$\theta/2\theta$ scan
Absorption correction:
ψ scan (North *et al.*, 1968)
$T_{\min} = 0.667$, $T_{\max} = 0.713$
5913 measured reflections
4536 independent reflections
2996 reflections with $I > 2\sigma(I)$

$h = -1 \rightarrow 12$
$k = -1 \rightarrow 13$
$l = -25 \rightarrow 25$
3 standard reflections every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.118$
$S = 1.056$
4536 reflections
273 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0547P)^2 + 0.3604P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.009$
$\Delta\rho_{\max} = 0.28$ e Å^{-3}
$\Delta\rho_{\min} = -0.37$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Cu1—O1	1.893 (2)	Cu1—N2	2.005 (2)
Cu1—O2	1.963 (2)	Cu1—O3	2.239 (2)
Cu1—N1	1.995 (2)		
O1—Cu1—O2	93.32 (9)	N1—Cu1—N2	81.69 (9)
O1—Cu1—N1	90.36 (9)	O1—Cu1—O3	95.60 (9)
O2—Cu1—N1	169.73 (9)	O2—Cu1—O3	84.65 (9)
O1—Cu1—N2	165.9 (1)	N1—Cu1—O3	104.54 (9)
O2—Cu1—N2	92.68 (9)	N2—Cu1—O3	97.64 (9)
O1—C13—C18—C19	6.2 (5)	O2—C19—C18—C13	−3.0 (5)

Data collection: *SHELXTL/PC* (Sheldrick, 1994). Cell refinement: *SHELXTL/PC*. Data reduction: *SHELXTL/PC*. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ZORTEP* (Zsolnai, 1997). Software used to prepare material for publication: *CIFTAB* in *SHELXL97*.

We would like to acknowledge Sylvain Bernès from USAI–Facultad de Química for collection of the data.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1120). Services for accessing these data are described at the back of the journal.

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Aqua(4,7-diphenyl-1,10-phenanthroline)(salicylaldehydato)copper(II) nitrate monohydrate

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Abstract

Each Cu^{II} ion in the title compound, aqua(4,7-diphenyl-1,10-phenanthroline-*N*,*N'*)(2-formylphenolato-*O*,*O'*)copper(II) nitrate monohydrate, $[Cu(C_7H_5O_2)(C_{24}H_{16}N_2)(H_2O)]NO_3 \cdot H_2O$, displays a slightly distorted square-pyramidal coordination site where the O atom from one water molecule is in the apical position [at 2.306 (4) Å], and both the O atoms [at 1.970 (3) and 1.939 (3) Å] of the salicylaldehydate and the N atoms [at 1.994 (3) and 1.998 (2) Å] of the phenanthroline molecule define its base. The five-membered chelate ring formed by the phenanthroline ligand and the Cu atom is roughly planar, while the chelate ring formed by the salicylaldehydate ligand and the Cu atom is planar, with a slight distortion towards an envelope conformation. Hydrogen bonding and π–π^* orbital interactions seem to determine the crystal packing. The complex is cationic and the nitrate ion is not coordinated.

Comment

Our study of the IR spectroscopic properties of several mixed phenanthroline and *O*-donor complexes has led us to prepare and crystallize the $[Cu(H_2O)(salal)(4,7\text{-di-}\varphi\text{-fen})]NO_3 \cdot H_2O$ complex (salal is salicylaldehydate

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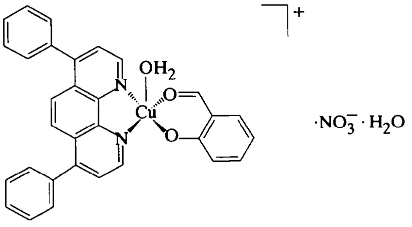
and 4,7-di-φ-fen is 4,7-diphenyl-1,10-phenanthroline), (I), among others.



(I)

The coordination sphere of the Cu^{II} ion (Fig. 1) is composed of five ligand atoms, with an N_2O_3-type atom coordination in a distorted square-pyramidal coordination site, where the water molecule is in the apical position, and the aromatic phenanthroline N and the salicylaldehydate O atoms lie in a plane with a slight tetrahedral distortion [N1 −0.060 (2), N2 0.061 (2), O1 0.056 (2) and O2 −0.058 (2) Å; the Cu1 atom is −0.104 (2) Å out of the plane formed by N1, N2, O1 and O2, and the apical O atom of the bonded water molecule is −2.404 (4) Å from this plane].

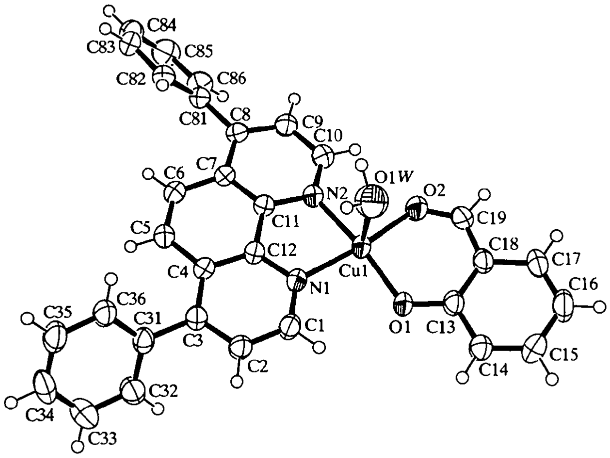


Fig. 1. *ZORTEP* plot (Zsolnai, 1997) of the molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

There are some other relevant planes, among them, the chelate ring formed by the N1, C11, C12, N2 and Cu1 atoms, and that formed by the salicylaldehydate moiety (O1, C13, C19, O2 and Cu1). The first plane is only slightly distorted (r.m.s. deviation of the fitted atoms is 0.0222 Å), while the second is more distorted (r.m.s. deviation of the fitted atoms is 0.0849 Å). A greater distortion is expected for the salicylaldehydate ring as it is six-membered. However, when the sixth member is included (O1, C13, C18, C19, O2 and Cu1), the r.m.s. deviation only changes to 0.0917 Å. This is consistent with aromaticity in the salicylaldehydate molecule.

The angle between the planes formed by the metal and the coordinated atoms, *i.e.* Cu1/N1/N2 and Cu1/O1/O2, is 9.9 (3)°.

Examination of the the main metal–ligand distances shows that the Cu—N distances are longer than the Cu—O1 distances, as observed in many related complexes with the salicylaldehydate ligand (Garland *et al.*, 1986, 1987; Li *et al.* 1995; Solans *et al.*, 1987; Gasque *et al.*, 1999).

Similar behavior has been observed in aminoacidate complexes (Aoki & Yamasaky, 1980; Antolini *et al.*, 1985; Solans *et al.*, 1992, 1993).

The distance from the metal to the apical O atom of the coordinated water in (I) [2.306 (4) Å] is longer than that to the apical O atom of the nitrate ion in the $[Cu(NO_3)(salal)(5,6\text{-dm-phen})]$ complex [2.239 (2) Å; Gasque *et al.*, 1999], but shorter than that in unsubstituted phenanthroline (2.496 Å; Li *et al.*, 1995).

Molecules in the crystal are arranged so as to form pairs in which the phenanthroline molecules and the salicylaldehydate moieties lie approximately parallel to one another. The average distance between the phenanthroline and salicylaldehydate planes is 3.041 (6) Å. Distances between planes were calculated as the average distance from each atom of one of the molecules to the plane defined by the other. Additionally, hydrogen-bond interactions between water molecules and the O atoms of the salicylaldehydate ligand can account partially for the crystal packing. Thus, it is observed that crystal packing is influenced by both hydrogen bonding and π–π* orbital interactions among the phenanthroline and salicylaldehydate units. In the crystal, the shortest distance from the nitrate ion to the Cu atom is 4.176 Å.

Experimental

The title complex was obtained by mixing $Cu(NO_3)_2$ (2.5 ml, 0.1 *M*) with 4,7,-diphenyl-1,10-phenanthroline (0.25 mmol) in ethanol and salicylaldehyde (salalH, 2.5 ml, 0.1 *M*) dissolved in a 50:50 mixture of ethanol/water. This solution was neutralized with aqueous NH_4OH (0.5 *M*) and left standing until crystals had formed. The isolated product (prismatic dark-green crystals) was filtered off, washed with ethanol and vacuum dried. Crystals suitable for X-ray analysis were obtained from the batch.

Crystal data

$[Cu(C_7H_5O_2)(C_{24}H_{16}N_2)$-
$(H_2O)]NO_3{\cdot}H_2O$
$M_r = 615.08$
Triclinic
$P\overline{1}$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 2$–$25°$

$a = 10.670\,(1)$ Å
$b = 11.752\,(1)$ Å
$c = 12.099\,(1)$ Å
$\alpha = 83.93\,(1)°$
$\beta = 72.21\,(1)°$
$\gamma = 74.02\,(1)°$
$V = 1388.4\,(2)$ Å^3
$Z = 2$
$D_x = 1.471$ Mg m^{-3}
D_m not measured

$\mu = 0.841$ mm^{-1}
$T = 293\,(2)$ K
Prismatic
0.5 × 0.5 × 0.3 mm
Green

Data collection

Siemens *P*4/PC diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.733$, $T_{\max} = 0.777$
5723 measured reflections
4867 independent reflections
3572 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.024$
$\theta_{\max} = 25°$
$h = -1 \rightarrow 12$
$k = -13 \rightarrow 13$
$l = -13 \rightarrow 14$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.144$
$S = 1.019$
4867 reflections
393 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0734P)^2 + 1.0087P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.017$
$\Delta\rho_{\max} = 0.53$ e Å^{-3}
$\Delta\rho_{\min} = -0.50$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Cu1—O1	1.907 (3)	Cu1—N2	1.998 (3)
Cu1—O2	1.939 (3)	Cu1—O1*W*	2.306 (4)
Cu1—N1	1.994 (3)		
O1—Cu1—O2	93.8 (1)	N1—Cu1—N2	82.0 (1)
O1—Cu1—N1	93.8 (1)	O1—Cu1—O1*W*	98.5 (1)
O2—Cu1—N1	171.8 (1)	O2—Cu1—O1*W*	88.8 (2)
O1—Cu1—N2	169.6 (1)	N1—Cu1—O1*W*	93.4 (1)
O2—Cu1—N2	90.0 (1)	N2—Cu1—O1*W*	91.3 (1)
O1—C13—C18—C19	−2.4 (6)	O2—C19—C18—C13	4.2 (7)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*···O4	0.97	1.87	2.770 (8)	154
O1*W*—H1*W*···N3	0.97	2.58	3.462 (7)	151
O1*W*—H2*W*···O2*W*	0.94	1.94	2.879 (7)	172
O2*W*—H3*W*···O5$^{\rm i}$	1.01	2.10	3.033 (9)	154
O2*W*—H3*W*···O3$^{\rm i}$	1.01	2.12	2.987 (8)	144
O2*W*—H3*W*···N3$^{\rm i}$	1.01	2.44	3.415 (9)	163
O2*W*—H4*W*···O3	1.00	1.95	2.880 (9)	153

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

All H atoms attached to C atoms were refined using a riding model, while water H atoms were placed in fixed positions with refined $U_{\rm iso}$ values.

Data collection: *SHELXTL/PC* (Siemens, 1994). Cell refinement: *SHELXTL/PC*. Data reduction: *SHELXTL/PC*. Program(s) used to solve structure: *SHELX*97 (Sheldrick, 1997). Program(s) used to refine structure: *SHELX*97. Molecular graphics: *ZORTEP* (Zsolnai, 1997). Software used to prepare material for publication: *CIFTAB* in *SHELX*97.

We would like to acknowledge Sylvain Bernès from USAI–Facultad de Química for collection of the data.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1122). Services for accessing these data are described at the back of the journal.

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Tetrakis(μ-phenylacetato-*O*:*O*′)bis[(quinoline-*N*)cobalt(II)]

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Abstract

The centrosymmetric title molecule, $[Co_2(C_8H_7O_2)_4(C_9H_7N)_2]$, contains two Co$^{\rm II}$ centres bridged by four phenylacetate ligands in *syn–syn* bridging modes.

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