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Synthesis and Structure of Chlorobis[3,6-di(2-pyridyl)pyridazine]copper(II) Chloride Pentahydrate

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Abstract

Crystals of $[Cu(C_{14}H_{10}N_4)_2Cl]Cl.5H_2O$, M_r = 693·05, are triclinic, space group $P\bar{1}$, with a = 14·429 (12), b = 14·636 (8), c = 7·540 (10) Å, α = 90·87 (6), β = 96·24 (5), γ = 104·28 (4)°, Z = 2. V = 1533 (3) Å^3, D_c = 1·502 g cm^{-3}, $F(000)$ = 714, $\bar{\lambda}$(Cu $K\alpha$) = 1·54178 Å, μ(Cu $K\alpha$) = 30·62 cm^{-1}. The structure has been determined from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares to R = 0·046 for 3875 observed reflections. The structure consists of mononuclear $[Cu(C_{14}H_{10}N_4)_2Cl]^+$ cations, Cl^- anions and water molecules linked by hydrogen bonds. The Cu atom is in a trigonal-bipyramidal arrangement involving one Cl atom and four N atoms from two independent tetranitrogenated organic ligands acting as bidentate chelates. In both ligands the two pyridyl N atoms are on opposite sides with respect to the N–N bond of the pyridazine ring.

Introduction

Bidentate chelating systems such as 2,2′-bipyridine and 1,10-phenanthroline are studied in several laboratories and a great deal of research effort is concentrated in this field. The results of these investigations have recently been reviewed (McKenzie, 1971; Gillard, 1975), confirming the constant interest in this class of compounds.

In this light we have undertaken the study of metal complexes with polydentate nitrogenated ligands such as 3,6-di(2-pyridyl)pyridazine (dppn), which contains another N atom as donor (from a third conjugated ring) with respect to 2,2′-bipyridine and 1,10-phenanthroline. The crystal structure of the mononuclear complex $[Cu(dppn)_2Cl]Cl.5H_2O$ is now reported.

Experimental

The ligand was prepared as described in the literature (Butte & Case, 1961).

A warm solution of $CuCl_2.2H_2O$ (0·25 mmol) in water (25 ml) and 0·5 mmol of ligand dissolved in warm acetone (50 ml) were mixed in a beaker. The reaction mixture was kept warm and stirred for 15 min; green crystals precipitated on cooling. The crude product was filtered and recrystallized from water–acetone (1:2) (yield 80%).

Analysis: calculated for $C_{28}H_{30}Cl_2CuN_8O_5$: C 48·51, H 4·33, N 16·17%; found: C 49·34, H 4·49, N, 16·08%.

Cell parameters were first determined from rotation and Weissenberg photographs and then refined from diffractometer data.

Intensity data

Intensity data were collected on a Siemens AED single-crystal diffractometer, with Ni-filtered Cu $K\alpha$ radiation and the θ–2θ scan technique. A flattened crystal, having dimensions of *ca* 0·03 × 0·13 × 0·24 mm, was aligned with its [001] axis along the φ axis of the diffractometer and all the reflections with $2\theta \leq 140°$ were measured. Of 5809 independent reflections, 3875 with $I \geq 2\sigma(I)$ were used in the analysis. Corrections for Lorentz and polarization factors were made in the usual way, but no correction was applied for absorption effects. The first absolute scaling and the overall temperature factor were obtained by Wilson's method.

Structure determination and refinement

The structure was solved by Patterson and Fourier methods and the refinement was carried out by least-squares full-matrix cycles using the *SHELX*

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Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (*Hamilton*, 1959) *for the non-hydrogen atoms, with e.s.d.'s in parentheses*

	x	y	z	B_{eq} (Å^2)
Cu	3284 (1)	7194 (1)	−1396 (1)	3·68 (3)
Cl(1)	3166 (1)	6522 (1)	1377 (2)	4·70 (8)
Cl(2)	7472 (1)	8109 (1)	872 (2)	4·07 (6)
O_w(1)	504 (4)	584 (3)	−2625 (7)	5·0 (2)
O_w(2)	4909 (4)	7400 (4)	4394 (8)	6·2 (3)
O_w(3)	6782 (4)	7158 (3)	4445 (7)	5·3 (3)
O_w(4)	208 (4)	1285 (4)	4014 (7)	5·2 (2)
O_w(5)	1751 (4)	2592 (4)	2638 (8)	5·9 (3)
N(11)	3999 (3)	8577 (3)	−1765 (5)	2·26 (17)
N(21)	4863 (3)	8836 (3)	−2350 (5)	2·35 (17)
N(31)	6483 (3)	10927 (3)	−3629 (6)	3·3 (2)
N(41)	2264 (3)	7832 (3)	−1018 (6)	2·96 (19)
N(12)	2553 (3)	6323 (3)	−3521 (5)	2·50 (17)
N(22)	1715 (3)	6395 (3)	−4345 (6)	2·75 (18)
N(32)	−102 (3)	5259 (3)	−7824 (6)	3·4 (2)
N(42)	4263 (3)	6516 (3)	−1877 (6)	2·73 (18)
C(11)	3488 (3)	9193 (3)	−1466 (6)	2·32 (19)
C(21)	3849 (4)	10157 (3)	−1691 (7)	2·8 (2)
C(31)	4732 (4)	10430 (3)	−2261 (7)	2·8 (2)
C(41)	5230 (3)	9752 (3)	−2594 (6)	2·3 (2)
C(51)	6191 (3)	10013 (3)	−3248 (7)	2·6 (2)
C(61)	6741 (4)	9380 (4)	−3422 (8)	3·2 (3)
C(71)	7622 (4)	9680 (5)	−4068 (9)	4·7 (3)
C(81)	7928 (4)	10615 (5)	−4445 (9)	4·1 (3)
C(91)	7343 (4)	11194 (4)	−4207 (8)	5·0 (3)
C(101)	2521 (3)	8779 (3)	−942 (6)	6·2 (2)
C(111)	1917 (4)	9310 (4)	−447 (7)	5·3 (3)
C(121)	1018 (4)	8850 (4)	−25 (8)	5·2 (3)
C(131)	743 (4)	7884 (4)	−168 (8)	5·9 (3)
C(141)	1377 (4)	7396 (4)	−665 (8)	2·3 (3)
C(12)	2956 (3)	5635 (3)	−3909 (6)	2·4 (2)
C(22)	2484 (4)	4914 (3)	−5188 (7)	3·3 (2)
C(32)	1627 (4)	4979 (4)	−6030 (7)	3·0 (2)
C(42)	1263 (3)	5748 (3)	−5623 (7)	2·5 (2)
C(52)	348 (3)	5901 (3)	−6527 (7)	2·8 (2)
C(62)	2 (4)	6665 (4)	−6059 (8)	3·4 (2)
C(72)	−832 (4)	6772 (4)	−6965 (8)	2·7 (3)
C(82)	−1312 (4)	6124 (4)	−8322 (8)	2·3 (3)
C(92)	−919 (4)	5388 (4)	−8683 (8)	2·8 (3)
C(102)	3926 (3)	5724 (3)	−2935 (6)	2·8 (2)
C(112)	4468 (4)	5076 (4)	−3095 (7)	2·3 (2)
C(122)	5382 (4)	5258 (4)	−2206 (8)	2·6 (3)
C(132)	5744 (4)	6088 (4)	−1211 (8)	3·2 (3)
C(142)	5161 (4)	6693 (4)	−1069 (8)	4·2 (3)

system of computer programs (Sheldrick, 1976) for the non-hydrogen atoms. A subsequent ΔF map revealed the positions of all the H atoms. Further least-squares cycles were then computed including the H atoms with isotropic thermal parameters. Unit weights were used in all stages of the refinement by analysing the variations of $|\Delta F|$ as a function of $|F_o|$. The final R index was 0·046 (observed reflections only). Final atomic coordinates for the heavy atoms and for the H atoms are given in Tables 1 and 2 respectively.*

* Lists of structure factors and anisotropic thermal parameters are available from the authors and have also been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36566 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Fractional atomic coordinates* ($\times 10^3$) *and isotropic thermal parameters for the hydrogen atoms with e.s.d.'s in parentheses*

	x	y	z	U (Å^2)
H(1)	43 (5)	95 (5)	−353 (9)	0·04 (2)
H(2)	113 (5)	92 (4)	−216 (8)	0·09 (2)
H(3)	454 (5)	728 (5)	350 (10)	0·11 (3)
H(4)	447 (5)	768 (5)	482 (9)	0·15 (2)
H(5)	627 (5)	744 (4)	484 (8)	0·06 (2)
H(6)	686 (5)	735 (5)	328 (9)	0·10 (2)
H(7)	73 (5)	160 (5)	330 (8)	0·08 (2)
H(8)	−2 (5)	80 (5)	328 (9)	0·07 (2)
H(9)	235 (5)	267 (5)	341 (9)	0·07 (2)
H(10)	193 (5)	219 (5)	195 (9)	0·09 (3)
H(21)	351 (4)	1065 (4)	−136 (7)	0·025 (14)
H(31)	496 (3)	1107 (4)	−262 (6)	0·074 (13)
H(61)	650 (4)	879 (4)	−313 (7)	0·037 (15)
H(71)	807 (4)	928 (4)	−410 (8)	0·066 (17)
H(81)	848 (4)	1082 (4)	−486 (8)	0·061 (18)
H(91)	756 (4)	1190 (4)	−437 (7)	0·070 (16)
H(111)	208 (4)	998 (4)	−46 (7)	0·055 (15)
H(121)	50 (4)	919 (4)	19 (7)	0·071 (16)
H(131)	13 (4)	757 (4)	1 (7)	0·064 (16)
H(141)	118 (4)	664 (4)	−68 (7)	0·073 (16)
H(22)	278 (3)	440 (4)	−534 (6)	0·040 (13)
H(32)	132 (4)	459 (4)	−694 (7)	0·048 (14)
H(62)	32 (4)	706 (4)	−517 (7)	0·058 (15)
H(72)	−109 (4)	721 (4)	−675 (7)	0·056 (16)
H(82)	−194 (4)	620 (4)	−901 (7)	0·056 (15)
H(92)	−119 (4)	499 (4)	−960 (7)	0·062 (16)
H(112)	420 (4)	456 (4)	−370 (7)	0·062 (15)
H(122)	589 (4)	485 (4)	−241 (7)	0·058 (15)
H(132)	644 (4)	624 (4)	−55 (7)	0·055 (15)
H(142)	536 (4)	725 (4)	−21 (7)	0·036 (16)

All the calculations were carried out on the Cyber 76 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale (Bologna) with the financial support of the University of Parma.

Discussion

Crystals of the present compound consist of mononuclear $[Cu(C_{14}H_{10}N_4)_2Cl]^+$ cations, Cl^- counter ions and water molecules. In the cation the Cu atom is pentacoordinated, being surrounded in a trigonal-bipyramidal arrangement by a Cl atom and by four N atoms from two independent tetranitrogenated dppn molecules. These, acting as bidentate chelating ligands, form five-membered rings with the metal. A view of the complex, with the atomic-labelling system, is given in Fig. 1; bond distances and angles are reported in Table 3. The Cl atom, Cl(1), and the two N atoms, N(11) and N(12), from two different ligands, lie in the equatorial plane of the bipyramid [Cu is slightly displaced (0·033 Å) from this plane towards N(42)]; the other two N atoms, N(41) and N(42), deviate slightly from the normal to this plane [the Cu–N(41) and Cu–N(42) directions form angles of 10·0 and 12·5°, respectively,

Table 3. *Bond distances* (Å) *and angles* (°)

(*a*) In the coordination polyhedron

Cu–N(11)	2·071 (5)	Cu–N(41)	1·970 (5)
Cu–N(12)	2·052 (4)	Cu–N(42)	1·976 (5)
Cu–Cl(1)	2·329 (2)		

N(11)–Cu–N(12)	120·9 (2)	N(41)–Cu–Cl(1)	90·9 (1)
N(12)–Cu–Cl(1)	114·7 (1)	N(42)–Cu–N(11)	101·5 (2)
N(11)–Cu–Cl(1)	124·3 (1)	N(42)–Cu–N(12)	79·8 (2)
N(41)–Cu–N(11)	80·0 (2)	N(42)–Cu–Cl(1)	90·3 (1)
N(41)–Cu–N(12)	97·3 (2)	N(42)–Cu–N(41)	177·1 (2)

(*b*) In the organic ligands

N(11)–N(21)	1·336 (6)	N(12)–N(22)	1·327 (6)
N(11)–C(11)	1·329 (6)	N(12)–C(12)	1·325 (6)
C(11)–C(21)	1·398 (7)	C(12)–C(22)	1·407 (7)
C(21)–C(31)	1·357 (8)	C(22)–C(32)	1·353 (8)
C(31)–C(41)	1·396 (7)	C(32)–C(42)	1·398 (8)
C(41)–N(21)	1·338 (6)	C(42)–N(22)	1·335 (7)
C(11)–C(101)	1·477 (6)	C(12)–C(102)	1·483 (6)
C(41)–C(51)	1·485 (6)	C(42)–C(52)	1·488 (6)
C(51)–C(61)	1·374 (7)	C(52)–C(62)	1·388 (8)
C(61)–C(71)	1·383 (8)	C(62)–C(72)	1·363 (8)
C(71)–C(81)	1·375 (9)	C(72)–C(82)	1·385 (8)
C(81)–C(91)	1·358 (9)	C(82)–C(92)	1·372 (8)
C(91)–N(31)	1·329 (7)	C(92)–N(32)	1·339 (7)
N(31)–C(51)	1·345 (6)	N(32)–C(52)	1·339 (7)
C(101)–N(41)	1·342 (6)	C(102)–N(42)	1·351 (6)
C(101)–C(111)	1·378 (7)	C(102)–C(112)	1·382 (7)
C(111)–C(121)	1·379 (8)	C(112)–C(122)	1·374 (8)
C(121)–C(131)	1·370 (9)	C(122)–C(132)	1·373 (9)
C(131)–C(141)	1·370 (8)	C(132)–C(142)	1·374 (8)
C(141)–N(41)	1·339 (7)	C(142)–N(42)	1·332 (7)
C(21)–H(21)	1·01 (6)	C(22)–H(22)	0·96 (6)
C(31)–H(31)	0·97 (6)	C(32)–H(32)	0·89 (6)
C(61)–H(61)	0·89 (6)	C(62)–H(62)	0·89 (6)
C(71)–H(71)	0·98 (6)	C(72)–H(72)	0·84 (6)
C(81)–H(81)	0·87 (6)	C(82)–H(82)	1·03 (6)
C(91)–H(91)	1·02 (6)	C(92)–H(92)	0·89 (6)
C(111)–H(111)	0·95 (6)	C(112)–H(112)	0·86 (6)
C(121)–H(121)	1·02 (6)	C(122)–H(122)	1·07 (6)
C(131)–H(131)	0·92 (6)	C(132)–H(132)	1·04 (6)
C(141)–H(141)	1·07 (6)	C(142)–H(142)	1·00 (6)

N(21)–N(11)–C(11)	122·2 (4)	N(22)–N(12)–C(12)	122·8 (4)
N(11)–C(11)–C(21)	121·2 (4)	N(12)–C(12)–C(22)	120·7 (4)
N(11)–C(11)–C(101)	115·2 (4)	N(12)–C(12)–C(102)	114·3 (4)
C(21)–C(11)–C(101)	123·6 (4)	C(22)–C(12)–C(102)	125·1 (4)
C(11)–C(21)–C(31)	117·1 (4)	C(12)–C(22)–C(32)	117·0 (5)
C(21)–C(31)–C(41)	119·5 (4)	C(22)–C(32)–C(42)	119·6 (5)
C(31)–C(41)–N(21)	121·7 (4)	C(32)–C(42)–N(22)	121·4 (4)
C(31)–C(41)–C(51)	121·5 (4)	C(32)–C(42)–C(52)	123·5 (5)
N(21)–C(41)–C(51)	116·8 (4)	N(22)–C(42)–C(52)	115·0 (4)
C(41)–N(21)–N(11)	118·3 (4)	C(42)–N(22)–N(12)	118·5 (4)
C(41)–C(51)–C(61)	123·0 (4)	C(42)–C(52)–C(62)	121·7 (5)
C(41)–C(51)–N(31)	114·2 (4)	C(42)–C(52)–N(32)	115·2 (4)
N(31)–C(51)–C(61)	122·9 (4)	N(32)–C(52)–C(62)	123·1 (5)
C(51)–C(61)–C(71)	119·1 (6)	C(52)–C(62)–C(72)	118·6 (5)
C(61)–C(71)–C(81)	118·2 (6)	C(62)–C(72)–C(82)	119·8 (6)
C(71)–C(81)–C(91)	118·6 (6)	C(72)–C(82)–C(92)	117·5 (5)
C(81)–C(91)–N(31)	124·9 (6)	C(82)–C(92)–N(32)	124·5 (5)
C(91)–N(31)–C(51)	116·2 (5)	C(92)–N(32)–C(52)	116·5 (5)
C(11)–C(101)–N(41)	114·4 (4)	C(12)–C(102)–C(112)	124·2 (4)
C(11)–C(101)–C(111)	123·5 (4)	N(42)–C(102)–C(12)	114·4 (4)
N(41)–C(101)–C(111)	122·2 (4)	N(42)–C(102)–C(112)	121·4 (4)
C(101)–C(111)–C(121)	118·7 (5)	C(102)–C(112)–C(122)	119·2 (5)
C(111)–C(121)–C(131)	119·1 (5)	C(112)–C(122)–C(132)	119·4 (6)
C(121)–C(131)–C(141)	119·4 (5)	C(122)–C(132)–C(142)	118·7 (5)
C(131)–C(141)–N(41)	122·1 (5)	C(132)–C(142)–N(42)	122·8 (5)
C(141)–N(41)–C(101)	118·4 (5)	C(142)–N(42)–C(102)	118·4 (5)

(*c*) In the water molecules

$O_w(1)$–H(1)	0·89 (7)	$O_w(3)$–H(6)	0·94 (7)
$O_w(1)$–H(2)	0·94 (7)	$O_w(4)$–H(7)	1·00 (7)
$O_w(2)$–H(3)	0·80 (7)	$O_w(4)$–H(8)	0·87 (7)
$O_w(2)$–H(4)	0·92 (7)	$O_w(5)$–H(9)	0·97 (7)
$O_w(3)$–H(5)	1·00 (7)	$O_w(5)$–H(10)	0·88 (7)

Table 3 (*cont.*)

H(1)–$O_w(1)$–H(2)	97 (6)	H(7)–$O_w(4)$–H(8)	96 (6)
H(3)–$O_w(2)$–H(4)	86 (7)	H(9)–$O_w(5)$–H(10)	89 (6)
H(5)–$O_w(3)$–H(6)	106 (6)		

(*d*) Hydrogen bonds

$O_w(1)$–H(1)···$O_w(4^{i})$	2·778 (7)	$O_w(1)$–H(1)–$O_w(4^{i})$	158 (7)
H(1)···$O_w(4^{i})$	1·94 (7)	H(1)–$O_w(1)$–$O_w(4^{i})$	15 (5)
$O_w(1)$–H(2)···$Cl(2^{ii})$	3·204 (6)	$O_w(1)$–H(2)–$Cl(2^{ii})$	171 (5)
H(2)···$Cl(2^{ii})$	2·27 (7)	H(2)–$O_w(1)$–$Cl(2^{ii})$	6 (4)
$O_w(2)$–H(3)···Cl(1)	3·198 (6)	$O_w(2)$–H(3)–Cl(1)	162 (7)
H(3)···Cl(1)	2·43 (7)	H(3)–$O_w(2)$–Cl(1)	14 (5)
$O_w(3)$–H(5)···$O_w(2)$	2·807 (8)	$O_w(3)$–H(5)–$O_w(2)$	143 (5)
H(5)···$O_w(2)$	1·94 (7)	H(5)–$O_w(3)$–$O_w(2)$	24 (4)
$O_w(3)$–H(6)···Cl(2)	3·194 (5)	$O_w(3)$–H(6)–Cl(2)	163 (6)
H(6)···Cl(2)	2·29 (7)	H(6)–$O_w(3)$–Cl(2)	12 (4)
$O_w(4)$ H(7)···$O_w(5)$	2·856 (8)	$O_w(4)$–H(7)–$O_w(5)$	157 (6)
H(7)···$O_w(5)$	1·91 (7)	H(7)–$O_w(4)$–$O_w(5)$	15 (4)
$O_w(4)$–H(8)···$O_w(1^{iii})$	2·816 (8)	$O_w(4)$–H(8)–$O_w(1^{iii})$	155 (6)
H(8)···$O_w(1^{iii})$	2·01 (7)	H(8)–$O_w(4)$–$O_w(1^{iii})$	18 (5)
$O_w(5)$–H(9)···$O_w(3^{iv})$	2·834 (8)	$O_w(5)$–H(9)–$O_w(3^{iv})$	159 (6)
H(9)···$O_w(3^{iv})$	1·91 (7)	H(9)–$O_w(5)$–$O_w(3^{iv})$	14 (4)
$O_w(5)$–H(10)–$Cl(2^{ii})$	3·232 (6)	$O_w(5)$–H(10)–$Cl(2^{ii})$	148 (6)
H(10)···$Cl(2^{ii})$	2·45 (7)	H(10)–$O_w(5)$–$Cl(2^{ii})$	24 (5)

Symmetry code

(i)	$x, y, -1 + z$	(iii)	$-x, -y, -z$
(ii)	$1 - x, 1 - y, -z$	(iv)	$1 - x, 1 - y, 1 - z$

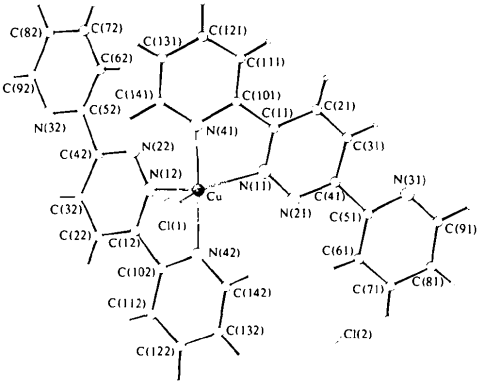

Fig. 1. View of the $[Cu(C_{14}H_{10}N_4)_2Cl]^+$ cation with the atomic-labelling system.

with the normal to the plane]. The Cu–Cl(1) bond distance [2·329 (2) Å] is quite regular and consistent with the Cu–Cl covalent bond (1·33 + 0·99 = 2·32 Å); the two Cu–N bond distances from the same ligand are significantly different but corresponding bonds from the two ligands are equivalent. The mean values for these two Cu–N distances are 1·973 (5) and 2·062 (5) Å respectively, the two shorter involving the N(41) and N(42) atoms at the apices of the bipyramid.

The complex possesses approximate C_2 symmetry, the idealized twofold axis passing along the Cu–Cl(1) bond.

The bite angles of the two ligands [N(41)–Cu–N(11) and N(42)–Cu–N(12)] are 80·0 (2) and 79·8 (2)°. In each ligand the two non-coordinating N atoms (one from pyridine and one from pyridazine) are mutually *trans*, as also found in

the structure of bis[3,6-di(2-pyridyl)pyridazine]-dinitratomanganese(II), $[Mn(dppn)_2(NO_3)_2]$ (Andrew, Blake & Fraser, 1975), the only other reported complex with dppn as ligand. The chelating behaviour of dppn in the present complex is similar to that of the 2,2′-bipyridyl (bpy) ligand.

In the structure of chlorobis(2,2′-bipyridyl)-copper(II) chloride hexahydrate, $[Cu(bpy)_2Cl]Cl.6H_2O$ (Stephens & Tucker, 1973), the Cu is also in a trigonal-bipyramidal arrangement with Cu–N distances ranging from 1·98 to 2·08 Å, the two shorter ones *trans* with respect to the Cu atom and the two longer ones in the equatorial plane; the mean bite angle is 79·5°. In the structures of bis(2,2′-bipyridyl)iodocopper(II) iodide, $[Cu(bpy)_2I]I$ (Barclay, Hoskins & Kennard, 1963), and bis(2,2′-bipyridyl)nitritocopper(II) nitrate, $[Cu(bpy)_2NO_2]NO_3$ (Procter & Stephens, 1969), where the arrangement of the two bipyridyl ligands is very similar to that found in the chloride derivative, different Cu–N bonds (1·96–2·10 and 1·99–2·08 Å) and mean bite angles of 82 and 80·7° have also been found. In dinitrito(2,2′-bipyridyl)copper(II), $[Cu(bpy)(NO_2)_2]$ (Stephens, 1969), only one bipyridyl ligand chelates to Cu in a nearly square-planar arrangement and the two Cu–N bonds are equivalent (1·980 and 1·984 Å); the bite angle of 81·3° shows no variation from the other reported values.

Neither dppn ligand is planar, but each individual ring is planar. In each ligand the pyridine and pyridazine rings involved in the chelation are twisted, about the exocyclic C–C bond, by the same angle (8·5°); this value is larger than those (2 and 7°) found in $[Mn(dppn)_2(NO_3)_2]$. Values of 10, 11·2 and 3·2° have been found in $[Cu(bpy)_2I]I$, $[Cu(bpy)_2NO_2]NO_3$ and $[Cu(bpy)(NO_2)_2]$ respectively, while in $[Cu(bpy)_2Cl]Cl.6H_2O$ the bpy ligands are planar (the mean value of the twist angle is 0·8°). The uncoordinated pyridyl groups are twisted about the corresponding exocyclic C–C bond by 5·7 and 3·7° in the present complex for the ligands defined by N(11),N(21) and N(12),N(22) respectively. {Values of 10 and 12° have been found in $[Mn(dppn)_2(NO_3)_2]$.} The larger twist angle of the coordinated pyridyl groups with respect to those of the uncoordinated groups may be due to the necessity to minimize the steric hindrance between the H atoms at C atoms adjacent to the C–C bond of the chelate rings; this is confirmed by the large angles C(111)–C(101)–C(11) 123·5, C(101)–C(11)–C(21) 123·6, C(112)–C(102)–C(12) 124·2, and C(102)–C(12)–C(22) 125·1°. The uncoordinated pyridyl N atoms, in both ligands, are on opposite sides with respect to the pyridazine N–N bond, to avoid these H interactions.

These data show that the structure of the complex $[Cu(dppn)_2Cl]^+$ is strictly analogous to that of $[Cu(bpy)_2Cl]^+$, even if this result is not obvious from a comparison of the electronic properties of the two chelating ligands. The dppn ligand, in fact, possesses a second N atom in an α position with respect to the chelating system and a third conjugate ring, so that it is very hard to forecast the same behaviour as for bpy on complexation.

The magnetic moment of the present complex is 2·03 BM (1 BM $\equiv 9{\cdot}27 \times 10^{-24}$ JT^{-1}), a value close to those reported for the pentacoordinated bpy complexes which are in the range 1·81–1·97 BM (Harris, Lockyer & Waterman, 1961).

Packing of the complexes in the crystals (Fig. 2) is determined by a network of hydrogen bonds involving water molecules, and ionic and coordinated Cl atoms.

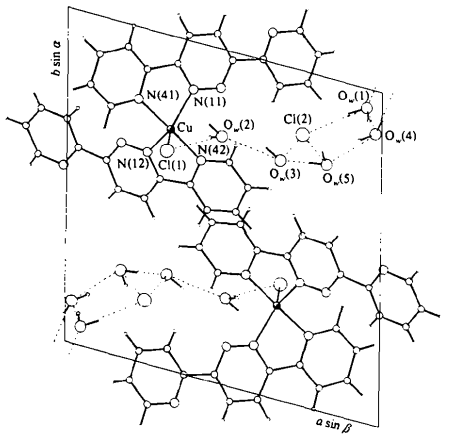

Fig. 2. Projection along **c** of the structure of $[Cu(C_{14}H_{10}N_4)_2Cl]Cl.5H_2O$

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