Fe(Co)1—O11	2.046 (6)	Fe(Co)3—O3	2.160 (7)
Fe(Co)1—O16	2.012 (6)	Fe(Co)3—O8	2.043 (7)
Fe(Co)2—O4	1.898 (6)	Fe(Co)3—O9	2.025 (6)
Fe(Co)2—O2	2.145 (8)	Fe(Co)3—O14	2.027 (6)
Fe(Co)2—O6	2.035 (6)	Fe(Co)3—O15	2.027 (7)
Fe(Co)1—Fe(Co)2—Fe(Co)3	59.80 (4)	Fe(Co)1—O4—Fe(Co)2	120.2 (3)
Fe(Co)1—Fe(Co)3—Fe(Co)2	59.95 (4)	Fe(Co)1—O4—Fe(Co)3	119.9 (3)
Fe(Co)2—Fe(Co)1—Fe(Co)3	60.26 (4)	Fe(Co)2—O4—Fe(Co)3	119.9 (4)

Cell constants were automatically obtained and refined for the internally centered cell (*I*2/*a*) [$a = 15.286\,(1)$, $b = 13.838\,(1)$, $c = 22.605\,(1)$ Å and $\beta = 91.161\,(4)°$], and reflections were collected with the setting. For comparison of the structure with that of the corresponding trinuclear iron complex, the structure was solved after revising the cell constants and reflection data to those for *C*2/*c*. Refinements were performed for the three cases (Co1/Fe2/Fe3, Fe1/Co2/Fe3 and Fe1/Fe2/Co3) by locating one Co and two Fe atoms at the three Fe(Co) sites. In the three cases, refinement converged to $R = 0.062$ and there was no significant difference in geometry between them. The structure was therefore refined by locating an Fe atom of site occupancy 0.667 and a constrained Co atom of site occupancy 0.333 at each metal position. Peaks corresponding to H-atom positions could not be seen in difference Fourier syntheses and no theoretical calculations were performed to obtain the positions of H atoms. The five largest positive peaks in the final difference Fourier map were located near water molecules of crystallization.

Data collection: *CAD*-4 *Express* (Enraf–Nonius, 1992). Cell refinement: *SET*4 in *CAD*-4 *Express*. Data reduction: *DATA* in *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIR*88 (Burla *et al.*, 1989). Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *DRAW* in *MolEN*. Software used to prepare material for publication: *OMEGA* in *MolEN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1083). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Di-μ-chloro-bis[(diethylenetriamine)-copper(II)] Dinitrate

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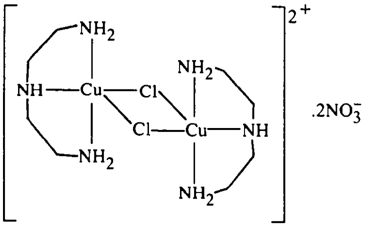
Abstract

The crystal structure of the title compound, di-μ-chloro-bis{[*N*-(2-aminoethyl)-1,2-ethanediamine-*N*,*N*′,*N*″]-copper(II)} dinitrate, $[Cu_2Cl_2(dien)_2](NO_3)_2$ (dien is diethylenetriamine; $C_4H_{13}N_3$), consists of chloride-bridged copper(II) dimers. Each copper ion is five-coordinate with geometry that is approximately square-pyramidal. Hydrogen bonding involving the three O atoms of the nitrate counteranions and the three H atoms of the amine groups of the organic ligand stabilizes the crystal packing.

Comment

Polynuclear copper(II) halide systems are of interest from both the inorganic and bio-inorganic viewpoints, particularly with respect to the study of the structural parameters which may have an influence on the strength and sign of magnetic coupling (Rojo, Arriortua, Ruiz, Darriet, Villeneuve & Beltrán-Porter, 1987). Cu^{II} atoms are also present in several metalloproteins and so the study of model systems is useful for the interpretation of their biological functions (Fee, 1975).

The ligands selected to block the metal have been shown to play an important role in determining the final structure and, consequently, the structural parameters. In this sense, the use of rigid aromatic amine ligands gives rise to minor variations in certain parameters, such as the bridging angles, which have a great influence on the final magnetic behaviour (Rojo, Arriortua, Mesa, Cortés, Villeneuve & Beltrán-Porter, 1987). The use of a non-rigid aliphatic ligand would lead to a wider range of values for these parameters and so we decided to use diethylenetriamine (dien) as a ligand and prepared the title compound, (I).



(I)

A view of the dimeric unit of (I) is shown in Fig. 1. The structure consists of centrosymmetric dinuclear $[Cu_2(dien)_2Cl_2]^{2+}$ cations and NO_3^- counterions. The copper(II) ions in the dimer are linked by two Cl atoms. Each copper(II) cation is pentacoordinated by one dien molecule (N1, N2 and N3) and two Cl atoms [Cl and Cl^i; symmetry code: (i) $-x$, $-y$, $-z$]. The coordination sphere around the central Cu^{II} atom is a distorted square pyramid where the three N atoms (N1, N2 and N3) and a Cl atom form the basal plane, while the other Cl atom (Cl^i) occupies the apical position.

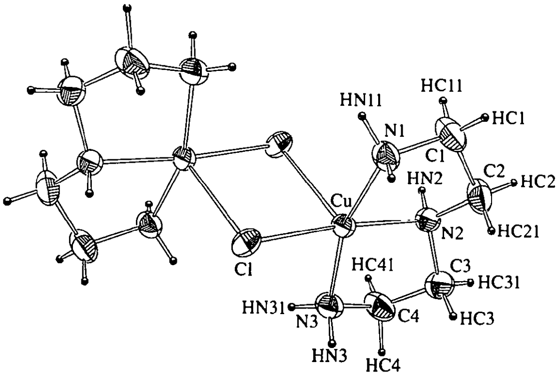


Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the dimeric $[Cu_2(dien)_2Cl_2]^{2+}$ cation showing the atomic numbering scheme and displacement ellipsoids plotted at the 50% probability level.

The distances from the three N atoms to the copper ion are very similar [Cu—N1 2.014 (2), Cu—N2 2.017 (1) and Cu—N3 2.004 (2) Å]. The Cu—Cl apical bond is much longer than the basal one [2.646 (1) *versus* 2.318 (1) Å], a feature which appears frequently in copper(II) crystal chemistry and which characterizes the square-pyramidal configuration. The same feature has been observed in the dimer $[Cu_2(terpy)_2Cl_2](PF_6)_2$ (Rojo, Arriortua, Ruiz, Darriet, Villeneuve & Beltrán-Porter, 1987) and in the monomer $[Cu(terpy)Cl_2].H_2O$ (Rojo, Vlasse & Beltrán-Porter, 1983), where terpy is 2,2′,2″-terpyridine.

The existence of an inversion centre causes the Cu—Cl$_2$—Cu^i bridging unit to form a plane. In this dimeric unit, the copper cations are separated from each other by 3.537 (1) Å and the Cu—Cl—Cu^i and Cl—Cu—Cl^i angles are 90.62 (1) and 89.38 (2)°, respectively.

A highly planar configuration is observed for the nitrate ion. The values of the N—O bond distances and O—N—O bond angles (approximately 1.233 Å and 120°, respectively) are in good agreement with those found in the literature (Anderson, Packard & Wicholas, 1976; Anderson, 1975).

The cationic complex $[Cu_2(dien)_2Cl_2]^{2+}$ dimers are linked *via* hydrogen bonds between the dien ligands and the nitrate anions (Table 3).

Experimental

Prismatic blue crystals of the title compound were obtained by slow evaporation of a water/ethanol solution containing copper(II) nitrate, diethylenetriamine (dien) and sodium chloride in stoichiometric proportions.

Crystal data

$[CuCl(C_4H_{13}N_3)]NO_3$
$M_r = 264.17$
Monoclinic
$P2_1/n$
$a = 6.680 (1)$ Å
$b = 13.996 (2)$ Å
$c = 10.816 (1)$ Å
$\beta = 104.22 (1)°$
$V = 980.2 (2)$ Å^3
$Z = 4$
$D_x = 1.790$ Mg m^{-3}
$D_m = 1.785 (3)$ Mg m^{-3}
D_m measured by flotation

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 9–13°$
$\mu = 2.484$ mm^{-1}
$T = 293 (2)$ K
Prismatic
0.46 × 0.34 × 0.24 mm
Blue

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
3070 measured reflections
2850 independent reflections
2386 observed reflections [$I > 2\sigma(I)$]

$R_{int} = 0.0133$
$\theta_{max} = 29.96°$
$h = 0 \rightarrow 9$
$k = -4 \rightarrow 19$
$l = -15 \rightarrow 14$
3 standard reflections
frequency: 60 min
intensity decay: 4%

Refinement

Refinement on F^2
$R(F) = 0.0222$
$wR(F^2) = 0.0737$
$S = 0.651$
2850 reflections
158 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0758P)^2 + 0.3302P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.004$
$\Delta\rho_{max} = 0.359$ e Å^{-3}
$\Delta\rho_{min} = -0.385$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cu	0.18516 (3)	0.05095 (1)	0.12858 (2)	0.02618 (7)
N1	0.0833 (3)	0.00157 (11)	0.27710 (15)	0.0338 (3)
N2	0.2328 (2)	0.17316 (10)	0.23040 (13)	0.0284 (3)
N3	0.3585 (2)	0.11378 (11)	0.0247 (2)	0.0346 (3)
C1	0.0746 (4)	0.0806 (2)	0.3661 (2)	0.0455 (4)
C2	0.2501 (4)	0.14821 (14)	0.3648 (2)	0.0412 (4)
C3	0.4157 (3)	0.21983 (13)	0.2053 (2)	0.0372 (4)
C4	0.3925 (3)	0.21528 (13)	0.0636 (2)	0.0419 (4)
Cl	0.17170 (6)	−0.09649 (3)	0.02918 (4)	0.03071 (9)
N4	0.5780 (2)	−0.10128 (12)	0.29428 (14)	0.0380 (3)
O1	0.4514 (2)	−0.12719 (12)	0.35345 (15)	0.0499 (4)
O2	0.5907 (3)	−0.01556 (14)	0.2662 (2)	0.0689 (5)
O3	0.6891 (4)	−0.1599 (2)	0.2604 (2)	0.0907 (8)

Table 2. *Selected geometric parameters (Å, °)*

Cu—N3	2.004 (2)	N2—C2	1.472 (2)
Cu—N1	2.014 (2)	N3—C4	1.483 (2)
Cu—N2	2.017 (1)	C1—C2	1.509 (3)
Cu—Cl	2.318 (1)	C3—C4	1.503 (3)
Cu—Cl$^{\rm i}$	2.646 (1)	Cl—Cu$^{\rm i}$	2.646 (1)
Cu—Cu$^{\rm i}$	3.537 (1)	N4—O3	1.221 (2)
N1—C1	1.476 (2)	N4—O1	1.233 (2)
N2—C3	1.468 (2)	N4—O2	1.246 (3)
N3—Cu—N1	162.27 (7)	C3—N2—Cu	107.66 (10)
N3—Cu—N2	84.18 (6)	C2—N2—Cu	107.57 (11)
N1—Cu—N2	83.94 (6)	C4—N3—Cu	109.30 (11)
N3—Cu—Cl	95.31 (5)	N1—C1—C2	108.0 (2)
N1—Cu—Cl	94.71 (4)	N2—C2—C1	106.6 (2)
N2—Cu—Cl	172.32 (4)	N2—C3—C4	106.73 (15)
N3—Cu—Cl$^{\rm i}$	94.93 (5)	N3—C4—C3	107.46 (15)
N1—Cu—Cl$^{\rm i}$	99.77 (5)	Cu—Cl—Cu$^{\rm i}$	90.62 (1)
N2—Cu—Cl$^{\rm i}$	98.30 (4)	O3—N4—O1	120.2 (2)
Cl—Cu—Cl$^{\rm i}$	89.38 (2)	O3—N4—O2	119.4 (2)
C1—N1—Cu	109.8 (1)	O1—N4—O2	120.4 (2)
C3—N2—C2	114.9 (2)		

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

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—HN1$\cdots$O1	0.87 (2)	2.17 (3)	2.996 (7)	159 (3)
N2—HN2$\cdots$O1$^{\rm i}$	0.89 (2)	2.39 (2)	3.098 (2)	137 (2)
N1—HN11$\cdots$O3$^{\rm ii}$	0.90 (3)	2.60 (3)	3.441 (3)	157 (2)
N1—HN11$\cdots$O2$^{\rm ii}$	0.90 (3)	2.48 (3)	3.272 (3)	146 (2)
N3—HN31$\cdots$O3$^{\rm iii}$	0.88 (2)	2.29 (3)	3.089 (3)	151 (2)
N3—HN3$\cdots$Cl$^{\rm iii}$	0.88 (2)	2.63 (3)	3.338 (2)	138 (2)

Symmetry codes: (i) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $x-1, y, z$; (iii) $1-x, -y, -z$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *Xtal*3.2 (Hall, Flack & Stewart, 1992). 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: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1250). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Paucity of Hydrogen Bonds in Ferrocene-1,1′-diylbis[bis(4-methoxyphenyl)methanol]–Methanol (3/2)

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Abstract

In the 3:2 adduct formed between ferrocene-1,1′-diylbis[bis(4-methoxyphenyl)methanol] and methanol, $3[\mathrm{Fe(C_{20}H_{19}O_3)_2}].2\mathrm{CH_4O}$, the ferrocenediol occupies two types of site. Ferrocenediol molecules in general positions form intramolecular O—H$\cdots$O hydrogen bonds and are hydrogen-bonded to methanol molecules by a single O—H$\cdots$O hydrogen bond, while ferrocenediol molecules lying across centres of inversion form no O—H$\cdots$O hydrogen bonds. Overall, only half of the hydroxyl groups in the asymmetric unit act as donors in O—H$\cdots$O hydrogen bonds, while none of the seven independent methoxy groups acts as acceptors of O—H$\cdots$O hydrogen bonds.