$a = 17.000$ (2) Å
$b = 14.369$ (2) Å
$c = 13.485$ (2) Å
$\beta = 91.32$ (1)°
$V = 3293.1$ (8) Å^3
$Z = 8$
$D_x = 1.586$ Mg m^{-3}
D_m not measured

$\mu = 1.435$ mm^{-1}
$T = 298$ (2) K
Block
0.5 × 0.4 × 0.2 mm
Brown

Data collection

Stoe IPDS diffractometer
Area-detector scans
Absorption correction: numerical (*X-RED* in *IPDS*; Stoe & Cie, 1996)
$T_{\min} = 0.778$, $T_{\max} = 0.891$
32 839 measured reflections
8343 independent reflections
6272 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.044$
$\theta_{\max} = 29.49°$
$h = -23 \rightarrow 22$
$k = -18 \rightarrow 19$
$l = -17 \rightarrow 17$
3 standard reflections
frequency: 90 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.121$
$S = 1.215$
7704 reflections
569 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0400P)^2 + 1.6555P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.432$ e Å^{-3}
$\Delta\rho_{\min} = -0.454$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0087 (7)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Ni1—N1	1.909 (2)	Ni2—N4	1.913 (2)
Ni1—N2	1.916 (2)	Ni2—N3	1.919 (2)
Ni1—S2	2.1454 (8)	Ni2—S3	2.1610 (9)
Ni1—S1	2.1733 (8)	Ni2—S4	2.1686 (9)
S1—C1	1.708 (3)	S3—C1*A*	1.712 (3)
S2—C17	1.731 (3)	S4—C17*A*	1.721 (3)
N2—C11	1.291 (4)	N3—C7*A*	1.270 (4)
N2—C10	1.462 (4)	N3—C8*A*	1.472 (4)
N1—C7	1.265 (4)	N4—C11*A*	1.267 (4)
N1—C8	1.452 (4)	N4—C10*A*	1.445 (4)
N1—Ni1—N2	90.70 (10)	N4—Ni2—N3	90.67 (10)
N2—Ni1—S2	96.66 (7)	N3—Ni2—S3	94.36 (8)
N1—Ni1—S1	90.07 (8)	N4—Ni2—S4	92.36 (8)
S2—Ni1—S1	83.60 (3)	S3—Ni2—S4	83.14 (4)

Data collection: *EXPOSE* in *IPDS* (Stoe & Cie, 1996). Cell refinement: *CELL* in *IPDS*. Data reduction: *INTEGRATE* in *IPDS*. 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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1011). Services for accessing these data are described at the back of the journal.

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(5,6-Dimethyl-1,10-phenanthroline)(nitrato)(salicylaldehydato)copper(II)

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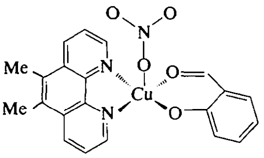
Abstract

The Cu$^{\rm II}$ ion of the title complex, (5,6-dimethyl-1,10-phenanthroline-*N*,*N*′)(2-formylphenolato-*O*,*O*′)(nitrato-*O*)copper(II), $[\mathrm{Cu(C_7H_5O_2)(NO_3)(C_{14}H_{12}N_2)}]$, displays a slightly distorted square-pyramidal coordination site, where one O atom from the nitrate ion is coordinated in the apical position [at 2.239 (2) Å], and both O atoms from the salicylaldehydate [at 1.893 (2) and 1.963 (2) Å] and both N atoms from the phenanthroline molecule [at 1.995 (2) and 2.005 (2) Å] define its base. The five-membered chelate ring ($\mathrm{CuC_2N_2}$) in the phenanthroline

moiety is roughly planar, while the CuC_3O_2 ring in the salicylaldehyde moiety is planar with a slight distortion toward an envelope conformation. The crystal packing seems to be determined by π–π^* interactions.

Comment

Our study of the IR spectroscopic properties of several mixed phenanthroline and oxygen-donor complexes has led us to prepare and crystallize the title complex, [$Cu(NO_3)$(salal)(5,6-dm-phen)], (I), among others (salal is salicylaldehydate and 5,6-dm-phen is 5,6-dimethylphenanthroline).



(I)

Fig. 1 shows a molecule of (I) with the atom-numbering scheme. Selected bond lengths and angles are shown in Table 1. The coordination sphere of the Cu^{II} ion consists of five ligand atoms, two N and three O, in a distorted square-pyramidal geometry. The nitrate ion is in the apical position, while both the aromatic N atoms from the phenanthroline and the O atoms from the salicylaldehydate lie at the base. There is a very slight tetrahedral distortion [N1 0.026 (1), N2 −0.025 (1), O1 −0.025 (1) and O2 0.024 (1) Å], with atom Cu1 0.182 (1) Å out of the plane formed by N1, N2, O1 and O2. Other relevant planes can be defined, among them the chelate ring formed by N1, C12, C11, N2 and Cu1, and that formed by the salicylaldehydate moiety (O1, C13, C19, O2 and Cu1). Both are only slightly distorted (r.m.s. deviations to the fitted atoms are 0.020 and 0.079 Å, respectively). Being six-membered, the salicylaldehydate–copper ring would be expected to have a greater distortion but, when the sixth member in this ring is included (O1, C13, C18, C19, O2 and Cu1), the r.m.s. deviation remains almost the same, at 0.088 Å. This, of course, has to do with aromaticity in the molecule. Finally, the angle between the planes formed by the metal and the coordinated atoms, Cu1/N1/N2 and Cu1/O1/O2, is 15.0 (1)°.

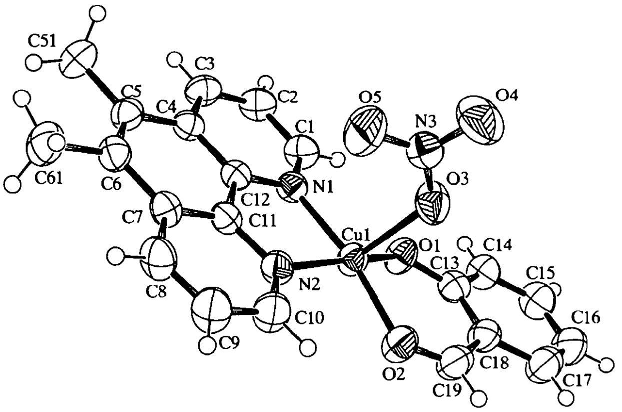


Fig. 1. *ZORTEP* (Zsolnai, 1997) plot of the molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

Examination of the main metal–ligand distances shows that the Cu—N distances are longer than the Cu—O1 distance, as observed in many related salicylaldehydate complexes (Garland *et al.*, 1986, 1987; Li *et al.*, 1995; Solans *et al.*, 1987). Similar behaviour 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 from the nitrate ion [2.239 (2) Å] is smaller than that observed in other related complexes (2.496 Å for the unsubstituted phenanthroline; Li *et al.*, 1995).

Molecules in the crystal are arranged in chains formed by parallel stacking of the phenanthroline molecules. The average distance between phenanthroline planes is 3.42 (5) Å. The fact that hydrogen bonding is absent in this crystal, and the presence of the previously mentioned interaction between phenanthroline molecules, suggests that crystal packing is determined by π–π^* interaction between phenanthroline units.

Experimental

The title complex was obtained by mixing $Cu(NO_3)_2$ (0.1 *M*, 2.5 ml) with 5,6-dimethyl-1,10-phenanthroline (0.25 mmol in ethanol) and salicylaldehyde (0.1 *M*, 2.5 ml) 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 formed. Prismatic dark-green crystals of the product were isolated, filtered, washed with ethanol and vacuum dried. Suitable crystals for X-ray analysis were obtained from the batch.

Crystal data

[$Cu(C_7H_5O_2)(NO_3)$-($C_{14}H_{12}N_2$)]
$M_r = 454.92$
Monoclinic
$P2_1/n$
$a = 9.573\,(1)$ Å
$b = 10.190\,(1)$ Å
$c = 19.213\,(2)$ Å
$\beta = 90.32\,(1)°$
$V = 1874.2\,(3)$ Å^3
$Z = 4$
$D_x = 1.612$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 2$–$28°$
$\mu = 1.21$ mm^{-1}
$T = 293\,(2)$ K
Prismatic
0.58 × 0.33 × 0.28 mm
Dark green

Data collection

Siemens *P*4/PC diffractometer

$R_{\text{int}} = 0.029$
$\theta_{\text{max}} = 28°$

$\theta/2\theta$ 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: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ZORTEP* (Zsolnai, 1997). Software used to prepare material for publication: *CIFTAB* in *SHELXL*97.

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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