

Cie, 1988c); program(s) used to solve structures: *Xtal3.2 SIMPEL* (Hall *et al.*, 1992); program(s) used to refine structures: *Xtal3.2 CRYLSQ*; molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *Xtal3.2 BONDLA CIFIO*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1347). Services for accessing these data are described at the back of the journal.

## References

- Bergerhoff, G. (1996). *DIAMOND. Visual Crystal Structure Information System*. Gerhard-Domagk-Straße 1, Bonn, Germany.
- Cotton, S. (1991). In *Lanthanides and Actinides*. Oxford University Press.
- Evans, C. H. (1990). In *Biochemistry of the Lanthanides*. New York: Plenum Press.
- Hall, S. R., Flack, H. D. & Stewart, J. M. (1992). Editors. *Xtal3.2 User's Manual*. Universities of Western Australia, Australia, Geneva, Switzerland, and Maryland, USA.
- Lippard, S. J. (1967). *Prog. Inorg. Chem.* **8**, 109–193.
- Niinisto, L. (1987). *Inorg. Chim. Acta*, **140**, 339–343.
- Panagiotopoulos, A., Zafiroopoulos, T. F., Perlepes, S. P., Bakalbassis, E., Masson-Ramade, I., Kahn, O. & Terzis, A. (1995). *Inorg. Chem.* **34**, 4918–4920.
- Pope, G. W., Steinbach, J. F. & Wagner, W. F. (1961). *J. Inorg. Nucl. Chem.* **20**, 304–313.
- Stoe & Cie (1988a). *DIF4. Diffractometer Control Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.
- Stoe & Cie (1988b). *EMPIR. Data Setup for Empirical Absorption Correction*. Version 6.2. Stoe & Cie, Darmstadt, Germany.
- Stoe & Cie (1988c). *REDU4. Data Reduction Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.
- Watson, W. H., Williams, R. J. & Stemple, N. R. (1972). *J. Inorg. Nucl. Chem.* **34**, 501–508.

*Acta Cryst.* (1998). **C54**, 1236–1238

## Aqua(2-ethylpyridine-*N*)(*N*-salicylidene-glycinato-*O,N,O'*)copper(II)

SALAM A. WARDA

Department of Chemistry, University of Marburg, Hans-Meerwein-Straße, 35032 Marburg, Germany. E-mail: warda@ax1501.chemie.uni-marburg.de

(Received 30 January 1998; accepted 26 March 1998)

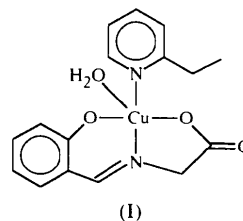
## Abstract

In the title compound, [Cu(C<sub>9</sub>H<sub>7</sub>NO<sub>3</sub>)(C<sub>7</sub>H<sub>9</sub>N)(H<sub>2</sub>O)], the copper(II) centre has a square-pyramidal environment with a tridentate *N*-salicylidene-glycinato Schiff base dianion and a 2-ethylpyridine ligand coordinated in the basal plane. The apex of the pyramid is occupied

by the O atom of the coordinated water molecule at a distance of 2.388 (3) Å. The monomeric units are associated through hydrogen bonds, forming infinite chains. There are two magnetically different copper(II) polyhedra.

## Comment

The tetrameric structure of (4-ethylpyridine)(*N*-salicylidene-glycinato)copper(II), which crystallizes with a tetragonal unit cell, has been reported recently (Warda, 1997). In this communication, the structure of the closely related title complex, aqua(2-ethylpyridine)(*N*-salicylidene-glycinato)copper(II), (I), is reported.



The Cu<sup>II</sup> ion has square-pyramidal [4+1] coordination geometry, with the tridentate Schiff base *N*-salicylidene-glycinato dianion and the monodentate 2-ethylpyridine ligand in the basal plane (Fig. 1). The apical position is occupied by a water O atom at a distance of 2.388 (3) Å. It is noteworthy that coordination of water to Cu<sup>II</sup> is invariably at the apical site of a tetragonally elongated square pyramid. This seems to be a general result for five-coordinate Cu<sup>II</sup> complexes (Warda, 1998, and references therein).

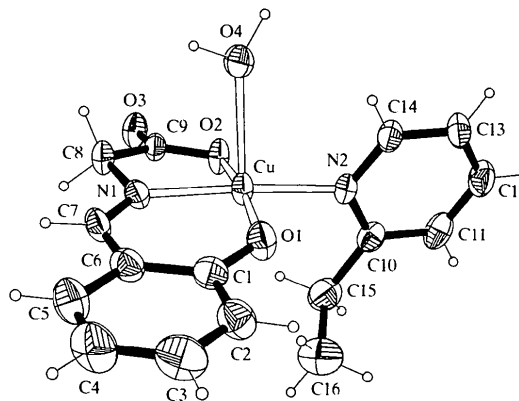


Fig. 1. The asymmetric unit of the title compound with the atomic numbering scheme. Ellipsoids are drawn at the 50% probability level.

The pyridine ring is inclined with respect to the basal plane (through atoms O1, O2, N1 and N2) at an angle of 80.0 (1)° and the Cu atom lies 0.155 (1) Å out of this plane, displaced towards the O4 atom (*PLATON*;

Spek, 1994). The Cu—N and Cu—O bond distances in the equatorial plane [Cu—N 1.930 (3) and 2.003 (3) Å, and Cu—O 1.911 (2) and 1.976 (2) Å] do not differ significantly from those of the other members in this series (Warda, 1998, and references therein).

The monomers are associated through hydrogen bonding, forming a chain *via* O4—H41...O3 interactions that is connected by O4—H42...O2 hydrogen bonds to a second (inverted) chain. These chains run parallel to [001]. The former hydrogen bond is much shorter than the latter [O4...O3 2.749 (4) and O4...O2 2.924 (4) Å].

In the title compound, the copper(II) polyhedra are arranged in two magnetically inequivalent orientations with  $2\gamma$  of 17.9 (2)°; the *g* tensor is slightly affected by this value, indicating a distorted ferrodistoritive ordering ( $0 < 2\gamma < 45^\circ$ ;  $2\gamma$  is the angle describing the orientation of the main axes of the polyhedra with respect to one another and should therefore be carefully distinguished from the cell parameter with the same symbol). The value of the *g* tensor allows the tilting angle between differently oriented copper(II) polyhedra to be estimated as 19°, which is in good agreement with the X-ray data.

It is worth comparing the monoclinic structure in this report with the closely related orthorhombic structure of polymeric (3-ethylpyridine)(*N*-salicylidenglycinato)copper(II) (Warda, 1994). The position of the substituent in the pyridine ligand has a crucial effect on the metric of the lattice, which is monoclinic in the present case (2-ethylpyridine), but is orthorhombic in the 3-ethylpyridine (Warda, 1994) and tetragonal in the 4-ethylpyridine compound (Warda, 1997).

## Experimental

The title compound was synthesized from aqua(*N*-salicylidenglycinato)copper(II) hemihydrate according to the methods of Ueki *et al.* (1967) and Warda (1994), with 2-ethylpyridine in a 1:3 ethanol–water mixture at 333 K. Dark-green prismatic crystals grew within a few days.

### Crystal data

[Cu(C<sub>9</sub>H<sub>7</sub>NO<sub>3</sub>)(C<sub>7</sub>H<sub>9</sub>N)·(H<sub>2</sub>O)]

*M<sub>r</sub>* = 365.86

Monoclinic

*P*2<sub>1</sub>/*c*

*a* = 14.7592 (15) Å

*b* = 10.7763 (11) Å

*c* = 10.0983 (7) Å

$\beta$  = 92.473 (7)°

*V* = 1604.6 (3) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 1.514 Mg m<sup>-3</sup>

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

Mo *K*α radiation

$\lambda$  = 0.71073 Å

Cell parameters from 25 reflections

$\theta$  = 18.93–22.10°

$\mu$  = 1.382 mm<sup>-1</sup>

*T* = 293 (2) K

Prism

0.36 × 0.12 × 0.05 mm

Dark green

### Data collection

Enraf–Nonius CAD-4 diffractometer

*R<sub>int</sub>* = 0.013

$\theta_{\max}$  = 25.06°

$\omega$  scans

Absorption correction:

$\psi$  scans (Siemens, 1996a)

*T<sub>min</sub>* = 0.636, *T<sub>max</sub>* = 0.937

3009 measured reflections

2846 independent reflections

1904 reflections with

*I* > 2σ(*I*)

*h* = -17 → 3

*k* = -5 → 12

*l* = -12 → 12

2 standard reflections

frequency: 120 min

intensity decay: none

### Refinement

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

*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.043

*wR* (*F*<sup>2</sup>) = 0.095

2846 reflections

214 parameters

H atoms: see below

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0508*P*)<sup>2</sup>]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

(Δ/σ)<sub>max</sub> < 0.001

Δρ<sub>max</sub> = 0.44 e Å<sup>-3</sup>

(1.14 Å from Cu)

Δρ<sub>min</sub> = -0.54 e Å<sup>-3</sup>

(0.95 Å from Cu)

Extinction correction: none

Scattering factors from

*International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Cu—O1	1.911 (2)	Cu—N2	2.003 (3)
Cu—N1	1.930 (3)	Cu—O4	2.388 (3)
Cu—O2	1.976 (2)		
O1—Cu—N1	92.97 (12)	O2—Cu—N2	90.45 (10)
O1—Cu—O2	169.93 (11)	O1—Cu—O4	99.72 (11)
N1—Cu—O2	83.70 (11)	N1—Cu—O4	89.38 (11)
O1—Cu—N2	91.87 (11)	O2—Cu—O4	89.77 (11)
N1—Cu—N2	171.94 (12)	N2—Cu—O4	96.15 (11)

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>
O4—H41...O3 <sup>i</sup>	0.89 (1)	1.91 (1)	2.749 (4)	157 (1)
O4—H42...O2 <sup>ii</sup>	0.89 (1)	2.04 (1)	2.924 (4)	171 (1)

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

All H atoms, except the water H atoms, were included at calculated positions and refined using a riding model. The *U*<sub>iso</sub> for H atoms of CH and CH<sub>2</sub> or the CH<sub>3</sub> groups were taken as 1.2*U*<sub>eq</sub> or 1.5*U*<sub>eq</sub> of the carrier atoms, respectively. Atoms H41 and H42 were found from the difference Fourier syntheses and refined with *U*<sub>iso</sub> = 1.2*U*<sub>eq</sub>(water O); O—H distances were restrained to be equal.

Data collection: CAD-4 EXPRESS (Enraf–Nonius, 1994). Cell refinement: CAD-4 EXPRESS. Data reduction: XCAD4 (Harms, 1997). Program(s) used to solve structure: SHELXS97 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997). Molecular graphics: XP (Siemens, 1996b). Software used to prepare material for publication: SHELXL97.

We thank the head of the X-ray diffraction section, Professor Dr W. Massa (University of Marburg), for making diffractometer time available.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1284). Services for accessing these data are described at the back of the journal.

## References

Enraf–Nonius (1994). CAD-4 EXPRESS. Version 5.1. Enraf–Nonius, Delft, The Netherlands.

- Harms, K. (1997). *XCAD4. Program for the Reduction of CAD-4 Diffractometer Data*. University of Marburg, Germany.
- Reinen, D. & Atanasov, M. (1991). *Magn. Res. Rev.* **15**, 167–239.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97. Release 97-1. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Siemens (1996a). *XPREP in SHELXTL. Program for Data Preparation and Reciprocal Space Exploration*. Version 5.05. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1996b). *XP in SHELXTL. Molecular Graphics Program*. Version 5.06. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Spek, A. L. (1994). *PLATON. Program for Molecular Geometry*. University of Utrecht, The Netherlands.
- Ueki, T., Ashida, T., Sasada, Y. & Kakudo, M. (1967). *Acta Cryst.* **22**, 870–878.
- Warda, S. A. (1994). *Bioanorganische Kupfer(II) Komplexe mit dreizähligen O,N,O Chelat-Dianionen und additiven einzähligen Donorliganden*. Aachen: Verlag Shaker.
- Warda, S. A. (1997). *Acta Cryst.* **C53**, 697–699.
- Warda, S. A. (1998). *Acta Cryst.* **C54**, 187–189.

*Acta Cryst.* (1998). **C54**, 1238–1240

## Dibromo(diethyl ether-*O*)(diisopropylamine-*N*)magnesium(II)

KENNETH W. HENDERSON AND ALAN R. KENNEDY

*Department of Pure & Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL, Scotland. E-mail: a.r.kennedy@ccsun.strath.ac.uk*

(Received 27 January 1998; accepted 3 March 1998)

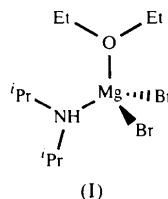
### Abstract

The coordination geometry at the Mg atom in the title complex, [MgBr<sub>2</sub>{(C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>NH}]{(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O}], is shown to be distorted tetrahedral. The presence of a secondary amine ligand is unusual in its derivation from an amide. It is also unusual to find both an ether and a simple amine solvating the same magnesium centre [Mg1—N1 2.158 (3) and Mg1—O1 2.041 (3) Å].

### Comment

As part of our continuing investigations of the organometallic complexes present during the course of Mg-mediated enolization reactions (Allan *et al.*, 1997, 1998), we were interested in preparing a range of halomagnesium enolate complexes. This was attempted by the reaction of Hauser bases (R<sub>2</sub>NMgX, where R = alkyl or aryl, and X = halide) with ketones carrying an α-proton. Unless the reaction conditions for this transformation are very tightly controlled, the halomagnesium enolate complexes undergo a dismutation

reaction into the respective dihalides and dienolates. This paper discusses the structure of one such dihalide, [MgBr<sub>2</sub>(OEt<sub>2</sub>)(NH<sup>*i*</sup>Pr<sub>2</sub>)], (I), which is unusual in that the rehydrogenated amine is present as a donor ligand.



The crystal structure consists of monomeric molecular units, with the closest intermolecular interaction being that of N1—H1···Br2<sup>i</sup> [N1···Br2<sup>i</sup> 3.659 (3), H1···Br2<sup>i</sup> 2.78 Å and N1—H1···Br2<sup>i</sup> 163°; symmetry code: (i) 2 - x, 1 - y, -z]. The coordination geometry about the Mg atom is distorted tetrahedral, the largest deviation from ideal geometry being the wide N1—Mg1—Br1 angle of 120.35 (11)° (Table 1). That the angle from N1 to the second bromide ligand is smaller [N1—Mg1—Br2 102.28 (10)°] is a consequence of the molecular conformation adopted by (I). The substituents about the Mg—N bond are eclipsed [O1—Mg1—N1—C4 6.7 (3), Br1—Mg1—N1—C1 -12.9 (3) and Br2—Mg1—N1—H1 4.2°]. Thus, the Br1—Mg1—N1 angle opens to relieve the steric interaction between Br1 and the *syn*-isopropyl group. In contrast, as Br2 lies *syn* to H1, there is little steric repulsion (Br2···H1 3.25 Å). The wider angle at Mg1 from Br2 to O1, as opposed to that from Br1, may similarly be explained by the steric strain imposed by Br2 being *syn* to an ethyl group [Br2—Mg1—O1—C7 -5.4 (3)°].

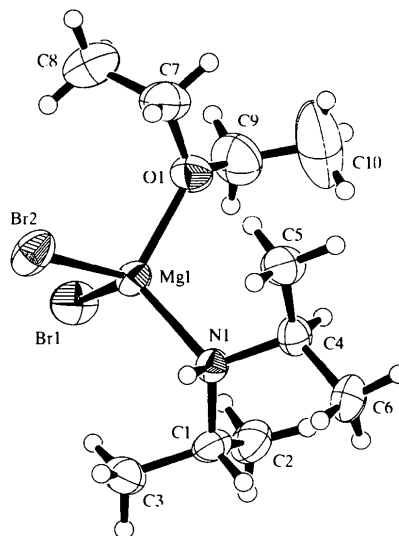


Fig. 1. ORTEP (Johnson, 1976) view of (I). Non-H atoms are shown as 40% probability ellipsoids and H atoms as small spheres of arbitrary radii.