de 4 atomes est parfaitement plan avec des angles N–H···N compris entre 116° et 144° et des distances H···N comprises entre 2,21 et 2,51 Å, valeurs inférieures à la somme des rayons de van der Waals. Il semble donc que nous soyons en présence de liaisons hydrogène N–H···N bifurquées.

Empilement des molécules

Les angles dièdres des plans des différentes molécules avec le plan *ab* sont respectivement de 33,4°; 27,8°; 28,9°; 35,1° pour les molécules 1, 2, 3, 4. Le paramètre *c* étant faible, les molécules forment des piles suivant **c**, la distance entre deux molécules voisines d'une même pile est voisine de 3,5 Å. Ce sont les molécules 4 qui sont les plus rapprochées. De plus, elles sont orientées de telle manière que l'hétérocycle de l'une se superpose au cycle benzénique de celle qui s'en déduit par une translation *c*. Les distances interatomiques les plus courtes entre ces deux molécules ont été portées dans le Tableau 6. Parmi les piles formées par les différentes molécules, on peut en distinguer deux sortes. D'une part, celles formées par les molécules 1, 2, 4 qui sont disposées de telle manière que leur hétérocycle soient en regard; elles n'échangent entre elles aucune liaison hydrogène caractérisée mais sont impliquées dans les géométries particulières décrites au paragraphe précédent faisant intervenir des contacts H···N.

Tableau 6. *Distances interatomiques entre deux molécules* 4

Le premier atome est pris dans le motif de base le deuxiéme s'en déduit par une translation *c*.

N(34)···C′(94)	3,55 Å
N(34)···C′(84)	3,40
N(24)···C′(84)	3,40
N(14)···C′(74)	3,56
N(14)···C′(84)	3,53

D'autre part celle formée par les molécules 3 qui échangent une liaison hydrogène avec les molécules 1 et 2, on pourrait donc décrire la structure comme étant formée par des piles de 3 molécules (molécules 1, 2, 4), ces ensembles étant reliés par l'intermédiaire des piles correspondant aux molécules 3, grâce à des liaisons hydrogène. Chaque molécule 3 participe à 2 liaisons hydrogène avec les molécules 1 et 2 de deux ensembles distincts.

Nous remercions M Elguéro du Laboratoire de M Jacquier de nous avoir proposé ce travail et pour l'intérêt qu'il a accordé à nos résultats.

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$(-)_{589}$-[*l*-*N*,*N*,*N*′,*N*′-Tetrakis-(2′-aminoethyl)-1,2-diaminopropane]cobalt(III) Hexacyanocobaltate(III) Trihydrate

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$(-)_{589}$-[Co($C_{11}H_{30}N_6$)] [Co(CN)$_6$].3H_2O, orthorhombic, $P2_12_12_1$, $a=10\cdot855(5)$, $b=26\cdot59(1)$, $c=8\cdot705(3)$ Å, $Z=4$, $D_m=1\cdot520$, $D_x=1\cdot532$ g cm^{-3}. The absolute configuration of $(-)_{589}$-[Co(*l*-mepenten)]$^{3+}$ determined with reference to the known absolute configuration of the ligand is skew chelate pairs $\Delta\Lambda\Delta$. The conformations of the chelate rings in [Co(*l*-mepenten)]$^{3+}$ agree well with the prediction based on the conformational analysis.

Introduction

$(-)_{589}$-[Co(*l*-mepenten)] [Co(CN)$_6$].3H_2O was kindly supplied by Professor K. Yamasaki of Nagoya University. The crystal used for X-ray analysis was an orange-red rhombic thin plate and had the dimensions $0\cdot36\times0\cdot32\times0\cdot07$ mm. Two series of integrated equi-inclination Weissenberg photographs were taken with Fe $K\alpha$ radiation ($\lambda=1\cdot937$ Å) around the *a* axis up to the sixth layer and around the *c* axis up to the second layer, the multiple-film technique being used. Exposure time was as long as about 200h because of weak intensities of higher-order reflexions. Intensities were estimated visually and converted to $|F|$ by applying Lorentz and polarization corrections. No corrections were made for absorption. 819 independent reflexions were collected. The structure was solved by the heavy-atom method. The coordinates of all the non-hydrogen atoms were refined by assuming anisotropic thermal motion. After inclusion of the hydrogen atoms whose positions were obtained by calculation, the final R value decreased to 0·11 for the 819 observed reflexions. A weighting scheme, $w=0·2$ for $|F_o|$'s smaller than 5·0 and $w=1$ for other $|F_o|$'s was employed. The observed and calculated structure amplitudes are compared in Table 1.* The positional and thermal parameters are given in Tables 2 and 3 respectively with their estimated standard deviations.

Table 2. *Final positional parameters with their standard deviations in parentheses* ($\times 10^4$)

	x	y	z
Co(1)	5324 (5)	3757 (3)	6401 (8)
Co(2)	4862 (6)	1181 (3)	7731 (8)
N(1)	3909 (46)	274 (18)	9275 (67)
N(2)	5807 (49)	2075 (19)	6225 (92)
N(3)	2250 (31)	1475 (14)	7169 (49)
N(4)	7462 (36)	893 (16)	8364 (55)
N(5)	4814 (50)	631 (20)	4710 (63)
N(6)	4895 (43)	1727 (20)	10694 (72)
N(7)	6839 (29)	4227 (13)	6010 (40)
N(8)	6035 (19)	3659 (13)	8420 (36)
N(9)	3804 (27)	3403 (14)	6974 (45)
N(10)	4602 (24)	3687 (13)	4327 (36)
N(11)	4262 (30)	4363 (13)	6814 (43)
N(12)	6393 (26)	3142 (12)	5939 (35)
C(1)	4261 (41)	598 (17)	8726 (61)
C(2)	5452 (45)	1775 (15)	6795 (60)
C(3)	3162 (35)	1349 (23)	7414 (59)
C(4)	6516 (35)	993 (18)	8091 (61)
C(5)	4792 (88)	867 (19)	5750 (73)
C(6)	4880 (80)	1520 (21)	9644 (76)
C(7)	4996 (34)	3505 (13)	9517 (41)
C(8)	4203 (41)	3156 (19)	8517 (60)
C(9)	6608 (41)	4143 (19)	8985 (53)
C(10)	7461 (41)	4281 (24)	7622 (60)
C(11)	3496 (40)	3039 (18)	5763 (45)
C(12)	3432 (56)	3358 (21)	4252 (65)
C(13)	7488 (36)	3204 (20)	6895 (51)
C(14)	6965 (33)	3258 (18)	8554 (52)
C(15)	2776 (31)	3745 (20)	7452 (52)
C(16)	2876 (36)	4255 (19)	6719 (61)
C(17)	3087 (46)	2893 (23)	9342 (60)
O(1)	3656 (43)	4768 (16)	−330 (51)
O(2)	4422 (62)	4831 (19)	3301 (66)
O(3)	5417 (31)	2476 (16)	2939 (60)

Discussion

The absolute configuration was determined from the known absolute configuration of the asymmetric carbon atom (Yoshikawa, Fujii & Yamasaki, 1967). Fig. 1 shows a perspective drawing of the complex cation, which correctly represents its absolute configuration. It can be designated as skew chelate pairs *ΔΛΔ* (*IUPAC Information Bulletin,* 1968). The interatomic distances and bond angles within the complex ions are listed in Table 4. The ligand acts as a sexidentate and forms a complex ion similar to [Co(penten)]$^{3+}$ (Muto, Marumo & Saito, 1970). The cobalt atom is surrounded octahedrally by six nitrogen atoms. The distortion of the coordination octahedron is very much like that observed in [Co(penten)]$^{3+}$. The two nitrogen atoms N(8) and N(9) are coordinated at distances of 1·94 and 1·96 Å, being shorter than the other four N–Co distances. The angle N(8)Co(1)N(9) is 92°, though the average value of other NCoN angles is 83°. In $(+)_{589}$-[Co(penten)]$^{3+}$ the corresponding angle is 8·95° and the average NCoN angle is 85·2°. The methyl group is equatorial with respect to the average plane of the chelate ring. The five chelate rings are not planar. The deviations of the carbon atoms from the plane formed by the cobalt atom and the two nitrogen atoms are listed in Table 5. According to the constraints due to fused-ring formation, the two carbon atoms are both on the same side of the plane defined by Co and the two N atoms in rings *B*, *C* and *E*. The six CN groups in the complex ion [Co$(CN)_6$]$^{3-}$ are arranged at the apices of a slightly distorted octahedron around the metal atom. The interatomic distances and bond angles are quite normal. A projection of the structure along the c axis is shown in Fig. 2. A complex cation is surrounded by four complex anions nearly tetrahedrally. Broken lines indicate some close contacts.

The conformation of each chelate ring is listed in Table 5. The conformation of the unique ring *A* is λ. Those of rings *B* and *C* are δ, whereas they are λ in rings *D* and *E*. In $(-)_{589}$-[*l*-mepenten)]$^{3+}$ the conformations of the chelate rings are enantiomeric with those in $(+)_{589}$-[Co(penten)]$^{3+}$ except the ring *E*. If this chelate ring takes the δ conformation, retaining the other atomic arrangement unchanged, the dis-

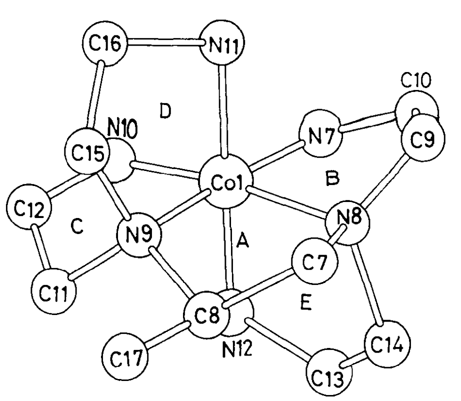

Fig. 1. A perspective drawing of the complex ion, $(-)_{589}$-[Co(*l*-mepenten)]$^{3+}$.

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* Table 1 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30343 (6pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Final thermal parameters with their standard deviations in parentheses*

The values have been multiplied by 10^4 and refer to the expression: $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(1)	65 (5)	18 (1)	149 (12)	0 (3)	−4 (9)	−1 (4)
Co(2)	73 (6)	19 (1)	167 (12)	−2 (3)	4 (8)	−1 (5)
N(1)	238 (74)	28 (11)	413 (137)	22 (24)	69 (95)	52 (38)
N(2)	257 (86)	26 (12)	724 (293)	28 (27)	286 (144)	52 (48)
N(3)	84 (41)	31 (11)	213 (96)	12 (17)	−19 (57)	21 (28)
N(4)	125 (72)	26 (16)	369 (140)	18 (30)	−77 (98)	−33 (37)
N(5)	200 (72)	52 (16)	387 (140)	6 (31)	−103 (98)	−16 (37)
N(6)	129 (59)	51 (14)	596 (167)	31 (27)	−38 (95)	−62 (42)
N(7)	70 (35)	18 (8)	73 (71)	−13 (15)	−16 (46)	−1 (22)
N(8)	−34 (23)	21 (8)	83 (63)	−6 (13)	−61 (39)	−6 (21)
N(9)	24 (31)	32 (10)	164 (90)	−5 (15)	4 (50)	10 (25)
N(10)	24 (28)	15 (7)	136 (66)	1 (17)	−72 (42)	2 (21)
N(11)	97 (40)	16 (8)	131 (85)	7 (15)	17 (49)	19 (21)
N(12)	35 (31)	14 (7)	37 (64)	−16 (14)	−34 (40)	3 (19)
C(1)	129 (60)	17 (10)	186 (118)	0 (21)	−47 (79)	−16 (39)
C(2)	156 (62)	10 (8)	259 (127)	28 (22)	111 (88)	25 (27)
C(3)	63 (44)	44 (15)	145 (99)	18 (25)	2 (59)	25 (39)
C(4)	57 (45)	26 (13)	224 (117)	28 (20)	−15 (65)	13 (32)
C(5)	539 (161)	12 (10)	313 (144)	29 (44)	12 (179)	−18 (33)
C(6)	374 (127)	31 (14)	381 (164)	−2 (41)	−99 (157)	−94 (41)
C(7)	35 (40)	18 (8)	−22 (61)	4 (18)	52 (47)	−7 (20)
C(8)	121 (59)	27 (12)	162 (115)	20 (23)	29 (75)	−3 (33)
C(9)	118 (58)	21 (11)	95 (198)	−25 (22)	−5 (69)	3 (30)
C(10)	50 (47)	67 (18)	116 (105)	−45 (27)	61 (63)	−32 (41)
C(11)	89 (52)	22 (12)	86 (91)	0 (22)	18 (63)	−2 (30)
C(12)	234 (87)	28 (13)	151 (111)	−39 (30)	−138 (92)	3 (35)
C(13)	28 (39)	49 (16)	44 (84)	10 (23)	−24 (57)	9 (31)
C(14)	29 (38)	32 (12)	86 (89)	25 (19)	−17 (57)	7 (30)
C(15)	58 (42)	30 (10)	114 (87)	32 (24)	62 (57)	−65 (32)
C(16)	48 (46)	26 (12)	23 (126)	21 (19)	−23 (71)	1 (33)
C(17)	15 (69)	43 (16)	112 (102)	−50 (29)	72 (78)	−28 (38)
O(1)	299 (69)	35 (12)	305 (110)	5 (23)	46 (84)	−2 (31)
O(2)	577 (131)	56 (17)	456 (146)	49 (39)	−232 (136)	27 (39)
O(3)	111 (51)	59 (12)	410 (111)	−10 (21)	−20 (79)	−78 (31)

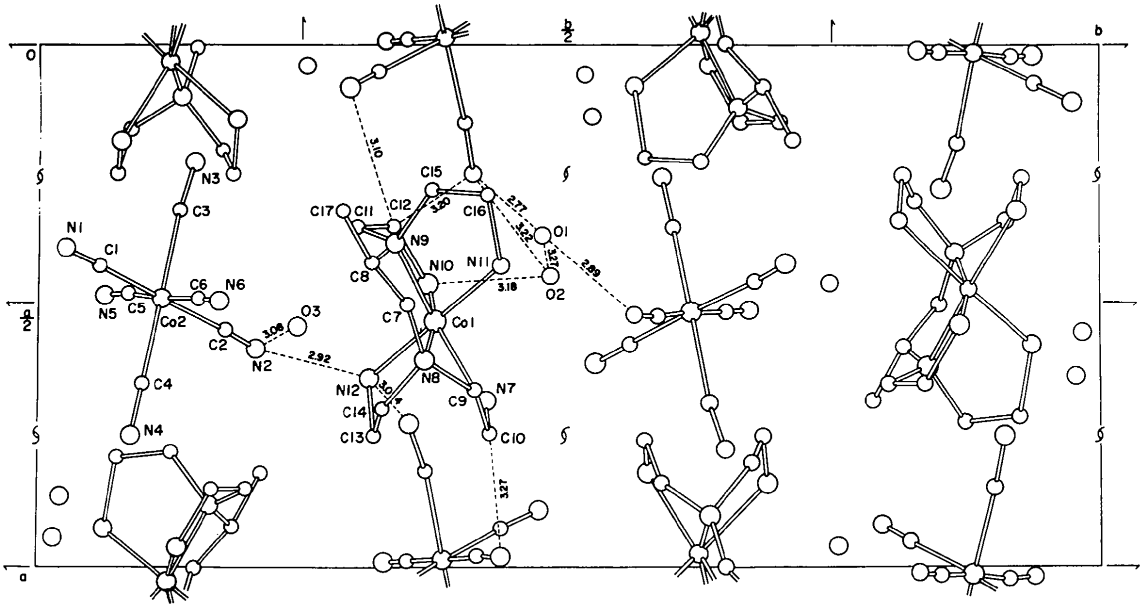

Fig. 2. A projection of the structure along the *c* axis. Broken lines indicate some close contacts.

Table 4. *Interatomic distances and angles within the complex ion* $(-)_{589}$-[Co(*l-mepenten*)]$^{3+}$, *with their estimated standard deviations*

Co(1)–N(7)	2·09 (3) Å	N(7)—C(10)	1·56 (6) Å
Co(1)–N(8)	1·94 (3)	N(8)—C(7)	1·53 (4)
Co(1)–N(9)	1·96 (3)	N(8)—C(9)	1·51 (6)
Co(1)–N(10)	1·98 (3)	N(8)—C(14)	1·47 (5)
Co(1)–N(11)	2·01 (3)	N(9)—C(8)	1·56 (6)
Co(1)–N(12)	2·04 (3)	N(9)—C(11)	1·47 (6)
C(7)—C(8)	1·54 (6)	N(9)—C(15)	1·50 (5)
C(9)—C(10)	1·55 (7)	N(10)–C(12)	1·55 (6)
C(11)–C(12)	1·57 (7)	N(11)–C(16)	1·53 (5)
C(13)–C(14)	1·56 (6)	N(12)–C(13)	1·46 (5)
C(15)–C(16)	1·50 (7)	C(8)—C(17)	1·57 (7)

Table 4 (*cont.*)

N(7)—Co(1)–N(8)	85 (1)°	N(7)—Co(1)–N(9)	171 (1)°
N(7)—Co(1)–N(10)	103 (1)	N(7)—Co(1)–N(11)	90 (1)
N(7)—Co(1)–N(12)	90 (1)	N(8)—Co(1)–N(9)	92 (1)
N(8)—Co(1)–N(10)	167 (1)	N(8)—Co(1)–N(11)	100 (1)
N(8)—Co(1)–N(12)	81 (1)	N(9)—Co(1)–N(10)	82 (1)
N(9)—Co(1)–N(11)	82 (1)	N(9)—Co(1)–N(12)	98 (1)
N(10)–Co(1)–N(11)	91 (1)	N(10)–Co(1)–N(12)	88 (1)
N(11)–Co(1)–N(12)	179 (1)	Co(1)–N(7)—C(10)	104 (2)
Co(1)–N(8)—C(7)	108 (2)	Co(1)–N(8)—C(9)	110 (1)
Co(1)–N(8)—C(14)	116 (2)	Co(1)–N(9)—C(8)	101 (2)
Co(1)–N(9)—C(11)	109 (2)	Co(1)–N(9)—C(15)	114 (1)
Co(1)–N(10)–C(12)	115 (2)	Co(1)–N(11)–C(16)	114 (2)
Co(1)–N(12)–C(13)	105 (2)	C(7)—N(8)—C(9)	109 (2)
C(7)—N(8)—C(14)	105 (2)	C(8)—N(9)—C(11)	114 (2)
C(8)—N(9)—C(15)	103 (3)	C(9)—N(8)—C(14)	108 (2)
C(11)–N(9)—C(15)	116 (3)	N(7)—C(10)–C(9)	114 (3)
N(8)—C(7)—C(8)	103 (3)	N(8)—C(9)—C(10)	102 (3)
N(8)—C(14)–C(13)	104 (3)	N(9)—C(8)—C(7)	113 (2)
N(9)—C(11)–C(12)	105 (2)	N(9)—C(15)–C(16)	112 (3)
N(10)–C(12)–C(11)	104 (4)	N(11)–C(16)–C(15)	102 (3)
N(12)–C(13)–C(14)	104 (3)	N(9)—C(8)—C(17)	112 (3)
C(7)—C(8)—C(17)	116 (4)		

Table 5. *Deviations of the carbon atoms from the plane formed by the central cobalt atom and the two nitrogen atoms*

Ring	Atom	Shift	Ring conformation
A	C(7)	−0·39 Å	λ
	C(8)	0·33	
	C(17)	0·23	
B	C(9)	−0·85	δ
	C(10)	−0·24	
C	C(11)	0·81	δ
	C(12)	0·19	
D	C(15)	−0·07	λ
	C(16)	0·52	
E	C(13)	−0·80	λ
	C(14)	−0·10	

tances, C(13)–C(10) and C(13)–N(7), will be as short as 2·5 and 2·5 Å, respectively. The distances between the nitrogen atom N(12) in the ring *E* and N(2) and N(3) of [Co(CN)$_6$]$^{3-}$ are respectively 2·92 and 3·04 Å. These distances as well as the proposed position of the hydrogen atoms indicate that there exist NH···N hydrogen bonds between these atoms. Similar hydrogen bonds are recognized in crystals of [Co(penten)]-[Co(CN)$_6$].2H_2O. If the conformation of the chelate ring is inverted, the two hydrogen atoms bonded to N(12) are oriented along directions irrelevant to hydrogen-bond formation. Gollogly & Hawkins (1967) performed a conformational analysis of [Co(*l*-mepenten)]$^{3+}$. The predicted structure can be summarized as follows. (i) The methyl group is bonded in the equatorial position with respect to the chelate ring. (ii) Ring *A* has only one possible conformation and rings *B* and *C* have a single conformation type which nevertheless permits a small range of conformations with similar bond angle and torsional strains. (iii) As to rings *D* and *E*, they exist in either of two distinct conformations which experience similar structural strain. The geometry of the complex cation revealed by the present study agrees very well with the prediction described above. The ring *E* takes the λ conformation in $\Delta\Lambda\Delta$-[Co(*l*-mepenten)]$^{3+}$, while it is δ in $\Delta\Lambda\Delta$-[Co(penten)]$^{3+}$. This is in accordance with prediction (iii).

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