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[μ-*rel*-(3*R*,6*S*)-10,22-Dichloro-3,6-dimethyl-3,6,14,18-tetraazatricyclo[18.3.1.1^{8,12}]pentacosa-1(24),8,10,12(25),13,18,20,22-octane-24,25-diolato-$\kappa^4N^3,N^6,O^{24},O^{25}$:$\kappa^4N^{14},N^{18},O^{24},O^{25}$]dicopper(II) perchlorate

Huan Liu,[a] Yi-Zhi Li,[b] Dan Hu,[a] Zhi-Quan Pan[a]* and Xue-Lei Hu[a]

[a]Hubei Key Laboratory of Novel Chemical Reactor & Green Chemical Technology, Wuhan Institute of Technology, Wuhan 430073, People's Republic of China, and [b]State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, Nanjing University, Nanjing 210093, People's Republic of China

Correspondence e-mail: zhiqpan@163.com

Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.011 Å
R factor = 0.061
wR factor = 0.126
Data-to-parameter ratio = 14.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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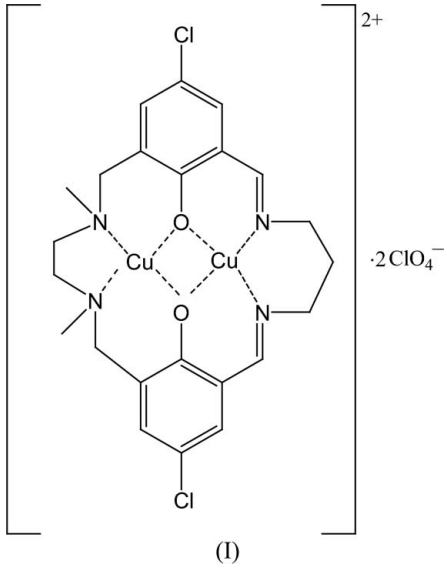
The title complex, $[Cu_2(C_{23}H_{26}Cl_2N_4O_2)](ClO_4)_2$, has been synthesized by condensation between *N*,*N*′-dimethyl-*N*,*N*′-bis(3-formyl-5-chlorosalicylidene)ethylenediamine and 1,3-propanediamine in the presence of copper(II). The complex is a phenol-based macrocyclic dinuclear complex, with the two Cu^{II} ions in $N(amine)_2O_2$ and $N(imine)_2O_2$ sites, and a Cu···Cu separation of 3.0138 (14) Å.

Comment

The study of dinuclear metal complexes is one of ongoing interest (Ōkawa *et al.*, 1998; McCollum *et al.*, 1996; Hori *et al.*, 2001). We have been studying macrocyclic systems with $N(amine)_2O_2$ and $N(imine)_2O_2$ metal-binding sites for a variety of diamines in order to investigate the relationship between topological structure and chelate ring size (Plieger *et al.*, 2004; Ramachandran *et al.*, 2004; Yonemura *et al.*, 1996). In this paper, we report the synthesis and structure of the title compound, (I).



(I)

The structure of (I) is shown in Fig. 1. Selected bond distances and angles relevant to the Cu^{II} coordination geometries are listed in Table 1. Atom Cu1 is coordinated by two amine and two phenoxide donors, while Cu2 is coordinated by two imine and two phenoxide donors. The perchlorate anions coordinate weakly to Cu1 with Cu—O distances of 2.824 (5) (Cu1—O6) and 2.511 (6) Å (Cu1—O7). The dihedral angle between the $N(amine)_2O_2$ and $N(imine)_2O_2$ planes is 1.2 (3)°. The deviations of Cu1 and Cu2 from these planes are 0.1180 (9) and 0.0338 (9) Å, respec-

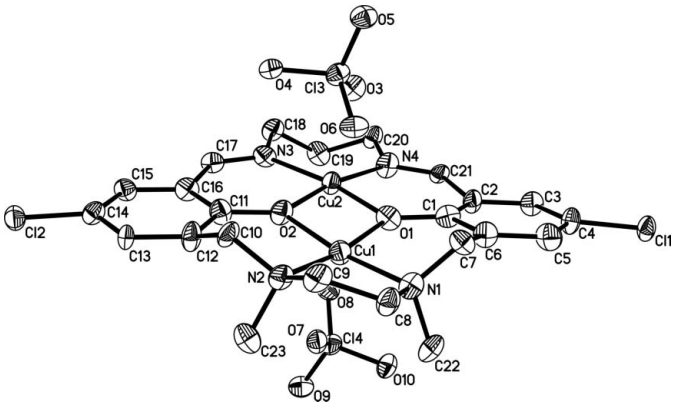


Figure 1
A view of the title complex cation, showing the atom labelling for the non-H atoms and 30% probability ellipsoids. H atoms have been omitted for clarity.

tively. The two methyl groups attached to atoms N1 and N2 are *cis* to each other. The Cu1···Cu2 separation is 3.0138 (14) Å.

Experimental

Caution: the perchlorate salts described below may be explosive and should be handled with great care! *N*,*N*′-Dimethyl-*N*,*N*′-bis(3-formyl-5-chlorosalicylidene)ethylenediamine (H_2L) was synthesized according to a literature method (Yonemura *et al.*, 1997). A mixture of H_2L and $(CH_3COO)_2CuH_2O$ (1:1) in acetonitrile was stirred for 6 h at ambient temperature. To this solution, an equivalent amount of $Cu(ClO_4)_2{\cdot}6H_2O$ and propane-1,3-diamine dissolved in acetonitrile was added with stirring. The resulting dark-green solution was concentrated to afford bottle green needle crystals. IR (KBr, ν cm^{-1}): 3430 (O—H), 1625 (C═N), 1097 and 623 (ClO_4^-).

Crystal data

$[Cu_2(C_{23}H_{26}Cl_2N_4O_2)](ClO_4)_2$
M_r = 787.36
Monoclinic, $P2_1$
a = 8.7105 (16) Å
b = 9.5778 (18) Å
c = 18.104 (3) Å
β = 100.761 (18)°
V = 1483.8 (5) Å^3
Z = 2
D_x = 1.762 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 1.85 mm^{-1}
T = 298 (2) K
Block, green
0.32 × 0.26 × 0.24 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.57, T_{max} = 0.64
15477 measured reflections
5798 independent reflections
4438 reflections with $I > 2\sigma(I)$
R_{int} = 0.055
θ_{max} = 26.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.061
$wR(F^2)$ = 0.126
S = 1.00
5798 reflections
390 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 1.88P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.67 e Å^{-3}
Absolute structure: Flack (1983), 2706 Friedel pairs
Flack parameter: 0.06 (2)

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.900 (5)	Cu2—O1	1.941 (5)
Cu1—N2	1.960 (6)	Cu2—N3	1.960 (6)
Cu1—N1	1.968 (6)	Cu2—O2	1.988 (5)
Cu2—N4	1.915 (6)		
O2—Cu1—O1	78.9 (2)	N4—Cu2—O1	93.3 (2)
O2—Cu1—N2	96.0 (2)	N4—Cu2—N3	99.0 (3)
O1—Cu1—N2	170.9 (3)	O1—Cu2—N3	167.5 (2)
O2—Cu1—N1	172.1 (3)	N4—Cu2—O2	168.7 (2)
O1—Cu1—N1	95.9 (3)	O1—Cu2—O2	75.6 (2)
N2—Cu1—N1	88.4 (3)	N3—Cu2—O2	91.9 (2)

All H atoms were placed in calculated positions, with C—H = 0.93–0.97 Å and O—H = 0.85 Å, and included in the refinement in the riding-model approximation, with U_{iso}(H) = 1.2–1.5U_{eq}(C,O).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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