

THE STEREOCHEMISTRY OF THE BIS [N-(2-CARBAMOYLETHYL)-IMINODIACETATE] COBALT(III) COMPLEX

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A complex with the composition $K[Co(ceida)_2] \cdot 2 H_2O$ was isolated from solution after reaction of N-(2-carbamoylethyl)iminodiacetic acid, H_2ceida , with $CoCl_2$ in an aqueous solution of CH_3COOK after oxidation with H_2O_2 . Its structure was studied in D_2O solution using 1H and ^{13}C NMR spectroscopy and by X-ray diffraction of the crystalline substance. Both methods indicate that the complex anion is centrosymmetric in the octahedral complex. The ligand is coordinated by two oxygen atoms of the carboxylic groups and the nitrogen atom of the imino group. The amide group is not coordinated. Of the three possible isomers, only the *trans*-facial isomer was isolated. The uncoordinated ceida chain can assume two different conformations in the crystal. The K^+ cations and molecules of water of crystallization are disordered.

A great many amino acids have a side chain containing functional groups with donor atoms that can coordinate to a central atom. The amide group is a biologically important group that can coordinate with both oxygen and nitrogen atoms¹. Previous works^{2,3} have studied the complexing equilibria of amino acid containing an amide group — N-(carbamoylethyl)iminodiacetic acid, H_2ceida , $(HOOC-CH_2-)_2N-CH_2-CH_2-CONH_2$ with divalent metal ions considering coordination of the amide group in complexes of the ML and ML_2 type. In octahedral complexes, ML_2 , one of the groups, either the carboxyl or the amide, cannot be coordinated. The $[Co(ceida)_2]^-$ ion can exist in three geometric isomers with the nitrogen atoms in the *cis* or *trans* positions. In the *trans* isomer, the ligand can be coordinated either facially or meridionally (Fig. 1). This work gives the results of study of the stereochemistry of the $[Co(ceida)_2]^-$ complex in aqueous solution and in the crystalline form.

EXPERIMENTAL

Synthesis of N-(Carbamoylethyl)iminodiacetic Acid, H_2ceida ⁴
Sodium hydroxide (1.6 g, 40 mmol) is dissolved in 8 ml of water and 2.66 g (20 mmol) of iminodiacetic acid are added. The resulting solution is mixed with a solution of 2.12 g (20 mmol)

3-chloropropionamide in 8 ml of 50 vol. % ethanol and the mixture is left to react for 16 h at 55°C with constant stirring with a reflux condenser. The pH of the reaction mixture is maintained at 8.0–8.5 by gradual addition of 1.68 g (20 mmol) of NaHCO_3 . After completion of the reaction, the mixture is cooled and acidified with dil. HCl (1 : 1) to pH 3. The precipitated substance is filtered off and the filtrate is again acidified to pH 1.5 and left to stand in the cold. The precipitated product is filtered off and recrystallized twice from water at 80°C.

Preparation of $\text{K}[\text{Co}(\text{ceida})_2] \cdot 2 \text{H}_2\text{O}$

The reaction mixture of 2.04 g (10 mmol) H_2ceida , 1.2 g (5 mmol) $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$, 3.0 g (30 mmol) CH_3COOK and 0.25 g active carbon is heated to 90°C, 0.5 ml of 30% H_2O_2 are added and the mixture is left to react for 30 min at this temperature. The mixture is filtered and the filtrate is left to stand in the air. The red-purple crystals formed are filtered off and recrystallized from hot water. Analysis for $\text{K}[\text{Co}(\text{ceida})_2] \cdot 2 \text{H}_2\text{O}$ (538.4) calculated: 31.23% C, 4.49% H, 10.95% Co 10.40% N; found: 30.62% C, 4.23% H, 10.47% Co, 10.17% N.

It was found by electrophoresis that the complex ion has a charge of -1 . A complex with the same composition and same charge was also obtained for an equimolar ratio of $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ and H_2ceida .

NMR Measurements

The ^{13}C NMR spectra were measured on a JEOL FX-100 spectrometer with a working frequency of 25.05 MHz. The samples were dissolved in D_2O , the pH was adjusted using KOD, and *p*-dioxan was added as an internal reference ($\delta = 67.4$ ppm). The ^1H NMR spectra were obtained using a Bruker AM-300 spectrometer at 300.13 MHz. The solvent was D_2O and TSP was employed as an internal reference. All the measurements were carried out at laboratory temperature.

X-Ray Analysis

The analysis was carried out using crystals with deformed cubic shape with dimensions of 0.3 mm, D_m was found by flotation and the Weissenberg photographs did not exhibit any symmetry. The measurements were carried out using a Syntex P2₁ diffractometer with a graphite

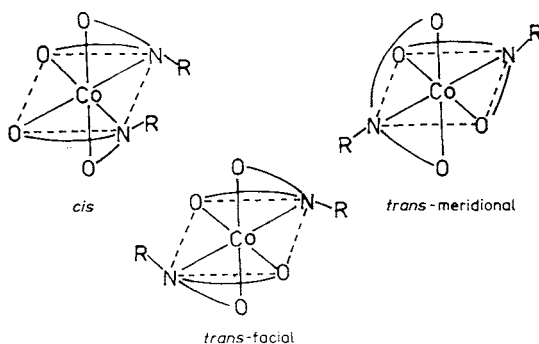


FIG. 1
Schematic depiction of the geometric isomers of $[\text{Co}(\text{ceida})_2]^-$

monochromator, and the lattice parameters were found from the positional angles of 10 reflections, $5 < 2\theta < 16^\circ$. Crystal data: triclinic, PI , $a = 1.1065(25)$, $b = 1.2964(26)$, $c = 0.9046(21)$ nm, $\alpha = 99.90(17)$, $\beta = 95.17(20)$, $\gamma = 122.69(14)^\circ$, $V = 1.0493(20)$ nm³, $D_m = 1.75(1)$, $D_x = 1.704$ Mg m⁻³, $Z = 2$, $\lambda(\text{MoK}\alpha) = 0.071069$ nm, $\mu = 1.081$ mm⁻¹, $F(000) = 556$, room temperature.

Measuring conditions: $\omega - 2\theta$ technique, scanning rate $4.88 - 29.3^\circ$, 2θ min⁻¹, scanning range $2^\circ + 2\theta(K\alpha 1) - 2\theta(K\alpha 2)$, the background at each end of the scan for the half of scanning time, two standard reflections (0, 2, 0) and (0, -1, 0) monitored after recording of each 98 reflections did not change significantly during the experiment. 2945 reflections were measured for $2\theta < 50^\circ$, $h = -10$ to 10, $k = -11$ to 11, $l = 0$ to 9, 2881 independent, 521 unobserved for $I < 1.96\sigma(I)$, $R_{\text{int}} = 0.02$. Correction was carried out for the Lorentz and polarization factors; corrections for absorption and extinction were neglected. The structure was solved by the heavy atom method in the PI and PI space groups. The Co-K vectors could not be localized on the Patterson map. Refinement was carried out on the $|F_0|$ by block-diagonal least squares method, anisotropic parameters for the heavier atoms, hydrogen atoms fixed in the calculated positions ($B = 0.04$ nm²), the weighting scheme $w^{-1} = \sigma^2(F) + (0.02|F_0|)^2$, $\sigma(F)$ from pulse statistics. The K⁺ cations and molecules of crystalline water could not be unambiguously localized in either PI or PI . A working hypothesis was selected in which 2K⁺ cations and the molecules of crystalline water are statistically distributed over four positions and the character of the disorder was partly solved by a combination of differential synthesis and refinement of the occupation factors. $(\Delta/\sigma)_{\text{max}} = 0.1$, $R = 0.0758$ for the observed and 0.091 for all the reflections, the wR values are 0.0925 and 0.094. $(\Delta\rho)_{\text{max}} = 540$ e nm⁻³, $(\Delta\rho)_{\text{min}} = -870$ e nm⁻³. The scattering factors for the neutral atoms were taken from the International Tables for X-ray Crystallography⁵. All calculations were carried out with the XRC83 program system⁶ on the EC-1 033 computer. The refined positional parameters are given in Table I. The occupation factors for K(1), K(2), O(10), O(11), O(12) are 0.53(2), 0.63(2), 1.15(7), 0.76(12), 0.44(3). The anisotropic parameters are listed in Table II. Tables of the calculated and measured structural factors can be obtained on request from the first of the authors.

RESULTS AND DISCUSSION

The structure in solution of the prepared compound was found from the NMR spectra. Table III lists the ¹³C chemical shifts of the free and protonated (ceida)²⁻ anions and of those bonded in the complex. The number of ¹³C signals for the complex $[\text{Co}(\text{ceida})_2]^-$ anion is the same as for the (ceida)²⁻ anion, indicating that both ligand molecules are coordinated in the same way in the complex. ¹H NMR spectroscopy was employed to distinguish between the geometric isomers. In the *trans*-facial isomers, all the acetate CH₂ groups have the same chemical environment, so that only the AB pattern can be expected in the spectrum. In the *cis*- and *trans*-meridional isomers, the chemical environment around the CH₂ group is different and thus two AB patterns can be expected. Only a single AB pattern was observed in the NMR spectrum of $[\text{Co}(\text{ceida})_2]^-$ for the protons of the acetate CH₂ groups ($\delta_A = 4.31$ ppm, $\delta_B = 3.77$ ppm, $J_{AB} = 16.7$ Hz) and two multiplets for the protons of the other CH₂ groups ($\delta = 3.89$ ppm and 3.04 ppm). It follows from the spectra that the *trans*-facial isomer of $[\text{Co}(\text{ceida})_2]^-$ is present in solution.

TABLE I

Final atomic coordinates ($\cdot 10^4$) with estimated standard deviations in parentheses and equivalent isotropic thermal parameters B_{eq} (10^{-22} m^2) defined as $B_{\text{eq}} = 4/3 \sum_i \sum_j B_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$

Atom	x/a	y/b	z/c	B_{eq}
Co(1)	0(0)	0(0)	0(0)	2·04
O(1)	1 003(2)	1 785(2)	634(3)	2·69
O(2)	2 807(3)	3 501(2)	2 378(3)	4·03
O(3)	-1 389(3)	-156(2)	1 183(3)	2·74
O(4)	-2 107(3)	-618(3)	3 322(3)	3·66
O(5)	5 095(3)	838(3)	2 838(3)	3·64
N(1)	1 189(3)	140(3)	1 899(3)	2·04
N(3)	4 649(4)	1 263(3)	5 199(4)	3·58
C(1)	2 423(4)	1 556(3)	2 514(4)	3·42
C(2)	2 034(4)	2 345(3)	1 812(4)	2·62
C(3)	154(4)	-326(4)	2 967(4)	3·18
C(4)	-1 189(4)	-352(3)	2 506(4)	2·25
C(5)	1 831(4)	-605(4)	1 669(4)	2·88
C(6)	2 668(4)	-585(4)	3 201(4)	3·15
C(7)	4 252(4)	573(3)	3 716(4)	2·56
Co(2)	0(0)	5 000(0)	5 000(0)	2·27
O(101)	-1 648(3)	3 861(2)	5 729(3)	3·26
O(102)	-2 686(3)	3 689(3)	7 728(3)	5·42
O(103)	-936(3)	5 816(2)	4 517(3)	3·45
O(104)	-749(3)	7 615(3)	5 114(3)	4·36
O(105)	4 808(3)	7 175(3)	9 380(3)	4·52
N(101)	760(3)	6 211(3)	7 063(3)	2·87
N(103)	5 376(3)	8 957(3)	10 979(4)	3·56
C(101)	-384(4)	5 605(4)	7 997(4)	3·05
C(102)	-1 675(4)	4 276(3)	7 101(4)	2·96
C(103)	836(4)	7 351(3)	6 723(4)	2·82
C(104)	-352(4)	6 906(3)	5 383(4)	3·00
C(105)	2 222(4)	6 533(3)	7 779(4)	2·48
C(106)	2 942(4)	7 563(3)	9 307(4)	2·99
C(107)	4 462(4)	7 890(3)	9 888(4)	2·65
K(1)	4 263(3)	5 303(2)	750(3)	6·63
K(2)	4 289(2)	5 245(3)	5 523(3)	10·57
O(10)	6 269(7)	6 666(5)	3 328(8)	20·46
O(11)	9 072(12)	6 429(6)	1 470(8)	18·34
O(12)	6 915(10)	5 428(8)	15(13)	9·36

TABLE II

Coefficients of anisotropic temperature factors ($\cdot 10^4$). Estimated standard deviations are given in parentheses. Temperature factor is of the form $T = \exp[-(B_{11} \cdot h^2 + \dots + B_{12} \cdot hk + \dots)]$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co(1)	74(1)	51(1)	46(1)	74(1)	4(1)	19(1)
O(1)	89(3)	50(2)	89(4)	88(5)	-40(6)	-5(5)
O(2)	142(4)	53(3)	130(5)	88(6)	-58(7)	17(6)
O(3)	115(4)	90(3)	54(3)	151(6)	37(6)	54(5)
O(4)	97(4)	123(3)	86(4)	129(6)	50(7)	86(6)
O(5)	101(4)	103(3)	113(4)	118(6)	90(7)	79(6)
N(1)	75(4)	53(3)	52(4)	76(6)	25(7)	43(6)
N(3)	158(5)	82(4)	77(5)	159(8)	-7(8)	17(7)
C(1)	127(6)	49(4)	102(6)	78(8)	-29(10)	36(8)
C(2)	67(5)	61(4)	89(6)	67(7)	20(9)	31(8)
C(3)	93(5)	117(5)	88(6)	149(9)	53(9)	116(9)
C(4)	74(5)	52(4)	72(5)	77(7)	36(8)	23(7)
C(5)	106(6)	82(4)	76(6)	136(9)	14(9)	37(8)
C(6)	113(6)	70(4)	86(6)	102(8)	2(10)	55(8)
C(7)	75(5)	69(4)	85(6)	99(7)	1(9)	42(8)
Co(2)	89(1)	44(1)	60(1)	73(1)	10(2)	23(1)
O(101)	111(4)	54(3)	89(4)	62(5)	46(7)	9(5)
O(102)	142(5)	94(3)	132(5)	20(6)	110(8)	38(7)
O(103)	144(4)	72(3)	88(4)	151(6)	-57(7)	-9(5)
O(104)	193(5)	77(3)	139(5)	185(7)	-2(8)	40(6)
O(105)	111(4)	99(3)	164(5)	125(6)	-21(8)	9(7)
N(101)	107(4)	57(3)	56(4)	65(6)	26(7)	19(6)
N(103)	103(5)	70(4)	91(5)	62(7)	-12(8)	22(7)
C(101)	76(5)	79(4)	69(6)	61(8)	21(9)	24(8)
C(102)	92(5)	58(4)	86(6)	64(8)	0(9)	41(8)
C(103)	128(6)	48(4)	97(6)	127(8)	-5(10)	34(8)
C(104)	133(6)	55(4)	76(6)	117(8)	9(10)	8(8)
C(105)	62(5)	66(4)	69(5)	71(7)	-6(8)	12(7)
C(106)	86(5)	68(4)	107(6)	97(8)	35(10)	24(8)
C(107)	94(5)	59(4)	104(6)	117(8)	37(9)	28(8)
K(1)	226(4)	157(3)	182(4)	189(6)	100()	186(6)
K(2)	162(4)	255(4)	305(6)	76(6)	-124(7)	177(8)
O(10)	704(19)	200(8)	740(22)	319(19)	-268(33)	236(21)
O(11)	1 159(40)	161(9)	315(17)	592(31)	609(41)	287(20)
O(12)	260(18)	137(12)	397(27)	186(24)	68(35)	100(28)

The crystal structure consists of two complex $[\text{Co}(\text{ceida})_2]^-$ anions (*A*, *B*), the K^+ cation and a molecule of crystalline water. The cobalt atoms occupy two independent symmetry centres of the crystal lattice, so that the complex anions are exactly centrosymmetric. The coordination number of Co(III) is 6 and the coordination sphere contains the oxygen atoms of the carboxyl groups and two nitrogen

TABLE III

The ^{13}C chemical shifts (ppm) of the free, protonated and coordinated ceida^{2-} anion in D_2O solutions; $(\text{HOOC}-\overset{1}{\text{CH}_2}-\overset{2}{\text{N}}-\overset{3}{\text{CH}_2}-\overset{4}{\text{CH}_2}-\overset{5}{\text{CO}}-\text{NH}_2)$

Compound	pH of solution	δ , ppm				
		C-1	C-2	C-3	C-4	C-5
ceida^{2-}	13	180.1	59.0	50.7	33.6	179.3
Hceida^-	5.5	171.1	58.0	52.6	30.0	175.3
$[\text{Co}(\text{ceida})_2]^-$	8.6	183.4	65.7	59.1	30.4	176.5

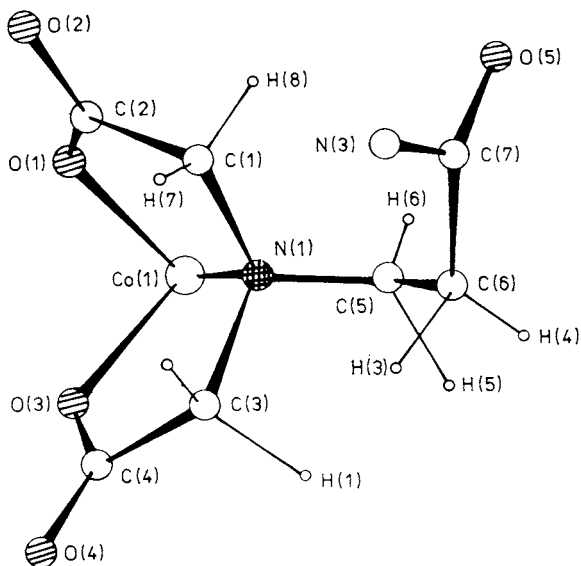


FIG. 2

The molecular structure and atomic numbering in the $[\text{Co}(\text{ceida})_2]^-$ anion *A*. Only the symmetrically independent part is depicted. The second half of the atoms is generated through the centre of symmetry

atoms from the two ligand molecules. The amide group is not coordinated and the ligands are *trans*-facially coordinated (Figs 2, 3). Most complexes of iminodiacetic acid (ida) and its derivatives have *trans*-facial coordination: $\text{Li}_2[\text{Ni}(\text{ida})_2] \cdot 4 \text{H}_2\text{O}$, $\text{Cs}[\text{Ni}(\text{ida})_2] \cdot 4 \text{H}_2\text{O}$ (ref.⁷), $\text{Li}_2[\text{Zn}(\text{ida})_2] \cdot 4 \text{H}_2\text{O}$ (ref.⁸), $\text{Na}_2[\text{Co}(\text{ida})_2] \cdot 7 \text{H}_2\text{O}$ (ref.⁹), $\text{K}_2[\text{Cu}(\text{ida})_2] \cdot 3 \text{H}_2\text{O}$ (ref.¹⁰), $\text{Na}[\text{Cr}(\text{N-isopropyl-ida})_2] \cdot 2 \text{H}_2\text{O}$ (ref.¹¹), $\text{K}[\text{Cr}(\text{N-tert-butyl-ida})_2] \cdot 4 \text{H}_2\text{O}$ (ref.¹²), $\text{K}_4[\text{Co}(\text{ida})_2] \cdot 2.5 \text{H}_2\text{O}$ (ref.¹³), $\text{Na}_2[\text{Ni}(\text{N-hydroxyethyl-ida})_2] \cdot 4 \text{H}_2\text{O}$, $\text{Cs}_2[\text{Co}(\text{N-hydroxyethyl-ida})_2] \cdot 4 \text{H}_2\text{O}$ (ref.¹⁴). The *cis* configuration is found in the crystals of $\text{K}_2[\text{Zn}(\text{ida})_2] \cdot 3 \text{H}_2\text{O}$ (ref.¹⁵), $\text{K}[\text{Co}(\text{ida})_2] \cdot 2.5 \text{H}_2\text{O}$ (ref.¹⁶) and $\text{K}[\text{Cr}(\text{ida})_2] \cdot 3 \text{H}_2\text{O}$ (ref.¹⁷). The steric repulsion between the uncoordinated chains makes the *cis* configuration less favourable in the N-substituted ida complexes¹⁴.

The Co(III) coordination polyhedra are slightly deformed octahedra. The bonding angles in the coordination sphere vary from 84 to 90° (Table IV). The conformation of the glycine rings is close to the *gauche* form in which the cobalt atom deviates from the central plane on one side and the nitrogen atom on the other side. The —Co(2)—O(101)—C(102)—C(101)—N(101)—ring is an exception as it is almost planar. The degree of puckering of the glycine ring expressed as the sum of the bonding angles is 537.0°, 536.8°, 539.9°, and 529.0° for the rings containing the O(1), O(3), O(101), and O(103) atoms, respectively (the sum of the angles for a planar

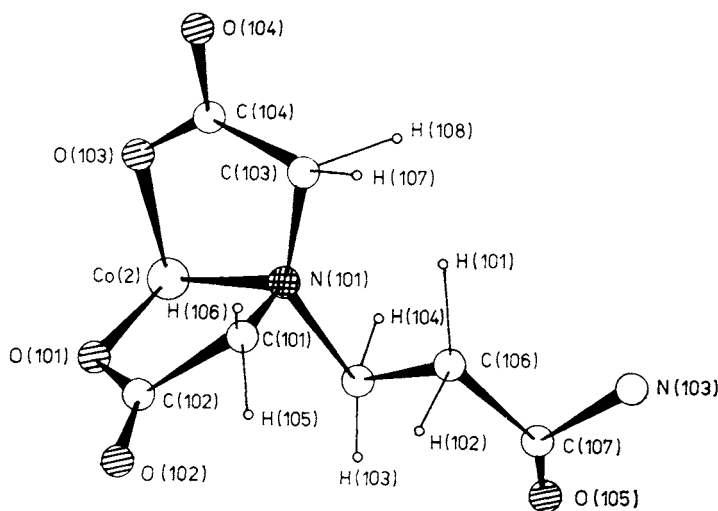


FIG. 3

The molecular structure and atomic numbering in the $[\text{Co}(\text{ceida})_2]^-$ anion *B*. Only the symmetrically independent part is depicted. The second half of the atoms is generated through the centre of symmetry

TABLE IV

Interatomic distances (nm), bond angles ($^{\circ}$), and torsion angles ($^{\circ}$) with standard deviations in parentheses

Interatomic distances			
Co(1)—O(1)	0·1889(3)	N(1)—C(1)	0·1532(5)
Co(1)—O(3)	0·1993(3)	N(1)—C(3)	0·1505(6)
Co(1)—N(1)	0·1986(3)	N(1)—C(5)	0·1476(6)
O(1)—C(2)	0·1259(5)	N(3)—C(7)	0·1360(5)
O(2)—C(2)	0·1230(5)	C(1)—C(2)	0·1511(6)
O(3)—C(4)	0·1290(4)	C(3)—C(4)	0·1487(7)
O(4)—C(4)	0·1241(5)	C(5)—C(6)	0·1584(6)
O(5)—C(7)	0·1225(5)	C(6)—C(7)	0·1520(6)
Co(2)—O(101)	0·1893(3)	N(101)—C(101)	0·1510(6)
Co(2)—O(103)	0·1909(3)	N(101)—C(103)	0·1520(5)
Co(2)—N(101)	0·1985(3)	N(101)—C(105)	0·1484(6)
O(101)—C(102)	0·1274(5)	N(103)—C(107)	0·1322(5)
O(102)—C(102)	0·1223(6)	C(101)—C(102)	0·1523(6)
O(103)—C(104)	0·1253(5)	C(103)—C(104)	0·1477(6)
O(104)—C(104)	0·1261(6)	C(105)—C(106)	0·1531(5)
O(105)—C(107)	0·1219(6)	C(106)—C(107)	0·1509(7)
K(1)—O(2)	2·787(4)	K(2)—O(2)	2·972(4)
K(1)—O(10)	2·627(8)	K(2)—O(2)	2·962(4)
K(1)—O(102)	2·987(5)	K(2)—O(10)	2·636(7)
K(1)—O(12)	2·992(13)	K(2)—K(2)	2·218(4)
K(1)—O(105)	2·716(4)	K(1)—K(1)	2·557(4)
Bond angles			
O(1)—Co(1)—O(3)	89·20(12)	O(101)—Co(2)—O(103)	89·79(12)
O(1)—Co(1)—N(1)	87·39(12)	O(101)—Co(2)—N(101)	87·74(13)
O(3)—Co(1)—N(1)	86·79(12)	O(103)—Co(2)—N(101)	84·56(13)
Co(1)—O(1)—C(2)	115·80(25)	Co(2)—O(101)—C(102)	115·66(26)
Co(1)—O(3)—C(4)	115·11(25)	Co(2)—O(103)—C(104)	113·84(27)
Co(1)—N(1)—C(1)	105·42(23)	Co(2)—N(101)—C(101)	107·10(24)
Co(1)—N(1)—C(3)	105·45(24)	Co(2)—N(101)—C(103)	103·27(24)
Co(1)—N(1)—C(5)	114·72(24)	Co(2)—N(101)—C(105)	110·53(24)
C(1)—N(1)—C(3)	111·96(31)	C(101)—N(101)—C(103)	109·85(31)
C(3)—N(1)—C(5)	109·47(31)	C(103)—N(101)—C(105)	112·43(31)
N(1)—C(1)—C(2)	110·54(34)	N(101)—C(101)—C(102)	111·70(34)
O(1)—C(2)—O(2)	124·53(38)	O(101)—C(102)—O(102)	124·27(40)
O(1)—C(2)—C(1)	117·84(36)	O(101)—C(102)—C(101)	117·71(36)
O(2)—C(2)—C(1)	117·49(37)	O(102)—C(102)—C(101)	117·98(38)
N(1)—C(3)—C(4)	112·63(34)	N(101)—C(103)—C(104)	109·10(34)

TABLE IV
(Continued)

O(2)—C(4)—O(4)	121·87(36)	O(103)—C(104)—O(104)	121·20(40)
O(3)—C(4)—C(3)	116·77(35)	O(103)—C(104)—C(103)	118·19(38)
O(4)—C(4)—C(3)	121·25(36)	O(104)—C(104)—C(103)	120·60(39)
N(1)—C(5)—C(6)	114·71(33)	N(101)—C(105)—C(106)	113·28(33)
C(5)—C(6)—C(7)	112·33(35)	C(105)—C(106)—C(107)	109·41(34)
O(5)—C(7)—N(3)	123·50(39)	O(105)—C(107)—N(103)	121·97(40)
O(5)—C(7)—C(6)	121·15(37)	O(105)—C(107)—C(106)	120·45(38)
N(3)—C(7)—C(6)	115·35(36)	N(103)—C(107)—C(106)	117·57(37)

Torsion angles

O(1)—Co(1)—N(1)—C(3)	105·2(2)	O(101)—Co(2)—N(101)—C(103)	-118·7(3)
O(2)—C(2)—O(1)—Co(1)	179·6(3)	O(102)—C(102)—O(101)—Co(2)	176·6(4)
Co(1)—N(1)—C(5)—C(6)	-175·2(3)	Co(2)—N(101)—C(105)—C(106)	174·4(2)
O(2)—C(2)—C(1)—N(1)	168·6(4)	O(102)—C(102)—C(101)—N(101)	-179·1(4)
C(2)—C(1)—N(1)—C(5)	142·0(3)	C(102)—C(101)—N(101)—C(105)	-119·4(4)
C(2)—C(1)—N(1)—C(3)	-96·2(4)	C(103)—N(101)—C(101)—C(102)	114·1(4)
C(3)—N(1)—C(5)—C(6)	-56·9(4)	C(103)—N(101)—C(105)—C(106)	59·6(4)
N(1)—C(5)—C(6)—C(7)	-84·4(5)	N(101)—C(105)—C(106)—C(107)	-176·1(3)
C(5)—C(6)—C(7)—N(3)	127·6(4)	C(105)—C(106)—C(107)—N(103)	164·0(3)
C(5)—C(6)—C(7)—O(5)	-53·1(6)	C(105)—C(106)—C(107)—C(105)	-17·3(5)
O(1)—Co(1)—N(1)—C(5)	-134·3(3)	O(101)—Co(2)—N(101)—C(105)	120·9(2)
O(4)—C(4)—C(3)—N(1)	-174·4(3)	O(104)—C(104)—C(103)—N(101)	162·3(4)
C(1)—N(1)—C(3)—C(4)	96·9(4)	C(104)—C(103)—N(101)—C(101)	-82·2(4)
C(1)—N(1)—Co(1)—O(3)	-102·7(3)	C(101)—N(101)—Co(2)—O(103)	87·3(3)
C(6)—C(5)—N(1)—C(3)	-56·9(4)	C(101)—N(101)—C(105)—C(106)	-65·5(4)
C(5)—N(1)—Co(1)—O(3)	136·4(3)	O(103)—Co(2)—N(101)—C(105)	-149·1(2)
O(1)—Co(1)—O(3)—C(4)	-99·9(2)	O(101)—Co(2)—O(103)—C(104)	109·3(3)
C(2)—O(1)—Co(1)—O(3)	92·9(3)	C(102)—O(101)—Co(2)—O(103)	-82·1(3)
C(4)—C(3)—N(1)—C(5)	-141·2(3)	C(104)—C(103)—N(101)—C(105)	151·0(3)
O(4)—C(4)—O(3)—Co(1)	-171·5(3)	O(104)—C(104)—O(103)—Co(2)	172·6(3)

ring is 540°). The carbon atom of the condensed chelate ring is located in the pseudo-axial position and the carbon atoms in the uncoordinated chain in the pseudo-equatorial position.

The complex anions *A* and *B* differ in the conformation of the uncoordinated chain. The conformation for the Co—N—C—C—CO—NH₂ fragment is *trans-gauche* for the anion containing the Co(1) atom and *trans-trans* for the Co(2) atom.

The character of disorder of the K⁺ ions can be interpreted by an arrangement in which the complex anions form two centrosymmetric cavities in which the energy

TABLE V

Interatomic distances (nm) characterizing the hydrogen bonds. Symmetry codes: (i) $1 - x$, $1 - y$, $-z$, (ii) $-x$, $-y$, $1 - z$, (iii) $x - 1$, $y - 1$, z , (iv) x , $y - 1$, $1 + z$, (v) $x - 1$, y , z

Interatomic distances X...Y			
O(2)...O(104 ⁱ)	2.72(1)	O(103)...O(101 ^{iv})	3.00(1)
O(4)...N(3 ⁱⁱ)	2.99(1)	O(104)...O(101 ^v)	3.00(1)
O(4)...O(101 ⁱⁱⁱ)	2.97(1)	O(101)...O(104)	2.15(2)
O(5)...N(103 ^{iv})	2.89(1)		

minimum for K^+ is not located at the centre of symmetry and both energetically favourable positions in the cavity are statistically occupied by K^+ ions. The crystal structure is stabilized by both ionic forces and a system of hydrogen bonds, given in Table V. The character of the disorder indicated that the number of molecules of crystalline water is variable.

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