*Inorganica Chimica Acta*, 40 (1980) 71–77
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# Crystal and Molecular Structure of Chloro[1,11-bis(2-pyridyl)2,6,10-triazaundecane]-cobalt(III) Tetrachlorocobaltate(II) Hemihydrate, [Co(picditn)Cl] $CoCl_4 \cdot 1/2H_2O$

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Received September 11, 1979

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*The structure of the title compound has been determined by counter data. The crystals are orthorhombic, space group $P2_12_12_1$ with* a = *16.069(8),* b = *13.215(6),* c = *11.490(5)* Å, Z = *4. The structure has been refined by full-matrix least-squares to a final conventional R value of 0.049. The coordination geometry of the complex cation is near regular octahedral, with the pentadentate ligand present in the α,β configuration and with a Cl* trans *to an 'angular' secondary nitrogen. The absolute configuration of the complex ion can be designed as* Λ *while the two optically active N(2) and N(4) are* R *and* S *respectively.*

## Introduction

As part of our study of the ways in which the sensitivity of chloropenta-aminecobalt(III) complexes towards base hydrolysis depends upon the nature of the nitrogen donors, the extent of chelation, and the detailed stereochemistry of the multidentate amine system [1], we have been investigating the complexes derived from the pentadentate ligands, 1,9-bis(2-pyridyl)2,5,8-triazanonane(picdien), and 1,11-bis(2-pyridyl)2,6,10-triazaundecane(picditn). The red orange $[Co(picdien)Cl]^+$ cation is so sensitive to base hydrolysis that even at pH = 2 more than 97% of the hydrolysis goes by way of the hydroxide catalysed path [2]. The red-purple $[Co(picditn)Cl]^{2+}$ cation, on the other hand, is some two orders of magnitude less sensitive to base hydrolysis and at least 20 times more labile to acid hydrolysis [2, 3]. The spectra of these two species are similar to the pair isomers of $[Co(tetren)Cl]^+$ (tetren = 1,11-diamino-3,6,9-triazaundecane) reported by House and Garner [4] but in that case, the reactivity difference between the species is small [5]. In order to establish how much of the reactivity difference between the picdien and picditn complexes was due to changes in ring size and how much was due to ligand geometry it was necessary to establish the stereochemistry of the complexes. This paper reports the structure of the $[Co(picditn)Cl]^{2+}$ cation. The structure of the $[Co(picdien)Cl]^{2+}$ cation and the kinetics will be reported elsewhere.

## Experimental

### X-ray Structure Analysis

The data crystal of [Co(picditn)Cl] $CoCl_4 \cdot 0.5H_2O$, size 0.2 × 0.08 × 0.07 mm, was obtained from Dr. R. Henderson. The preparation and properties were reported elsewhere [3]. Intensity data were collected using a Philips PW 1100 four-circle diffractometer in the range $6 \leqslant 2\theta \leqslant 50°$, with $MoK\bar{\alpha}$ radiation (graphite monochromator; $\theta/2\theta$ scan mode; scan width 1.2°; scan speed 0.03° $s^{-1}$). During the data collection two standard reflections were measured every 120 min to check the stability of the crystal and electronics. Using the criterion $I \geqslant 3\sigma(I)$, where $\sigma(I)$ is the estimated standard deviation derived from counting statistics, 1590 of the 3370 intensities recorded were deemed independent and observable and only these were used in the solution and refinement of the structure. Corrections were made for Lorentz, polarization and X-ray absorption-effects [6].

### Crystal data

$C_{18}H_{28}N_5O_{0.5}Cl_5Co_2$, $M = 616.59$. Orthorhombic, space group $P2_12_12_1$, $a = 16.069(8)$, $b = 13.215(6)$, $c = 11.490(5)$ Å, $U = 2439.9$ Å$^3$, F(000) = 1256 e,

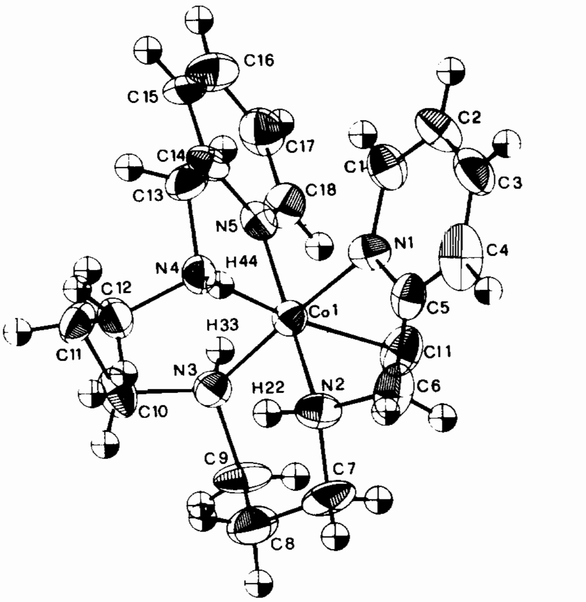

Fig. 1. Stereochemical arrangement of the cation together with the atom nomenclature.

$D_o$ = 1.66, $D_c$ = 1.678 g $cm^{-3}$ for $Z$ = 4, $\mathrm{MoK}\bar{\alpha}$ radiation $\lambda$ = 0.71069 Å, $\mu(\mathrm{MoK}\bar{\alpha})$ = 19.6 $cm^{-1}$.

### *Structure solution and refinement*

The molecular structure of the complex was solved by difference density syntheses following successful location of the Co atoms from a three-dimensional Patterson synthesis. A full-matrix least-squares refinement in F was computed. The function $\Sigma w(|F_o|-|F_c|)^2$ was minimized in which w = 1.

Throughout the analysis the scattering factors of International Tables for X-ray Crystallography were used [7]; both the real and imaginary components of anomalous dispersion were included for cobalt only [2]. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were located in calculated idealized positions (C–H = 0.95 Å), but not varied.

The final conventional $R_1$ value for the 1590 observed reflections, with $I \geqslant 3\sigma(I)$, was 0.049.

As pointed out by Ibers and Hamilton [8] the absolute configuration of the present complex may be determined from the anomalous scattering effect even though no Bijvoet pairs of reflections (hkl and hkl) have been measured. Consequently the refinement was repeated with the direction of the *a, b* and *c* axes reversed. The resulting value of the reliability factor $R_2$ then was 0.055. This significantly higher discrepancy index confirmed that the original model, which was chosen so that the optically active nitrogen atoms N(2) and N(4) were S and R respectively, indeed was of correct handedness. In addition application of Hamilton's R-factor ratio test [9] gives R = $R_2/R_1$ = 1.122. Comparison with the theoretical value of acceptance of the second configuration with a 99.5% probability ($R_{1.1310.0.005}$ = 1.003) indicates

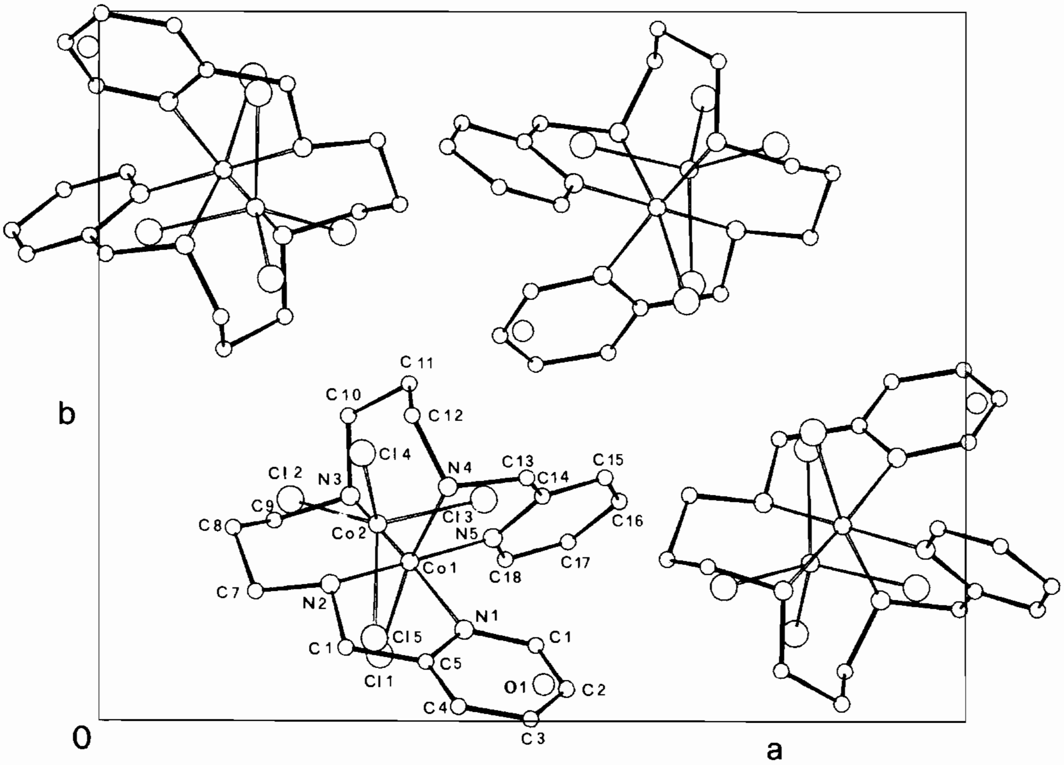

Fig. 2. Crystal packing, as viewed down the *c* axis.

TABLE I. Atomic Coordinates.

*Atomic coordinates (×$10^4$, for hydrogen atoms ×$10^3$) with e.s.d.s in parentheses*

| | x | y | z | | x | y | z |
|---|---|---|---|---|---|---|---|
| Co(2) | 3203(1) | 2775(1) | 7771(1) | | | | |
| Cl(2) | 2201(2) | 3116(3) | 6420(3) | | | | |
| Cl(3) | 4428(2) | 3122(3) | 6870(4) | | | | |
| Cl(4) | 3023(3) | 3771(3) | 9326(3) | | | | |
| Cl(5) | 3169(3) | 1157(3) | 8311(4) | | | | |
| Co(1) | 3573(1) | 2239(1) | 3088(2) | | | | |
| Cl(1) | 3231(3) | 927(3) | 1954(3) | | | | |
| N(1) | 4204(7) | 1280(9) | 4059(10) | | | | |
| C(1) | 5031(10) | 1059(11) | 3978(13) | H(1) | 5357 | 1337 | 3367 |
| C(2) | 5384(10) | 443(12) | 4759(13) | H(2) | 5959 | 288 | 4678 |
| C(3) | 4972(11) | 33(12) | 5633(16) | H(3) | 5242 | −361 | 6213 |
| C(4) | 4138(13) | 204(12) | 5692(12) | H(4) | 3805 | −113 | 6270 |
| C(5) | 3763(9) | 831(11) | 4879(12) | | | | |
| C(6) | 2840(10) | 1026(12) | 4854(13) | H(61) | 2644 | 1125 | 5625 |
| | | | | H(62) | 2571 | 455 | 4521 |
| N(2) | 2659(7) | 1918(9) | 4149(10) | H(22) | 2645 | 2525 | 4591 |
| C(7) | 1801(9) | 1817(12) | 3685(15) | H(71) | 1424 | 1749 | 4317 |
| | | | | H(72) | 1776 | 1230 | 3210 |
| C(8) | 1544(9) | 2723(13) | 2978(15) | H(81) | 970 | 2662 | 2795 |
| | | | | H(82) | 1630 | 3311 | 3439 |
| C(9) | 2014(7) | 2828(13) | 1882(13) | H(91) | 2019 | 2204 | 1471 |
| | | | | H(92) | 1747 | 3330 | 1424 |
| N(3) | 2889(7) | 3165(8) | 2125(10) | H(33) | 3267 | 3065 | 1500 |
| C(10) | 2866(10) | 4295(10) | 2254(13) | H(101) | 2362 | 4452 | 2646 |
| | | | | H(102) | 2862 | 4597 | 1503 |
| C(11) | 3565(9) | 4754(10) | 2958(13) | H(111) | 4077 | 4619 | 2575 |
| | | | | H(112) | 3483 | 5464 | 3007 |
| C(12) | 3601(10) | 4302(10) | 4152(12) | H(121) | 3049 | 4217 | 4431 |
| | | | | H(122) | 3896 | 4747 | 4655 |
| N(4) | 4015(7) | 3297(8) | 4137(11) | H(44) | 3910 | 3053 | 4900 |
| C(13) | 4924(9) | 3423(12) | 3872(13) | H(131) | 5079 | 4105 | 4015 |
| | | | | H(132) | 5236 | 2988 | 4366 |
| N(5) | 4532(7) | 2579(8) | 2127(9) | | | | |
| C(14) | 5106(8) | 3167(11) | 2638(12) | | | | |
| C(15) | 5828(8) | 3427(11) | 2100(16) | H(15) | 6224 | 3850 | 2475 |
| C(16) | 5994(10) | 3095(13) | 1010(14) | H(16) | 6509 | 3237 | 637 |
| C(17) | 5400(11) | 2525(12) | 458(15) | H(17) | 5483 | 2312 | −323 |
| C(18) | 4676(9) | 2274(12) | 1044(12) | H(18) | 4270 | 1874 | 656 |
| O(1) | 5122(14) | 509(16) | 8773(19) | | | | |

*Anisotropic thermal parameters (×$10^3$) with e.s.d.s in parentheses*

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Co(2) | 30.8(9) | 23.4(8) | 23.6(8) | 0.8(9) | 0.8(8) | −0.4(8) |
| Cl(2) | 43(2) | 55(2) | 37(2) | 7(2) | −5(2) | −8(2) |
| Cl(3) | 42(2) | 83(3) | 46(2) | 1(2) | 2(2) | 4(2) |
| Cl(4) | 68(3) | 59(3) | 37(2) | 4(2) | −1(2) | −10(2) |
| Cl(5) | 80(3) | 39(2) | 86(3) | 3(2) | 15(3) | 5(2) |
| Co(1) | 33.4(1.0) | 32.1(9) | 31.1(9) | −0.9(9) | 0.5(9) | −2.1(1.0) |
| Cl(1) | 67(3) | 47(2) | 43(2) | −13(2) | 6(3) | −11(2) |
| N(1) | 34(7) | 47(7) | 26(6) | 0(6) | 8(6) | −11(6) |
| C(1) | 56(11) | 41(9) | 37(9) | 8(8) | −1(8) | 6(7) |
| C(2) | 50(10) | 55(10) | 41(9) | 22(8) | 5(8) | 8(8) |
| C(3) | 59(12) | 43(10) | 68(12) | 18(9) | −19(10) | 1(9) |

*(continued overleaf)*

TABLE I. *(continued)*

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| C(4) | 118(16) | 49(10) | 13(7) | −2(11) | 4(9) | 1(7) |
| C(5) | 57(11) | 31(8) | 29(8) | −4(7) | 8(7) | −9(7) |
| C(6) | 81(12) | 42(9) | 37(9) | −12(9) | 30(9) | 3(7) |
| N(2) | 32(7) | 56(8) | 34(7) | 1(6) | 12(6) | 3(6) |
| C(7) | 32(8) | 76(11) | 65(10) | −17(9) | 24(7) | −1(9) |
| C(8) | 38(8) | 67(10) | 80(11) | −9(8) | −11(9) | 20(12) |
| C(9) | 25(7) | 89(10) | 49(9) | −8(8) | −19(7) | 4(10) |
| N(3) | 35(6) | 38(6) | 39(7) | 0(5) | 6(6) | 7(6) |
| C(10) | 66(10) | 40(8) | 38(8) | 13(8) | −4(8) | −13(7) |
| C(11) | 46(8) | 34(7) | 48(9) | −12(7) | −3(9) | 9(8) |
| C(12) | 44(9) | 33(8) | 46(8) | 6(7) | 1(4) | −1(7) |
| N(4) | 40(7) | 30(7) | 43(7) | 2(6) | −9(6) | −3(6) |
| C(13) | 36(8) | 48(10) | 53(10) | −9(8) | −13(8) | 3(8) |
| N(5) | 39(6) | 35(7) | 28(6) | 7(5) | −7(6) | −5(5) |
| C(14) | 34(7) | 47(8) | 31(7) | 12(7) | −6(7) | 9(7) |
| C(15) | 22(7) | 48(8) | 80(12) | −4(7) | 8(8) | 13(10) |
| C(16) | 39(9) | 73(12) | 53(9) | −4(9) | 15(8) | 7(9) |
| C(17) | 59(12) | 53(12) | 56(9) | 7(8) | 19(9) | −1(8) |
| C(18) | 53(10) | 44(8) | 37(8) | −4(9) | 7(7) | −6(8) |

TABLE II. Interatomic Distances (A) and Angles (°) with their e.s.d.s in Parentheses.

| | | | |
|---|---|---|---|
| Co(1)–Cl(1) | 2.237(4) | C(9)–N(3) | 1.50(2) |
| Co(1)–N(1) | 1.97(1) | N(3)–C(10) | 1.50(2) |
| Co(1)–N(2) | 1.96(1) | C(10)–C(11) | 1.51(2) |
| Co(1)–N(3) | 1.98(1) | C(11)–C(12) | 1.50(2) |
| Co(1)–N(4) | 1.98(1) | C(12)–N(4) | 1.49(2) |
| Co(1)–N(5) | 1.95(1) | N(4)–C(13) | 1.50(2) |
| N(1)–C(1) | 1.36(2) | C(13)–C(14) | 1.49(2) |
| N(1)–C(5) | 1.32(2) | C(14)–C(15) | 1.36(2) |
| C(1)–C(2) | 1.34(2) | C(15)–C(16) | 1.35(2) |
| C(2)–C(3) | 1.32(2) | C(16)–C(17) | 1.37(2) |
| C(3)–C(4) | 1.36(2) | C(17)–C(18) | 1.38(2) |
| C(4)–C(5) | 1.39(2) | C(18)–N(5) | 1.33(2) |
| C(5)–C(6) | 1.50(2) | C(14)–N(5) | 1.34(2) |
| C(6)–N(2) | 1.46(2) | Co(2)–Cl(2) | 2.282(4) |
| N(2)–C(7) | 1.48(2) | Co(2)–Cl(3) | 2.272(4) |
| C(7)–C(8) | 1.50(2) | Co(2)–Cl(4) | 2.238(4) |
| C(8)–C(9) | 1.48(2) | Co(2)–Cl(5) | 2.226(4) |
| | | | |
| N(1)–Co(1)–N(2) | 83.9(5) | C(6)–N(2)–C(7) | 108(1) |
| N(2)–Co(1)–N(3) | 93.7(5) | Co(1)–N(2)–C(7) | 120(1) |
| N(3)–Co(1)–N(4) | 95.9(4) | N(2)–C(7)–C(8) | 112(1) |
| N(3)–Co(1)–N(5) | 88.8(5) | C(7)–C(8)–C(9) | 113(2) |
| N(3)–Co(1)–Cl(1) | 91.0(3) | C(8)–C(9)–N(3) | 110(1) |
| N(2)–Co(1)–N(4) | 92.5(5) | C(9)–N(3)–Co(1) | 116(1) |
| N(2)–Co(1)–Cl(1) | 90.5(4) | C(9)–N(3)–C(10) | 107(1) |
| N(1)–Co(1)–N(4) | 85.7(5) | Co(1)–N(3)–C(10) | 125(1) |
| N(1)–Co(1)–Cl(1) | 87.6(3) | N(3)–C(10)–C(11) | 116(1) |
| N(1)–Co(1)–N(5) | 93.6(5) | C(10)–C(11)–C(12) | 111(1) |
| N(4)–Co(1)–N(5) | 84.2(5) | C(11)–C(12)–N(4) | 111(1) |
| N(5)–Co(1)–Cl(1) | 92.5(3) | C(12)–N(4)–Co(1) | 119(1) |
| Co(1)–N(1)–C(5) | 115(1) | Co(1)–N(4)–C(13) | 108(1) |
| N(1)–C(5)–C(6) | 116(1) | N(4)–C(13)–C(14) | 111(1) |

*(continued on facing page)*

TABLE II. *(continued)*

| | | | |
|---|---|---|---|
| C(4)–C(5)–C(6) | 123(2) | C(13)–C(14)–N(5) | 115(1) |
| C(5)–N(1)–C(1) | 118(1) | C(14)–N(5)–Co(1) | 115(1) |
| N(1)–C(1)–C(2) | 120(2) | Co(1)–N(5)–C(18) | 127(1) |
| C(1)–C(2)–C(3) | 123(2) | C(18)–N(5)–C(14) | 118(1) |
| C(2)–C(3)–C(4) | 118(2) | N(5)–C(14)–C(15) | 122(1) |
| Co(1)–N(1)–C(1) | 127(1) | C(12)–N(4)–C(13) | 110(1) |
| | | C(13)–C(14)–C(15) | 123(1) |
| C(3)–C(4)–C(5) | 120(2) | C(14)–C(15)–C(16) | 121(1) |
| C(4)–C(5)–N(1) | 121(2) | C(15)–C(16)–C(17) | 118(2) |
| C(5)–C(6)–N(2) | 110(1) | C(16)–C(17)–C(18) | 120(2) |
| C(6)–N(2)–Co(1) | 112(1) | C(17)–C(18)–N(5) | 122(2) |
| Cl(2)–Co(2)–Cl(3) | 105.1(2) | Cl(3)–Co(2)–Cl(5) | 110.0(2) |
| Cl(2)–Co(2)–Cl(4) | 109.6(2) | Cl(3)–Co(2)–Cl(4) | 111.0(2) |
| Cl(2)–Co(2)–Cl(5) | 111.2(2) | Cl(4)–Co(2)–Cl(5) | 109.8(2) |

TABLE III. Least-squares Planes with Deviations (Å) of the Relevant Atoms in Square Brackets. The equation of a plane in the direct space is given by PX + QY + RZ = S.

| | P | Q | R | S |
|---|---|---|---|---|
| | 4.0081 | 9.9675 | 6.9785 | 5.8304 |
| *Plane (1)* | | | | |
| N(1), N(2), N(3), N(5), Co(1) | | | | |
| N(1) −0.037, N(2) 0.042, N(3) −0.035, N(5) 0.041, Co(1) −0.012, N(4) 1.952, Cl(1) −2.248 | | | | |
| *Plane (2)* | 2.9993 | 10.3969 | 6.7604 | 5.3089 |
| N(1), C(1), C(2), C(3), C(4), C(5) | | | | |
| N(1) 0.027, C(1) −0.010, C(2) −0.016, C(3) 0.025, C(1) −0.008, C(5) −0.018 | | | | |
| *Plane (3)* | −7.0379 | 10.8721 | −4.1639 | −1.2573 |
| N(5), C(14), C(15), C(16), C(17), C(18) | | | | |
| N(5) −0.014, C(14) 0.009, C(15) 0.007, C(16) −0.017, C(17) 0.011, C(18) 0.004 | | | | |
| *Plane (4)* | 4.4973 | 9.9208 | 6.8756 | 5.9513 |
| Co(1), N(1), N(2) | | | | |
| C(5) −0.080, C(6) −0.319 | | | | |
| *Plane (5)* | 4.2477 | 10.1304 | 6.7241 | 5.8623 |
| Co(1), N(2), N(3) | | | | |
| C(7) −0.779, C(8) −0.446, C(9) −0.876 | | | | |
| *Plane (6)* | 12.4509 | 1.8259 | −7.0878 | 2.6688 |
| Co(1), N(3), N(4) | | | | |
| C(10) 0.086, C(11) 0.541, C(12) −0.342 | | | | |
| *Plane (7)* | −0.5440 | 0.6891 | −0.4788 | −2.7831 |
| Co(1), N(4), N(5) | | | | |
| C(13) −0.534, C(14) −0.247 | | | | |
| *Angles (°) between the planes* | | | | |
| 1–2 4.2 1–3 73.1 2–3 69.4 | | | | |

TABLE IV. Torsion Angles (°).[a]

| | |
|---|---|
| N(1)–C(5)–C(6)–N(2) | −18 |
| C(5)–C(6)–N(2)–C(7) | 154 |
| C(6)–N(2)–C(7)–C(8) | 178 |
| N(2)–C(7)–C(8)–C(9) | 67 |
| C(7)–C(8)–C(9)–N(3) | −72 |
| C(8)–C(9)–N(3)–C(10) | −83 |
| C(9)–N(3)–C(10)–C(11) | 156 |
| N(3)–C(10)–C(11)–C(12) | −57 |
| C(10)–C(11)–C(12)–N(4) | 79 |
| C(11)–C(12)–N(4)–C(13) | 69 |
| C(12)–N(4)–C(13)–C(14) | −102 |
| N(4)–C(13)–C(14)–N(5) | −21 |

[a] The torsion angle W(IJKL) is defined as the angle between the vector KL when viewed down JK. It is positive if clockwise and negative if counter-clockwise.

TABLE V. Helicity of the Conformation [12] for All Chelate Rings.

| Ring | Conformation | Helicity |
|---|---|---|
| N(1)–Co–N(2) | envelope | $\delta$ |
| N(2)–Co–N(3) | chair | nonhelical |
| N(3)–Co–N(4) | chair | $\lambda$ |
| N(4)–Co–N(5) | envelope | $\delta$ |

the configuration presented in this study to be the correct one.

The calculations were carried out on the CYBER 76 computer of the 'Centro di Calcolo Interuniversitario Italia Nord Orientale' with the SHELX-76 system of crystallographic programs [10].

## Results and Discussion

The stereochemical arrangement of the complex cation is shown in Fig. 1 along with the atom nomenclature and the crystal packing arrangement is illustrated in Fig. 2.

The final positional and thermal parameters of the atoms are listed in Table I. In Table II bond lengths and valence angles, uncorrected for changes due to thermal vibrations are given. Some least-squares planes and torsion angles are shown in Tables III and IV respectively.

The coordination geometry of the cation is near regular octahedral with the pentadentate picditn ligand present in the $\alpha,\beta$ configuration [11].

In particular two secondary-nitrogens along with the two pyridine nitrogen atoms of the picditn ligand are found to occupy the equatorial plane. The chlorine and the remaining secondary-nitrogen of picditn in axial position complete the coordination about the cobalt atom. The absolute configuration of the complex ion can be designed as $\Lambda$ [12]. Only two, *i.e.* N(2) and N(4), of the three secondary nitrogen atoms of the picditn ligand exhibit chirality; the configuration of the 'flat' nitrogen N(2) is R, whereas that of N(4) is S. The hydrogens on N(2) and N(3) point away from the coordinated chlorine Cl(1).

Inspection of the Co–N bond distances in the picditn–cobalt moiety shows that the bonds to the terminal trigonal nitrogens [Co–N(1) = 1.97(1), Co–N(5) = 1.95(1) Å] are significantly longer than predicted from radii-sum rules [13], although similar values have been already found in several crystal structures of cobalt complexes containing the pyridine ligand [14–16]. The bonds to the 'flat' and 'angular' secondary nitrogens [Co–N(2) = 1.96(1), Co–N(3) = 1.98(1), Co–N(4) = 1.98(1) Å] lie in the middle of the range of observed Co–N (tetrahedral) lengths (1.89 to 2.06 Å) [17].

There are no significant intraligand angular distorsions in the polyamine skeleton. In fact within the picditn chelate all internal angles at C and N are close to the regular tetrahedral value. The angles subtended by the two terminal five-membered chelate rings at the metal ion are similar, 83.9(5) and 84.2(5)°, and compare well with the values found in analogous compounds [16, 18]. The corresponding angles in the two central six-membered rings are significantly larger, 93.7(5) and 95.9(4)°.

All C–C and C–N distances are reasonably close to their usual values [13].

The conformation along with the helicity [12] adopted by the chelate rings are reported in Table V. The torsion angle values about the non-rigid bonds of the picditn ligand are presented in Table IV.

The Co–Cl(1) bond distance, 2.237(4) Å, is only slightly longer than the sum of appropriate covalent radii [13] and agrees closely with the Co–Cl bonds in several Co(III) complexes [15, 16]. The $CoCl_4$ anion takes a nearly regular tetrahedral configuration with a mean Co–Cl distance of 2.254(4) Å. This value agrees with those in several observed crystal structures [15]. The crystal packing arrangement, which is shown in Fig. 2, is mainly determined by coulombic forces, N–H···Cl hydrogen bonds and van der Waals interactions. In particular the cations and anions are linked in one dimensional chains approximately parallel to *c* by a hydrogen bonding system between N(2), N(3)′, N(4), C(10)′ of the cation and Cl(2), Cl(3), Cl(4) of the anion. The main features of these hydrogen bonds are reported in Table VI. The chains are connected together

TABLE VI. Possible Hydrogen-bonding Interactions.

| | | | | | |
|---|---|---|---|---|---|
| Cl(2)···N(2) | 3.14 | Cl(2)···H(22) | 2.35 | Cl(2)···H(22)–N(2) | 140° |
| Cl(3)···N(4) | 3.22 | Cl(3)···H(44) | 2.41 | Cl(3)···H(44)–N(4) | 142° |
| Cl(4)···N(3)$^{I}$ | 3.32 | Cl(4)···H(33)$^{I}$ | 2.70 | Cl(4)···H(33)$^{I}$–N(3)$^{I}$ | 124° |
| Cl(4)···C(10)$^{I}$ | 3.44 | Cl(4)···H(102)$^{I}$ | 2.74 | Cl(4)···H(102)$^{I}$–C(10)$^{I}$ | 131° |
| C(11)···Cl(2)$^{II}$ | 3.54 | H(112)···Cl(2)$^{II}$ | 2.84 | C(11)–H(112)···Cl(2)$^{II}$ | 132° |
| C(11)···Cl(4)$^{II}$ | 3.58 | H(112)···Cl(4)$^{II}$ | 3.03 | C(11)–H(112)···Cl(4)$^{II}$ | 118° |
| C(10)···Cl(2)$^{II}$ | 3.55 | H(102)···Cl(2)$^{II}$ | 3.03 | C(10)–H(102)···Cl(2)$^{II}$ | 117° |
| C(8)···Cl(3)$^{III}$ | 3.58 | H(81)···Cl(3)$^{III}$ | 2.71 | C(8)–H(81)···Cl(3)$^{III}$ | 153° |
| C(2)···Cl(4)$^{IV}$ | 3.54 | H(2)···Cl(4)$^{IV}$ | 2.83 | C(2)–H(2)···Cl(4)$^{IV}$ | 132° |

*Key for symmetry*

| | | | |
|---|---|---|---|
| I | x, y, 1 + z | II | ½ − x, 1 − y, −½ + z |
| III | −½ + x, ½ − y, 1 − z | IV | 1 − x, −½ + y, 1 − z |

through some more feeble interactions involving hydrogens belonging to carbon atoms of the cation and chlorine atoms of the anions (see Table VI).

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