

bonding interaction, the general arrangement of the bridge is similar.

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Structure of Mononuclear Bis{aqua[2,2'-(1,3,4-oxadiazole-2,5-diyl)dipyridine-N,N']}copper(II) Diperchlorate

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Abstract. [Cu(C₁₂H₈N₄O)₂(H₂O)₂](ClO₄)₂, *M_r* = 746.5, monoclinic, *P*₂₁/*n*, *a* = 13.579 (2), *b* = 10.904 (3), *c* = 10.329 (2) Å, β = 103.5°, *V* = 1487.1 Å³, *Z* = 2, *D_x* = 1.667, *D_m* = 1.67 g cm⁻³, λ(Mo *K*α) = 0.7107 Å, μ = 9.38 cm⁻¹, *F*(000) = 722, *R* = 0.053 for 769 reflexions. The structure consists of alternate layers of mononuclear centrosymmetric cations and ClO₄⁻ anions. Each ligand is bidentate, linked to the Cu atoms through one N atom of the oxadiazole and the N atom of one of the pyridines. The two water molecules complete a square-bipyramidal surrounding of the metal ion.

Introduction. Symmetrical 2,5-disubstituted-1,3,4-oxadiazoles are reported to show a broad spectrum of biological activities (Sharma & Tandon, 1984). No report on these kinds of molecules as ligands in metal compounds has appeared so far. In order to investigate the coordination mode in this type of compound, we selected 2,2'-(1,3,4-oxadiazole-2,5-diyl)dipyridine (odp).

Coordination compounds with 2,2'-(1,2,4-triazole-3,5-diyl)dipyridine have been identified (Keij, de Graff, Haasnoot & Reedijk, 1984); the crystal struc-

ture determination of an Ni compound showed the dinucleating properties of this ligand. Surprisingly, in spite of the similarity of the ligand structure, a mononuclear compound was obtained in our case.

Experimental. The odp ligand was synthesized according to Sharma & Tandon (1984). 0.18 g (8 × 10⁻⁴ mol) odp was added to a warm solution of 0.3 g (8 × 10⁻⁴ mol) Cu(ClO₄)₂·6H₂O in 40 ml of water. Green crystals appeared on standing for several days and were isolated by filtration.

Air stable tabular crystal mounted on glass rod. Unit-cell dimensions refined from 25 reflexions (4 < θ < 6°). Philips PW 1100 automated diffractometer. 1595 reflexions with 2 < θ < 20°, 0 < *h* < 13, 0 < *k* < 10, 0 < *l* < 10, 769 unique reflexions [*I* > 3σ(*I*)], *R_{int}* = 0.040; three standards (120, 211, 301) stable throughout data collection.

Observed reflexions limited by 0*k*0 (*k* = 2*n*) and *h*0*l* (*h* + *l* = 2*n*) leading to the non-standard space group *P*₂₁/*n*.

Crystal size: 0.155 × 0.3 × 0.02 mm with corresponding faces of the type (100), (010) and (001). Absorption correction applied, transmission factors:

Table 1. Atomic coordinates ($\times 10^4$) for all non-H atoms and equivalent isotropic thermal parameters (\AA^2) with e.s.d.'s in parentheses

$$B_{\text{eq}} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	B_{eq}
Cu	5000	5000	5000	4.26
O(1)	3461 (6)	5538 (7)	3501 (8)	7.84
N(1)	5266 (6)	3841 (8)	3662 (8)	4.35
N(2)	5697 (6)	3754 (9)	2568 (9)	5.09
C(1)	4963 (8)	2749 (12)	3871 (11)	4.44
O(2)	5140 (5)	1922 (6)	2991 (7)	4.51
C(2)	4463 (6)	2487 (8)	4937 (10)	3.54
C(3)	4116 (10)	1369 (10)	5234 (13)	5.12
C(4)	3670 (10)	1278 (12)	6282 (15)	5.53
C(5)	3579 (8)	2272 (12)	7050 (11)	4.92
C(6)	3952 (8)	3384 (11)	6680 (11)	4.60
N(3)	4373 (5)	3488 (6)	5658 (8)	3.85
C(7)	5624 (8)	2628 (12)	2193 (11)	4.46
C(8)	5908 (7)	2070 (11)	1085 (10)	4.27
N(4)	6027 (7)	866 (9)	1125 (10)	6.12
C(9)	6288 (14)	398 (14)	70 (21)	7.82
C(10)	6406 (11)	1007 (18)	-996 (16)	7.26
C(11)	6273 (10)	2249 (16)	-1025 (14)	6.70
C(12)	6019 (10)	2794 (13)	47 (14)	6.47
Cl	7711 (3)	1647 (3)	5667 (3)	5.73
O(3)	8085 (9)	2516 (10)	6566 (13)	13.29
O(4)	6755 (7)	1388 (12)	5787 (15)	15.86
O(5)	8173 (18)	607 (16)	6151 (20)	15.22
O(6)	7438 (17)	2046 (15)	4414 (20)	16.45
O(7)	8398 (20)	1303 (16)	4895 (19)	15.00

Table 2. Characteristic bond lengths (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

Cu—N(1)	1.966 (6)	N(3)—C(2)	1.343 (19)
Cu—N(3)	2.043 (6)	C(7)—C(8)	1.426 (16)
Cu—O(1)	2.365 (6)	C(8)—N(4)	1.323 (10)
N(1)—N(2)	1.393 (13)	N(4)—C(9)	1.324 (10)
N(2)—C(7)	1.284 (15)	C(9)—C(10)	1.328 (25)
C(7)—O(2)	1.400 (14)	C(10)—C(11)	1.365 (23)
O(1)—C(1)	1.341 (13)	C(11)—C(12)	1.371 (21)
C(1)—C(2)	1.451 (15)	C(12)—C(8)	1.368 (18)
C(2)—C(3)	1.373 (16)	Cl—O(3)	1.41 (2)
C(3)—C(4)	1.344 (21)	Cl—O(4)	1.35 (2)
C(4)—C(5)	1.09 (9)	Cl—O(5)	1.34 (2)
C(5)—C(6)	1.402 (17)	Cl—O(6)	1.39 (5)
C(6)—N(3)	1.317 (15)	Cl—O(7)	1.39 (4)
N(1)—Cu—N(3)	82.8 (5)	N(1)—N(2)—C(7)	107.0 (7)
N(1)—Cu—O(1)	88.8 (5)	C(7)—O(2)—N(1)	102.2 (8)
N(3)—Cu—O(1)	92.6 (5)	O(2)—C(1)—N(1)	113.1 (9)
C(1)—N(1)—N(2)	106.4 (9)	C(2)—C(1)—O(2)	124.8 (10)

max. = 0.9814, min. = 0.8748. Cu and Cl atoms located from Patterson map and direct methods, as well as odp cluster atoms. Successive difference Fourier syntheses displayed the O atoms of the water molecule and of the ClO_4 anion and finally the odp H atoms. The ClO_4 geometry is not clearly resolved: the best configuration, around the Cl position, gives a statistical disorder with two O positions fully occupied and three others with partial occupancy.

Least-squares refinement on F with anisotropic temperature factors for all non-H atoms. The H atoms were refined with a common temperature factor (using the free variable scheme). Final $R = 0.053$ (unit weight); max. Δ/σ in final refinement cycle = 0.07. Weights in final difference Fourier syn-

thesis: max. 0.32, min. -0.30 e \AA^{-3} . Atomic scattering factors and anomalous-dispersion corrections included in *SHELX76* (Sheldrick, 1976) for all atoms but Cu (*International Tables for X-ray Crystallography*). CII-Mini 6 computer was used.

Discussion. Atomic positions are given in Table 1, characteristic bond lengths and angles in Table 2.* The cation configuration and the atomic numbering scheme are shown in Fig. 1.

The structure of the centrosymmetric cation consists of a copper ion bridging two odp molecules, each linked by one nitrogen atom N(1) of the oxadiazole ring and its *syn*-nitrogen atom N(3) of the neighbouring pyridine ring. This part of the cation lies in plane (a) (Table 3) including also the C(8) linking atom of the non-chelated pyridine ring; in this ring the N(4) atom is *trans*-located from the non-bonded N(2) atom of the central oxadiazole and a planar configuration is kept (b) (Table 3) with an (a)–(b) interplane angle of 22.7° .

Two water molecules complete a square-bipyramidal surrounding of the metal ion (mean Cu—N = 2.009, Cu—O = 2.365 \AA).

In the ClO_4 anion, the bond lengths remain coherent but the angles are not significant. The disorder seems to be of the dynamic type according

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52390 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

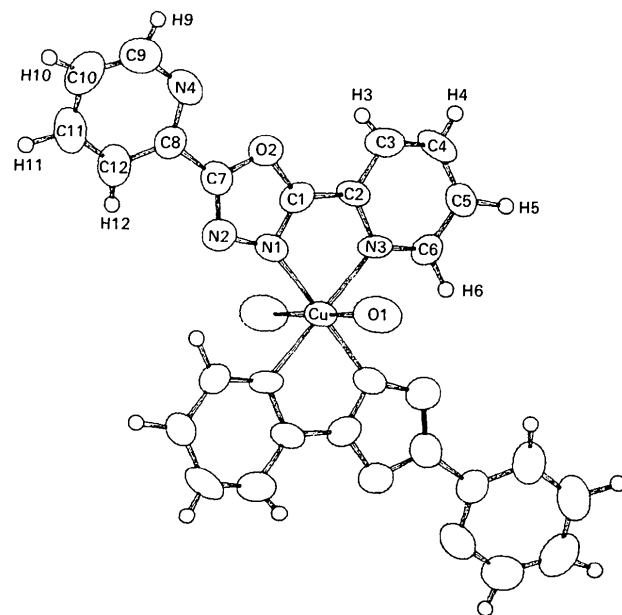


Fig. 1. Atom numbering in the mononuclear centrosymmetric cation.

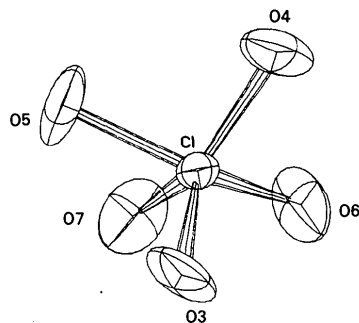
Table 3. Equations of mean planes and distances of the atoms from the planes (Å)

(a) $0.7684x - 0.2101y + 0.6044z = 6.1808$

N(1)	-0.021	C(3)	0.017
N(2)	-0.013	C(4)	0.006
C(7)	0.011	C(5)	0.007
O(2)	0.004	C(6)	-0.015
C(1)	0.001	N(3)	-0.030
C(2)	-0.011	Cu	0.000

(b) $0.8912x + 0.1242y + 0.4361z = 7.6704$

C(8)	0.002	C(10)	-0.004
N(4)	-0.008	C(11)	-0.003
C(9)	0.009	C(12)	0.003

Fig. 2. Disordered positions in the ClO₄⁻ anion.

to the elongated form of the thermal ellipsoids; the oxygen atoms O(5), O(6) and O(7) are refined respectively with 0.75, 0.75 and 0.5 occupancy factors; see Fig. 2.

The whole crystal structure can be described by alternative layers of [Cu(odp)₂(H₂O)₂]²⁺ and ClO₄⁻, probably linked by hydrogen bonds of the type O(1)⋯O(5) = 2.64 Å.

The mononuclear complex in [Cu(odp)₂(H₂O)₂](ClO₄)₂ will be used to initiate an interesting structural study of a new polynuclear complex family.

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Structures of Chromium(III) Cyclam Complexes. 2. Structure of *trans*-Dibromo(1,4,8,11-tetraazacyclotetradecane)chromium(III) Bromide

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Abstract. [CrBr₂(C₁₀H₂₄N₄)]Br, *M_r* = 492.0, tetragonal, *P*4₂/*m*, *a* = 7.860 (1), *c* = 13.507 (2) Å, *V* = 834.5 (3) Å³, *Z* = 2, *D_x* = 1.96 g cm⁻³, λ(Cu *K*α) = 1.54184 Å, μ = 119.4 cm⁻¹, *F*(000) = 483.96, room temperature, *R* = 0.0722 for 637 observed reflections. The cyclam moiety exists in a chair conformation with exact 2/*m* symmetry. The twofold axis passes through Cr and bisects the C(1)—C(1') and C(1'')—C(1''') bonds of the five-membered chelate

rings; the mirror plane also passes through Cr and contains atoms C(4) and C(4') of the cyclam moiety. The Br⋯Br' vector is tilted by 2.4° from the perpendicular to the CrN₄ plane.

Introduction. Quadrate complexes (*i.e.* *MBA*₂) of metals with *B* = quadridentate cyclic ligand have been extensively studied because they essentially have a stable four-donor-atom plane allowing for kinetic, photochemical and spectroscopic evaluation of the *A*₂ ligands. When the effective crystal field is

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