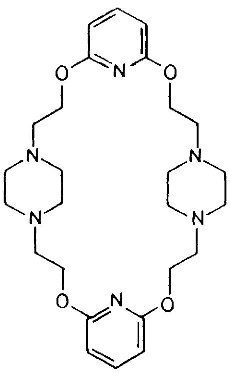
The Crystal Structures of a Macrocycle containing 2,6-Pyridino and Piperazino Subunits and of the Tetrachlorocobaltate(II) Salt of its Diprotonated Cation

By **Frank R. Fronczek, Veronica K. Majestic,** and **George R. Newkome,*** Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, U.S.A.
William E. Hunter and **Jerry L. Atwood**, Department of Chemistry, University of Alabama University, Alabama 35486, U.S.A.

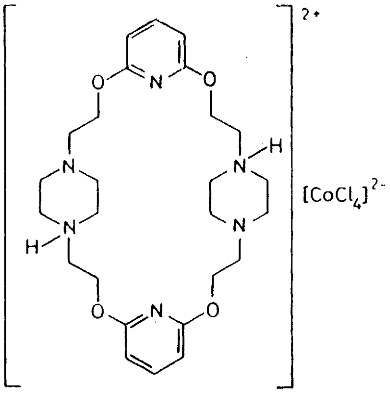
The multiheteromacrocycle $C_{26}H_{38}N_6O_4$ is prepared by reaction of 2,6-dichloropyridine with *NN'*-bis-(2-hydroxyethyl)piperazine. Counter data obtained from crystals of space group $P2_1/c$ having a = 10.498(3), b = 4.748(2), c = 26.032(8) Å, β = 96.42(2)°, and Z = 2 were used in the refinement, which converged with R 0.043 for 1 060 observed data. The molecule possesses crystallographic C_i symmetry with the piperazino subunits in the chair conformation. Reaction of this macrocycle with $CoCl_2$ has led to diprotonation. Crystals of $[C_{26}H_{40}N_6O_4][CoCl_4]$ conform to space group $P2_1/c$ with a = 15.258(6), b = 28.676(12), c = 15.538(5) Å, β = 107.18(3)°, and Z = 8. Refinement using 2 239 observed data measured on a diffractometer has yielded R 0.108. The crystal structure consists of $[C_{26}H_{40}N_6O_4]^{2+}$ ions having essentially identical conformations to the macrocycle $C_{26}H_{38}N_6O_4$, each forming two hydrogen bonds to tetrahedral $[CoCl_4]^{2-}$ ions. The Co–Cl distances within the complex anions average 2.260(8) Å. The array of $[CoCl_4]^{2-}$ anions approximates a C-centred structure with the true b axis halved.

DURING the course of our studies of macrocycles possessing one or more subheterocyclic ring(s),[1] we combined the 2,6-pyridino and 1,4-piperazino moieties into a macrocyclic framework. Synthesis of the 2 : 2-macrocycle (1) was accomplished by treatment of 2,6-dichloropyridine with the dianion of *NN'*-bis-(2-hydroxyethyl)piperazine in xylene at 140 °C for 24 h, following standard synthetic procedures.[2]

CPK models of (1) suggested that a novel cavity could be realized if the piperazine ring(s) possessed the boat conformation(s). Treatment of (1) with methanolic cobalt(II) chloride afforded a blue, cobalt-containing, crystalline product. The structure elucidation of the macrocycle (1) and characterization of the blue product (2) are described in this paper.



(1)



(2)

EXPERIMENTAL

Preparation of Macrocycle (1).—To a mixture of *NN'*-bis-(2-hydroxyethyl)piperazine (19 mmol) and excess of oil-free sodium hydride in xylene, 2,6-dichloropyridine (19 mmol) in xylene was added. The mixture was refluxed for 2 h and worked up by previously described procedures [2,3] to afford crystals (10%) of (1), m.p. 240 °C; δ ($CDCl_3$) 2.67 (16 H, s, NCH_2), 2.78 (8 H, m, NCH_2–CH_2–O), 4.46 (8 H, m, OCH_2), 6.27 (4 H, d, 3,5-pyr-H, *J* 8 Hz), and 7.45 (2 H, t, 4-pyrH, *J* 8 Hz); $\nu_{max.}$ (KBr) 1 575, 1 248, and 1 147 cm^{-1}; (Found: C, 62.65; H, 7.5; N, 16.75%; M^+, 498. Calc. for $C_{26}H_{38}N_6O_4$: C, 62.65; H, 7.6; N, 16.85; *M*, 498).

Preparation of Salt (2).—A sample (24.9 mg, 50 µmol) of macrocycle (1) was dissolved in refluxing ethyl acetate–methanol (3 : 1; 50.0 ml), to which $CoCl_2 \cdot 6H_2O$ (119 mg, 500 µmol) was added. The dark blue solution was refluxed for 4 h; dark blue crystals grew on the walls of the reaction vessel. The volume was reduced *in vacuo* and the mixture was allowed to stand overnight, then the salt was filtered, washed with ethyl acetate, and dried *in vacuo* to give dark blue crystals (66%), m.p. 255 °C (decomp.) (Found: C, 44.3; H, 5.5; N, 12.1. Calc. for $C_{26}H_{40}Cl_4CoN_6O_4$: C, 44.5; H, 5.75; N, 11.95%).

Data Collection for Macrocycle (1).—Crystals of (1) were grown by evaporation from CH_2Cl_2, and were well formed, multifaceted, colourless, and fairly equant. A crystal of dimensions 0.55 × 0.63 × 0.52 mm was mounted in a thin-walled glass capillary in random orientation on an Enraf-Nonius CAD4 diffractometer. All measurements were made using graphite-monochromatized Mo-K_α radiation (λ 0.710 73 Å) at 24 °C. Unit-cell dimensions and crystal orientation were determined from the diffractometer co-ordinates of 15 accurately-centred reflections with $\theta > 15°$.

Crystal data. $C_{26}H_{38}N_6O_4$, $M = 498.6$, space group $P2_1/c$, $a = 10.498(3)$, $b = 4.748(2)$, $c = 26.032(8)$ Å, $\beta = 96.42(2)°$, $U = 1\,289.4(8)$ Å^3, $Z = 2$, $D_c = 1.284(1)$ g cm^{-3}, μ(Mo-K_α) = 0.83 cm^{-1}.

Intensity data were collected by the ω—2θ scan technique using a scintillation counter equipped with pulse-height discriminator circuits adjusted to accept 95% of the Mo-K_α profile. All reflections in one quadrant for which $2° \leqslant 2\theta \leqslant 44°$ were measured at least once. The 2θ scan width was computed for each reflection as (0.8° + 0.20tanθ) to account for $\alpha_1 - \alpha_2$ splitting. The scan was then extended on both ends by 25% with the counts collected during these extensions taken as measurements of backgrounds. The width of the receiving aperture was varied as a function of angle [(4.0 + 2.11tanθ) mm]. A rapid (20 deg. min^{-1}) pre-scan was made for each reflection. If the pre-scan intensity exceeded 4 000 counts, it was accepted as the final measurement; if it totalled fewer than 30 counts, the intensity was flagged as unobserved; if it was intermediate between these values, the reflection was re-measured at a scan speed appropriate to yield a net intensity of 4 000 counts. An upper limit of 240 s was set for the scan time spent on any reflection. During data collection, three reflections, (0010), ($\bar{8}$00), and (0$\bar{2}$0), were periodically re-measured every 75 reflections as a monitor of crystal and instrument stability. These standards exhibited no significant decrease during the course of the experiment.

A total of 2 660 intensities were measured in the above manner, of which 1 060 were considered as ' observed ' by the diffractometer, and used in further calculations. Lorentz and polarization corrections were applied to the data, but errors due to absorption were judged to be insignificant.

Data Collection for Salt (2).—Data collection for this compound was the same as that for the macrocycle (1).

Crystal data. $C_{26}H_{40}Cl_4CoN_6O_4$, M = 701.3, space group $P2_1/c$, a = 15.258(6), b = 28.676(12), c = 15.538 (5) Å, β = 107.18(3)°, U = 6 495(4) Å^3, Z = 8, D_c = 1.432(1) g cm^{-3}, μ(Mo-K_α) = 8.96 cm^{-1}. Crystal size, 0.12 × 0.08 × 0.04 mm; angular limits, $2° \leqslant 2\theta \leqslant 42°$; scan width function, (0.90° + 0.20 tanθ); aperture function, (4.0 + 2.11 tanθ) mm; pre-scan intensity maximum, 2 000 counts; minimum, 10 counts; maximum time, 240 s; standards, (0100) and (800); 7 816 measurements; 2 239 observed.

Structure Solutions and Refinements.—Macrocycle (1). The space group is uniquely determined by systematic absences $0k0$ with k odd and $h0l$ with l odd, and $Z = 2$ requires that the molecule be centrosymmetric. The structure was solved by routine application of the multiple-solution direct-phasing method [4] using program MULTAN 74. All 18 non-hydrogen atoms of the structure were located from the highest overall figure-of-merit E-map. Machine calculations were conducted on an IBM 3033 computer using primarily the X-RAY 72 system of programs.[5]

The model was refined by blocked matrix least squares techniques using unit weights, and the function minimized was $\Sigma(|F_o|-|F_c|)^2$. Non-hydrogen atoms were treated anisotropically, while hydrogen atoms were fixed in calculated positions, 1.08 Å distant from the carbon atoms to which they are bonded, with thermal parameters refined isotropically. Neutral atom scattering factors for C, N, and O were taken from the compilation of Cromer and Mann; [6] H atom scattering factors were those of Stewart *et al.*[7] Secondary extinction was a problem; an extinction coefficient was included in the refinement. It refined to a value $65\sigma > 0$, with considerable improvement in the fit to the data. Refinement converged with $R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$ = 0.043 and goodness of fit = $\{[|F_o|-|F_c|^2/(\text{NOBS}-\text{NVAR})]\}^{\frac{1}{2}}$ = 0.95 for NOBS = 1 060 observations and NVAR = 183 variables. A difference-Fourier synthesis calculated at the conclusion of the refinement exhibited no feature greater than ±0.22 e Å^{-3}. Refined co-ordinates for the non-hydrogen atoms are given in Table 1; anisotropic temperature factors for these atoms, parameters for hydrogen atoms and thermal parameters are given in Supplementary Publication No. SUP 22946 (22 pp.).*

Salt (2). Solving the structure of this compound was difficult, due to the weakness of the diffraction pattern, uncertainty of the identity of the compound, and the existence of a superlattice, which obscured the correct space group and cell dimensions. The positions of the two independent cobalt atoms near $0,0,\frac{1}{4}$ and $\frac{1}{2},\frac{1}{4},\frac{1}{4}$ in $P2_1/c$ create an approximate unit cell which resembles space group $C2/c$ with b = 14.34 Å. The true cell was not recognized until careful examination of precession photographs revealed weak nets of reflections with k odd and a few non-extinct h odd reflections in the k even nets of the $P2_1/c$ cell. Once the correct space group and cell dimensions were realized, the problem was simplified to that of locating the two independent formula units in the asymmetric unit based upon very weak and limited data. The two $[CoCl_4]^{2-}$ anions were located based upon a Patterson map, and the 72 atoms of the two independent macrocyclic cations were eventually located by standard Fourier procedures.

TABLE 1

Co-ordinates (× 10^4) and equivalent isotropic temperature factor [a] for macrocycle $C_{26}H_{38}N_6O_4$ (1)

Atom	X	Y	Z	U_{eq}
O(1)	8 795(2)	7 630(4)	7 182(1)	0.048(2)
O(2)	6 295(2)	12 620(5)	5 920(1)	0.055(2)
N(1)	7 547(2)	10 087(5)	6 545(1)	0.042(2)
N(2)	11 302(2)	7 659(4)	6 271(1)	0.038(2)
N(3)	12 607(2)	8 359(5)	5 358(1)	0.039(2)
C(1)	7 799(3)	9 413(5)	7 036(1)	0.041(2)
C(2)	7 107(3)	10 350(6)	7 425(1)	0.049(2)
C(3)	6 110(3)	12 163(8)	7 287(2)	0.054(2)
C(4)	5 823(3)	12 982(7)	6 777(1)	0.053(2)
C(5)	6 570(3)	11 863(6)	6 422(1)	0.044(2)
C(6)	9 541(3)	6 600(5)	6 786(1)	0.045(2)
C(7)	10 513(3)	8 724(6)	6 658(1)	0.043(2)
C(8)	12 483(3)	9 326(7)	6 278(1)	0.049(2)
C(9)	13 305(3)	8 210(8)	5 879(1)	0.053(2)
C(10)	10 613(3)	7 835(7)	5 748(1)	0.049(2)
C(11)	11 426(3)	6 747(6)	5 352(1)	0.047(2)
C(12)	13 405(3)	7 350(7)	4 971(1)	0.048(2)
C(13)	12 910(3)	8 502(8)	4 442(1)	0.054(2)

[a] $U_{eq} = (U_1U_2U_3)^{1/3}$, where the U_i values are principle radii of the thermal ellipsoids.

The model was refined by blocked least-squares techniques, employing unit weights, and minimizing the function $\Sigma(|F_o|-|F_c|)^2$. Cobalt and chlorine were treated anisotropically, while C, N, and O were refined isotropically. The 76 hydrogen atoms bonded to carbon were placed in calculated positions, the four hydrogen atoms bonded to nitrogen were placed in positions deduced from the hydrogen-bonding pattern, and no hydrogen atoms were refined. Convergence was achieved with R 0.108 and goodness of fit = 2.4 for NOBS = 2 239 and NVAR = 380. A difference-Fourier synthesis calculated at the conclusion of the refinement exhibited no residuals greater than ±0.30 e Å^{-3}. Co-ordinates and isotropic or equivalent isotropic temperature factors are listed in Table 2; anisotropic temperature factors, assigned hydrogen atom co-ordinates, and thermal parameters are given in SUP 22946.

DISCUSSION

Structure Descriptions.—Macrocycle (1). The conformation of the unprotonated macrocycle is illustrated in the stereopair [8] in Figure 1. Notable features are its crystallographic C_i point symmetry and the chair conformation of the piperazine subrings. The conformation of the 2,6-disubstitution of the pyridine subrings is

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 2*, 1980, Index Issue.

essentially *cis* to the nitrogen atom, as uniformly found in a series of related compounds recently investigated.[2,9]

Distances and angles involving bonds between positionally refined atoms are listed in Table 3; no unusual bonding is noted. Average bond distances for some chemically equivalent bonds are: 1.328(4) for aromatic C–N, 1.383(3) for aromatic C–C, 1.464(2) for aliphatic C–N, and 1.511(4) Å for aliphatic C–C bonds. Bond angles about the piperazine nitrogen atoms average 110.1(5) Å. Important torsion angles are given in Table 4. No unusually close intermolecular contacts exist in the crystal.

TABLE 2

Co-ordinates (× 10^4) and thermal parameters [a] for $[C_{26}H_{40}N_6O_4]^{2+}[CoCl_4]^{2-}$ (2)

Atom	X	Y	Z	U_{iso} or U_{eq}
Co(1)	−0 171(3)	0 262(2)	2 412(3)	0.049(4)
Co(2)	4 809(3)	7 788(2)	2 540(3)	0.046(3)
Cl(1)	−1 496(6)	0 649(4)	2 212(7)	0.069(8)
Cl(2)	−0 421(6)	−0.292(3)	1 319(6)	0.054(6)
Cl(3)	4 660(7)	7 272(5)	1 427(9)	0.089(10)
Cl(4)	3 491(7)	8 218(5)	2 202(7)	0.073(8)
Cl(5)	0 136(6)	−0 175(4)	3 684(7)	0.068(8)
Cl(6)	1 048(6)	0 721(4)	2 507(7)	0.073(8)
Cl(7)	6 068(7)	8 236(4)	2 816(7)	0.084(6)
Cl(8)	5 039(8)	7 388(5)	3 833(7)	0.094(9)
N(1)	1 936(18)	2 025(9)	24(17)	0.052(8)
N(2)	3 282(17)	2 130(9)	3 546(16)	0.046(7)
N(3)	3 389(16)	1 131(8)	3 571(15)	0.039(7)
N(4)	6 762(19)	468(10)	5 130(18)	0.059(8)
N(5)	1 819(17)	4 632(9)	1 225(17)	0.050(8)
N(6)	1 592(19)	3 623(10)	1 135(18)	0.061(8)
N(7)	9 475(18)	2 602(9)	3 757(17)	0.048(8)
N(8)	7 726(15)	2 109(8)	985(15)	0.032(6)
N(9)	6 356(17)	1 606(9)	1 539(16)	0.046(7)
N(10)	5 736(18)	169(10)	1 137(18)	0.049(8)
N(11)	7 586(17)	4 560(9)	4 017(16)	0.045(7)
N(12)	8 756(14)	4 028(7)	3 286(14)	0.024(6)
O(1)	2 823(15)	3 339(8)	4 225(14)	0.057(6)
O(2)	4 018(14)	−104(7)	3 956(13)	0.051(6)
O(3)	7 470(17)	836(9)	4 245(17)	0.082(8)
O(4)	1 134(13)	2 382(7)	834(13)	0.044(6)
O(5)	8 778(14)	2 192(7)	4 608(14)	0.054(6)
O(6)	4 945(15)	582(8)	1 943(15)	0.064(7)
O(7)	3 534(15)	4 695(8)	4 610(15)	0.065(7)
O(8)	10 141(15)	3 030(8)	2 833(14)	0.061(7)
C(1)	1 437(23)	1 961(12)	503(22)	0.058(10)
C(2)	1 078(21)	1 578(12)	774(20)	0.043(9)
C(3)	1 429(22)	1 191(12)	425(22)	0.052(10)
C(4)	1 966(19)	3 824(9)	4 891(18)	0.029(8)
C(5)	2 243(22)	3 351(12)	4 704(22)	0.057(10)
C(6)	3 308(21)	2 894(11)	4 184(20)	0.048(9)
C(7)	2 801(21)	2 567(11)	3 564(20)	0.045(10)
C(8)	2 863(20)	1 888(11)	2 704(20)	0.042(9)
C(9)	3 351(21)	1 387(11)	2 709(20)	0.041(9)
C(10)	3 327(23)	1 873(12)	4 380(21)	0.054(10)
C(11)	3 876(24)	1 410(13)	4 365(22)	0.059(10)
C(12)	3 838(24)	684(13)	3 528(23)	0.067(11)
C(13)	3 595(22)	326(12)	4 099(21)	0.055(10)
C(14)	6 213(19)	491(10)	5 637(18)	0.033(8)
C(15)	5 863(21)	920(11)	5 907(20)	0.044(9)
C(16)	6 145(21)	1 309(11)	5 556(21)	0.046(9)
C(17)	6 645(26)	1 269(14)	5 003(25)	0.078(12)
C(18)	6 972(26)	862(15)	4 818(26)	0.079(12)
C(19)	8 099(25)	410(13)	4 326(23)	0.058(11)
C(20)	2 459(22)	5 053(12)	1 314(22)	0.055(10)
C(21)	1 780(26)	4 326(14)	419(25)	0.064(12)
C(22)	1 203(25)	3 945(13)	363(24)	0.058(11)
C(23)	2 290(23)	4 294(12)	2 036(22)	0.057(10)
C(24)	1 633(20)	3 882(10)	1 938(19)	0.040(9)
C(25)	1 111(20)	3 191(11)	1 108(19)	0.041(8)
C(26)	1 498(22)	2 828(12)	628(21)	0.052(10)
C(27)	9 930(20)	2 628(11)	3 135(19)	0.035(9)
C(28)	10 122(22)	2 247(12)	2 703(22)	0.051(10)
C(29)	9 959(20)	1 821(11)	2 975(20)	0.043(9)
C(30)	9 443(22)	1 774(12)	3 615(21)	0.048(10)
C(31)	9 282(24)	2 127(14)	4 003(24)	0.065(11)
C(32)	8 553(22)	2 392(12)	−65(22)	0.057(10)
C(33)	8 050(22)	2 507(11)	590(21)	0.047(9)
C(34)	7 527(22)	2 214(12)	1 780(21)	0.053(10)
C(35)	7 210(24)	1 816(13)	2 238(23)	0.064(11)
C(36)	6 863(19)	1 897(10)	292(18)	0.032(8)
C(37)	6 585(22)	1 454(12)	679(21)	0.052(10)
C(38)	6 100(24)	1 163(13)	2 043(23)	0.065(11)
C(39)	5 131(23)	974(12)	1 471(22)	0.054(10)
C(40)	5 200(26)	168(14)	1 683(26)	0.072(12)
C(41)	4 944(27)	−265(16)	2 034(27)	0.082(13)
C(42)	4 763(23)	4 341(13)	3 196(23)	0.055(10)
C(43)	4 313(22)	4 301(12)	3 807(22)	0.052(10)
C(44)	4 056(19)	4 748(11)	4 072(18)	0.032(8)
C(45)	6 755(20)	4 854(10)	5 050(19)	0.042(9)
C(46)	7 320(20)	5 007(11)	4 453(20)	0.042(9)
C(47)	8 355(22)	4 340(12)	4 525(22)	0.055(10)
C(48)	8 576(18)	3 920(10)	4 152(18)	0.029(8)
C(49)	7 742(18)	4 704(10)	3 166(17)	0.028(8)
C(50)	7 948(25)	4 241(13)	2 688(24)	0.071(11)
C(51)	9 000(20)	3 595(10)	2 815(19)	0.038(8)
C(52)	9 949(21)	3 443(11)	3 243(20)	0.045(9)

[a] The definition of the isotropic temperature factor is $\exp(-8\pi^2 U_{iso}\sin^2\theta/\lambda^2)$.

Salt (2). The precision of the determination of the $[C_{26}H_{40}N_6O_4]^{2+}[CoCl_4]^{2-}$ crystal structure is insufficient to allow meaningful comment about bond distances or angles. The standard deviations in typical bond distances within the macrocyclic cation are *ca.* 0.06—0.08 Å, and typical bond angle e.s.d.s are 2—4°. The determination does, however, reveal the identity of the substance, the conformation of the macrocyclic cation, and the packing of ions into the crystal. Comparison of the two independent macrocyclic cations of the asymmetric unit reveals their conformations to be quite similar to each

TABLE 3

Distances (Å) and angles (°) in macrocycle $C_{26}H_{38}N_6O_4$ (1)

Atoms	Distance or angle	Atoms	Distance or angle
O(1)–C(1)	1.362(3)	C(2)–C(3)	1.372(5)
O(1)–C(6)	1.446(3)	C(1)–C(2)–C(3)	116.9(3)
C(1)–O(1)–C(6)	118.0(2)	C(3)–C(4)	1.388(5)
O(2)–C(5)	1.353(4)	C(2)–C(3)–C(4)	120.5(3)
O(2)–C(13)	1.432(4)	C(4)–C(5)	1.381(4)
C(5)–O(2)–C(13)	117.0(2)	C(3)–C(4)–C(5)	117.1(3)
N(1)–C(1)	1.319(4)	O(2)–C(5)–N(1)	118.2(2)
N(1)–C(5)	1.337(4)	O(2)–C(5)–C(4)	117.8(3)
C(1)–N(1)–C(5)	116.8(2)	N(1)–C(5)–C(4)	124.0(3)
N(2)–C(7)	1.464(4)	C(6)–C(7)	1.501(4)
N(2)–C(8)	1.472(4)	O(1)–C(6)–C(7)	111.5(2)
N(2)–C(10)	1.467(5)	N(2)–C(7)–C(6)	111.8(2)
C(7)–N(2)–C(8)	110.3(2)	C(8)–C(9)	1.516(5)
C(7)–N(2)–C(10)	111.0(2)	N(2)–C(8)–C(9)	110.1(2)
C(8)–N(2)–C(10)	108.1(2)	N(3)–C(9)–C(8)	110.6(3)
N(3)–C(9)	1.466(3)	C(10)–C(11)	1.504(4)
N(3)–C(11)	1.454(4)	N(2)–C(10)–C(11)	111.1(3)
N(3)–C(12)	1.461(4)	N(3)–C(11)–C(10)	111.2(2)
C(9)–N(3)–C(11)	108.8(2)	C(12)–C(13)	1.513(5)
C(9)–N(3)–C(12)	110.7(2)	N(3)–C(12)–C(13)	110.0(2)
C(11)–N(3)–C(12)	111.9(3)	O(2)–C(13)–C(12)	107.2(2)
C(1)–C(2)	1.390(4)		
O(1)–C(1)–N(1)	119.2(2)		
O(1)–C(1)–C(2)	116.1(2)		
N(1)–C(1)–C(2)	124.6(3)		

other and to the conformation of the unprotonated macrocycle in the crystal of (1). The two independent $[CoCl_4]^{2-}$ ions are essentially regular tetrahedra with Co–Cl distances averaging 2.262(8) and 2.258(9) Å.

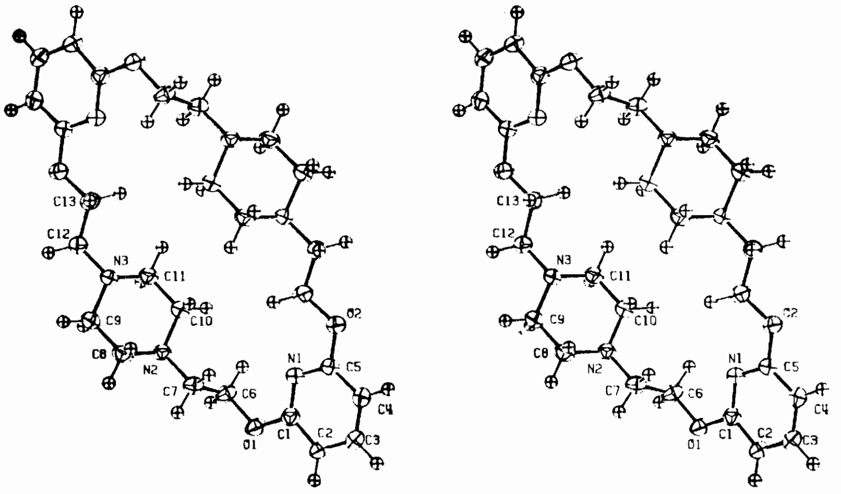

FIGURE 1 Stereoscopic representation of the unprotonated macrocycle. Ellipsoids are drawn at the 40% probability level, and hydrogen atoms are represented by spheres of arbitrary radius

Packing within the crystal is typical of ionic compounds, and is determined by the formation of N–H · · · Cl hydrogen bonds between cations and anions. Distribution of ions within the unit cell is illustrated in Figure 2.

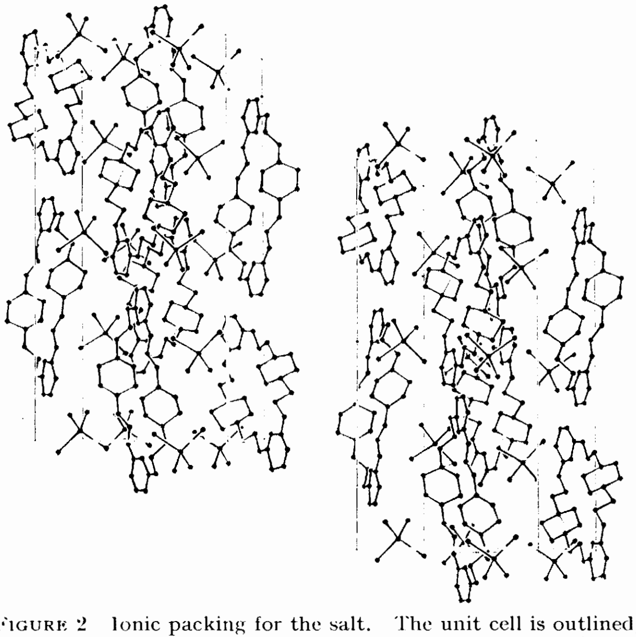

FIGURE 2 Ionic packing for the salt. The unit cell is outlined, and hydrogen bonds are indicated. For the sake of clarity, hydrogen atoms have been omitted. The origin is at lower left (foreground). the *a* axis points into the paper, and *b* is nearest vertical

Each macrocyclic cation is surrounded by six $[CoCl_4]^{2-}$ anions, and is hydrogen-bonded to two of them. The hydrogen bonds are approximately linear, and N · · · Cl distances fall within the range 3.09(4)—3.17(4) Å, averaging 3.13(2) Å, thus these forces appear to be strong. Each complex anion forms contacts to portions of six macrocyclic cations, accepting hydrogen bonds from two of them.

Examination of Figure 2 clarifies the troublesome pseudosymmetry. Not only do the two $[CoCl_4]^{2-}$ anions have nearly identical orientations in the unit cell, they also are situated near 0,0,$\frac{1}{4}$ and $\frac{1}{2},\frac{1}{4},\frac{1}{4}$, giving rise to the approximate *C*-centred structure with subcell one-half the volume of the real unit cell. The macrocyclic cations do not conform to this pseudosymmetry, and are mainly responsible for the weak *k* odd reflections.

Conclusions.—The multiheteromacrocycle (1), prepared by a simple procedure, was originally envisioned as a possible tetradentate chelating agent for transition metal ions. Model building indicates that, if both piperazine rings were placed in the ' boat ' conformation, all four piperazine nitrogen atoms might be expected to co-ordinate the same metal ion, and thus form a stable complex. The results of the crystal structure analysis of this macrocycle have shown that the piperizine rings exist in the ' chair ' conformation in the solid, and the molecule is actually not very flexible. Attempted preparation of a Co^{II} complex of this macrocycle has led to diprotonation instead of complexation. The acid responsible for protonation of the relatively strongly basic macrocycle is undoubtedly an aquacobalt(II) complex.

TABLE 4

Torsion angles within the piperazino-ring of the unprotonated macrocycle (1)

Atoms	Torsion angle (°)
N(2)–C(8)–C(9)–N(3)	59.9(3)
C(8)–C(9)–N(3)–C(11)	−57.9(4)
C(9)–N(3)–C(11)–C(10)	57.9(4)
N(3)–C(11)–C(10)–N(2)	−59.7(3)
C(11)–C(10)–N(2)–C(8)	58.8(4)
C(10)–N(2)–C(8)–C(9)	−58.8(4)

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