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(Pyrazole-κN^2)[N-salicylidene-κO-(S)-alaninato-$\kappa^2 N,O$]copper(II) Dihydrate and (Pyrazole-κN^2)[N-salicylidene-κO-(R,S)-alaninato-$\kappa^2 N,O$]copper(II) Pyrazole Solvate

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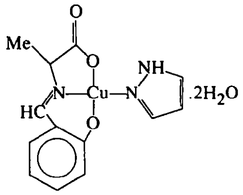
Abstract

In both {N-[(2-hydroxyphenyl)methylene]-(S)-alaninato-O,N,O'}(pyrazole-N^2)copper(II) dihydrate, $[Cu(C_{10}H_9NO_3)(C_3H_4N_2)].2H_2O$, (I), and {$N$-[(2-hydroxyphenyl)methylene]-(R,S)-alaninato-O,N,O'}(pyrazole-N^2)copper(II) pyrazole solvate, $[Cu(C_{10}H_9NO_3)(C_3H_4N_2)].C_3H_4N_2$, (II), the Cu^{II} ion adopts a similar axially distorted square-pyramidal coordination. The basal plane is formed by the tridentate Schiff base N-salicylidenealaninato dianion (TSB^{2-}) and the pyrazole ligand. The apex of the pyramid is occupied by a carboxylic O atom from the neighbouring chelate. The cooperative ordering and the apical distance [2.978 (3) Å in (I) compared with 2.366 (3) Å in (II)] are the two main differences between the two complexes. The stacked Cu(TSB) complexes within (I) form polymeric chains by translation parallel to [100]. The apically bridged Cu(TSB) complexes of (II) form zigzag chains parallel to [010] *via* the 2_1 operator. The influence of the configuration at the chiral C atoms as well as the effect of uncoordinated water and pyrazole molecules on the cooperative ordering are discussed.

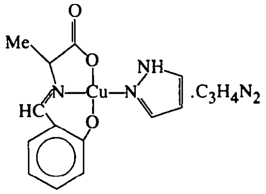
Comment

In complexes of general formula [Cu(TSB)(L)].H_2O, three donor atoms (O, N and O) of the TSB^{2-} dianion and a donor atom (O, N or S) of the neutral ligand L form a square-planar coordination around the Cu^{II} ion. Furthermore, an elongated square pyramid may be obtained by weak additional bonding of an O atom from the adjacent complex. Thus, either carboxylato-bridged chains (Ueki, Ashida, Sasada & Kakudo, 1967) or phenolic oxygen-bridged dimers (Warda, 1994) will result. Isolated complexes are obtained if an additional neutral molecule (*e.g.* water) coordinates at the apical position (Ueki, Ashida, Sasada & Kakudo, 1969).

The X-ray crystal structure investigations of the adducts of [N-salicylidene-(S)-alaninato]copper(II) with one pyrazole and two water molecules, (I), and of [N-salicylidene-(R,S)-alaninato]copper(II) with two pyrazole molecules, (II), were undertaken in order to detect whether water and pyrazole act as ligands or as solvent molecules. Kettmann, Frešova, Bláhová & Krätsmár-Šmogrovič (1993) reported recently the crystal structure of the optically active S enantiomer of complex (II). The influence of the chiral C atoms on the cooperative ordering of molecules was also of interest. Cooperative ordering, especially of Jahn–Teller ions, has been described using the term ferrodistortive for a parallel (2γ = 0°) and antiferrodistortive for a perpendicular (2γ = 90°) orientation; the angle 2γ describes the orientation of the main axes of polyhedra with respect to one another (Reinen & Friebel, 1979).



(I)



(II)

Complexes (I) and (II) both show axially extended square-planar coordination around the Cu^{II} ions. The atoms in the basal plane of the square-pyramid around the Cu^{II} atom belong to the Schiff base dianion (O1, N1 and O2) and the coordinated pyrazole molecule (N2) (Fig. 1). The apex is occupied by a carboxylic O atom from the adjacent molecule. There is a major difference, however, between the apical Cu—O distances in complexes (I) [2.798 (3) Å] and (II) [2.366(3) Å]. The different strength of axial interactions is reflected by the different displacements of the Cu atom from the basal plane towards the apices of the pyramids [0.084 (3) Å in (I) and 0.210 (3) Å in (II)].

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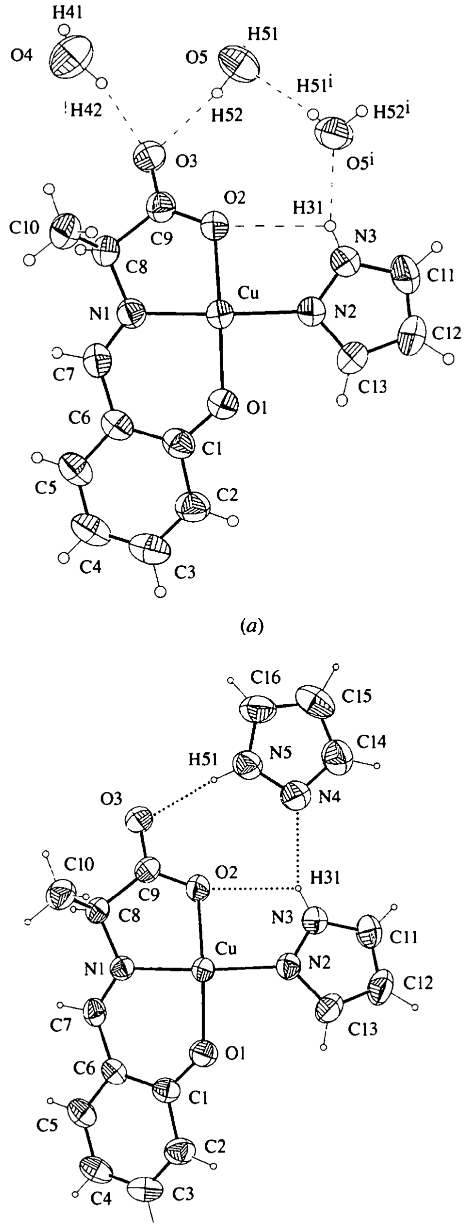

Fig. 1. The molecular structures of complexes (*a*) (I) and (*b*) (II) (both with 50% probability ellipsoids) showing the atomic numbering schemes. [Symmetry code: (i) $x - \frac{1}{2}, \frac{1}{2} - y, -z$.]

The presence of an optically active ligand leads to a chiral space group in complex (I). The four magnetically non-equivalent Cu^{II} ions are related to one another by three 2_1 axes. Carboxylate bridging leads to chains of molecules related by translation along **a** (ferrodistortive stacking), with each Cu^{II} ion belonging to a different chain. The interchain Cu···Cu distance is 4.878 (1) Å, corresponding to the lattice constant *a*. These chains are similar to those found in pyrazole[*N*-salicylidene-(*S*)-alaninato]copper(II)–pyrazole (Kettmann, Frešová, Bláhová & Krätšmár-Šmogrovič, 1993). They are stacked along [010] to form layers, which are connected by hydrogen bonds (Table 2) *via* layers of water molecules (Fig. 2) similar to the structure of diaqua(*N*-salicylideneglycinato)copper(II) dihydrate (Ueki, Ashida, Sasada & Kakudo, 1969).

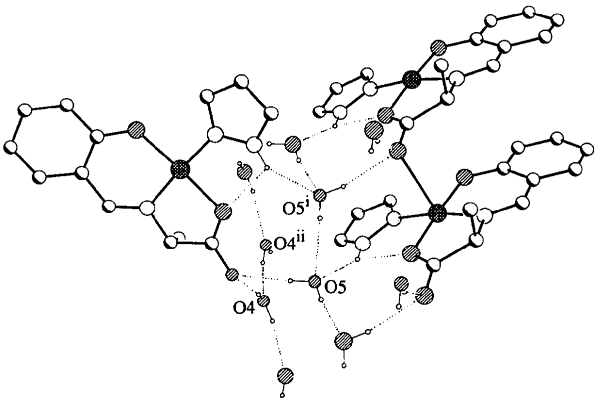

Fig. 2. View of part of the three-dimensional network of complex (I). The dotted lines indicate inter- and intramolecular hydrogen bonds. [Symmetry codes: (i) $x - \frac{1}{2}, \frac{1}{2} - y, -z$; (ii) $x - \frac{1}{2}, -\frac{1}{2} - y, -z$.]

Single-crystal electron paramagnetic resonance (EPR) investigations show four distinct signals corresponding to the four points of general position, *i.e.* there is no coupling between the four magnetically non-equivalent Cu^{II} ions. This leads to the observation of molecular *g* tensors. The reason for this behaviour, in spite of the nearly antiferrodistortive tilting of their basal planes towards one another, is the large Cu···Cu distance from one chain to another [minimum distance of 8.445 (2) Å].

In complex (II), the uncoordinated pyrazole molecule is connected *via* hydrogen bonds in the same manner as the solvent water molecules in complex (I) (Fig. 1 and Table 4). The carboxylate bridging is associated with the 2_1 operator. The tilting angle between the basal planes of neighbouring Cu^{II} coordination pyramids is 2γ = 73.4 (2)° (Fig. 3). This corresponds to distorted antiferrodistortive ordering. This type of chain is frequently found for (*N*-salicylideneglycinato)copper(II) complexes in conjunction with various neutral ligands. In the unit cell, two different chains exist, one containing only the *R* form and the other only the *S* form. The apical Cu—O distance within such a zigzag chain is markedly shorter than in chains of ferrodistortively stacked molecules. The shortest Cu···Cu distance within the zigzag chain is 6.1312 (7) Å [*cf.* minimum interchain distance of 7.5359 (7) Å]. EPR spectroscopy detects dipolar coupling between neighbouring Cu^{II} ions of the same chain. A tilting angle of 2γ = 73.5° was derived from the observed components of the crystal *g* values (Warda, 1994). This is in excellent agreement with the angle determined by X-ray structure analysis.

In conclusion, the configuration of the asymmetric C8 atom seems to influence the cooperative ordering of the (*N*-salicylidenealaninato)copper(II) complexes in such a way that the (*S*)-alaninato group leads to Cu^{II} complexes with carboxylato-bridged chains of ferrodistortively ordered molecules. This type of ordering has so far only been found in pyrazole[*N*-salicylidene-(*S*)-alaninato]copper(II)–pyrazole (Kettmann, Frešová, Bláhová & Krätsmár-Šmogrovič, 1993) and complex (I). The substitution of solvent pyrazole by two water molecules has no influence on the resulting structure. The use of the racemic Schiff base instead of the *S* enantiomer in the synthesis of pyrazole(*N*-salicylidene-alaninato)copper(II)–pyrazole leads from ferrodistortive to disturbed antiferrodistortive ordering in the chains. Further investigation of this behaviour is planned.

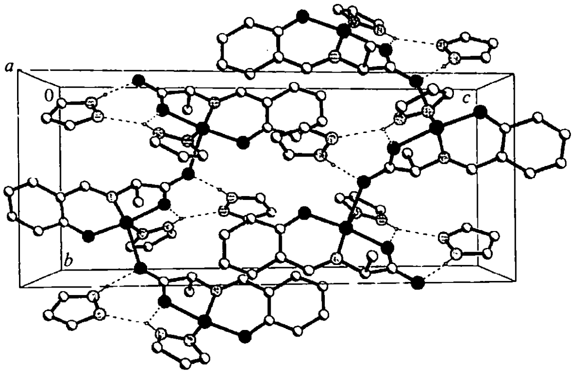

Fig. 3 A view of complex (II) showing the polymeric chains and hydrogen bonds.

Experimental

The title complexes (I) and (II) were prepared by the reaction of the corresponding optically active and racemic (*N*-salicylidenealaninato)copper(II) hydrates with pyrazole in a copper:pyrazole ratio of 1:1.5 at 333 K. Diluted methanol (65%) and diluted ethanol (50%) were used as solvents for the preparation of complexes (I) and (II), respectively. After filtration and slow cooling to 268 K, dark green crystals appeared.

Compound (I)

Crystal data

$[Cu(C_{10}H_9NO_3)$-
$(C_3H_4N_2)].2H_2O$
$M_r = 358.84$
Orthorhombic
$P2_12_12_1$
$a = 4.8781 (10)$ Å
$b = 10.4750 (10)$ Å
$c = 30.2952 (10)$ Å
$V = 1548.0 (4)$ Å^3
$Z = 4$
$D_x = 1.540$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 17.27–19.64°$
$\mu = 2.245$ mm^{-1}
$T = 293 (2)$ K
Needle
0.4 × 0.2 × 0.1 mm
Dark green

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2461 measured reflections
2325 independent reflections
2258 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.0534$
$\theta_{\rm max} = 64.94°$
$h = -5 \rightarrow 5$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 35$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0423$
$wR(F^2) = 0.1166$
$S = 1.037$
2325 reflections
200 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0967P)^2 + 0.284P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.571$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.446$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0007 (4)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)
Flack parameter = −0.06 (4)

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

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

	x	y	z	$U_{\rm eq}$
Cu	0.06061 (9)	0.16423 (4)	0.130096 (14)	0.0420 (2)
O1	−0.2122 (6)	0.1833 (2)	0.17449 (8)	0.0539 (6)
N1	0.2075 (6)	0.0111 (2)	0.15603 (8)	0.0414 (6)
C1	−0.2209 (8)	0.1241 (3)	0.21259 (11)	0.0459 (7)
O2	0.3544 (5)	0.1432 (2)	0.08696 (8)	0.0470 (5)
N2	−0.0374 (6)	0.3318 (3)	0.10599 (9)	0.0452 (6)
C2	−0.4135 (8)	0.1652 (4)	0.24433 (12)	0.0535 (8)
O3	0.7228 (5)	0.0253 (3)	0.07299 (9)	0.0590 (7)
N3	0.0921 (7)	0.3912 (3)	0.07305 (10)	0.0525 (7)
C3	−0.4302 (9)	0.1100 (4)	0.28489 (12)	0.0622 (10)
O4	0.7799 (7)	−0.1973 (3)	0.01322 (12)	0.0776 (9)
C4	−0.2544 (10)	0.0103 (5)	0.29708 (13)	0.0652 (10)
O5	0.8992 (6)	0.1761 (3)	0.00006 (9)	0.0699 (8)
C5	−0.0713 (9)	−0.0348 (4)	0.26644 (12)	0.0585 (9)
C6	−0.0488 (7)	0.0198 (3)	0.22416 (11)	0.0461 (7)
C7	0.1546 (7)	−0.0315 (3)	0.19452 (12)	0.0478 (8)
C8	0.4170 (7)	−0.0496 (3)	0.12855 (11)	0.0453 (7)
C9	0.5071 (7)	0.0471 (3)	0.09327 (11)	0.0443 (7)
C10	0.3002 (9)	−0.1690 (4)	0.10620 (13)	0.0591 (9)
C11	−0.0197 (10)	0.5045 (4)	0.06490 (14)	0.0688 (12)
C12	−0.2276 (12)	0.5201 (4)	0.09355 (17)	0.0759 (14)
C13	−0.2350 (9)	0.4102 (4)	0.11841 (13)	0.0617 (10)

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

Cu—O1	1.902 (2)	Cu—N2	1.960 (3)
Cu—N1	1.924 (3)	Cu—O3$^{\rm i}$	2.798 (3)
Cu—O2	1.952 (2)		
O1—Cu—N1	93.40 (11)	O2—Cu—N2	91.76 (10)
O1—Cu—O2	177.03 (10)	O1—Cu—O3$^{\rm i}$	94.58 (10)
N1—Cu—O2	84.59 (11)	N1—Cu—O3$^{\rm i}$	92.20 (10)
O1—Cu—N2	89.93 (11)	O2—Cu—O3$^{\rm i}$	87.69 (9)
N1—Cu—N2	171.57 (12)	N2—Cu—O3$^{\rm i}$	95.26 (10)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H31···O2	0.860	2.502	2.927 (4)	111.4
N3—H31···O5^{i}	0.860	2.006	2.766 (4)	146.7
O4—H41···O4^{ii}	0.760	2.076	2.794 (5)	157.8
O4—H42···O3	0.941	2.049	2.966 (5)	164.2
O5—H51···O3^{iii}	0.751	2.157	2.889 (5)	165.0
O5—H52···O3	0.799	2.079	2.849 (4)	162.1

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

Compound (II)

Crystal data

$[Cu(C_{10}H_9NO_3)(C_3H_4N_2)].C_3H_4N_2$
$M_r = 390.89$
Monoclinic
$P2_1/n$
$a = 10.3223\ (5)$ Å
$b = 8.3892\ (3)$ Å
$c = 19.9025\ (9)$ Å
$\beta = 97.533\ (4)°$
$V = 1708.6\ (3)$ Å^3
$Z = 4$
$D_x = 1.520$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 17.24–19.58°$
$\mu = 2.036$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.35 × 0.25 × 0.15 mm
Dark green

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2605 measured reflections
2524 independent reflections
2478 observed reflections $[I > 2\sigma(I)]$

$R_{int} = 0.0523$
$\theta_{max} = 59.87°$
$h = -11 \rightarrow 11$
$k = -9 \rightarrow 0$
$l = 0 \rightarrow 22$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0681$
$wR(F^2) = 0.1833$
$S = 1.145$
2524 reflections
227 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.1311P)^2 + 1.2995P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 1.450$ e Å^{-3}
$\Delta\rho_{min} = -0.974$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0073 (10)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (II)*

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

	x	y	z	U_{eq}
Cu	0.39772 (5)	0.24319 (5)	0.34282 (2)	0.0348 (3)
O1	0.4406 (3)	0.3184 (3)	0.43277 (11)	0.0446 (7)
O2	0.3528 (2)	0.1429 (3)	0.25317 (12)	0.0463 (7)
O3	0.2163 (3)	−0.0212 (3)	0.19377 (12)	0.0482 (7)
N1	0.2663 (3)	0.0990 (3)	0.36704 (13)	0.0334 (7)
N2	0.5667 (3)	0.3142 (4)	0.31467 (14)	0.0371 (7)
N3	0.6049 (3)	0.2761 (4)	0.25509 (17)	0.0422 (8)
N4	0.4832 (3)	0.1847 (5)	0.11912 (17)	0.0587 (9)
N5	0.3716 (3)	0.1087 (4)	0.09822 (16)	0.0512 (8)
C1	0.4218 (4)	0.2388 (4)	0.48733 (19)	0.0362 (9)
C2	0.4867 (4)	0.2899 (5)	0.55041 (19)	0.0452 (9)
C3	0.4772 (4)	0.2070 (5)	0.60904 (19)	0.0508 (10)
C4	0.4021 (4)	0.0696 (5)	0.60852 (18)	0.0482 (10)
C5	0.3343 (4)	0.0200 (4)	0.54837 (17)	0.0434 (9)
C6	0.3405 (3)	0.1020 (4)	0.48704 (16)	0.0348 (8)
C7	0.2644 (3)	0.0425 (4)	0.42709 (16)	0.0365 (8)
C8	0.1823 (3)	0.0320 (4)	0.30860 (17)	0.0371 (8)
C9	0.2547 (3)	0.0496 (4)	0.24761 (17)	0.0362 (8)
C10	0.0534 (3)	0.1241 (5)	0.2981 (2)	0.0510 (10)
C11	0.7267 (4)	0.3238 (6)	0.2522 (2)	0.0580 (11)
C12	0.7710 (4)	0.3974 (6)	0.3119 (2)	0.0605 (11)
C13	0.6677 (4)	0.3896 (5)	0.3493 (2)	0.0468 (9)
C14	0.5248 (6)	0.2340 (6)	0.0629 (3)	0.0647 (14)
C15	0.4378 (5)	0.1921 (7)	0.0064 (2)	0.0703 (13)
C16	0.3424 (5)	0.1111 (6)	0.0313 (2)	0.0648 (13)

Table 5. *Selected geometric parameters (Å, °) for (II)*

Cu—O1	1.895 (2)	Cu—N2	1.992 (3)
Cu—N1	1.925 (3)	Cu—O3^{i}	2.366 (3)
Cu—O2	1.973 (2)	O3—Cu^{ii}	2.366 (3)
O1—Cu—N1	93.31 (11)	O2—Cu—N2	89.08 (10)
O1—Cu—O2	174.16 (11)	O1—Cu—O3^{i}	93.30 (10)
N1—Cu—O2	82.44 (10)	N1—Cu—O3^{i}	105.28 (11)
O1—Cu—N2	93.51 (11)	O2—Cu—O3^{i}	91.69 (11)
N1—Cu—N2	158.44 (12)	N2—Cu—O3^{i}	94.71 (11)

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

Table 6. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···A	D—H	H···A	D···A	D—H···A
N3—H31···O2	0.860	2.375	2.828 (4)	113.3
N3—H31···N4	0.860	2.136	2.932 (5)	153.8
N5—H51···O3	0.860	2.002	2.858 (4)	173.8

Intensities were corrected for Lorentz and polarization factors (Harms, 1994). The structures were solved by the Patterson method and subsequent refinement used *SHELXL*93 (Sheldrick, 1993). Anisotropic displacement parameters were fixed for all non-H atoms. Isotropic displacement parameters were fixed for all H atoms. Geometrical analysis was performed using *PLATON* (Spek, 1990) and *SHELXL*93.

For both compounds, data collection: *CAD*-4 *Express Software* (Enraf–Nonius, 1992); cell refinement: *CAD*-4 *Express Software*; data reduction: *XCAD*-4 (Harms, 1994); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*96 (Sheldrick, 1996*a*); molecular graphics: *XP* in *SHELXTL*96 (Sheldrick, 1996*b*); software used to prepare material for publication: *SHELXL*96.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1116). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Aquabis(salicylaldoximato)zinc

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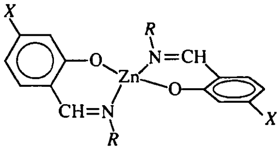
Abstract

The crystal structure of aqua(2-hydroxybenzaldehyde oximato-*N*,*O*)zinc(II), $[Zn(C_7H_6NO_2)_2(H_2O)]$, is formed by discrete molecules. The coordination polyhedron of the Zn atom is a distorted trigonal bipyramid with a ZnN_2O_3 chromophore.

Comment

As far as the structures of zinc complexes of type (1) are known, the vast majority are monomeric with a tetrahedral N_2O_2 coordination of zinc: *R*† = Et, Pr (*X* = OMe), ^{i}Pr, Bu and $(CH_2)_3SEt$ (Dreher, Elias & Paulus, 1987); *R* = Ph and 4-MePh (Xia-Lan, Hong-Li & Fang-Ming, 1992); *R* = 4-MePh (Sogo *et al.*, 1988); *R* = CH(Ph)Me (Sakiyama, Okawa, Matsumoto & Kida, 1990); *R* = 4-MeOPh (*X* = heptoxy) (Polishchuk *et al.*, 1991); *R* = 2,2,6,6-tetramethyl-1-oxypiperidine-4-yl (Gusejnova & Mamedov, 1978); *R* = 2-pyridyl (Vasilchenko *et al.*, 1994). The methyl derivative (*R* = Me) is the only example of a dimeric complex with a Zn_2O_2 unit and distorted trigonal bipyramidal N_2O_3-coordinated Zn atoms (Orioli, Di Vaira & Sacconi, 1966). We report here on the structure of the salicylaldoximato (sald) complex (*R* = OH) which is monomeric but has a five-coordinated Zn atom as a result of solvation.



(1)

The title structure consists of a racemic mixture of two stereoisomers. The labelling scheme of the molecule is shown in Fig. 1. The Zn atom is five-coordinated by two sald anions and one water molecule (in the equatorial plane). The coordination polyhedron is described by a distorted trigonal bipyramid. In this trigonal bipyramid, the two axial Zn—O1 and Zn—O11 bonds are of practically the same length [2.041 (4) and 2.047 (4) Å, respectively] and are almost collinear [O1—Zn—O11 172.70 (15)°]. The two equatorial Zn—N1 and Zn—N11 bonds have the same lengths as the axial Zn—O bonds [2.040 (5) and 2.042 (5) Å, respectively]. The third equatorial Zn—O3 distance of 1.942 (4) Å is significantly shorter than the other two. The out-of-plane angles lie within the range 87.4 (2)–94.0 (2)°, whereas the bond angles in the equatorial plane lie within the range 117.0 (2)–122.8 (2)°. The sum of the bond angles in the equatorial plane (360.0°) indicates coplanarity of the Zn atom with the three

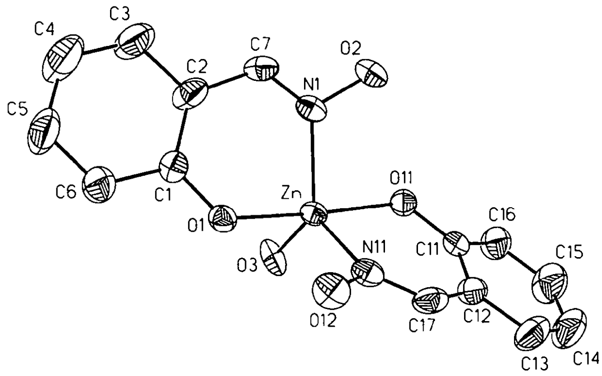


Fig. 1. *ORTEP* (Johnson, 1965) drawing of the title compound showing the labelling of the atoms. Displacement ellipsoids are plotted at the 40% probability level.

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† *X* = H unless otherwise stated.