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Aquadichloro-μ-[3,6-di(2-pyridyl)pyridazine-*N*,*N'*,*N''*,*N'''*]-μ-hydroxo-nitrato-*O*-dicopper(II) Dichloro-μ-[3,6-di(2-pyridyl)pyridazine-*N*,*N'*,*N''*,*N'''*]-μ-hydroxo-μ-nitrato-*O*,*O'*-dicopper(II) Sesquihydrate, $\{[Cu_2Cl_2(OH)(NO_3)(C_{14}H_{10}N_4)(H_2O)][Cu_2Cl_2(OH)(NO_3)(C_{14}H_{10}N_4)]\}.1{\cdot}5H_2O$

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Abstract. M_r (title formula) = 1067·56, triclinic, $P\bar{1}$, $a = 14{\cdot}500$ (3), $b = 13{\cdot}049$ (3), $c = 10{\cdot}874$ (2) Å, $\alpha = 84{\cdot}8$ (1), $\beta = 110{\cdot}1$ (1), $\gamma = 110{\cdot}5$ (1)°, $V = 1809$ (2) Å^3, $Z = 2$, D_m (by flotation) = 1·96, $D_x = 1{\cdot}959$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 26{\cdot}46$ cm^{-1}, $F(000) = 1066$, $T = 293$ K, final conventional R is 0·050 over the 2114 unique observed reflections. The asymmetric unit consists of two different neutral dinuclear complexes and of 1·5 solvent molecules. Both complexes contain the tetradentate organic ligand, a bridging hydroxo group and two terminal chlorine ligands. In one complex the copper atoms are five-coordinate, in a distorted square-pyramidal geometry, the two apical sites being occupied by the oxygen atoms of a monodentate nitrato group and of a water molecule, respectively. In the second complex the copper atoms are bridged by a bidentate nitrato group. Such complexes form a dimeric structure in which one of the copper atoms achieves a distorted octahedral geometry, because of a long interaction with the μ-hydroxo oxygen of the second monomeric unit.

Introduction. Binuclear copper(II) complexes with ligands containing nitrogen donor atoms have received increasing attention as models for biological copper(II) systems, concerning the relationships between their structural features and physico-chemical properties. In this field we have already studied complexes obtained using the quadridentate ligand 3,6-di(2-pyridyl)pyridazine and carried out structural determinations of some of them (Ghedini, De Munno, Denti, Manotti Lanfredi & Tiripicchio, 1982; Dapporto, De Munno, Bruno & Romeo, 1983; De Munno, Denti & Dapporto, 1983; Dapporto, De Munno, Sega & Mealli, 1984). As a further contribution we report here the crystal structure of the title complex.

Experimental. Crystals were prepared by treating $[Cu_2Cl_4(C_{14}H_{10}N_4)(H_2O)].H_2O$ (De Munno, Denti & Dapporto, 1983) with hot aqueous 0·001 mol dm^{-3} nitric acid and by slowly evaporating the resulting solution in air. Green parallelepiped crystals, 0·30 × 0·40 × 0·25 mm, Philips PW 1100 diffractometer, graphite monochromator, 25 reflections used for measuring lattice parameters with $7° < \theta < 15°$, no systematic loss of intensity of the three standard reflections $\bar{5}12$, $\bar{2}2\bar{1}$, $\bar{2}02$, 6355 unique measured reflections with $\theta < 25°$, 2114 with $I > 3\sigma(I)$, θ–2θ scan, $-15 \le h \le 15$, $-15 \le k \le 15$, $0 \le l \le 12$ indices collected, absorption corrected with numerical method according to *SHELX* (Sheldrick, 1976), transmission factors between 0·44 and 0·50, Lp correction, scattering factors for non-hydrogen atoms (*International Tables for X-ray Crystallography*, 1974, p. 99), and for H atoms (Stewart, Davidson & Simpson, 1965), anomalous-dispersion corrections (*International Tables for X-ray Crystallography*, 1974, p. 149); direct methods, full matrix, $\sum w(|F_o| - |F_c|)^2$ minimized, anisotropic thermal parameters for Cu and Cl, isotropic for the other atoms, H of the hydroxy groups and linked molecule (from ΔF synthesis) and the other hydrogens (calculated) given isotropic U of 0·04 Å^2

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and not refined; final $R = 0.050$, $R_w = 0.054$, $w = 1/\sigma^2$; max. $\Delta/\sigma = 0.056$, max. and min. $\Delta\rho$ excursions of ΔF synthesis 0·72 and −0·72 e Å^{-3}, respectively; VAX/VMS computer of the Università della Calabria; *SHELX* program (Sheldrick, 1976) and *XRAY* system of programs (Stewart, Kundell & Baldwin, 1970).*

Discussion. The asymmetric unit consists of two different binuclear complexes (*A* and *B*), and of 1·5 solvent water molecules. In both complexes each copper atom is coordinated – approximately on the same plane – by two nitrogen atoms of the organic ligand, by a terminal chlorine atom and by the oxygen atom of a μ-hydroxo group. In complex *A* (Fig. 1) both Cu(1) and Cu(2) atoms have a distorted square-pyramidal geometry, the apical sites being occupied by an oxygen atom of a monodentate nitrato group and by the oxygen atom of a ligating water molecule, respectively.

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and a full list of bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39030 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

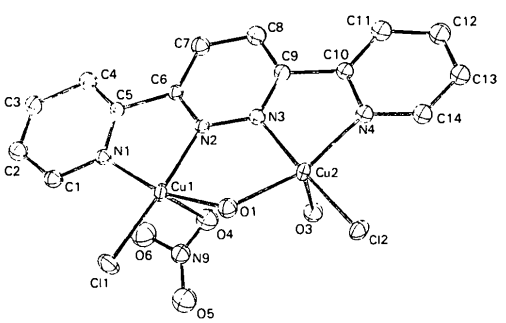

Fig. 1. Complex *A*.

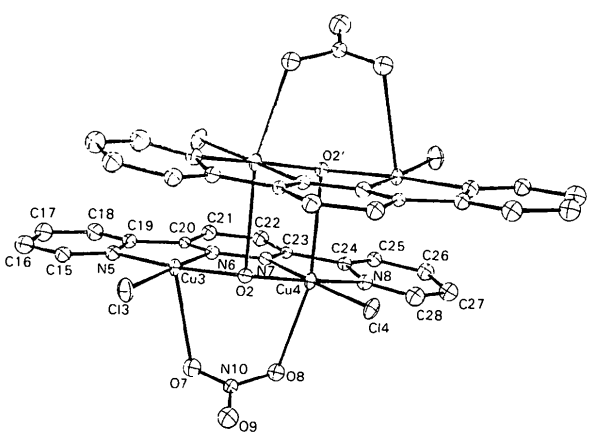

Fig. 2. Complex *B*.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic* (*Hamilton*, 1959) *thermal parameters* (Å^2 × 10^3) *for non-hydrogen atoms*

	x	*y*	*z*	U_{eq}
Cu(1)	6171 (2)	−401 (1)	−166 (2)	35 (1)
Cu(2)	5643 (1)	1816 (1)	−1599 (2)	35 (1)
Cu(3)	8863 (1)	6458 (1)	4991 (2)	30 (1)
Cu(4)	9488 (1)	4259 (1)	6256 (2)	30 (1)
Cl(1)	7156 (4)	−361 (4)	1909 (4)	59 (3)
Cl(2)	6231 (3)	3421 (3)	−530 (4)	49 (2)
Cl(3)	7675 (3)	6381 (3)	3026 (4)	57 (3)
Cl(4)	8861 (3)	2629 (3)	5201 (4)	40 (2)
N(1)	5835 (8)	−1988 (8)	−682 (10)	32 (3)
N(2)	5193 (9)	−528 (9)	−1996 (11)	36 (3)
N(3)	4963 (8)	384 (8)	−2550 (10)	31 (3)
N(4)	4745 (8)	2196 (9)	−3295 (10)	34 (3)
N(5)	9089 (9)	7968 (9)	5595 (11)	39 (3)
N(6)	9857 (8)	6534 (8)	6785 (10)	32 (3)
N(7)	10103 (8)	5643 (8)	7317 (10)	32 (3)
N(8)	10255 (9)	3797 (9)	8028 (11)	36 (3)
N(9)	8075 (12)	−154 (13)	−1266 (15)	59 (4)
N(10)	7383 (9)	4546 (9)	6357 (11)	33 (3)
O(1)	6142 (7)	1031 (8)	−91 (9)	45 (3)
O(2)	8901 (7)	5032 (7)	4816 (8)	30 (2)
O(3)	6914 (8)	1962 (8)	−2538 (10)	51 (3)
O(4)*	7249 (2)	46 (2)	−1872 (3)	83 (8)
O(4')*	7929 (3)	503 (3)	−2330 (4)	150 (4)
O(5)	8017 (1)	−1079 (1)	−1558 (2)	124 (6)
O(6)*	8943 (2)	384 (2)	−645 (2)	82 (8)
O(6')*	7821 (2)	271 (2)	−838 (3)	83 (8)
O(7)	7616 (8)	5520 (8)	6542 (10)	51 (3)
O(8)	7996 (8)	4072 (8)	7068 (10)	51 (3)
O(9)	6587 (9)	3994 (9)	5542 (11)	56 (3)
O(10)	7395 (19)	3697 (21)	2565 (24)	217 (10)
O(11)*	7246 (40)	2035 (44)	2346 (50)	231 (22)
C(1)	6282 (12)	−2677 (12)	40 (15)	48 (4)
C(2)	6018 (12)	−3744 (13)	−304 (16)	60 (4)
C(3)	5277 (11)	−4097 (12)	−1512 (12)	51 (4)
C(4)	4825 (12)	−3363 (12)	−2372 (16)	53 (4)
C(5)	5139 (11)	−2323 (11)	−1869 (13)	36 (3)
C(6)	4772 (9)	−1457 (10)	−2645 (12)	29 (3)
C(7)	4086 (11)	−1599 (12)	−3931 (14)	48 (4)
C(8)	3836 (12)	−692 (13)	−4534 (17)	56 (4)
C(9)	4303 (10)	288 (11)	−3755 (13)	37 (3)
C(10)	4191 (11)	1368 (12)	−4247 (14)	49 (4)
C(11)	3598 (12)	1521 (13)	−5460 (16)	55 (4)
C(12)	3532 (12)	2589 (12)	−5721 (16)	53 (4)
C(13)	4048 (12)	3370 (13)	−4819 (15)	55 (4)
C(14)	4660 (12)	3184 (13)	−3607 (16)	56 (4)
C(15)	8664 (11)	8656 (11)	4830 (14)	39 (3)
C(16)	8851 (12)	9697 (13)	5327 (15)	56 (44)
C(17)	9528 (12)	9977 (13)	6593 (15)	57 (4)
C(18)	9982 (12)	9305 (12)	7335 (15)	52 (4)
C(19)	9774 (10)	8279 (10)	6831 (12)	33 (3)
C(20)	10194 (10)	7444 (10)	7529 (13)	34 (3)
C(21)	10863 (10)	7513 (11)	8802 (13)	42 (4)
C(22)	11134 (11)	6655 (11)	9311 (14)	44 (4)
C(23)	10677 (9)	5674 (9)	8523 (11)	24 (3)
C(24)	10849 (9)	4632 (9)	8970 (12)	26 (3)
C(25)	11424 (11)	4417 (11)	10162 (14)	43 (4)
C(26)	11447 (12)	3374 (12)	10437 (15)	52 (4)
C(27)	10844 (11)	2541 (12)	9520 (14)	50 (4)
C(28)	10245 (12)	2807 (12)	8299 (15)	54 (4)

* These atoms have population parameter 0·5.

In complex *B* (Fig. 2) a bidentate nitrato group bridges the copper atoms Cu(3) and Cu(4), the latter being also bound to the oxygen O(2') of the μ-hydroxo group belonging to another molecule of the same kind. Therefore, complex *B* is a dimer where Cu(4) assumes a distorted octahedral six-coordinate geometry, whereas Cu(3) has a distorted square-pyramidal five coordination. Final atomic parameters are given in Table 1; bond distances and angles are reported in Table 2.

The structural features of complexes *A* and *B* are very similar to those already found for the previously

Table 2. *Bond distances* (Å) *and angles* (°)

Cu(1)–Cl(1)	2·211 (4)	Cu(3)–Cl(3)	2·221 (4)
Cu(1)–O(1)	1·893 (11)	Cu(3)–O(2)	1·909 (10)
Cu(1)–N(1)	2·040 (11)	Cu(3)–N(5)	2·014 (13)
Cu(1)–N(2)	1·988 (10)	Cu(3)–N(6)	1·973 (10)
Cu(1)–O(4)	2·72 (4)	Cu(3)–O(7)	2·791 (12)
Cu(1)–O(6′)	2·58 (4)	Cu(4)–Cl(4)	2·245 (4)
Cu(2)–Cl(2)	2·230 (4)	Cu(4)–O(2)	1·895 (8)
Cu(2)–O(1)	1·914 (9)	Cu(4)–O(2′)	2·800 (14)
Cu(3)–N(3)	1·973 (10)	Cu(4)–N(7)	1·982 (11)
Cu(2)–N(4)	1·994 (10)	Cu(4)–N(8)	2·024 (11)
Cu(2)–O(3)	2·343 (13)	Cu(4)–O(8)	2·535 (13)
N(1)–C(1)	1·330 (20)	N(5)–C(15)	1·332 (14)
N(1)–C(5)	1·331 (11)	N(5)–C(19)	1·363 (11)
N(2)–N(3)	1·38 (2)	N(6)–N(7)	1·36 (2)
N(2)–C(6)	1·296 (12)	N(6)–C(20)	1·341 (13)
N(3)–C(9)	1·316 (12)	N(7)–C(23)	1·283 (10)
N(4)–C(10)	1·381 (14)	N(8)–C(24)	1·384 (11)
N(4)–C(14)	1·34 (2)	N(8)–C(28)	1·30 (2)
C(1)–C(2)	1·36 (2)	C(15)–C(16)	1·41 (2)
C(2)–C(3)	1·37 (2)	C(16)–C(17)	1·38 (2)
C(3)–C(4)	1·44 (2)	C(17)–C(18)	1·33 (2)
C(4)–C(5)	1·37 (2)	C(18)–C(19)	1·39 (2)
C(5)–C(6)	1·49 (2)	C(19)–C(20)	1·46 (2)
C(6)–C(7)	1·39 (2)	C(20)–C(21)	1·38 (2)
C(7)–C(8)	1·40 (2)	C(21)–C(22)	1·33 (2)
C(8)–C(9)	1·42 (2)	C(22)–C(23)	1·42 (2)
C(9)–C(10)	1·50 (2)	C(23)–C(24)	1·48 (2)
C(10)–C(11)	1·35 (2)	C(24)–C(25)	1·34 (2)
C(11)–C(12)	1·43 (2)	C(25)–C(26)	1·38 (2)
C(12)–C(13)	1·30 (2)	C(26)–C(27)	1·37 (2)
C(13)–C(14)	1·37 (2)	C(27)–C(28)	1·40 (2)
N(9)–O(4)	1·26 (4)	N(10)–O(7)	1·21 (2)
N(9)–O(4′)	1·38 (4)	N(10)–O(8)	1·26 (2)
N(9)–O(5)	1·24 (3)	N(10)–O(9)	1·210 (13)
N(9)–O(6)	1·19 (3)		
N(9)–O(6′)	0·98 (4)		

Cu(1)–O(1)–Cu(2)	124·0 (5)	Cu(3)–O(2)–Cu(4)	123·2 (5)
Cl(1)–Cu(1)–O(1)	94·6 (3)	Cl(3)–Cu(3)–O(2)	94·5 (3)
Cl(1)–Cu(1)–N(1)	100·2 (3)	Cl(3)–Cu(3)–N(5)	99·3 (3)
Cl(1)–Cu(1)–N(2)	175·4 (4)	Cl(3)–Cu(3)–N(6)	176·5 (4)
Cl(1)–Cu(1)–O(4)	113·9 (6)	Cl(3)–Cu(3)–O(7)	101·9 (2)
Cl(1)–Cu(1)–O(6′)	89·9 (6)	O(2)–Cu(3)–N(5)	166·2 (4)
O(1)–Cu(1)–N(2)	87·2 (4)	O(2)–Cu(3)–N(6)	87·1 (4)
O(1)–Cu(1)–N(1)	164·0 (4)	O(2)–Cu(3)–O(7)	86·9 (4)
O(1)–Cu(1)–O(4)	95·8 (7)	N(6)–Cu(3)–N(5)	79·1 (5)
O(1)–Cu(1)–O(6′)	93·2 (8)	N(6)–Cu(3)–O(7)	75·1 (4)
N(2)–Cu(1)–N(1)	77·6 (4)	N(5)–Cu(3)–O(7)	90·7 (5)
N(2)–Cu(1)–O(4)	70·0 (7)	Cl(4)–Cu(4)–O(2)	97·0 (3)
N(2)–Cu(1)–O(6′)	94·2 (7)	Cl(4)–Cu(4)–N(7)	175·2 (3)
N(1)–Cu(1)–O(4)	83·7 (7)	Cl(4)–Cu(4)–N(8)	97·2 (3)
N(1)–Cu(1)–O(6′)	92·8 (8)	Cl(4)–Cu(4)–O(8)	99·4 (2)
Cl(2)–Cu(2)–O(1)	95·6 (3)	O(2)–Cu(4)–N(7)	87·8 (4)
Cl(2)–Cu(2)–N(3)	173·4 (4)	O(2)–Cu(4)–N(8)	165·8 (4)
Cl(2)–Cu(2)–N(4)	98·3 (3)	O(2)–Cu(4)–O(8)	88·7 (4)
Cl(2)–Cu(2)–O(3)	103·7 (3)	N(7)–Cu(4)–N(8)	78·1 (4)
O(1)–Cu(2)–N(3)	86·1 (4)	N(7)–Cu(4)–O(8)	80·9 (4)
O(1)–Cu(2)–N(4)	162·0 (4)	N(8)–Cu(4)–O(8)	89·0 (5)
O(1)–Cu(2)–O(3)	97·6 (4)	Cu(3)–N(5)–C(15)	123·5 (6)
N(3)–Cu(2)–N(4)	78·8 (4)	Cu(3)–N(5)–C(19)	115·1 (6)
N(3)–Cu(2)–O(3)	82·4 (4)	C(15)–N(5)–C(19)	121·3 (8)
N(4)–Cu(2)–O(3)	90·3 (5)	Cu(3)–N(6)–N(7)	120·9 (7)
Cu(1)–N(1)–C(1)	125·5 (6)	Cu(3)–N(6)–C(20)	118·7 (6)
Cu(1)–N(1)–C(5)	115·5 (6)	N(7)–N(6)–C(20)	119·9 (5)
C(1)–N(1)–C(5)	119·0 (9)	Cu(4)–N(7)–C(23)	120·1 (6)
Cu(1)–N(2)–C(6)	120·3 (5)	Cu(4)–N(7)–N(6)	119·4 (7)
Cu(1)–N(2)–N(3)	118·7 (8)	N(6)–N(7)–C(23)	120·4 (6)
C(6)–N(2)–N(3)	120·9 (5)	Cu(4)–N(8)–C(24)	115·4 (5)
N(2)–N(3)–Cu(2)	121·3 (7)	Cu(4)–N(8)–C(28)	124·5 (6)
N(2)–N(3)–C(9)	118·3 (6)	C(24)–N(8)–C(28)	120·0 (8)
Cu(2)–N(3)–C(9)	120·4 (6)	O(7)–N(10)–O(8)	118·3 (9)
Cu(2)–N(4)–C(14)	126·0 (6)	O(7)–N(10)–O(9)	123·9 (13)
C(10)–N(4)–C(14)	117·5 (9)	O(8)–N(10)–O(9)	117·8 (12)
Cu(2)–N(4)–C(10)	116·4 (6)		

reported aquatrichloro[3,6-di(2-pyridyl)pyridazine]-μ-hydroxo-dicopper(II) (Ghedini, De Munno, Denti, Manotti Lanfredi & Tiripicchio, 1982), in particular regarding the distortion undergone by the organic ligand. The presence of a bridging nitrato group in complex *B* does not seem to affect the geometry of the 3,6-di(2-pyridyl)pyridazine system to any relevant extent. The Cu(3)–O(7) and Cu(4)–O(8) bond distances [2·79 (1) and 2·54 (1) Å, respectively] are long in comparison with the corresponding distances (2·33 and 2·43 Å) observed for the complex cation aqua{1,4-bis(4-methyl-2-pyridylamino)phthalazine}-μ-hydroxo-dinitrato-dicopper(II) (Bautista, Dewan & Thompson, 1982), and could account for the small structural consequences connected with the presence of the μ-nitrato ligand. However, the observed Cu···Cu separations [3·346 (3) Å in complex *B* and 3·361 (4) Å in complex *A*] represent the smallest observed values for the intermetallic distance in complexes of the present kind. These are substantially longer than those found for a series of bis(2-pyridylamino)phthalazine-μ-hydroxo-dicopper(II) derivatives (Thompson, 1983), which are in the range 2·97–3·21 Å, in agreement with the higher flexibility of the ligand. The distance between the copper atom and the oxygen atom of the monodentate nitrato group in complex *A* also accounts for the tendency of the nitrato group to give weak bonds in these compounds, the bond lengths being 2·72 and 2·58 Å for Cu(1)–O(4) and Cu(1)–O(6′) respectively [the nitrate group is disordered into two positions generated by rotation around the N(9)–O(5) axis].

Some short contacts are found between the oxygen atom of water molecule O(11) and O(1), Cl(1), Cl(4): O(11)···O(1) = 2·75 (5), O(11)···Cl(1) = 3·16 (6), O(11)···Cl(4) = 3·14 (5) Å, and between the oxygen atom of water molecule O(10) and the chlorine atom Cl(2): O(10)···Cl(2) = 3·19 (2) Å.

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