yamasaki (1973).

are brittle and stable in air, but it was difficult to shape one into a sphere. Preliminary cell dimensions and the space group were determined from oscillation and Weissenberg photographs. A single crystal ( $0.2 \times 0.3 \times 0.3$  mm) was selected and the intensities of reflexions were recorded on a Rigaku four-circle diffractometer with Mo  $K\alpha$  radiation monochromated by a graphite plate, the  $\omega$ - $2\theta$  scan technique being used. 2583 independent reflexions with  $|F| > 3\sigma$  were measured and Lorentz and polarization corrections (but no absorption corrections) were applied.

The crystal data are:

$(+)_589\text{-Co}(\text{C}_{10}\text{H}_{28}\text{N}_6) \cdot \text{Co}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ , F.W. 560.4; monoclinic,  $a = 12.427(1)$ ,  $b = 11.008(1)$ ,  $c = 8.758(1)$  Å,  $\beta = 100.61(1)^\circ$ ,  $U = 1178$  Å<sup>3</sup>;  $Z = 2$ ,  $D_m = 1.58$ ,  $D_x = 1.58$

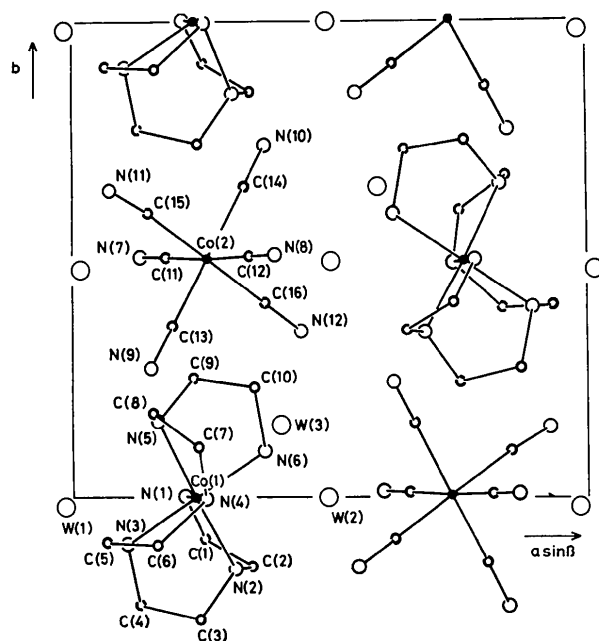


Fig. 1. A projection of the structure along the  $c$  axis.

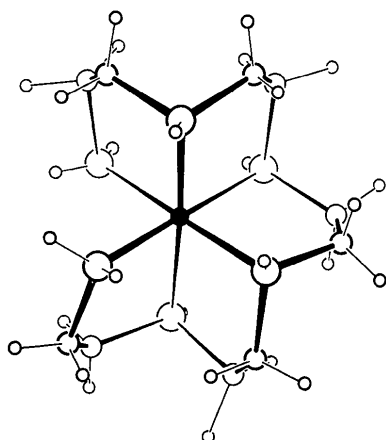


Fig. 2. A perspective drawing of the complex cation,  $(+)_589\text{-[Co(linpen)]}^{3+}$ .

$\text{g cm}^{-3}$ . Space group  $P2_1$  (No. 4). Linear absorption coefficient for Mo  $K\alpha$  ( $\lambda = 0.7107$  Å):  $\mu = 15.1$   $\text{cm}^{-1}$ .

### Structure determination

The structure was solved by the heavy-atom method using the sharpened Patterson function to locate the cobalt atoms. Refinement was by the least-squares method with block-diagonal approximation.

At a later stage of the refinement all the hydrogen atoms came out clearly on the difference synthesis. They were also included in the refinement. The final  $R$  value became 0.031 for the 2583 observed reflexions. At the final stage of the refinement positional shifts were all less than one half of the standard deviations of the positional parameters. Unit weight was given to all the reflexions. The scattering factors for Co, N, C and O as well as the corrections for anomalous scattering of cobalt were taken from *International Tables for X-ray Crystallography* (1962). For H the values given by Stewart, Davidson & Simpson (1965) were used. In order to determine the absolute configuration, the intensities of the reflexions of 43 Bijvoet pairs were measured with Cu  $K\alpha$  radiation, which can excite the cobalt atom. In Table 1 are compared the observed and calculated intensity ratios of the 12 Bijvoet pairs for which the observed  $|F(hkl)|$  and  $|F(\bar{h}\bar{k}\bar{l})|$  differed by more than 15%. All the observed  $|F|$ 's are

Table 1. Determination of the absolute configuration

$h$	$k$	$l$	$ F_o $	$ F_c $	$\frac{ F_o(hkl) }{ F_o(\bar{h}\bar{k}\bar{l}) }$	$\frac{ F_c(hkl) }{ F_c(\bar{h}\bar{k}\bar{l}) }$
6	1	0	33.2	31.8	1.23	1.22
$\bar{6}$	$\bar{1}$	0	27.0	26.0		
6	3	0	34.0	32.2	1.25	1.31
$\bar{6}$	$\bar{3}$	0	27.2	24.6		
4	1	1	11.3	14.0	0.32	0.39
$\bar{4}$	$\bar{1}$	$\bar{1}$	35.0	35.8		
8	1	1	32.3	31.3	1.45	1.29
$\bar{8}$	$\bar{1}$	$\bar{1}$	22.3	24.2		
4	2	1	43.7	40.5	1.19	1.22
$\bar{4}$	$\bar{2}$	$\bar{1}$	36.7	33.3		
6	2	1	41.6	39.6	1.24	1.23
$\bar{6}$	$\bar{2}$	$\bar{1}$	33.6	32.3		
8	2	1	16.7	18.7	0.60	0.67
$\bar{8}$	$\bar{2}$	$\bar{1}$	28.0	28.1		
0	3	1	15.0	7.6	0.69	0.31
0	$\bar{3}$	$\bar{1}$	21.8	24.2		
2	3	1	14.7	16.0	0.46	0.47
$\bar{2}$	$\bar{3}$	$\bar{1}$	32.3	33.9		
$\bar{8}$	2	2	24.2	23.8	1.38	1.23
8	$\bar{2}$	$\bar{2}$	17.6	19.4		
$\bar{2}$	1	3	34.4	34.9	0.82	0.83
2	$\bar{1}$	$\bar{3}$	41.8	41.8		
4	2	3	19.6	19.5	1.23	1.39
$\bar{4}$	$\bar{2}$	$\bar{3}$	15.9	15.2		

averaged for the two equivalent reflexions  $hkl$  and  $\bar{h}\bar{k}\bar{l}$ . The agreement in the table indicates that the complex ion (+)<sub>589</sub>-[Co(linpen)]<sup>3+</sup> has the absolute configuration  $AAAA$  (IUPAC, 1972), in agreement with the assignment by Yoshikawa & Yamasaki (1973). Observed and calculated structure amplitudes are compared in Table 2.\* The final atomic parameters are tabulated in Table 3, together with their estimated standard deviations.

### Description of the structure and discussion

The crystal is ionic, comprising [Co(linpen)]<sup>3+</sup> and [Co(CN)<sub>6</sub>]<sup>3-</sup> ions and water molecules. Fig. 1 represents a projection of the structure along the  $c$  axis. The complex cations and anions are arranged like those in sodium chloride. A perspective drawing of the complex cation is given in Fig. 2. It correctly represents the absolute configuration. The six nitrogen atoms of the ligand are coordinated to the central cobalt atom, and there exist five five-membered chelate rings. The cation has an approximate twofold axis of rotation,

through the cobalt atom and bisecting the C(5)–C(6) bond.

The bond distances and angles in the cation are listed in Table 4, together with their estimated standard deviations. The Co–N distances are in the range 1.936(4)–2.011(4) Å. However, the average value of 1.977(4) Å is similar to that of 1.978(4) Å in [Co(en)<sub>3</sub>]<sup>3+</sup> (Iwata, Nakatsu & Saito, 1969). The N–C and C–C distances are normal. The coordination octahedron is slightly distorted. The N–Co–N angles in the chelate rings are all smaller than 90°, and average 85.8(1)°. The angles Co–N–C and N–C–C are not much different from the tetrahedral angle. All the C–N–C angles, with a mean value of 112.9(3)°, are greater than the tetrahedral angle, indicating significant angular deformations due to the non-bonded interactions between the hydrogen atoms.

None of the five-membered chelate rings is planar. The conformations of the rings are  $\delta$ ,  $\lambda$ ,  $\delta$ ,  $\lambda$  and  $\delta$  in turn, as shown in Fig. 3. The deviations of the two carbon atoms from the plane defined by the cobalt and the two nitrogen atoms in each ring are not symmetrical with respect to the plane, as can be seen from Fig. 3. Rings  $A$ ,  $B$  and  $C$  have an unsymmetrical skew conformation, ring  $D$  is of an eclipsed envelope type and, in the ring  $E$ , the two carbon atoms are both on the same side of the NCoN plane. The dihedral

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Table 3. Atomic parameters

Atomic parameters for the non-hydrogen atoms ( $\times 10^4$ ). The  $U_{ij}$ 's are defined by:

$$\exp [-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots) \times 10^{-3}].$$

	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Co(1)	2383 (0)	0	2561 (1)	21 (0)	21 (0)	20 (0)	2 (0)	1 (0)	-2 (0)
Co(2)	2633 (0)	5074 (1)	7477 (1)	23 (0)	24 (0)	24 (0)	0 (0)	2 (0)	-3 (0)
N(1)	2168 (3)	206 (4)	285 (4)	39 (2)	22 (2)	25 (2)	-1 (2)	5 (1)	1 (2)
N(2)	3155 (3)	-1481 (4)	2249 (4)	34 (2)	21 (2)	28 (2)	8 (2)	5 (1)	-1 (2)
N(3)	1050 (3)	-968 (4)	2379 (4)	24 (2)	31 (2)	25 (2)	-4 (2)	0 (1)	4 (2)
N(4)	2492 (3)	-173 (4)	4851 (4)	30 (2)	32 (2)	20 (1)	5 (2)	1 (1)	-1 (2)
N(5)	1678 (3)	1614 (4)	2816 (4)	31 (2)	25 (2)	32 (2)	6 (2)	4 (2)	-3 (2)
N(6)	3746 (3)	989 (4)	2788 (4)	28 (2)	28 (2)	38 (2)	-3 (2)	3 (2)	-2 (2)
N(7)	1317 (3)	5098 (5)	4169 (4)	46 (2)	40 (2)	32 (2)	-2 (3)	1 (2)	3 (2)
N(8)	3962 (4)	5169 (6)	10765 (4)	54 (2)	55 (3)	33 (2)	3 (3)	-9 (2)	-7 (2)
N(9)	1539 (4)	2751 (5)	8273 (5)	48 (3)	44 (3)	35 (2)	-5 (2)	8 (2)	6 (2)
N(10)	3767 (4)	7433 (5)	6718 (7)	47 (3)	38 (3)	79 (4)	-8 (2)	1 (2)	8 (3)
N(11)	723 (4)	6497 (5)	8355 (6)	33 (2)	61 (3)	57 (3)	6 (2)	5 (2)	-28 (3)
N(12)	4443 (3)	3546 (5)	6598 (5)	33 (2)	52 (3)	45 (2)	6 (2)	4 (2)	-10 (2)
C(1)	2577 (4)	-863 (5)	-469 (5)	57 (3)	31 (2)	25 (2)	5 (2)	7 (2)	-5 (2)
C(2)	3478 (4)	-1448 (5)	681 (5)	42 (3)	35 (3)	35 (2)	10 (2)	18 (2)	-4 (2)
C(3)	2445 (5)	-2550 (5)	2465 (6)	56 (3)	20 (2)	56 (3)	2 (2)	26 (2)	0 (2)
C(4)	1279 (5)	-2235 (5)	1909 (6)	49 (3)	33 (3)	46 (3)	-13 (2)	16 (2)	-13 (2)
C(5)	651 (4)	-942 (5)	3895 (5)	27 (2)	42 (3)	37 (2)	1 (2)	12 (2)	4 (2)
C(6)	1620 (4)	-992 (5)	5178 (5)	50 (3)	41 (3)	25 (2)	0 (2)	12 (2)	7 (2)
C(7)	2444 (5)	1065 (5)	5532 (5)	68 (4)	38 (3)	23 (2)	2 (3)	10 (2)	-10 (2)
C(8)	1569 (5)	1786 (5)	4493 (6)	61 (4)	36 (3)	40 (3)	7 (3)	23 (3)	-7 (2)
C(9)	2361 (4)	2551 (4)	2261 (5)	62 (3)	17 (2)	31 (2)	3 (2)	12 (2)	-5 (2)
C(10)	3542 (4)	2324 (5)	2874 (6)	43 (3)	27 (2)	41 (3)	-11 (2)	6 (2)	-10 (2)
C(11)	1822 (3)	5101 (5)	5397 (4)	30 (2)	21 (2)	31 (2)	0 (2)	7 (1)	0 (2)
C(12)	3448 (4)	5135 (5)	9552 (5)	32 (2)	30 (3)	39 (2)	1 (2)	6 (2)	-3 (2)
C(13)	1942 (4)	3648 (5)	7978 (5)	35 (2)	30 (2)	22 (2)	3 (2)	2 (2)	-3 (2)
C(14)	3351 (4)	6558 (5)	7019 (6)	26 (2)	33 (3)	41 (3)	2 (2)	1 (2)	-3 (2)
C(15)	1479 (4)	6015 (5)	8053 (5)	37 (3)	31 (3)	31 (2)	-3 (2)	-3 (2)	-10 (2)
C(16)	3757 (4)	4152 (5)	6895 (5)	23 (2)	35 (2)	29 (2)	0 (2)	4 (2)	-1 (2)
O(1)	-169 (4)	-177 (6)	-986 (5)	59 (3)	94 (4)	60 (3)	-3 (3)	-14 (2)	18 (3)
O(2)	4902 (4)	72 (6)	5972 (5)	93 (3)	100 (4)	52 (2)	47 (4)	-22 (2)	-15 (3)
O(3)	4034 (3)	1560 (4)	-562 (5)	48 (2)	59 (3)	64 (3)	3 (2)	19 (2)	16 (2)

Table 3 (cont.)

Positional parameters for the hydrogen atoms ( $\times 10^3$ )

The isotropic temperature factor is defined by:  
 $\exp[-8\pi^2 U(\sin^2 \theta/\lambda^2)]$ . Mean value of  $U$  for the hydrogen atoms is 0.06 (2)  $\text{\AA}^2$ .

	<i>x</i>	<i>y</i>	<i>z</i>
H(1)	255 (4)	61 (5)	-4 (5)
H(2)	135 (5)	21 (7)	-19 (7)
H(3)	291 (5)	-58 (5)	-136 (6)
H(4)	183 (5)	-136 (6)	-93 (7)
H(5)	418 (5)	-95 (6)	71 (7)
H(6)	370 (4)	-233 (6)	41 (6)
H(7)	382 (3)	-152 (4)	288 (5)
H(8)	267 (6)	-266 (8)	334 (9)
H(9)	276 (4)	-330 (5)	208 (6)
H(10)	73 (4)	-284 (5)	229 (6)
H(11)	103 (4)	-219 (5)	88 (5)
H(12)	54 (5)	-72 (6)	161 (7)
H(13)	6 (4)	-158 (5)	389 (6)
H(14)	28 (4)	-14 (5)	397 (5)
H(15)	194 (6)	-173 (8)	530 (8)
H(16)	138 (6)	-83 (7)	609 (8)
H(17)	313 (4)	-51 (4)	528 (5)
H(18)	341 (5)	140 (6)	580 (7)
H(19)	222 (5)	98 (6)	657 (6)
H(20)	160 (4)	280 (5)	474 (6)
H(21)	88 (4)	148 (5)	448 (6)
H(22)	95 (4)	175 (5)	230 (6)
H(23)	215 (4)	317 (4)	249 (5)
H(24)	215 (4)	257 (5)	130 (6)
H(25)	376 (4)	253 (6)	369 (6)
H(26)	406 (4)	279 (5)	229 (6)
H(27)	430 (5)	76 (6)	374 (7)
H(28)	418 (6)	97 (8)	198 (8)
H(29)	-52 (7)	6 (11)	-194 (10)
H(30)	24 (4)	-84 (5)	-143 (6)
H(31)	496 (7)	-8 (11)	690 (10)
H(32)	514 (5)	91 (6)	607 (7)
H(33)	460 (5)	124 (6)	-76 (7)
H(34)	392 (9)	207 (11)	-99 (12)

angles about the C-C bond of the ligand are listed in Table 5. The mean value is 42.7°, much smaller than that in a typical *gauche* structure. The conformations of the chelate rings may be largely determined by the non-bonded hydrogen-hydrogen interactions. This has been verified by conformational analyses (private communication from Dr Y. Yoshikawa, to be published). The absolute configurations of the secondary nitrogen atoms agree with those expected (Yoshikawa & Yamasaki, 1973); *R* for N(2) and N(5), *S* for N(3) and N(4). The neighbouring chelate rings make approximately a right angle with one another. The dihedral angles between the NCoN planes of the chelate rings are listed in Table 5.

The octahedral coordination in the complex anion  $[\text{Co}(\text{CN})_6]^{3-}$  is also slightly distorted. The bond distances Co-C and C-N in the anion are normal, having mean values of 1.904(5) and 1.147(7)  $\text{\AA}$ , respectively. The average value of the Co-C-N angles are 177.2(3)°.

The water molecules are bonded to the nitrogen atoms of the complex cations by N-H...O hydrogen bonds with a mean value of 3.037(6)  $\text{\AA}$ . They are also close to the nitrogen atoms of the anions. Thus the

cations and anions are held together by the water molecules. Short contacts occur between the ligating atoms of the cations and the nitrogen atoms of the anions. The conformations of the chelate rings may be partly affected by these short contacts. The intermolecular short distances are listed in Table 6.

The calculations were performed on a FACOM 270-30 of this Institute with a local version of the

Table 4. Interatomic distances ( $\text{\AA}$ ) and bond angles (°) within the complex cation with their standard deviations in parentheses

Co(1)-N(1)	1.975 (3)	N(1)-Co(1)-N(2)	86.1 (1)
Co(1)-N(2)	1.936 (4)	N(2)-Co(1)-N(3)	88.0 (1)
Co(1)-N(3)	1.951 (4)	N(3)-Co(1)-N(4)	86.0 (1)
Co(1)-N(4)	1.995 (3)	N(4)-Co(1)-N(5)	85.6 (1)
Co(1)-N(5)	2.011 (4)	N(5)-Co(1)-N(6)	83.5 (1)
Co(1)-N(6)	1.993 (4)	Average	85.8 (1)
Average	1.977 (4)		
		Co(1)-N(1)-C(1)	111.3 (2)
N(1)-C(1)	1.484 (7)	Co(1)-N(2)-C(2)	109.4 (2)
N(2)-C(2)	1.500 (6)	Co(1)-N(2)-C(3)	108.9 (3)
N(2)-C(3)	1.504 (7)	Co(1)-N(3)-C(4)	109.2 (2)
N(3)-C(4)	1.497 (7)	Co(1)-N(3)-C(5)	109.3 (3)
N(3)-C(5)	1.501 (6)	Co(1)-N(4)-C(6)	109.7 (2)
N(4)-C(6)	1.477 (7)	Co(1)-N(4)-C(7)	108.3 (1)
N(4)-C(7)	1.493 (7)	Co(1)-N(5)-C(8)	109.8 (2)
N(5)-C(8)	1.511 (7)	Co(1)-N(5)-C(9)	107.0 (3)
N(5)-C(9)	1.474 (7)	Co(1)-N(6)-C(10)	113.2 (2)
N(6)-C(10)	1.496 (7)	Average	109.6 (2)
Average	1.494 (7)		
		N(1)-C(1)-C(2)	108.4 (3)
C(1)-C(2)	1.506 (7)	N(2)-C(2)-C(1)	109.3 (4)
C(3)-C(4)	1.482 (8)	N(2)-C(3)-C(4)	109.7 (3)
C(5)-C(6)	1.488 (6)	N(3)-C(4)-C(3)	110.6 (3)
C(7)-C(8)	1.509 (8)	N(3)-C(5)-C(6)	108.3 (4)
C(9)-C(10)	1.488 (7)	N(4)-C(6)-C(5)	110.6 (3)
Average	1.495 (7)	N(4)-C(7)-C(8)	108.5 (3)
		N(5)-C(8)-C(7)	109.6 (4)
		N(5)-C(9)-C(10)	110.7 (3)
		N(6)-C(10)-C(9)	108.1 (3)
		Average	109.4 (3)
		C(2)-N(2)-C(3)	113.3 (3)
		C(4)-N(3)-C(5)	111.8 (3)
		C(6)-N(4)-C(7)	113.3 (3)
		C(8)-N(5)-C(9)	113.1 (3)
		Average	112.9 (3)

Table 5. Dihedral angles (°) within the complex cation

N(1)-C(1)-C(2)-N(2)	42.2
N(2)-C(3)-C(4)-N(3)	40.8
N(3)-C(5)-C(6)-N(4)	43.6
N(4)-C(7)-C(8)-N(5)	45.5
N(5)-C(9)-C(10)-N(6)	41.3
Average	42.7

Angles between the chelate rings

	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>
<i>A</i>	88.4	87.8	5.2	89.5
<i>B</i>		83.0	85.2	2.4
<i>C</i>			83.3	85.2
<i>D</i>				86.4

Labelling of the chelate rings is given in Fig. 3(a).

Table 6. Relevant interatomic distances (Å) less than 3.5 Å outside the complex cation with their standard deviations in parentheses

Key to symmetry operations		
i	$x, -1+y, z$	
ii	$x, y, -1+z$	
iii	$x, -1+y, -1+z$	
iv	$1-x, \frac{1}{2}+y, 1-z$	
v	$1-x, -\frac{1}{2}+y, 1-z$	
vi	$-x, -\frac{1}{2}+y, 1-z$	
vii	$-x, -\frac{1}{2}+y, -z$	

Hydrogen bonds			
N(1)–H(1)····O(3)	2.963 (6)	O(1)····N(7 <sup>vi</sup> )	2.904 (5)
N(1)–H(2)····O(1)	2.943 (5)	O(1)····N(11 <sup>vi</sup> )	3.124 (7)
N(3)–H(12)····O(1)	3.177 (6)	O(2)····N(10 <sup>i</sup> )	3.346 (8)
N(4)–H(17)····O(2)	2.988 (6)	O(2)····N(12 <sup>v</sup> )	3.038 (7)
N(6)–H(27)····O(2)	3.063 (6)	O(3)····N(8 <sup>v</sup> )	2.956 (7)
N(6)–H(28)····O(3)	3.085 (6)	O(3)····N(9 <sup>ii</sup> )	3.348 (6)
Average	3.037 (6)	O(3)····N(12 <sup>ii</sup> )	3.419 (7)

N(1)····N(9 <sup>ii</sup> )	3.325 (6)	C(2)····N(12 <sup>v</sup> )	3.176 (6)
N(2)····N(12 <sup>v</sup> )	2.970 (5)	C(3)····N(7 <sup>i</sup> )	3.416 (7)
N(3)····N(9 <sup>vi</sup> )	3.462 (6)	C(4)····N(11 <sup>iii</sup> )	3.365 (7)
N(3)····N(11 <sup>vi</sup> )	3.479 (6)	C(5)····N(7 <sup>vi</sup> )	3.420 (7)
N(4)····N(10 <sup>i</sup> )	3.344 (6)	C(5)····N(9 <sup>vi</sup> )	3.344 (6)
N(5)····N(11 <sup>vi</sup> )	2.974 (6)	C(6)····N(10 <sup>i</sup> )	3.259 (7)
N(6)····N(10 <sup>v</sup> )	3.430 (6)	C(7)····N(9)	3.387 (7)
N(6)····N(12 <sup>v</sup> )	3.485 (6)	C(8)····N(9)	3.484 (7)
C(1)····O(1)	3.444 (7)	C(8)····N(11 <sup>vi</sup> )	3.437 (7)
C(1)····O(3)	3.232 (7)	C(9)····N(9 <sup>ii</sup> )	3.461 (6)
C(7)····O(2)	3.200 (8)	C(10)····N(10 <sup>v</sup> )	3.298 (7)
C(10)····O(3)	3.288 (7)	C(5)····C(11 <sup>vi</sup> )	3.443 (7)
O(2)····C(16 <sup>v</sup> )	3.414 (7)	C(5)····C(13 <sup>vi</sup> )	3.367 (6)
O(3)····C(12 <sup>v</sup> )	3.466 (6)		

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### References

- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- IUPAC (1972). *Nomenclature of Inorganic Chemistry*, 2nd ed., pp. 75–83. London: Butterworths.
- IWATA, M., NAKATSU, K. & SAITO, Y. (1969). *Acta Cryst.* **B25**, 2562–2571.

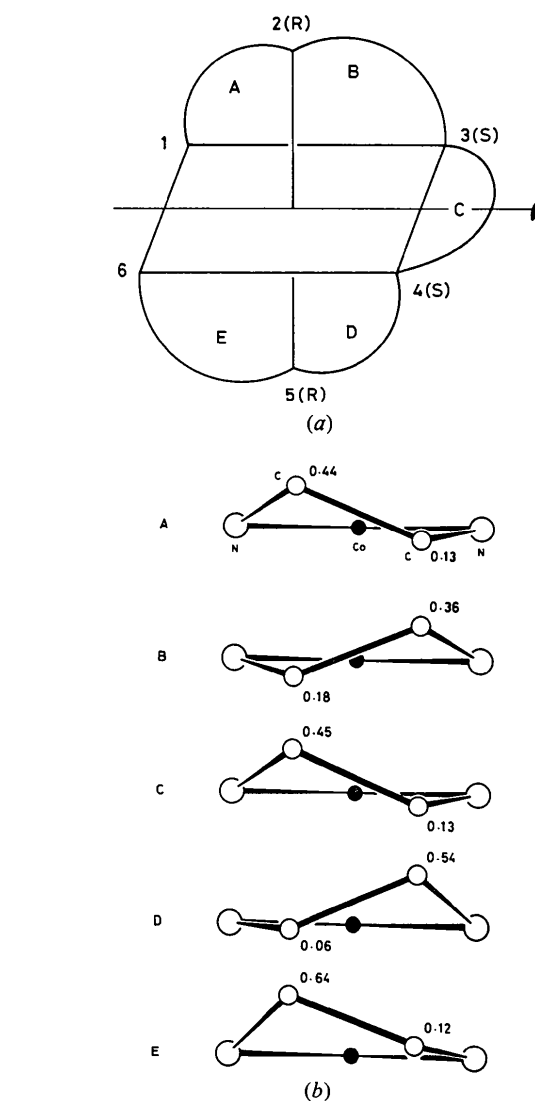


Fig. 3. (a) Labelling of the chelate rings, and absolute configurations of the secondary nitrogen atoms. (b) Conformations of the five chelate rings. Figures attached to each carbon atom indicate the distances from the NCoN plane in each ring.

- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- YOSHIKAWA, Y. & YAMASAKI, K. (1973). *Bull. Chem. Soc. Japan*, **46**, 3448–3452.