The Crystal Structure of (-) 589-*u-facial*-Bis(diethylenetriamine)cobalt(III) Hexacyanocobaltate(III) Dihydrate, (-)589-*u-facial*-[Co(dien)₂][Co(CN)₆].2H₂O

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The crystal structure of $(-)_{589}$ -u-facial-bis(diethylenetriamine)cobalt(III) hexacyanocobaltate(III) dihydrate, $(-)_{589}$ -u-facial-[Co(dien)₂] [Co(CN)₆] 2H₂O, has been determined from three-dimensional X-ray data collected by an automated four-circle diffractometer. The compound crystallizes in the orthorhombic system with a = 13.942, b = 32.370, c = 9.418 Å and Z = 8 in space group B22₁2. The structure has been refined by block-diagonal least-squares methods to an R value of 0.035 for 2510 reflexions. There are two isomeric complex cations in an asymmetric unit. They both have a twofold axis and the absolute configuration can be designated as skew chelate pairs $\Delta \Delta \Delta$. However, the conformations of the two chelate rings formed by a dien molecule in one complex ion are $\delta \lambda$, while those in the other are $\lambda \lambda$.

Introduction

All the possible isomers of bis(diethylenetriamine)cobalt(III) ion, $[Co(dien)_2]^{3+}$, were isolated and characterized by Keene, Searle, Yoshikawa, Imai & Yamasaki (1970). As part of a series of investigations on the structures of the complex cation in the $[Co(dien)_2]^{3+}$ system (Kobayashi, Marumo & Saito, 1972), the crystal of $(-)_{589}$ -u-facial- $[Co(dien)_2]$ $[Co(CN)_6]$. 2H₂O has been subjected to X-ray crystal analysis in order to establish the absolute configuration and conformational details.

Experimental

Orange red crystals of $(-)_{589}$ -*u-facial*-bis(diethylenetriamine)cobalt(III) hexacyanocobaltate(III) dihydrate were kindly supplied by Professor Yamasaki of Nagoya University. They belong to the orthorhombic system, with unit-cell dimensions: a=13.942 (3), b=32.370 (5) and c=9.418 (1) Å. The observed systematic

absences: hkl for $h+l \neq 2n$ and 0k0 for $k \neq 2n$, indicate the space group $B22_12$. There are eight formula units of $Co(C_4H_{13}N_3)_2Co(CN)_6.2H_2O$ in the unit cell $(D_x = 1.61 \text{ g cm}^{-3}, \tilde{D}_m = 1.59 \text{ g cm}^{-3})$. A crystal specimen shaped into a sphere of diameter 0.23 mm was mounted with the *a* axis parallel to the φ axis of a goniostat of a Rigaku automated four-circle diffractometer. The ω -scan technique was employed with a scanning speed of 2° per min in ω . Mo Ka radiation monochromated by a graphite crystal was used. Scanning range was calculated from the formula: 1.5° + 0.5° tan θ . Backgrounds were counted both at the beginning and at the end of each scan for 10 sec. 2758 independent intensities were measured up to $2\theta = 55^{\circ}$. 2510 of these had significantly non-zero intensities. The intensities were corrected for the Lorentz and polarization factors. No corrections were made for absorption in view of the small μr value of 0.2. The structure amplitudes obtained were put on an absolute scale by comparison with the calculated values at a later stage.



Fig. 1. Perspective drawings of the complex cations.

Determination and refinement of the structure

The structure was solved straightforwardly by the heavy-atom method. Positions of the cobalt atom were deduced from three-dimensional Patterson maps. The positions of the cobalt atoms were used to calculate structure factors, whose phases were used with the ob-

Table 1. Final positional parameters and their standard deviations (in parentheses)

The values have been multiplied by 104.

	x	У	Z
Co(1)	0 (0)	0 (0)	1005 (1)
$C_0(2)$	1685 (1)	2500 (O)	0 (0)
$C_0(3)$	484 (1)	1169 (0)	5552 (1)
N(1)	650 (4)	-334(1)	2445(5)
N(1)	772(2)	-334(1)	408 (5)
N(2)	123 (3)	-323(1)	-408(3)
N(3)	1087 (3)	388 (1)	924 (5)
N(4)	/12 (4)	2445 (2)	14// (6)
N(5)	2620 (3)	2487 (2)	1565 (5)
N(6)	1753 (4)	3104 (1)	223 (5)
N(7)	- 1398 (5)	731 (2)	6162 (9)
N(8)	2419 (4)	1582 (2)	5084 (7)
N(9)	- 410 (5)	1981 (2)	6501 (6)
N(10)	1300 (4)	372 (2)	4344 (6)
N(11)	- 101 (5)	1342 (2)	2518 (6)
N(12)	872 (4)	995 (2)	8655 (6)
CÙ	1478 (4)	-560(2)	1818 (7)
$\tilde{\mathbf{C}}(2)$	1207 (4)	-678(2)	316 (7)
cà	1394 (4)	-40(2)	-1152(6)
C(4)	1855 (4)	239(2)	-54(7)
C(5)	1143 (6)	2263(2)	2762 (7)
C(5)	2112(5)	2203(2) 2457(2)	2064 (6)
C(0)	2112(3)	2437(2)	1406 (7)
$C(\eta)$	3190(3)	2074 (2)	1490(7)
C(0)	2495 (5)	3220(2)	1207(7)
C(9)	-693(4)	890 (2)	5877 (7)
C(10)	1685 (4)	1427(2)	5277(5)
$C(\Pi)$	-66(5)	16/4 (2)	6145 (6)
C(12)	1019 (4)	665 (2)	4880 (6)
C(13)	124 (5)	1286 (2)	3668 (6)
C(14)	772 (4)	1057 (2)	7465 (6)
O(1)	-511(4)	1836 (1)	138 (6)
O(2)	2448 (6)	1412 (3)	2006 (7)
H(N11)	867 (49)	- 144 (19)	3251 (72)
H(N12)	190 (52)	- 516 (21)	2903 (75)
H(N21)	339 (49)	- 424 (20)	-1105 (74)
H(N31)	900 (47)	662 (20)	522 (75)
H(N32)	1392 (57)	408 (23)	1839 (85)
H(N41)	457 (54)	2722 (20)	1739 (77)
H(N42)	148 (56)	2270 (21)	1104 (79)
H(N51)	3046 (52)	2257 (21)	1536 (78)
H(N61)	1903 (51)	3240 (21)	- 706 (79)
H(N62)	1115 (50)	3213 (21)	491 (80)
H(C11)	2101 (52)	- 384 (20)	1842 (76)
H(C12)	1652 (50)	- 830 (21)	2385 (74)
H(C21)	1811 (44)	- 759 (19)	- 248 (72)
H(C22)	738 (45)	- 924 (19)	330 (70)
H(C31)	1012 (47)	139 (19)	-1884(69)
H(C32)	1913 (49)	- 208 (19)	- 1697 (74)
H(C41)	2169 (49)	492 (20)	- 525 (76)
H(C42)	2365 (48)	89 (20)	498 (70)
H(C51)	713 (49)	2330 (19)	3705 (74)
H(C52)	1233 (56)	1959 (22)	2637 (81)
H(C61)	1975 (52)	2726 (20)	3346 (77)
H(C62)	2519 (49)	2301 (20)	3637 (77)
H(C71)	3696 (52)	2842 (20)	632 (80)
H(C72)	3556 (49)	2928 (20)	2367 (73)
H(C81)	2843(51)	3479 (20)	900 (78)
H(C82)	2190 (53)	3311(21)	2197 (79)
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served |F(hkl)| to calculate a three-dimensional electron density synthesis. Successive Fourier syntheses revealed the complete structure. These atomic positions were refined using block-diagonal least-squares methods. The R value at this stage was 0.066, where anisotropic temperature factors were used. Difference synthesis was carried out, which revealed all the hydrogen atoms except those belonging to the two oxygen atoms. The final least-squares calculation was made including the contribution of these hydrogen atoms. Temperature factors for the hydrogen atoms were assumed to be isotropic. After several cycles of refinement the R value was reduced to 0.035 for the 2510 observed reflexions. At this stage positional shifts were all less than one fourth of the standard deviations of the positional parameters. Unit weight was given to all the reflexions. The atomic scattering factors were taken from International Tables for X-ray Crystallography (1962). The final set of coordinates and their estimated standard deviations are listed in Table 1. Corresponding thermal parameters are given in Table 2 with their estimated standard deviations. The observed and calculated structure amplitudes are listed in Table 3.

Table 2. Final thermal parameters and their standard deviations (in parentheses)

The values have been multiplied by $10^4\ \text{and}\ \text{refer}$ to the expression:

$\exp\left[-\left(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl\right)\right].$

Mean isotropic temperature factor of all the hydrogen atoms is 2.34 $Å^2$.

,,		0	0	0	0	0	0
5)		β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
5)	Co(1)	23 (0)	3 (0)	46 (1)	0 (0)	0 (0)	0 (0)
5)	Co(2)	28 (0)	4 (0)	48 (1)	0 (0)	0 (0)	-3(0)
5)	Co(3)	30 (0)	4 (0)	51 (1)	1 (0)	-6(1)	-1 (0)
5)	N(1)	37 (3)	5 (0)	63 (5)	1 (1)	7 (3)	-1(1)
/)	N(2)	28 (2)	4 (0)	60 (5)	0(1)	-3(3)	3 (1)
/2)	N(3)	29 (2)	5 (0)	73 (5)	-1(1)	-4(3)	0 (1)
75)	N(4)	43 (3)	8 (1)	92 (6)	-1(1)	21 (4)	-8(2)
/4)	N(5)	38 (2)	5 (0)	54 (4)	1 (1)	-11 (3)	1 (1)
75)	N(6)	52 (3)	5 (0)	66 (6)	2 (1)	-5 (4)	-4(1)
35)	N(7)	50 (4)	12(1)	202 (12)	-9(1)	2 (6)	-10 (2)
77)	N(8)	48 (3)	8(1)	95 (6)	-5(1)	-1 (4)	-2(2)
79)	N(9)	85 (5)	6 (1)	115 (7)	8(1)	-23 (5)	-9(2)
78)	N(10)	46 (3)	8(1)	111 (7)	5 (1)	- 14 (4)	-11 (2)
79)	N(11)	82 (5)	11 (1)	82 (6)	-4 (2)	-27 (5)	1 (2)
30)	N(12)	61 (4)	9 (1)	78 (6)	0(1)	-5(4)	9 (2)
76)	C (1)	37 (3)	6 (1)	90 (7)	3 (1)	17 (4)	-3(2)
74)	C(2)	39 (3)	6 (0)	90 (8)	3 (1)	3 (4)	0 (2)
72)	C(3)	34 (3)	7 (1)	83 (6)	-1(1)	13 (4)	0 (2)
70)	C(4)	31 (3)	6 (1)	105 (7)	-2(1)	13 (4)	1 (2)
59)	C(5)	67 (5)	9 (1)	82 (8)	-2(2)	21 (5)	1 (0)
74)	C(6)	65 (4)	8 (1)	56 (6)	-5(2)	-1 (4)	0 (2)
76)	C(7)	40 (3)	8 (1)	77 (7)	-5(1)	-11 (4)	1 (2)
70)	C(8)	73 (5)	5(1)	81 (7)	0(1)	-23 (5)	-4 (2)
74)	C(9)	40 (3)	6(1)	98 (8)	-1(1)	-8(4)	-6(2)
31)	C(10)	44 (3)	5(1)	46 (6)	0(1)	-2(3)	0(1)
77)	C(11)	43 (3)	6(1)	66 (6)	2 (1)	-13 (4)	1 (1)
77)	C(12)	34 (3)	6 (1)	61 (6)	0 (1)	-12 (4)	-2(1)
30)	C(13)	44 (3)	6(1)	77 (6)	0(1)	-6(4)	-4(1)
73)	C(14)	36 (3)	4 (0)	83 (7)	-1(1)	-9(4)	1 (1)
78)	O(1)	57 (3)	10 (1)	134 (7)	-6(1)	-16 (4)	0 (2)
79)	O(2)	159 (8)	46 (2)	122 (9)	64 (3)	68 (7)	35 (4)

Absolute configuration

The absolute configuration was determined by using the absorption-edge technique. Equi-inclination Weis-

senberg photographs were taken with Cu K α radiation. Table 4 lists some of the observed relations between intensities of hkl and $h\bar{k}l$ with calculated F values.

Table 3 (cont.)

K FO FC	I FO FC	A FO FO	* ** **	R FO FC	K FO FC	* fo fc	* PO *C	K FO FC	. +u rc	K FO IC	* FO FC	e fo fc	s fo fc
26 513 555 27 972 1016 28 620 617 79 242 246 30 151 153 31 174 388 32 421 410 33 536 5447 34 412 390 55 717 754 36 271 216 77 40 338 17 412 390 35 717 754 36 271 216 37 412 391 37 412 391 37 412 391 38 10 317 39 10 317 39 10 317 39 10 317 39 10 317 30 10 30 30 10 10 30 30 10 10 100 30 10 100 100 100 100 100 1000000000000	5/ 336 317 33 483 501 34 882 705 35 862 705 36 217 147 36 217 147 37 502 504 36 217 147 37 502 504 36 217 147 37 502 504 36 217 147 37 502 504 36 217 147 37 502 504 30 147 30 14	41 328 322 17 k 1 1 146 213 3 365 378 4 45 378 4 5 378 7 330 360 7 232 239 11 272 479 12 303 324 13 184 171	14 137 171 14 805 898 16 597 601 17 395 384 18 424 429 19 275 276 21 718 211 22 165 185 23 435 356 23 435 356 25 78 257 26 78 257 28 78 257 29 78 257 29 78 257 20 78 257	33 J64 336 9 C 1 0 324 347 1 900 918 2 1309 1350 3 395 440 4 1183 1219 5 226 237 5 401 422 7 341 357 6 401 422 7 341 357	9 714 719 10 1109 1130 11 1322 1372 12 725 730 13 439 490 14 478 454 15 831 850 16 1262 1258 17 703 711 18 853 883 19 1020 1039 20 650 629 20 56 299	17 404 418 18 201 217 19 769 830 20 515 534 21 549 576 24 357 303 24 357 303 25 317 327 26 311 329 27 403 401 28 444 99 28 446 951	24 35a 3a3 25 580 603 26 354 359 27 137 295 28 41a 475 29 606 61s 30 847 860 31 373 581 32 147 141 32 249 313 34 269 264 35 36 207 205 36 207 205 36	JO 714 714 JI 545 234 JJ 545 236 JJ 700 711 T3 42 413 J5 415 415 J5 415 415 J5 415 415 J7 744 23 J6 141 276 J7 744 23 J4 141 276 J7 744 23 J4 141 276 J7 744 23 J6 141 276 J7 744 23 J7 141 276 J7 141 27	14 244 271 19 412 472 20 248 473 21 96 78 22 555 555 23 295 400 24 255 400 24 255 400 25 127 141 12 4 0 C 532 545 2 149 414	12 656 689 13 497 502 14 1134 1133 15 461 473 16 409 428 17 797 842 18 99 112 19 248 224 20 282 280 21 917 932 22 893 891 25 200 205 26 225 225	30 1048 1040 31 406 428 34 130 107 36 133 140 37 435 435 6 € 0 1 522 547 3 1175 1138 4 104 1414 5 802 506 6 1074 1044	6 2810 2746 8 2370 2248 8 2370 2248 10 050 503 10 056 644 11 116 117 13 398 598 13 1327 1310 13 1327 1310 13 348 568 14 1327 134 15 348 568 16 1327 134 17 1264 1264 17 1264 1264 18 871 912	14 035 000 18 1610 1880 10 220 293 20 354 588 21 0354 083 22 033 403 23 573 403 24 547 801 25 141 100 26 140 101 26 140 101 27 140 101 26 140 101 27 140 100 100 100 100 100000000000000000
40 204 178	1 1942 1849	15 4 1	24 343 365	10 1334 1405	23 221 226	31 853 852	37 435 438	19 8 6	5 745 748	28 157 185	8 761 767	21 369 341	32 140 142
2 K 2 0 602 470	\$ 230 217 • 88 •98 5 916 692	n 107 151 1 302 309 2 473 478	0 1470 1501	12 920 955 13 149 157 14 769 802	25 297 313 26 409 445 27 642 643	33 235 209 35 66 38 36 424 418	41 212 220 1 F 1	1 279 241	7 615 638 8 454 447 10 311 315	30 994 1000 32 103 113	10 270 249 11 297 338	22 280 307 23 418 399 24 846 850 25 352 361	36 941 945 35 303 265 36 280 242
1 1+26 1849	N 277 544 7 460 410	3 430 441	2 397 385	15 520 563	28 355 351 29 355 355	37 483 461 38 162 147	0 192 35	0 603 605	11 234 229 12 1259 1261	35 444 405	13 265 238 14 1506 1512	26 358 352 27 846 865	37 404 371 39 461 450
4 965 855	10 227 196	7 50 - 47	5 597 644	18 1334 1357	31 182 204	40 313 307	2 769 737	2 377 349	14 232 447	0 414 414	15 1050 1078	29 341 336	41 147 168
6 766 782 7 5=0 518	11 342 376	10 146 379	7 730 768 8 1225 12-5	20 221 225 21 225 245 264	33 657 663 34 401 404	3 4 1	144 4092 5 2140 2016	• 221 239 • 413 •11	17 2+3 /46	1 319 309 2 1046 1062	10 1577 1599 20 713 776	31 107 75 33 582 608	C K U
9 2021 1962 10 184C 1847 11 1442 1476 12 536 500	13 251 247 14 1274 1244 15 076 200 16 1474 1493 17 1298 -103	13 54 84 14 466 474 15 313 311 18 466 476 14 465 465	4 635 641 10 427 431 11 666 710 12 189 193 13 382 410	22 306 312 23 181 179 24 210 217 25 372 374 26 1027 1080	35 499 497 36 413 380 37 187 178 38 196 196	0 1645 1651 1 1302 1154 2 1296 1161 3 1521 1458 4 1154 1112	6 1326 1206 7 014 722 8 387 507 9 341 294 10 549 502	7 222 217 8 214 224 9 365 355 10 267 275 11 148 160	19 412 413 20 894 913 21 220 234 22 432 440 23 250 207	3 237 201 4 714 737 5 345 342 6 1311 1370 7 1056 1116	21 837 878 22 467 476 23 635 660 24 784 808 26 293 294	34 556 543 35 458 451 36 309 318 38 341 337 40 249 241	• 1015 751 6 551 610 8 2902 2782 10 765 758 12 373 389
13 94 120	19 388 59) 20 198 189	21 loc 165 22 2-1 649	14 684 717	27 406 407	5 K 1	5 194 153	11 1649 1407	12 114 89 15 341 350	24 315 322	8 512 515 9 1046 1006	27 474 490 28 349 357	41 419 41 <i>8</i>	14 2246 2251 18 2636 2610
15 1162 1197 16 886 872 17 1441 1509 18 1147 1161	23 215 144 23 215 143 24 506 544 25 1285 322	13 4 1	16 730 739 17 663 685 18 273 251 19 295 272	30 77 100 31 287 292 32 359 385 34 815 790	0 227 249 1 1040 1811 2 790 790 3 384 364	7 1678 1614 8 804 790 9 733 742 10 884 853	13 1683 1458 14 914 386 15 808 791 16 902 384	14 160 ie3 14 K U	27 176 234 28 446 477 30 293 314	10 453 445 11 407 404 12 1181 1161 13 360 344	29 376 378 31 548 540 32 333 312 33 453 472	2 E 0 0 2337 2379 1 2360 2369	18 106 133 20 039 047 22 972 980 24 1437 1466
19 827 A30 20 627 624 21 363 367	40 778 764 47 477 5-1 48 285 223	1 344 644	20 234 212	35 247 218	+ 153+ 1502 5 458 8+6	11 1486 1450 1/ 758 739	17 951 971 18 904 884	2 /11 /26	10 4 3	14 1976 2030	36 612 605 37 240 206	2 2776 2735	26 878 846 28 1407 1487
22 385 363 23 936 960 24 975 497	30 749 '53 31 249 AV 37 506 64'	3 166 -AC - 181 1AT	23 182 200	0 771 803	7 1236 1259 8 543 495 9 1414 1408	14 2006 2039 15 1737 1761 16 1130 1095	20 1502 1511	5 297 281 6 343 377 7 215 220	1 631 628 2 741 755	17 435 445	39 149 136	6 339 418 7 2731 2612	32 1201 1200 34 453 453
25 V84 V42 26 739 723 27 578 575 28 358 364	33 +23 344 34 383 366 35 645 194 38 271 246	7 481 494 8 803 804 9 504 507	26 674 638 27 438 446 28 196 222 29 130 130	2 555 556 3 1407 1435 4 287 300 5 1461 1486	10 /33 735 11 1293 1263 12 1311 1310 13 387 602	17 617 597 18 618 650 19 1246 1269 20 549 535	23 827 870 24 302 769 25 769 777	+ 105 101 10 358 354 11 633 618 12 617 653	+ 1005 1112 5 204 226 6 661 704 7 705 749	20 572 380 21 180 212 22 1120 1167 23 791 809	0 517 461	9 2697 2565 10 2999 2960 11 556 512	38 551 560 40 219 222
29 483 465 30 446 445	37 120 114 38 582 592	1 345 401	30 334 324	6 142 136 7 770 767	14 390 396	21 635 650	27 032 648	15 227 249	8 299 294 10 230 241	26 92 97 28 253 243	3 1436 1846 4 1644 1568	13 1127 1155	

Table 4. The relationship between F(hkl) and $F(h\bar{k}l)$ in their calculated and observed values

Observed

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>

<

<

< >

>

<

 $F_{c}(h\bar{k}l)$

97

73

75

108

161

59

104

87

 $F_{c}(hkl)$

54

97

46

67

126

81

131

63

The two isomeric complex cations were found to have the absolute configurations illustrated in Fig. 1(*a*) and (*b*). Both complex cations can be designated as skew chelate pairs $\Delta A \Delta$ (*IUPAC Information Bulletin*, 1968).

Description of the structure and discussion

Perspective drawings of the complex cations are given in Fig. 1. The contents of one quarter of a unit cell as seen down the c axis are shown in Fig. 2. Bond



Fig. 2. Projection of the structure along the c axis.

h k

l

3 3

4

4

lengths and angles with their estimated standard deviations in the complex ions are given in Table 5.

Table 5. Interatomic distances and bond angles within the complex ions with their estimated standard deviations in parentheses

- · · · · · · · · · · · · · · · · · · ·			
$Co(1) \cdots N(1)$	1·957 (5) A	$Co(2) \cdots N(4)$	1·951 (5) Å
$Co(1) \cdots N(2)$	1.970 (4)	$Co(2) \cdots N(5)$	1.968(4)
$Co(1) \cdots N(3)$	1.969 (4)	$Co(2) \cdots N(6)$	1.970(4)
$C(1) \cdots N(1)$	1.489 (8)	$C(5) \cdots N(4)$	1.474(9)
$C(2) \cdots N(2)$	1.496(7)	$C(6) \cdots N(5)$	1.499 (7)
$C(3) \cdots N(2)$	1.487(7)	$C(7) \cdots N(5)$	1.486 (8)
$C(4) \cdots N(3)$	1.493 (8)	$C(8) \cdots N(6)$	1.482(9)
$C(1) \cdots C(2)$	1.514(9)	$C(5) \cdots C(6)$	1.402(0)
$C(3) \cdots C(4)$	1.517(8)	$C(7) \cdots C(8)$	1.515 (0)
C(J) = C(4)	1.517 (0)	C(7)	1.313 (9)
N(1)Co(1)N(2)	86·4 (2)°	$N(4)C_0(2)N(5)$	85.7 (2)°
$C_0(1)N(1)C(1)$	110.8(3)	$C_0(2)N(4)C(5)$	109.8(4)
N(1)C(1)C(2)	107.5(5)	N(4)C(5)C(6)	107.6(4)
C(1)C(2)N(2)	107 3 (3) 110.2 (2)	C(5)C(6)N(5)	1070(4)
C(1)C(2)N(2)	110.2(3)	C(3)C(0)N(3)	109.9(3)
$N(2)C_{2}(1)N(2)$	109.3(3)	C(0)N(3)C0(2)	110.3 (3)
N(2)CO(1)N(3)	85.4 (1)	N(5)CO(2)N(6)	84.9 (1)
Co(1)N(3)C(4)	111-8 (3)	Co(2)N(6)C(8)	111.8 (3)
N(3)C(4)C(3)	108.0 (4)	N(6)C(8)C(7)	109.7 (3)
C(4)C(3)N(2)	108.3 (4)	C(8)C(7)N(5)	107.6 (4)
C(3)N(2)Co(1)	108-2 (2)	C(7)N(5)Co(2)	107.6 (2)
$C_{\alpha}(3) \cdots C_{\alpha}(0)$	1.880 (6) Å	C(0),, $N(7)$	1.150 (0) 8
$C_0(3) = C(3)$	1.900 (C)	C(9) $N(7)$	1150 (9) A
$C_0(3) \cdots C(10)$	1.090 (0)	$C(10) \cdots N(8)$	1.153 (8)
$C_0(3) \cdots C(11)$	1.889 (5)	$C(11) \cdots N(9)$	1.154 (8)
$Co(3) \cdots C(12)$	1.903 (5)	$C(12) \cdots N(10)$	1.144 (8)
$Co(3) \cdots C(13)$	1.883 (6)	$C(13) \cdots N(11)$	1.142 (8)
$Co(3)\cdots C(14)$	1.881 (6)	$C(14) \cdots N(12)$	1.147 (8)
$C(9)C_0(3)C(11)$	90.3 (2)	$C(0)C_{0}(3)C(12)$	89.6 (2)
$C(0)C_0(3)C(13)$	00.0(2)	C(9)Co(3)C(12)	86.6 (2)
$C(11)C_{0}(2)C(13)$	90-9 (2) 80-8 (2)	C(3)C(3)C(14)	80.0(2)
C(11)CO(3)C(13)	09·0 (2)	C(11)Co(3)C(14)	88.3 (2)
C(12)CO(3)C(13)	0/.9(2)	C(12)Co(3)C(14)	94.0 (2)
C(10)CO(3)C(11)	91.0 (2)	C(10)Co(3)C(12)	89.2 (2)
C(10)Co(3)C(13)	91.0 (2)	C(10)Co(3)C(14)	91.6 (2)
Co(3)C(9)C(7)	175.8 (5)	Co(3)C(10)N(8)	178.7 (5)
Co(3)C(11)N(9)	179-3 (3)	Co(3)C(12)N(10)	173.0 (3)
Co(3)C(13)N(11)	177.3 (5)	Co(3)C(14)N(12)	174.5 (5)

The crystal is composed of complex cations, complex anions and water molecules. There are two crystallographically independent complex cations in an asymmetric unit. One lies on the diad axis parallel to the c axis and the other is on the diad axis parallel to the a axis. Two dien molecules are coordinated to the central cobalt atom by six nitrogen atoms, adopting u-facial configurations. Both cations can be designated



Fig. 3. Conformation of the chelate rings.

as skew chelate pairs $\Delta \Lambda \Delta$. This is in conformity with the results of a circular dichroism study (Keene *et al.*, 1970). However, the conformations of the two chelate rings formed by a dien molecule are different in the two cations in the asymmetric unit. In the complex cation A, which lies on the diad axis parallel to the c axis, they are $\delta \lambda$, whereas they are $\lambda \lambda$ in the complex ion B on the diad axis parallel to the a axis. The interatomic distances and bond angles in the two crystallographically independent complex cations correspond pretty well with each other, though the conformations of the chelate rings are different. Only the CNC angle at the secondary nitrogen atom is significantly different: CNC in A is 113.9°, while that in B is 110.4°. The C-C and C-N distances are in agree-

Table 6. Intermolecular distances less than 3.5 Å

Key to symmetry operations (1)*v*. z 0.5 + x, y, -0.5+z(2)-0.5 + z0.5 + x, (3) у, (4) -1 + zx, у, Symmetry operation applied to Distances second atom $O(1) \cdots N(4)$ 2·897 (7) Å (1) $O(1) \cdots N(11)$ 2.812 (8) (1) $O(1) \cdots N(4')$ 3.262 (7) (1) $O(1) \cdots N(6')$ 3.180 (7) (1) $O(2) \cdots N(8)$ 2.951 (9) (1) $O(2) \cdots C(5)$ 3.376 (12) (1)O(2) · · C(10)3.260 (8) (1) $O(2) \cdots N(6')$ 2.791 (9) (1) $O(2) \cdots C(8')$ 3.296 (10) (1) $N(1) \cdots N(10)$ 3.040 (7) (1)N(3) · · $\cdot N(10)$ 3.235 (7) (1) $C(5) \cdots N(11)$ 3.457 (9) (1) $C(6) \cdots N(8)$ 3.493 (9) (1) $N(1') \cdots N(10)$ 3.256 (7) (1) $N(1') \cdots N(11)$ 3.350 (7) (1) $N(1') \cdots C(12)$ 3.438 (7) (1) $N(1') \cdots C(13)$ 3.463(7)(1) $C(1') \cdots N(11)$ 3.244(9)(1) $C(2') \cdots N(11)$ 3.361 (8) (1) $O(1) \cdots N(8)$ 3.001 (7) (2) (2) (2) (3) (3) (3) $C(2') \cdots N(8)$ 3.505 (8) $C(3') \cdots N(10)$ 3.421 (8) $\vec{C}(4') \cdots N(10)$ 3.294 (8) $O(2) \cdots N(7)$ 2.843(11) $O(2) \cdots C(9)$ 3.262 (11) $C(4) \cdots N(7)$ 3.127 (9) $N(5) \cdots N(9)$ (3) 3.197 (8) (3) C(7) · · · N(9) 3.488 (9) (3) C(7')N(9) 3.464 (9) O(1) · · (4) · N(9) 3.461 (8) (4) (4) $N(3) \cdots N(12)$ 2.918(7) $C(3) \cdots N(12)$ 3.433 (8) $C(4) \cdots N(12)$ 3.056 (8) (4) $N(2') \cdots N(12)$ 3.232 (7) (4) (4) (4) $C(2') \cdots N(12)$ 3.450 (8) $C(3') \cdots N(7)$ 3.377 (9) $N(4') \cdots N(9)$ 3.086 (8) (4) $N(6') \cdots N(12)$ 3.335 (7) (4) $C(5') \cdots N(9)$ 3.340(10)(4) $C(8') \cdots N(8)$ 3.493 (9) (4) $C(8') \cdot \cdot \cdot N(12)$ 3.384 (9) (4)

ment, within experimental errors, with the values observed in the s-facial isomer (Kobayashi, Marumo & Saito, 1972). All the observed Co-N distances are normal for Co(III) complexes of linear aliphatic polyamines. The chelate rings formed by a dien ligand in the complex cation A have eclipsed envelope and symmetrical skew conformations, while those in the complex cation B are both eclipsed envelope conformations. They are shown in Fig. 3. The Newman projections along the C-C bonds are illustrated in Fig. 4. All the dihedral angles N-C-C-N are in the range $43 \sim 45^{\circ}$ and are much smaller than that in a typical gauche structure. The bond distances and angles in the hexacyanocobaltate(III) anion are listed in Table 5. They may be compared with those observed in $(-)_{589}$ -[Co(penten)] [Co(CN)₆] 2H₂O (Muto, Marumo & Saito, 1970). The closest approach between complex cations and anions occurs between the terminal nitrogen atom of the cation and the nitrogen atom of the anion: $N(3) \cdots N(12)$ and $N(4) \cdots N(9)$ are 2.918 and 3.086 Å respectively. The positions of hydrogen atoms attached to N(3) and N(4) suggest that N(3) \cdots N(12) and N(4) \cdots N(9) are hydrogen bonds. The water molecules are surrounded by two nitrogen atoms of the anion and a terminal nitrogen atom of the cation as indicated by broken lines in Fig. 2. These $N \cdots O$ distances are mostly less than 3 Å. Other interatomic distances less than 3.5 Å between complexes are listed in Table 6.

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Fig. 4. Newman projections along the C-C bonds in the chelate ring.

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The Crystal Structure of CsMnCl₃

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The crystal structure of CsMnCl₃, determined from Weissenberg data, is trigonal, space group R3m. The hexagonal cell contains 9 molecules and has dimensions a = 7.29 (1) and c = 27.48 (5) Å. The c parameter accommodates 9 close-packed layers of composition CsCl₃ and the Mn ions are octahedrally coordinated by Cl ions. The structure is closely related to that of CsNiCl₃.

Introduction

Many complex halides of composition CsMCl₃, where M represents a metal ion in the first transition series, have the same structure as CsNiCl₃ (Tishchenko, 1955), which consists of hexagonally close-packed CsCl₃ layers with Ni octahedrally coordinated by Cl ions such that the Ni–Cl octahedra share opposite faces to form infinite chains of composition $(\text{NiCl}_3)_n^n$ parallel to **c**, the space group being $P6_3/mmc$ with $a \simeq 7.2$ Å, $c/a \simeq 0.82$ and Z = 2. Recent work (Goodyear & Kennedy, 1972) has shown that CsMnBr₃ also has this structure.

An investigation of the unit cell of CsMnCl₃ by Kes-