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The Crystal Structure of a Five-Coordinate Copper(II) Macrocyclic Complex: Chloro-(2,7,12-trimethyl-3,7,11,17-tetraazabicyclo[11,3,1]heptadeca-1(17),2,11,13,15-pentaene)copper(II) Nitrate Dihydrate

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The structure of a five-coordinate copper(II) macrocyclic complex $Cu(C_{16}H_{24}N_4)(Cl)(NO_3).2H_2O$ has been elucidated by Patterson and Fourier methods and refined by least-squares calculations to R = 0·108 for 2190 independent counter reflexions. The triclinic cell, space group $P\bar{1}$, with a = 15·90 (5), b = 14·47 (5), c = 10·39 (5) Å, α = 103·4 (2)°, β = 88·6 (2)°, γ = 114·4 (2)° contains four molecules of the complex. The Cu atom has distorted square pyramidal coordination and is bonded to four N atoms of the macrocycle and an apical Cl^- ion. The average Cu–Cl distance is 2·50 Å. There is extensive hydrogen bonding *via* water molecules.

Introduction

Macrocyclic compounds are now established as an important class of ligand in chemical and biochemical systems. In particular, their potential tightness of binding as compared with acyclic ligands enables them to influence more strongly the metal ion which they chelate, and their rigidity enables their chemistry to be more easily interpreted. Macrocyclic ligands of the type CR, first prepared by Busch and coworkers (Curry & Busch, 1964; Cummings & Busch, 1970; Lindoy & Busch, 1971), leave one or more vacant coordination sites for further ligating groups.

Thus the effect of the metal's overall coordination geometry upon a small ligand molecule is open to study, giving results of chemical and indirectly of biochemical interest, in this case with respect to the thermodynamics (Prince & Woolley, 1972) and kinetics (Woolley, 1974) of bound species.

As X-ray structural data are limited to two compounds containing respectively Ni(II)CR and $Ni(II)CRH_4$ (reduced at the Schiff-base groups), we have examined the structure of a further derivative, containing Cu(II). The N atom in position 7 of the macrocycle is methylated and the ligand is referred to here as N–MeCR. The choice of the salt used was determined by the ease of obtaining crystals; amorphous particles were obtained with most counterions. We hope to extend this series further.

Experimental

The preparation of the derivative $Cu(N\text{–}MeCR)Cl(ClO_4)$ has been described (Prince, Stotter & Woolley, 1974). This compound was passed down an Amberlite column to replace perchlorate with chloride ions. To the resulting solution, two equivalents of $NaNO_3$ were added and the mixture allowed to evaporate slowly until crystals formed. These were dried at room temperature, as they returned to powder on warming.

Preliminary Weissenberg photographs showed that the crystals were triclinic. The odd layer-lines on the b-axis rotation photograph were extremely weak implying repetition of the structure with a period half that of the true repeat along b. Density measurement (density gradient column containing CCl_4 and m-xylene) indicated Z = 4.

Table 1. *Crystal data*

$Cu(C_{16}H_{24}N_4)(Cl)(NO_3).2H_2O$	
M.W.	469·0
Space group	$P\bar{1}$
a = 15·90 (5) Å	
b = 14·47 (5)	
c = 10·39 (5)	D_m = 1·48 g cm^{-3}
α = 103·4 (2)°	D_c = 1·47 g cm^{-3} for Z = 4
β = 88·6 (2)	
γ = 114·4 (2)	μ(Mo $K\alpha$) = 12·24 cm^{-1}
V = 2112·7 Å^3	$F(000)$ = 980·0

The first crystal selected for intensity measurements disintegrated in the X-ray beam. A second specimen cut into a rough cube of dimensions 0·38 × 0·43 × 0·25 mm was used for data collection with the X-ray generator operating at 0·75 kW (half the original power). Accurate cell parameters (Table 1) were obtained from a least-squares analysis of the settings of 25 reflexions measured on a Philips PW 1100 four-circle diffractometer. With graphite-monochromated Mo $K\alpha$ radia-

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tion ($\lambda = 0{\cdot}7107$ Å), a 2θ range from 6° to 38° was explored by the ω–2θ scan technique (scan width 1·4°θ, scan speed 0·1 °θ s^{-1}), counting the background for the same time as taken for the peak scan.

The large errors in the cell dimensions are due to the mosaic spread of the crystals. 3381 reflexions were counted, 1789 of which had $I_{\rm rel} < 1{\cdot}65\sigma(I_{\rm rel})$. Lorentz–polarization corrections were applied but, since the maximum value of μR was 0·3, no corrections for absorption were made (*International Tables for X-ray Crystallography*, 1968). Three reference reflexions were monitored after every 240 measured reflexions. Their intensities showed a rather high variation (up to 8%) due to crystal decomposition, resulting in rather poor-quality intensity data.

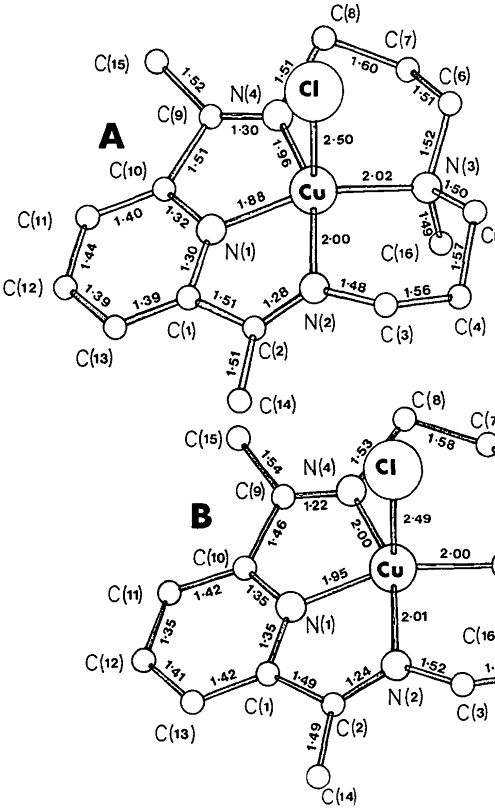

Fig. 1. Bond lengths (Å) in the two independent complexed macrocycles.

Solution and refinement of the structure

The structure was solved in the space group $P\bar{1}$. From the observation of weak odd layer-lines on the *b*-axis rotation photograph and the presence of four molecules in the cell, it was concluded that the Cu positions were related in pairs x,y,z and $x,\frac{1}{2}+y,z$ and the corresponding centrosymmetric positions. This model was consistent with the presence of a peak of height close to the origin height at $0,\frac{1}{2},0$ in the Patterson map. Analysis of rotation peaks gave four sets of positions for the two unique Cu atoms. An electron density map phased on one set revealed 27 peaks in chemically reasonable positions. All the remaining atoms were located in successive electron density maps. After several cycles of full-matrix least-squares refinement [X-RAY program system (1972)] with isotropic temperature factors assigned to all 56 non-hydrogen atoms of the asymmetric unit, R was 0·17. Several cycles of refinement with anisotropic temperature factors assigned to the Cu and Cl atoms yielded an average Δ/σ ratio of 0·14, indicating satisfactory convergence of all parameters. Since corresponding atoms of the two molecules comprising the asymmetric unit have coordinates differing only by approximately 0·5 in y, information about the differences between the individual molecules is contained in the reflexions of very weak intensity. Most of these reflexions had $I_{\rm rel} < 1{\cdot}65\sigma(I_{\rm rel})$. With the option that reflexions would be included if they calculated greater than the observed, 598 of these weak reflexions contributed in the last cycle of refinement. The final R, based on 2190 reflexions, was 0·108 with unit weight assigned to each reflexion.* The quality of the reflexion data did not warrant anisotropic refinement of the C, N and O atoms although a final difference map gave evidence of their anisotropic motion. H atoms were not located.

The scattering factors were those of the HFS model (Hanson, Herman, Lea & Skillman, 1964). Anomalous dispersion corrections were applied to the Cu and Cl scattering curves (*International Tables for X-ray Crystallography*, 1968). Final atomic positional and thermal parameters are listed in Table 2.

Table 2. *Final atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters* ($\times 10^3$)

Anisotropic temperature factors refer to the expression $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*) \times 10^3]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu*A*	2395 (2)	3925 (2)	3522 (3)	42 (2)	52 (2)	43 (2)	25 (2)	3 (1)	10 (2)
Cl*A*	2147 (5)	2396 (5)	4454 (7)	88 (5)	54 (4)	58 (5)	36 (4)	7 (4)	14 (4)
Cu*B*	2393 (2)	8923 (2)	3523 (3)	46 (2)	52 (2)	37 (2)	27 (2)	5 (1)	9 (1)
Cl*B*	2160 (5)	7400 (5)	4452 (6)	95 (5)	56 (4)	51 (4)	41 (4)	7 (4)	25 (3)

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* The observed and calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30849 (28 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2 (*cont.*)

	x	y	z	U_{iso}
N(1)*A*	3676 (13)	4728 (15)	3571 (19)	48 (6)
N(2)*A*	2610 (12)	4967 (14)	5266 (18)	41 (5)
N(3)*A*	1066 (13)	3641 (14)	3083 (19)	50 (6)
N(4)*A*	2654 (13)	3293 (14)	1768 (18)	43 (5)
C(1)*A*	4088 (16)	5531 (18)	4564 (23)	44 (6)
C(2)*A*	3444 (15)	5641 (17)	5620 (22)	41 (6)
C(3)*A*	1866 (17)	4851 (19)	6185 (25)	59 (7)
C(4)*A*	947 (20)	4623 (22)	5400 (29)	73 (9)
C(5)*A*	547 (19)	3572 (21)	4307 (27)	65 (8)
C(6)*A*	574 (19)	2563 (22)	2147 (29)	71 (9)
C(7)*A*	1000 (19)	2438 (21)	842 (28)	67 (8)
C(8)*A*	1954 (20)	2315 (22)	842 (29)	72 (9)
C(9)*A*	3511 (16)	3636 (17)	1478 (22)	42 (6)
C(10)*A*	4140 (15)	4557 (17)	2541 (22)	41 (6)
C(11)*A*	5079 (17)	5135 (19)	2425 (24)	49 (7)
C(12)*A*	5499 (18)	5955 (20)	3605 (26)	58 (8)
C(13)*A*	5027 (17)	6179 (18)	4685 (24)	50 (7)
C(14)*A*	3741 (17)	6428 (18)	6939 (24)	54 (7)
C(15)*A*	3924 (17)	3216 (19)	270 (25)	48 (7)
C(16)*A*	1033 (19)	4482 (21)	2507 (27)	67 (8)
N(5)*A*	2981 (18)	5045 (18)	−361 (24)	68 (7)
O(1)*A*	3747 (19)	5570 (20)	200 (26)	122 (9)
O(2)*A*	2883 (16)	4313 (18)	−1375 (24)	104 (7)
O(3)*A*	2305 (23)	5105 (24)	2 (31)	152 (11)
O(4)*A*	3743 (13)	1880 (14)	2765 (18)	74 (6)
O(5)*A*	1744 (17)	2227 (19)	7434 (27)	105 (8)
N(1)*B*	3721 (11)	9771 (12)	3585 (15)	24 (4)
N(2)*B*	2618 (12)	9966 (14)	5280 (18)	40 (5)
N(3)*B*	1076 (13)	8634 (15)	3080 (19)	51 (5)
N(4)*B*	2669 (13)	8296 (14)	1730 (18)	46 (5)
C(1)*B*	4123 (15)	10583 (17)	4642 (22)	38 (6)
C(2)*B*	3430 (15)	10610 (17)	5624 (21)	37 (6)
C(3)*B*	1843 (16)	9848 (18)	6195 (23)	46 (7)
C(4)*B*	946 (18)	9630 (20)	5416 (26)	59 (7)
C(5)*B*	580 (18)	8632 (20)	4348 (26)	62 (8)
C(6)*B*	604 (18)	7577 (20)	2179 (27)	62 (8)
C(7)*B*	993 (19)	7453 (21)	785 (28)	68 (8)
C(8)*B*	1914 (18)	7300 (20)	886 (26)	59 (7)
C(9)*B*	3480 (17)	8621 (18)	1487 (23)	46 (6)
C(10)*B*	4121 (15)	9522 (16)	2478 (21)	38 (6)
C(11)*B*	5087 (16)	10151 (18)	2518 (24)	47 (7)
C(12)*B*	5553 (18)	10962 (20)	3557 (26)	57 (7)
C(13)*B*	5090 (16)	11203 (18)	4675 (23)	48 (6)
C(14)*B*	3791 (18)	11434 (19)	6884 (26)	59 (7)
C(15)*B*	3897 (23)	8163 (26)	287 (34)	72 (11)
C(16)*B*	1045 (19)	9472 (21)	2467 (27)	68 (8)
N(5)*B*	2941 (23)	10014 (23)	−393 (31)	98 (9)
O(1)*B*	3687 (19)	10527 (20)	189 (26)	119 (8)
O(2)*B*	2893 (17)	9300 (19)	−1342 (25)	113 (8)
O(3)*B*	2276 (25)	10054 (26)	−36 (34)	168 (12)
O(4)*B*	3714 (13)	6877 (14)	2789 (19)	76 (6)
O(5)*B*	1752 (18)	7246 (19)	7437 (27)	104 (8)

Description of the structure and discussion

Bond lengths and angles are listed in Tables 3 and 4 respectively. All calculations were performed with the X-RAY 72 program system.

Two independent macrocycles and their associated ions comprise the asymmetric unit. For the purpose of general description, the structures of these two assemblages *A* and *B*, may be considered identical, every atom of macrocycle *B* being effectively generated from the corresponding *A* atom by the addition of 0·5 to y. In addition, two water molecules of crystallization are associated with each macrocycle.

Bond lengths in the ligands are shown in Fig. 1. For clarity, the nitrate ions and water molecules have been omitted. Cu is five-coordinate; four of the donor atoms are the N atoms of the macrocycle and the fifth is a

Table 3. *Bond lengths* (Å) *and their e.s.d.'s in parentheses*

Macrocycle *A*		Macrocycle *B*	
Cu—Cl	2·50 (1)	Cu—Cl	2·49 (1)
Cu—N(1)	1·88 (2)	Cu—N(1)	1·95 (2)
Cu—N(2)	2·00 (2)	Cu—N(2)	2·01 (2)
Cu—N(3)	2·02 (2)	Cu—N(3)	2·00 (2)
Cu—N(4)	1·96 (2)	Cu—N(4)	2·00 (2)
N(1)—C(1)	1·30 (3)	N(1)—C(1)	1·35 (2)
N(1)—C(10)	1·32 (3)	N(1)—C(10)	1·35 (3)
C(1)—C(13)	1·39 (3)	C(1)—C(13)	1·42 (3)
C(10)–C(11)	1·40 (3)	C(10)–C(11)	1·42 (3)
C(11)–C(12)	1·44 (3)	C(11)–C(12)	1·35 (3)
C(12)–C(13)	1·39 (4)	C(12)–C(13)	1·41 (4)
C(1)—C(2)	1·51 (3)	C(1)—C(2)	1·49 (3)
C(10)–C(9)	1·51 (3)	C(10)–C(9)	1·46 (3)
C(2)—C(14)	1·51 (3)	C(2)—C(14)	1·49 (3)
C(9)—C(15)	1·52 (4)	C(9)—C(15)	1·54 (4)
N(4)—C(9)	1·30 (3)	N(4)—C(9)	1·22 (3)
N(2)—C(2)	1·28 (3)	N(2)—C(2)	1·24 (3)
N(2)—C(3)	1·48 (3)	N(2)—C(3)	1·52 (3)
N(4)—C(8)	1·51 (3)	N(4)—C(8)	1·53 (3)
C(3)—C(4)	1·56 (4)	C(3)—C(4)	1·54 (4)
C(7)—C(8)	1·60 (5)	C(7)—C(8)	1·58 (5)
C(4)—C(5)	1·57 (4)	C(4)—C(5)	1·50 (3)
C(6)—C(7)	1·51 (4)	C(6)—C(7)	1·56 (4)
C(5)—N(3)	1·50 (3)	C(5)—N(3)	1·52 (3)
C(6)—N(3)	1·52 (3)	C(6)—N(3)	1·48 (3)
N(3)—C(16)	1·49 (4)	N(3)—C(16)	1·51 (4)
N(5)—O(1)	1·21 (3)	N(5)—O(1)	1·19 (4)
N(5)—O(2)	1·27 (3)	N(5)—O(2)	1·23 (4)
N(5)—O(3)	1·16 (5)	N(5)—O(3)	1·13 (6)

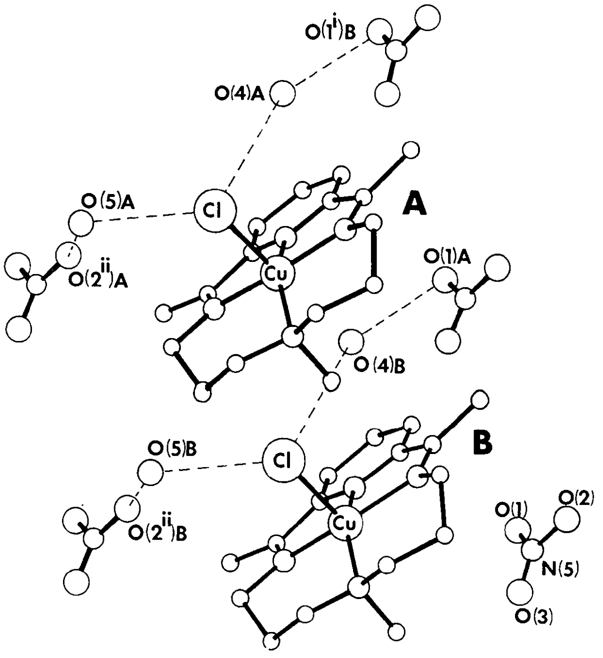

Fig. 2. Hydrogen bonding [involving hydrate oxygens O(4) and O(5)], represented by dashed lines.

Cl^- ion at the apex of a distorted square pyramid. The Cu–Cl distances of 2·50 (1) and 2·49 (1) Å are slightly longer than the analogous lengths (2·431 Å) found in bis-(6-hydroxypurine)copper(II) chloride trihydrate (Sletten, 1970). The closest approach of a water O to Cu is 4·2 Å.

Tension in the N-MeCR ring tends to bring about distortion of a notional square-planar donor configuration, resulting in (i) a reduction of the angles N(2)–Cu–N(1) and N(4)–Cu–N(1) and (ii) the movement of N(3) out of the plane of the other donors. Molecular models suggest that this latter movement encourages twisting about the Schiff base double bonds, resulting in an overall geometry for the five-coordinate complex which approaches trigonal bipyramidal (with N(2) and N(4) axial) rather than square pyramidal (with apical Cl). Opposing the distortion from square planar geometry is the tendency of Cu(II) toward short, strong equatorial bonds, attributable to the $d_{x^2-y^2}$ 'hole' in the d^9 ion.

This complex may be compared with the analogous low spin Ni(II)CR.Br (Fleischer & Hawkinson, 1968) and Ni(II)CRH.Br (Dewar & Fleischer, 1969) complexes and the angle N(1)–M–N(3) may be taken as a crude measure of the balance between the tension in the ligand, tending towards distortion away from square planar, and the metal's coordination inflexibility tending towards the square pyramidal configuration. (The angle N(2)–M–N(4) is distorted from 180° by

Table 4. *Bond angles* (°) *and their e.s.d.'s*

Macrocycle *A*		Macrocycle *B*	
N(1)—Cu——N(2)	79·4 (8)	N(1)—Cu——N(2)	78·4 (7)
N(2)—Cu——N(3)	98·0 (8)	N(2)—Cu——N(3)	98·8 (8)
N(3)—Cu——N(4)	98·2 (8)	N(3)—Cu——N(4)	98·3 (8)
N(4)—Cu——N(1)	79·6 (8)	N(4)—Cu——N(1)	79·6 (7)
N(1)—Cu——N(3)	152·0 (9)	N(1)—Cu——N(3)	151·6 (9)
N(2)—Cu——N(4)	158·5 (7)	N(2)—Cu——N(4)	157·5 (7)
N(1)—Cu——Cl	108·2 (8)	N(1)—Cu——Cl	108·0 (6)
N(2)—Cu——Cl	96·6 (7)	N(2)—Cu——Cl	96·3 (7)
N(3)—Cu——Cl	100·1 (7)	N(3)—Cu——Cl	100·4 (7)
N(4)—Cu——Cl	94·4 (7)	N(4)—Cu——Cl	94·9 (7)
Cu——N(1)—C(1)	120 (2)	Cu——N(1)—C(1)	118 (1)
Cu——N(1)—C(10)	120 (1)	Cu——N(1)—C(10)	115 (1)
Cu——N(2)—C(2)	117 (2)	Cu——N(2)—C(2)	117 (2)
Cu——N(2)—C(3)	121 (1)	Cu——N(2)—C(3)	120 (1)
Cu——N(4)—C(8)	124 (2)	Cu——N(4)—C(8)	119 (2)
Cu——N(4)—C(9)	117 (1)	Cu——N(4)—C(9)	117 (1)
N(1)—C(1)—C(2)	113 (2)	N(1)—C(1)—C(2)	110 (2)
C(1)—C(2)—N(2)	112 (2)	C(1)—C(2)—N(2)	116 (2)
C(2)—N(2)—C(3)	122 (2)	C(2)—N(2)—C(3)	123 (2)
N(2)—C(3)—C(4)	110 (2)	N(2)—C(3)—C(4)	110 (2)
C(3)—C(4)—C(5)	115 (3)	C(3)—C(4)—C(5)	115 (3)
C(4)—C(5)—N(3)	112 (2)	C(4)—C(5)—N(3)	117 (2)
Cu——N(3)—C(5)	110 (2)	Cu——N(3)—C(5)	109 (2)
Cu——N(3)—C(6)	110 (2)	Cu——N(3)—C(6)	110 (2)
C(5)—N(3)—C(6)	104 (2)	C(5)—N(3)—C(6)	108 (2)
Cu——N(3)—C(16)	110 (1)	Cu——N(3)—C(16)	110 (1)
C(6)—N(3)—C(16)	112 (2)	C(6)—N(3)—C(16)	112 (2)
C(5)—N(3)—C(16)	111 (2)	C(5)—N(3)—C(16)	110 (2)
N(3)—C(6)—C(7)	114 (2)	N(3)—C(6)—C(7)	115 (2)
C(6)—C(7)—C(8)	118 (3)	C(6)—C(7)—C(8)	110 (2)
C(7)—C(8)—N(4)	107 (2)	C(7)—C(8)—N(4)	110 (2)
C(8)—N(4)—C(9)	118 (2)	C(8)—N(4)—C(9)	123 (2)
N(4)—C(9)—C(10)	112 (2)	N(4)—C(9)—C(10)	116 (2)
C(9)—C(10)-N(1)	110 (2)	C(9)—C(10)-N(1)	113 (2)
N(1)—C(10)-C(11)	126 (2)	N(1)—C(10)-C(11)	114 (2)
C(10)-C(11)-C(12)	111 (2)	C(10)-C(11)-C(12)	122 (2)
C(11)-C(12)-C(13)	125 (2)	C(11)-C(12)-C(13)	120 (2)
C(12)-C(13)-C(1)	115 (2)	C(12)-C(13)-C(1)	118 (2)
C(13)-C(1)—N(1)	124 (2)	C(13)-C(1)—N(1)	118 (2)
C(1)—N(1)—C(10)	120 (2)	C(1)—N(1)—C(10)	127 (2)
C(13)-C(1)—C(2)	123 (2)	C(13)-C(1)—C(2)	132 (2)
C(9)—C(10)-C(11)	124 (2)	C(9)—C(10)-C(11)	132 (2)
C(1)—C(2)—C(14)	125 (2)	C(1)—C(2)—C(14)	116 (2)
C(10)-C(9)—C(15)	119 (2)	C(10)-C(9)—C(15)	117 (2)
N(2)—C(2)—C(14)	124 (2)	N(2)—C(2)—C(14)	128 (2)
N(4)—C(9)—C(15)	129 (2)	N(4)—C(9)—C(15)	127 (2)
O(1)—N(5)—O(2)	118 (3)	O(1)—N(5)—O(2)	116 (4)
O(2)—N(5)—O(3)	116 (2)	O(2)—N(5)—O(3)	119 (3)
O(1)—N(5)—O(3)	125 (3)	O(1)—N(5)—O(3)	125 (3)

Table 5. *Least-squares planes*

The equations of the planes are expressed in orthogonalized space as $PI+QJ+RK=S$.

Plane I: through atoms N(1)*A*, N(2)*A*, N(3)*A* and N(4)*A*.

Equation: $-0{\cdot}25384I+0{\cdot}75711J-0{\cdot}60195K=2{\cdot}28132$

Atoms included in the calculation	Distance from plane (Å)	Atoms not included in the calculation	Distance from plane (Å)
N(1)*A*	0·181	Cu*A*	−0·325
N(2)*A*	−0·147	Cl*A*	−2·819
N(3)*A*	0·117		
N(4)*A*	−0·150		

Plane II: through atoms N(1)*B*, N(2)*B*, N(3)*B* and N(4)*B*.

Equation: $-0{\cdot}26660I+0{\cdot}75738J-0{\cdot}59607K=8{\cdot}87094$

Atoms included in the calculation	Distance from plane (Å)	Atoms not included in the calculation	Distance from plane (Å)
N(1)*B*	0·184	Cu*B*	−0·332
N(2)*B*	−0·153	Cl*B*	−2·823
N(3)*B*	0·122		
N(4)*B*	−0·153		

Plane III: through atoms N(1)*A*, C(1)*A*, C(13)*A*, C(12)*A*, C(11)*A*, C(10)*A* of the pyridine ring in ligand *A*.

Equation: $-0{\cdot}53257I+0{\cdot}60879J-0{\cdot}58800K=0{\cdot}75632$

Atoms included in the calculation	Distance from plane (Å)	Atoms not included in the calculation	Distance from plane (Å)
N(1)*A*	−0·029	Cu*A*	0·055
C(1)*A*	0·032	C(2)*A*	0·059
C(13)*A*	−0·006		
C(12)*A*	−0·019		
C(11)*A*	0·020		
C(10)*A*	0·002	C(9)*A*	0·016

Plane IV: through atoms N(1)*B*, C(1)*B*, C(13)*B*, C(12)*B*, C(11)*B*, and C(10)*B* of the pyridine ring in ligand *B*.

Equation: $-0{\cdot}52307I+0{\cdot}61392J-0{\cdot}59118K=7{\cdot}24490$

Atoms included in the calculation	Distance from plane (Å)	Atoms not included in the calculation	Distance from plane (Å)
N(1)*B*	−0·025	Cu*B*	0·028
C(1)*B*	0·021	C(2)*B*	0·016
C(13)*B*	−0·008		
C(12)*B*	0·000		
C(11)*B*	−0·003		
C(10)*B*	0·016	C(9)*B*	0·013

Table 6. *Short contacts and hydrogen-bond data*

Symmetry code: (i) $x, y-1, z$
(ii) $x, y, z+1$

Cl*A*·····O(4)*A*	3·29 (2) Å	O(4)*A*···Cl*A*···O(5)*A*	126·0 (8)°
Cl*A*·····O(5)*A*	3·19 (3)		
Cl*B*·····O(4)*B*	3·22 (2)	O(4)*B*···Cl*B*···O(5)*B*	126·3 (8)
Cl*B*·····O(5)*B*	3·19 (3)		
O(4)*A*···O(1^{i})*B*	2·91 (2)	O(4)*B*···O(1)*A*	2·92 (3) Å
O(5)*A*···O(2^{ii})*A*	2·79 (2)	O(5)*B*···O(2^{ii})*B*	2·77 (3)

strong covalent bonds in the ligand, and variations in this angle are smaller and less informative). The angle N(1)–M–N(3) is expected to lie between 180° (square pyramid) and 120° (trigonal bipyramid). In fact its value is 152° in $(\mathrm{Cl.Cu.N\text{-}MeCR})^+$ and 164° and 172° in $(\mathrm{Br.Ni.CR})^+$ and $(\mathrm{Br.Ni.CRH})^+$ respectively. The difference between Cu and Ni in these examples may perhaps be attributable to the extra $d_{x^2-y^2}$ 'hole' of low spin Ni(II), and that between CR and CRH presumably due to the greater flexibility and slightly larger ring of CRH. In both Ni compounds the pyridine N–Ni distance is shorter than the others by 0·1 Å. Here a similar effect is observed, with a shortening between 0·05 and 0·1 Å.

Chemically equivalent bond lengths in the independent macrocycles are generally in fair agreement but some equivalent angles differ considerably, especially in and around the pyridine ring. Both pyridine rings are essentially planar (Table 5). There is close agreement between equivalent angles in the Cu coordination spheres (Table 4). The square pyramid is considerably distorted, the N–Cu–N angles ranging from 78 to 99°. A least-squares plane (Table 5) through the four donor N atoms shows that the diagonal atom pair N(1), N(3) is below the plane, while the pair N(2), N(4) is above. In each macrocycle, Cu lies about 0·3 Å out of this plane toward the coordinated Cl^- ion. The geometry is strikingly similar to that observed in bis-(6-hydroxypurine)copper(II) chloride trihydrate, in which Cu is displaced 0·29 Å from the analogous plane towards the apical Cl atom. Another feature of the latter structure is the presence of hydrogen bonds emanating from the apical Cl to two water molecules. This feature is present in this complex. The macrocyclic planes are interleaved by two water O atoms O(4) and O(5) (Fig. 2). Although H atoms were not located in the analysis, hydrogen bonding may be inferred from certain short contacts. Each water O is hydrogen bonded to the Cl^- ion and an O of the nitrate ion. Relevant data are listed in Table 6. Each Cl is therefore involved in two hydrogen bonds, the O···Cl···O angles being about 126° in both *A* and *B*. Two of the O···O contacts involving water and nitrate O atoms are just less than the van der Waals diameter of 2·8 Å while the other two just exceed this value.

All calculations were carried out on a Univac 1106 computer at the University of Cape Town.

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