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Acta Cryst. (1993). **C49**, 1932–1934

Structure of (Pyrazole- κN^2)[(S)-N-salicylidene- κO -alaninato(2-)- $\kappa N, \kappa O$]copper(II)-Pyrazole (1/1)

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(Received 14 December 1992; accepted 7 April 1993)

Abstract

Reaction of the parent aqua[(S)-N-salicylidene-alaninato]copper(II) dihydrate with an excess of pyrazole gives the title compound in which only one of the two pyrazole molecules is coordinated to Cu^{II} (the other is doubly hydrogen bonded to the complex molecule). The Cu^{II} coordination can be described as square pyramidal (4 + 1), the basal plane being formed by the heteroatoms of the tridentate Schiff base ligand and the N atom of the pyrazole molecule. A neighbouring chelate provides a semi-coordinating O(3) atom in the axial direction [Cu...O(3) = 2.595 (3) Å], thus forming polymeric chains along the *a* axis in the crystal. The title complex serves as a model to study the mechanism of a racemization reaction of amino acids catalyzed by vitamin B₆ (or salicylaldehyde) and metal ions. The results, combined with those obtained previously for potassium isocyanato[(R,S)-N-salicylidene-alaninato]cuprate(II), do not support the general

mechanism proposed earlier for the racemization reaction but instead suggest an active role for the nucleophilic solvent in the catalytic reaction.

Comment

This work is part of a more general study on the structural and chemical properties of copper complexes of Schiff bases derived from salicylaldehyde and amino acids. These complexes attract much attention owing to their biological importance since they serve as models for the more complicated key intermediates in the enzymatically catalyzed metabolic reactions of amino acids (Guirard & Snell, 1964; Bkouche-Waksman, Barbe & Kvik, 1988, and references therein). Recently, we reported (Krätzmár-Šmogrovič, Bláhová & Kettmann, 1991; Kettmann, Krätzmár-Šmogrovič & Švajlenová, 1990) that treatment of [Cu({sal-(S)-Ala}(H₂O))₂.2H₂O [sal-(S)-Ala = N-salicylidene-(S)-alaninato] with an excess of KOCN in hot dilute methanol led to a racemic product of composition K[Cu({sal-(RS)-Ala}(NCO))] (I). Although the title compound (II) was prepared under identical conditions, except for using pyrazole in place of KOCN, the racemization of the Schiff base ligand was not observed. To obtain a structural basis for understanding this difference in kinetic behaviour between (I) and (II), an X-ray analysis of (II) was undertaken.

The title complex was prepared by treatment of 3.1 g (10 mmol) of [Cu({sal-(S)-Ala}(H₂O))₂.2H₂O with 2.7 g (40 mmol) of pyrazole in dilute (65%) methanol at 233 K. After filtration and slow cooling to room temperature, dark-green single crystals appeared.

The numbering scheme is shown in Fig. 1, which also displays the overall conformation of the molecule and corresponds to the correct *S* enantiomer.

As generally found for this type of complex, the coordination geometry around Cu^{II} is axially distorted square pyramidal (4 + 1), the four basal atoms being O(1), N(1) and O(2) of the Schiff base ligand and the N(2) atom of one of the pyrazole molecules. The second, uncoordinated, pyrazole molecule associates with the complex through two hydrogen bonds. A neighbouring chelate provides the semi-coordinating O(3) atom in the axial direction [Cu...O(3)(*x* - 1, *y*, *z*) = 2.595 (3) Å] to complete the coordination. There is another contact shorter than the sum of the van der Waals radii, namely N(3)...O(2), so that the H atom on N(3) may be regarded as being involved in a bifurcated hydrogen bond.

The mean plane through the four basal atoms shows a slight tetrahedral distortion from planarity and the Cu atom is displaced from this plane by 0.145 (1) Å toward the apex of the pyramid. The

salicylideneimine moiety is almost planar but is canted relative to the basal coordination plane with a dihedral angle of $15.0(4)^\circ$, resulting in a significant warping of the six-membered chelate ring. The amino acid five-membered ring has a flat-envelope conformation with C(8) $0.243(4)$ Å out of the plane of the remaining four atoms. The carboxylate group rotates around the C(8)—C(10) bond by $19.8(4)^\circ$. Owing to the bifurcated hydrogen bonding of H(N3), the coordinated pyrazole molecule lies approximately in the basal plane [dihedral angle $8.8(4)^\circ$].

As in other related compounds (Bkouche-Waksman *et al.*, 1988), the Cu—O(1) distance of $1.890(2)$ Å is considerably shorter than the Cu—O(2) distance of $1.932(2)$ Å, indicating that more negative charge is localized on the phenolic O(1) atom than on the carboxy O(2) atom. An effect of the Cu coordination on the π -electron system within the *N*-sal-(*S*)-Ala moiety is evident in the C(7)=N(1) double bond [$1.267(5)$ Å], which is shortened compared to $1.303(5)$ Å reported for a similar bond in chloro(ethyl *N*-salicylidene-glycinato-*O*)(triphenyl)tin(IV), in which the imine N atom is uncoordinated, and even shorter than the normal double-bond range of 1.28 – 1.30 Å (Burke-Laing & Laing, 1976). The bond lengths and angles within the pyrazole molecules are close to those expected for coordinated and uncoordinated pyrazole (Berthou, Elguero & Rérat, 1970; Mighell, Santoro, Prince & Reimann, 1975).

The stereochemistry of the H atom at the C $^\alpha$ atom is of particular interest in connection with the mechanism of the racemization reaction of amino acids catalyzed by vitamin B $_6$ -amino acid-metal and related systems, since the key step in this reaction is release of the α proton. The general mechanism originally proposed by Metzler, Ikawa & Snell (1954) assumes displacement of electrons from the C $^\alpha$ —H bond, resulting in an increase in delocalization energy. As pointed out by Dunathan (1966), the geometric consequence of such an electron redistribution is a tendency of the bond to be cleaved in the catalytic reaction to become perpendicular to the plane of the π system. However, in the present molecule (II), a reverse effect is observed: it is the C $^\alpha$ —C $^\beta$ bond that is nearly perpendicular to the salicylideneimine plane, while the C $^\alpha$ H atom is positioned almost in this plane.

This observation might either rationalize the fact that (II) does not undergo racemization, or indicate that another mechanism, *e.g.* that proposed by Gillard & Wootton (1970), is operative. Since a very similar structure, including stereochemistry at the C $^\alpha$ atom, has been observed also for (I) (Kettmann *et al.*, 1990), we prefer the latter possibility. According to Gillard & Wootton (1970), in nucleophilic sol-

vents (alcohol, H $_2$ O *etc.*), carbanions are produced during a base-catalyzed addition-elimination sequence, the first, rate-limiting, step involving addition of the nucleophile to the Schiff base double bond. If this were true, then the difference in catalytic activity between (I) and (II) would be easily explained in terms of the difference in basicity of NCO $^-$ and pyrazole (pK_a 4.0 *versus* 2.5). The increase in the C=N bond order caused by coordination is also consistent with this reaction mechanism. Nevertheless, more details should be revealed in a charge-density study which is in progress in this laboratory.

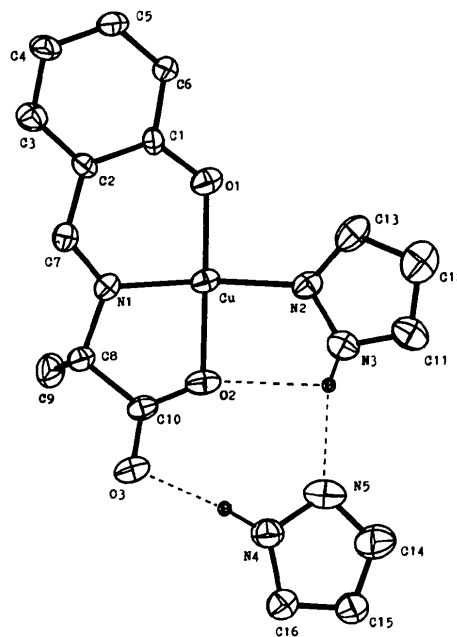


Fig. 1. Perspective drawing of the title compound and atom-numbering scheme. Thermal ellipsoids are drawn at the 40% probability level. Only polar H atoms involved in hydrogen bonds (indicated by dashed lines) are shown for clarity.

Experimental

Crystal data

[Cu(C $_{10}$ H $_9$ NO $_3$)(C $_3$ H $_4$ N $_2$)]·

C $_3$ H $_4$ N $_2$

$M_r = 390.9$

Monoclinic

$P2_1$

$a = 5.100(2)$ Å

$b = 10.051(4)$ Å

$c = 16.453(7)$ Å

$\beta = 94.82(5)^\circ$

$V = 840(1)$ Å 3

$Z = 2$

$D_x = 1.544$ Mg m $^{-3}$

$D_m = 1.55$ Mg m $^{-3}$

Density measured by flotation in CHBr $_3$ /cyclo-C $_6$ H $_{12}$

Mo K α radiation

$\lambda = 0.71069$ Å

Cell parameters from 15 reflections

$\theta = 8$ – 20°

$\mu = 1.38$ mm $^{-1}$

$T = 293$ K

Needle-like

$0.50 \times 0.20 \times 0.15$ mm

Dark green

Crystal source: crystallization from MeOH/H $_2$ O (4:1)

Data collection

Syntex P2 ₁ diffractometer	$R_{\text{int}} = 0.025$
$\theta/2\theta$ scans	$\theta_{\text{max}} = 27.5^\circ$
Absorption correction:	$h = 0 \rightarrow 6$
none	$k = 0 \rightarrow 13$
2105 measured reflections	$l = -21 \rightarrow 21$
1962 independent reflections	2 standard reflections
1444 observed reflections	frequency: 120 min
$[I > 2\sigma(I)]$	intensity variation: 5%

Refinement

Refinement on F	$(\Delta/\sigma)_{\text{max}} = 0.13$
Final $R = 0.041$	$\Delta\rho_{\text{max}} = 0.35 \text{ e } \text{Å}^{-3}$
$wR = 0.059$	$\Delta\rho_{\text{min}} = -0.40 \text{ e } \text{Å}^{-3}$
$S = 1.36$	Extinction correction: none
1444 reflections	Atomic scattering factors
294 parameters	from <i>International Tables</i>
All H-atom parameters re-	for <i>X-ray Crystallography</i>
efined	(1974, Vol. IV)
$w = 1/[\sigma^2(F) + 0.0009 F ^2]$	

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å^2)

	$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$			
	x	y	z	B_{eq}
Cu(1)	0.1039 (1)	-0.2480 (1)	0.2161 (1)	2.83 (1)
O(1)	-0.1780 (5)	-0.2785 (2)	0.1362 (1)	3.60 (7)
O(2)	0.4143 (4)	-0.2266 (3)	0.2907 (1)	3.81 (7)
O(3)	0.7881 (5)	-0.1196 (3)	0.3038 (2)	4.16 (7)
N(1)	0.2356 (5)	-0.0998 (3)	0.1616 (2)	2.81 (7)
N(2)	0.0420 (6)	-0.4207 (3)	0.2669 (2)	3.31 (7)
N(3)	0.2020 (6)	-0.4724 (4)	0.3278 (2)	3.85 (8)
C(1)	-0.2141 (6)	-0.2190 (3)	0.0655 (2)	2.90 (9)
C(2)	-0.0533 (7)	-0.1147 (4)	0.0397 (2)	3.24 (9)
C(3)	-0.1013 (8)	-0.0618 (5)	-0.0396 (2)	3.98 (11)
C(4)	-0.3071 (8)	-0.1062 (5)	-0.0910 (2)	4.19 (10)
C(5)	-0.4691 (7)	-0.2047 (5)	-0.0648 (2)	4.30 (12)
C(6)	-0.4283 (6)	-0.2600 (5)	0.0123 (2)	3.96 (9)
C(7)	0.1601 (7)	-0.0604 (4)	0.0903 (2)	3.16 (9)
C(8)	0.4583 (7)	-0.0361 (4)	0.2079 (2)	3.12 (9)
C(9)	0.3637 (9)	0.0894 (5)	0.2497 (3)	4.64 (12)
C(10)	0.5647 (6)	-0.1338 (4)	0.2723 (2)	3.18 (9)
C(11)	0.1248 (8)	-0.5913 (5)	0.3479 (3)	4.95 (13)
C(12)	-0.0967 (11)	-0.6207 (6)	0.2980 (3)	6.22 (16)
C(13)	-0.1411 (9)	-0.5094 (5)	0.2485 (3)	4.96 (13)
N(4)	0.8051 (6)	-0.3064 (4)	0.4377 (2)	4.58 (8)
N(5)	0.6095 (7)	-0.3922 (5)	0.4469 (2)	5.82 (13)
C(14)	0.6904 (10)	-0.4582 (7)	0.5134 (3)	6.25 (16)
C(15)	0.9322 (9)	-0.4226 (6)	0.5437 (3)	5.42 (14)
C(16)	1.0072 (10)	-0.3225 (6)	0.4961 (3)	5.16 (12)

Table 2. Selected geometric parameters (Å , $^\circ$)

Cu(1)—O(1)	1.890 (2)	C(7)—N(1)	1.267 (5)	
Cu(1)—O(2)	1.932 (2)	C(10)—O(2)	1.261 (5)	
Cu(1)—N(1)	1.890 (3)	C(10)—O(3)	1.220 (4)	
Cu(1)—N(2)	1.964 (3)			
O(1)—Cu(1)—N(1)	94.5 (1)	N(1)—Cu(1)—O(2)	84.8 (1)	
O(1)—Cu(1)—O(2)	174.2 (1)	N(1)—Cu(1)—N(2)	167.0 (1)	
O(1)—Cu(1)—N(2)	90.7 (1)	O(2)—Cu(1)—N(2)	88.9 (1)	
Cu—O(1)—C(1)—C(2)	-4.2 (5)	N(1)—Cu—O(1)—C(1)	8.2 (3)	
O(1)—C(1)—C(2)—C(7)	-2.6 (5)	C(7)—N(1)—C(8)—H(8)	-39.9 (3)	
C(1)—C(2)—C(7)—N(1)	2.2 (6)	C(7)—N(1)—C(8)—C(9)	83.3 (4)	
C(2)—C(7)—N(1)—Cu	5.0 (5)	N(1)—C(8)—C(10)—O(2)	-19.8 (4)	
C(7)—N(1)—Cu—O(1)	-8.6 (3)			
D—H...A	D—H	H...A	D...A	D—H...A
N(3)—H...N(5)	0.95 (5)	2.14 (6)	2.850 (5)	131 (5)
N(3)—H...O(2)	0.95 (5)	2.47 (7)	2.785 (5)	99 (4)
N(4)—H...O(3)	0.93 (5)	1.96 (5)	2.890 (5)	174 (4)

All calculations were performed with a local version of the NRC program system (*NRC Crystallographic Programs for the IBM360 System*, 1973).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, least-squares-planes' data and all bond lengths have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71245 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1037]

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Acta Cryst. (1993). **C49**, 1934–1936

Structure of the Ethylidene Cluster $\text{Os}_3(\mu\text{-H})_2(\mu\text{-CHCH}_3)(\text{CO})_9(\text{P}^i\text{Pr}_3)$

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(Received 16 October 1992; accepted February 1993)

Abstract

The title complex, nonacarbonyl- $1\kappa^3C, 2\kappa^3C, 3\kappa^3C$ - μ -ethylidene- $2\cdot 3\kappa^2C$ -di- μ -hydrido- $1\cdot 2\kappa^2H; 2\cdot 3\kappa^2H$ -triisopropylphosphine- $1\kappa P$ -triangulo-triosmium- $(3 Os—Os)$, contains an irregular Os_3 triangle [$\text{Os—Os} = 3.088(1)–2.797(1) \text{ Å}$], with an ethylidene and one hydrido ligand bridging two Os atoms, and a P^iPr_3 ligand coordinated in an equatorial position to the third Os atom. A second bridging hydride is