

**Data collection**

CAD-4 diffractometer  $\theta_{\max} = 28.46^\circ$   
 $\theta-2\theta$  scans  $h = 0 \rightarrow 8$   
 Absorption correction:  $k = -18 \rightarrow 18$   
 $\psi$  scan (Fair, 1990)  $l = -20 \rightarrow 20$   
 $T_{\min} = 0.529, T_{\max} = 0.573$  3 standard reflections  
 6468 measured reflections frequency: 420 min  
 6468 independent reflections intensity decay: 0.7%  
 4849 reflections with  
 $I > 2\sigma(I)$

**Refinement**

Refinement on  $F^2$   $(\Delta/\sigma)_{\max} = 0.018$   
 $R[F^2 > 2\sigma(F^2)] = 0.063$   $\Delta\rho_{\max} = 0.97 \text{ e } \text{\AA}^{-3}$   
 $wR(F^2) = 0.204$   $\Delta\rho_{\min} = -0.64 \text{ e } \text{\AA}^{-3}$   
 $S = 1.207$  Extinction correction: none  
 6468 reflections Scattering factors from  
 363 parameters *International Tables for*  
 H atoms constrained *Crystallography* (Vol. C)  
 $w = 1/[\sigma^2(F_o^2) + (0.0516P)^2$   
 $+ 8.8786P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Co1—N12	1.945 (6)	Co2—N23	1.947 (5)
Co1—N13	1.945 (5)	Co2—N22	1.949 (5)
Co1—N15	1.946 (5)	N21—O21A	1.224 (7)
Co1—N14	1.957 (5)	N21—O21B	1.230 (7)
Co1—N16	1.960 (5)	Co3—N31	1.924 (5)
Co1—N11	1.975 (5)	Co3—N32	1.950 (5)
N11—O11B	1.229 (7)	Co3—N33	1.953 (5)
N11—O11A	1.232 (7)	N31—O31B	1.229 (7)
N12—O12A	1.205 (8)	N31—O31A	1.233 (8)
Co2—N21	1.932 (5)		
N12—Co1—N13	89.1 (2)	N16—Co1—N11	89.1 (2)
N12—Co1—N15	90.8 (2)	O11B—N11—O11A	117.4 (5)
N13—Co1—N15	179.6 (2)	O11B—N11—Co1	121.7 (4)
N12—Co1—N14	90.3 (2)	O11A—N11—Co1	120.8 (4)
N13—Co1—N14	86.0 (2)	O12A—N12—Co1	120.4 (5)
N15—Co1—N14	93.6 (2)	N21—Co2—N23	90.6 (2)
N12—Co1—N16	90.1 (2)	N21—Co2—N22	89.8 (2)
N13—Co1—N16	94.9 (2)	N23—Co2—N22	86.0 (2)
N15—Co1—N16	85.5 (2)	O21A—N21—O21B	119.5 (5)
N14—Co1—N16	179.0 (2)	O21A—N21—Co2	120.1 (4)
N12—Co1—N11	178.1 (2)	O21B—N21—Co2	120.4 (4)
N13—Co1—N11	89.3 (2)	N31—Co3—N32	89.6 (2)
N15—Co1—N11	90.8 (2)	N31—Co3—N33	90.6 (2)
N14—Co1—N11	90.6 (2)	N32—Co3—N33	85.8 (2)

Table 2. Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N13—H13A $\cdots$ O31A	0.90	2.08	2.973 (7)	170
N14—H14A $\cdots$ O21A <sup>i</sup>	0.90	2.17	3.037 (8)	161
N15—H15A $\cdots$ O24 <sup>ii</sup>	0.90	2.09	2.969 (10)	164

Symmetry codes: (i)  $x, 1 + y, z$ ; (ii)  $1 + x, 1 + y, z$ .

H atoms were included as a riding model with C—H = 0.97  $\text{\AA}$  and N—H = 0.90  $\text{\AA}$ .

Data collection: *CAD-4 EXPRESS* (Straver, 1992). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1228). Services for accessing these data are described at the back of the journal.

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**A redetermination of bis(ethylenediamine-*N,N'*)bis(perchlorato-*O*)copper(II)**

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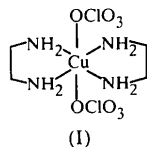
(Received 7 June 1999; accepted 7 September 1999)

**Abstract**

Reaction of copper(II) perchlorate with excess ethylenediamine (en) in aqueous solution gave the title complex, [Cu(ClO<sub>4</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>]. The cation is centrosymmetric with a mean Cu—N distance of 2.016 (2)  $\text{\AA}$ . There are semi-coordinate bonds to the perchlorate ions with a Cu—O distance of 2.579 (4)  $\text{\AA}$ . The N—Cu—N angle is 84.69 (9)°, as expected for chelating en. The structure is stabilized by hydrogen bonds from three of the perchlorate O atoms to amino H atoms within each molecule and between molecules, linking them into chains.

### Comment

Our interest in one-dimensional magnetic materials has led us to investigate compounds belonging to the NENP family [NENP is bis(ethylenediamine)nitronickel(II) perchlorate]. The structure of NENP (Meyer *et al.*, 1982), its general magnetic properties (Renard *et al.*, 1988) and its high field magnetization response (Katsumata *et al.*, 1989) show this compound to be an outstanding example of one which can be used to study the Haldane gap (Haldane, 1983). This compound is routinely prepared by disproportionation of the tris(ethylenediamine)nickel(II) complex with nickel perchlorate in the presence of sodium nitrite. We are interested in how corresponding chains with non- $S = 1$  spin ions and doping NENP with non- $S = 1$  ions will affect the magnetic behavior of the system. Our attempts to prepare the corresponding copper coordination polymer by the same route were thwarted by our inability to prepare the starting compound, tris(ethylenediamine)copper(II) perchlorate; in all cases, bis(ethylenediamine- $N,N'$ )bis(perchlorato- $O$ )copper(II), (I), resulted. The only previous report of the structure of complex (I) was a low resolution study by Pajunen (1967) and so we undertook to resolve this structure in the hope that it would yield some information on the instability of the tris-complex.



Complex (I) was isolated by slow evaporation of an aqueous solution. The crystals are square plates and are dichroic; when viewed perpendicular to the square face, the crystals appear purple, but when viewed parallel to that face they are pink. Complex (I) crystallizes in the triclinic space group  $P\bar{1}$  with the Cu atom at the origin (see Fig. 1) so that only one en ring and one perchlorate ion appear in the asymmetric unit.

A typical Jahn-Teller distortion results in the Cu atom having long semi-coordinate axial bonds to the perchlorate ions [Cu—O1 = 2.579(4) Å] at an angle of 88.0(1)° relative to the CuN<sub>4</sub> plane. The Cu—N bond distances are 2.012(2) Å and 2.019(2) Å to N4 and N1, respectively, and the angle between them is 84.69(9)°. One of the chelate rings is in the  $\lambda$  conformation and the other is in the  $\delta$  conformation. This also generates a pseudo-mirror in the molecules, which lies between the two en rings and passes through the Cu and Cl atoms. The data are in good agreement with those reported by Pajunen (1967) with a substantially reduced  $R$  factor and are comparable to those for the tetrafluoroborate complex (Brown *et al.*, 1968). The higher quality and more extensive data set allowed for location and refinement of the amino H atoms, which are responsible for stabilizing the lattice through hydrogen bonding.

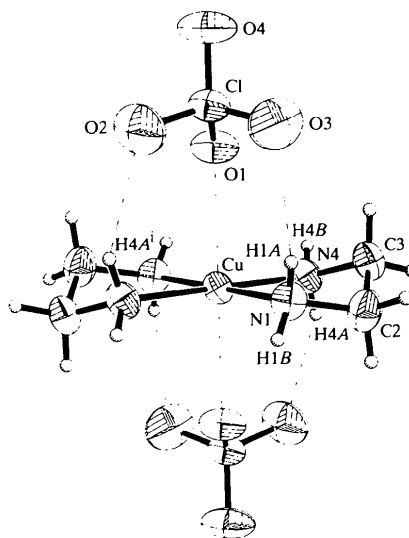


Fig. 1. The molecular structure of (I) showing the intramolecular hydrogen bonds and 50% probability displacement ellipsoids. H atoms are drawn as spheres of arbitrary radii [symmetry code: (i)  $-x, -y, -z$ ].

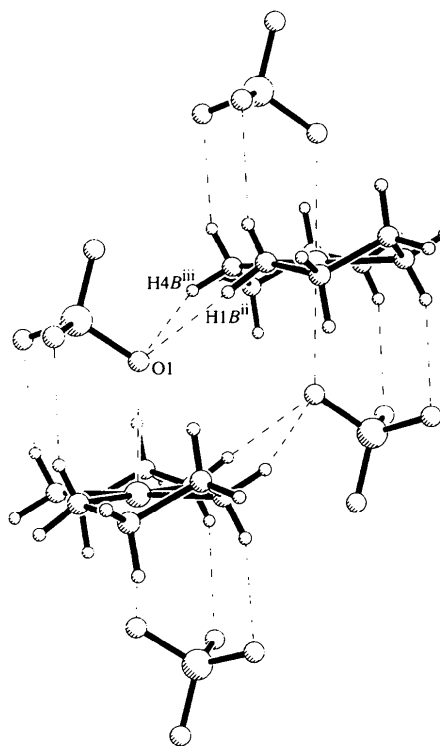


Fig. 2. The structure of two units in the chain showing the intermolecular hydrogen bonding [symmetry codes: (ii)  $x+1, y, z$ ; (iii)  $-x+1, -y, -z$ ].

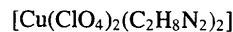
The position of the perchlorate ions in the molecular unit is stabilized by hydrogen bonds between the amino H atoms and two of the perchlorate O atoms (see Fig. 1). Hydrogen bonds are found between O3 and H1A, and

between O2 and H4A. The lattice is further stabilized by hydrogen bonding between an O atom of one molecule and two amino H atoms of an adjacent molecule (Fig. 2). These bonds occur through O1, the oxygen coordinated to the Cu atom, and link the molecules into chains parallel to the *a* axis. The combination of elongation of the axial bonds due to the Jahn–Teller effect and the stabilization of the lattice due to the hydrogen bonding in (I) may explain the failure to prepare the desired tris(ethylenediamine) complex.

## Experimental

Complex (I) was prepared from an aqueous solution of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (6.5 mmol) in water (10 ml) to which ethylenediamine (13.1 mmol) had been added. Slow evaporation yielded square plates which were dichroic (pink/purple). A final yield of 85.3% was obtained after recovering three crops.

### Crystal data



*M<sub>r</sub>* = 382.65

Triclinic

*P* $\bar{1}$

*a* = 5.7100 (8) Å

*b* = 7.8019 (15) Å

*c* = 7.9527 (7) Å

$\alpha$  = 75.319 (12)°

$\beta$  = 79.168 (9)°

$\gamma$  = 77.967 (16)°

*V* = 331.75 (8) Å<sup>3</sup>

*Z* = 1

*D<sub>x</sub>* = 1.915 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

Mo *K*α radiation

$\lambda$  = 0.71073 Å

Cell parameters from 15 reflections

$\theta$  = 9.65–12.98°

$\mu$  = 2.089 mm<sup>-1</sup>

*T* = 293 (2) K

Square plate

0.30 × 0.30 × 0.18 mm

Dichroic pink/purple

### Data collection

Enraf–Nonius CAD-4 diffractometer

$\theta/2\theta$  scans

Absorption correction:  $\psi$  scan (Fair, 1990)

*T<sub>min</sub>* = 0.608, *T<sub>max</sub>* = 0.687

2002 measured reflections

2002 independent reflections

1918 reflections with

*I* > 2σ(*I*)

$\theta_{\max}$  = 30.37°

*h* = 0 → 8

*k* = -10 → 11

*l* = -10 → 11

3 standard reflections

frequency: 90 min

intensity decay: 5.9%

### Refinement

Refinement on *F*<sup>2</sup>

$R[F^2 > 2\sigma(F^2)] = 0.041$

$wR(F^2) = 0.146$

*S* = 1.179

2002 reflections

101 parameters

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0973P)^2 + 0.1165P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.003$

$\Delta\rho_{\max} = 0.73 \text{ e } \text{Å}^{-3}$

$\Delta\rho_{\min} = -0.84 \text{ e } \text{Å}^{-3}$

Extinction correction:

*SHELXL97* (Sheldrick, 1997)

Extinction coefficient:

0.36 (3)

Scattering factors from

*International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Cu—N4	2.012 (2)	Cl—O2	1.419 (3)
Cu—N1	2.019 (2)	Cl—O4	1.421 (2)
N1—C2	1.486 (4)	Cl—O3	1.428 (3)
C2—C3	1.505 (4)	Cl—O1	1.453 (2)
C3—N4	1.478 (3)		
N4—Cu—N1	84.69 (9)	N4—C3—C2	107.2 (2)
C2—N1—Cu	108.29 (16)	C3—N4—Cu	108.61 (16)
N1—C2—C3	108.4 (2)		

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1A...O3	0.82 (4)	2.39 (4)	3.135 (4)	152 (4)
N1—H1B...O1 <sup>i</sup>	0.91 (4)	2.39 (4)	3.225 (3)	151 (3)
N4—H4A...O2 <sup>ii</sup>	0.89 (4)	2.38 (4)	3.174 (4)	149 (3)
N4—H4B...O1 <sup>iii</sup>	0.96 (4)	2.37 (4)	3.202 (3)	145 (3)

Symmetry codes: (i) *x* - 1, *y*, *z*; (ii) -*x*, -*y*, -*z*; (iii) 1 - *x*, -*y*, -*z*.

All H atoms were assigned a *U<sub>iso</sub>* of 1.2 times that of the atom to which they were bonded. H atoms attached to C were placed in calculated positions with a C—H bond length of 0.97 Å. The atomic coordinates of amino-H atoms were refined.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1222). Services for accessing these data are described at the back of the journal.

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