solve structures: *SIR*92 (Altomare *et al.*, 1994) in *KRYSTAL* (Hazell, 1995); program(s) used to refine structures: modified *ORFLS* (Busing *et al.*, 1962) in *KRYSTAL*; molecular graphics: *ORTEP*III (Burnett & Johnson, 1996) in *KRYSTAL*; software used to prepare material for publication: *KRYSTAL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1224). Services for accessing these data are described at the back of the journal.

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Bis(di-2-pyridylmethanediol-*N*,*O*,*N*′)-copper(II) Diperchlorate

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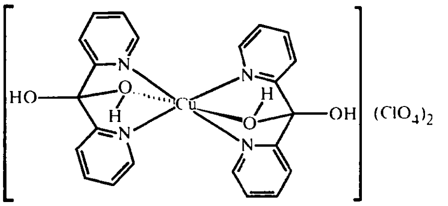
Abstract

Di-2-pyridyl ketone reacts with diaquatetrakis(betaine)-dicopper tetraperchlorate in water to form centrosymmetric bis(di-2-pyridylmethanediol)copper(II) diperchlorate, $[Cu(C_{11}H_{10}N_2O_2)_2](ClO_4)_2$, whose metal atom is *N*,*O*,*N*′-chelated by the two di-2-pyridylmethanediol ligands in an elongated octahedral CuN_4O_2 geometry. The hydroxyl groups are hydrogen bonded to the perchlorate anion.

Comment

Di-2-pyridyl ketone (hereafter DPK) functions either as a bidentate *N*,*N*′-donor or as a tridentate *N*,*O*,*N*′-donor towards metal ions, depending on the reaction medium used in the synthesis of the complexes (Deveson *et al.*, 1996), and several mononuclear and polynuclear transition metal–DPK complexes have been reported (Wang *et al.*, 1986; Sommerer *et al.*, 1993). The ligand undergoes alcoholysis to the acetal, $[(NC_5H_4)_2C(OR)(OH)]$ (R = alkyl), whose existence has been documented through its metal complexes (Bayers *et al.*, 1985; Baggio *et al.*, 1993; Papadopoulos *et al.*, 1996; Tangoulis *et al.*, 1996). The $[(NC_5H_4)_2C(OH)_2]$ homologue is trapped in the title complex, (I), which was obtained in the attempt to prepare a copper–DPK–betaine complex.



(I)

The title complex consists of bis(di-2-pyridylmethanediol)copper(II) cations and perchlorate anions. The Cu^{II} atom, which is located at an inversion centre, is chelated by the N, O and N′ atoms of the ligand, being surrounded by four N and two O atoms in an elongated octahedral CuN_4O_2 environment. The distortion arises from the deviation of the N1—Cu1—N2 [88.2 (1)°] and O1—Cu1—N1 [74.7 (1)°] angles from the idealized 90° value. The Cu—N bond lengths [2.009 (2) and 2.010 (2) Å] are similar to those [1.994 (5)–2.098 (5) Å] found in the di-2-pyridyl ketal complexes of nickel(II) and copper(II) (Wang *et al.*, 1986).

The title complex is structurally different from bis(di-2-pyridyl-1-hydroxymethoxy)cobalt(III) perchlorate trihydrate, where the Co^{III} atom is coordinated by a pair of the tridentate ligands, with the two Co—O bonds in a *cis* arrangement (Tong *et al.*, 1998). In contrast, in the present case, the two Cu—O bonds [2.454 (2) Å], being in a *trans* arrangement, significantly exceed the Cu—N bond distances, a feature which can be attributed to the Jahn–Teller effect, which usually manifests itself in d^9 metal systems. The hydroxyl groups are both involved as donors in hydrogen bonds with the perchlorate anion (Table 2).

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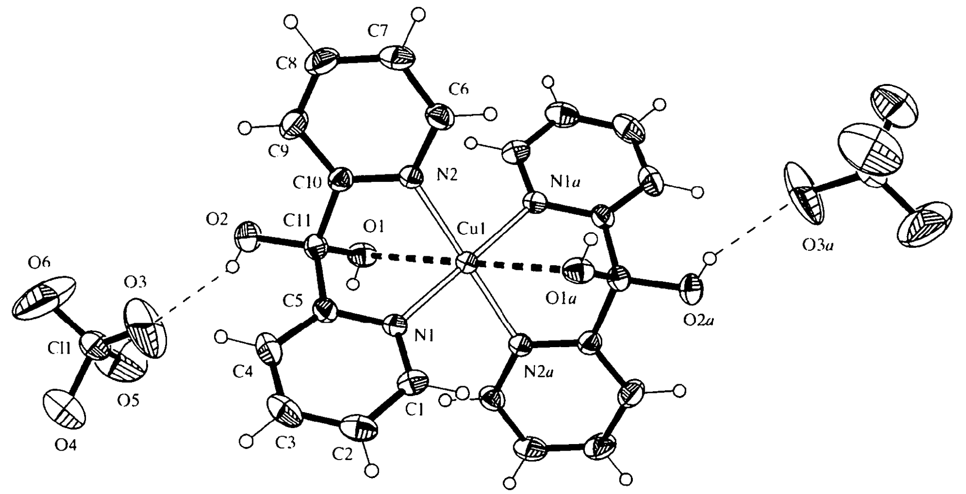

Fig. 1. *ORTEP*II (Johnson, 1976) plot of the title compound with ellipsoids at the 35% probability level. Suffix *a* on atom labels represents symmetry operation $-x$, $-y$, $-z$.

Experimental

DPK (1.0 mmol) was dissolved in water (2 ml) and the solution mixed with an aqueous solution containing $[Cu_2(\text{betaine})_4(H_2O)_2](ClO_4)_4$ (0.5 mmol). The mixture was heated to 333 K. Lilac blocks were deposited from the solution after several days. $[Cu_2(\text{betaine})_4(H_2O)_2](ClO_4)_4$ was prepared according to Chen & Mak (1993).

Crystal data

$[Cu(C_{11}H_{10}N_2O_2)_2](ClO_4)_2$
$M_r = 666.86$
Monoclinic
$P2_1/n$
$a = 7.8466\ (3)$ Å
$b = 13.6602\ (4)$ Å
$c = 12.2522\ (5)$ Å
$\beta = 100.830\ (4)°$
$V = 1289.88\ (8)$ Å^3
$Z = 2$
$D_x = 1.717$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12.0–15.0°$
$\mu = 1.127$ mm^{-1}
$T = 298\ (2)$ K
Regular block
0.44 × 0.36 × 0.32 mm
Lilac

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.613$, $T_{max} = 0.697$
3990 measured reflections
3746 independent reflections

3037 reflections with $I > 2\sigma(I)$
$R_{int} = 0.011$
$\theta_{max} = 29.96°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 19$
$l = -17 \rightarrow 16$
3 standard reflections frequency: 60 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.131$
$S = 1.026$
3746 reflections
195 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0707P)^2 + 0.9966P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.54$ e Å^{-3}
$\Delta\rho_{min} = -0.48$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cu1—N1	2.009 (2)	O1—C11	1.425 (3)
Cu1—N2	2.010 (2)	O2—C11	1.379 (3)
Cu1—O1	2.454 (2)		
N1—Cu1—N2'	91.8 (1)	C1—N1—Cu1	123.3 (2)
N1—Cu1—N2	88.2 (1)	C5—N1—Cu1	117.1 (2)
N1—Cu1—O1	74.7 (1)	C10—N2—Cu1	116.6 (2)
N2—Cu1—O1	72.4 (1)	C6—N2—Cu1	124.6 (2)
C11—O1—Cu1	92.8 (1)		

Symmetry code: (i) $-x, -y, -z$.

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
O2—H21···O3	2.11 (4)	2.750 (4)	153 (4)
O1—H11···O4'	2.26 (4)	2.932 (4)	155 (4)
O1—H11···O5'	2.39 (4)	3.028 (5)	149 (4)

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

H atoms were refined as a riding model with $U(H) = 1.5U_{eq}(C)$. The hydroxyl H atoms were located and refined.

Data collection: *CAD*-4 *VAX/PC* (Enraf–Nonius, 1988). Cell refinement: *CAD*-4 *VAX/PC*. Data reduction: *Xtal*3.0 (Hall & Stewart, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Triethylenetetraminehexaacetic Acid Complex of Lead

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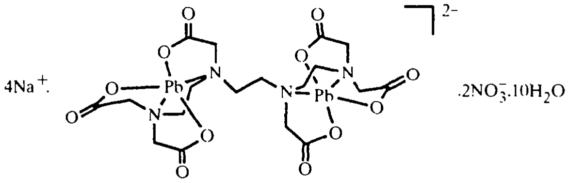
Abstract

In the title compound, tetrasodium μ-[3,6,9,12-tetrakis(carboxymethyl)-3,6,9,12-tetraazatetradecanedioato-$1\kappa^5O^1,N^3,O^3,N^6,O^6:2\kappa^5N^9,O^9,N^{12},O^{12},O^{14}$]dilead dinitrate decahydrate, $Na_4[Pb_2(C_{18}H_{24}N_4O_{12})](NO_3)_2\cdot 10H_2O$, the Pb^{2+} ions have highly distorted bonding geometry, with a primary coordination number of five and two secondary intermolecular contacts. The Pb—N bond distances range from 2.505 (4) to 2.641 (4) Å, and the Pb—O bond distances range from 2.454 (3) to 2.559 (3) Å. The binuclear lead complexes sit on inversion centers and are bridged to form polymeric structures. The polymers are linked into sheets *via* N···O contacts.

Comment

The use of metal-ion chelation for remediation of soils and waters contaminated with toxic metal ions (Pb, Cd, Hg) is finding increasing application. Extractants such as nitrilotriacetic acid, H_3NTA, ethylenediaminetetraacetic acid, H_4EDTA, and diethylenetriaminepentaacetic acid, H_5DTPA, have commonly been used for extraction of lead (Barbarick & Workman, 1987; Elliott & Brown, 1989; Raghavan *et al.*, 1989). Polymeric aminocarboxylate systems with multiple metal-binding sites are also of interest for waste-water treatment (Geckeler & Volchek, 1996). Surprisingly, only a few structural studies of this class of molecules with heavy metals have been reported in the literature (Harrison & Steel, 1982; Solans *et al.*, 1985). Characterization of metal-ion binding in these simple yet effective molecular extractants will enhance our ability to design new chelator systems based on this functional group. We report herein the structure of a triethylenetetraminehexaacetic acid (H_6TTHA) complex of lead, (1).



(1)

Tetrasodium triethylenetetraminehexaacetatodilead dinitrate decahydrate, (1), contains a binuclear complex that forms weak dibridged polymeric structures. Further weak intermolecular bonding leads to a sheet-like structure. As shown in Fig. 1, all ten donor atoms of the TTHA ligand are utilized in binding the two Pb^{2+} ions, and the ligand has an inversion center at the midpoint of the central ethylene bridge (C9—C9′). The ligand bond distances and angles are typical (Fallon & Gatehouse, 1974, 1976; Leverett, 1974). The other four reported TTHA–metal complexes (*M* = VO, Cr, Cu, Sb) are discrete molecules with very similar ligand geometries (Allen & Kennard, 1993; Fallon & Gatehouse, 1974, 1976; Leverett, 1974). The lead salt reported here has a polymeric structure and the ligand geometry differs from that reported in other M_2TTHA complexes in that