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A Model for Vitamin B₆–Amino-Acid-Related Metal Complexes. Neutron Diffraction Study of Aqua(*N*-salicylidene-glycinato)copper(II) Hemihydrate at 130 K*

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Abstract

A neutron diffraction study of aqua(*N*-salicylidene-glycinato)copper(II) hemihydrate, [Cu(C₉H₇NO₃)(H₂O)]·0.5H₂O, *M_r* = 267.7, a model for vitamin B₆–amino-acid-related metal complexes, has been carried out at 130 K. Least-squares refinement based on 3800 reflections [(sinθ/λ)_{max} = 0.786 Å⁻¹] converged at *R*(*F*²) = 4.5%. The crystal is monoclinic, space group *C2/c*, *Z* = 8 with cell parameters at 130 K: *a* = 17.030 (3), *b* = 6.665 (1), *c* = 17.469 (5) Å, β = 111.13 (1)°, *V* = 1849.50 Å³. The bond distances between non-H atoms have been determined with estimated standard deviations in the range 0.0008–0.0012 Å; the corresponding values for distances involving H atoms are 0.0017–0.0020 Å. The presence of a Cu^{II} ion does not significantly change the bond distances around the α-C atom from those observed in glycine or glycyglycine. There are, however, indications of differences in distance and direction relative to the π system for the two α-C–H bonds. These bond vectors are inclined at angles of 30 and 71° to the plane of the conjugated π system. A planar conjugated π-system is stabilized by chelation to the Cu ion.

Introduction

Pyridoxal [vitamin B₆, formula (1)] amino-acid Schiff bases are key intermediates in the metabolic reactions

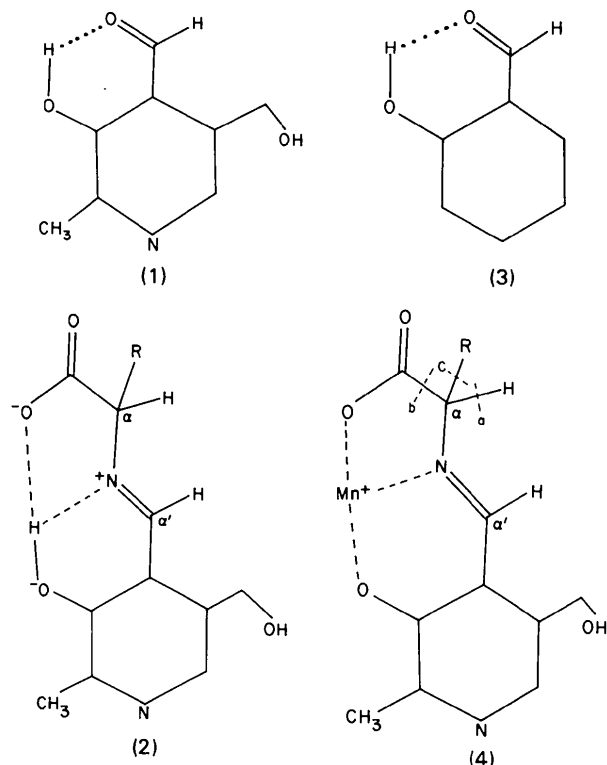
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of amino acids catalyzed by enzymes, which require pyridoxal phosphate as a cofactor. These reactions are transamination, decarboxylation, α-, β-elimination, racemization, etc. (Guirard & Snell, 1964). Many of these reactions are related to non-enzymatic model reactions in which pyridoxal is the catalyst and a metal ion replaces the apoenzymatic protein (Braunstein & Shemyakin, 1953; Metzler, Ikawa & Snell, 1954; Longenecker & Snell, 1957; Dunathan, 1971; Holm, 1973). Formula (2) gives one of the important forms of these Schiff bases. When a metal ion is present, it replaces the hydroxyl proton (4), and the structure is stabilized by bonding to the N atom and to the carboxylate and phenolate O atoms. The three donor atoms are locked in, resulting in a planar conformation of the tridentate ligand. A strong electron-withdrawal effect on the C atoms adjacent to the azomethine N is proposed. The planar conformation facilitates the electron transfer through the conjugation of the pyridine ring and the azomethine group with the amino-acid side chain (Martell, 1982). The result is a labilization of one of the three bonds *a*, *b*, *c* on the α-C atom of the amino-acid moiety, preparing it for the catalytic reaction. Catalytic activities are also observed with derivatives of salicylaldehyde, (3) (Ikawa & Snell, 1954; Eichhorn & Marchand, 1956; Ando & Emoto, 1969, 1975), although they are not effective transamination substrates (Wroblewski & Long, 1977). The key question is: What is the mechanism of activation of the amino-acid pyridoxal metal intermediate complexes? Inductive effects leading to bond weakening at the α-C atom of the amino-acid moiety as the main driving force for reactions have been discussed by Perault, Pullman & Valdemoro (1961), who calculated the energy changes associated with the different transition states of the Schiff bases. They considered the variations of resonance energy associated with the formation of the transitional Schiff bases and the

electronic distribution in these transitional forms as the essential factors responsible for the mechanism of the reactions.



Since the first studies in solution referenced above, many of metal intermediates (derived from pyridoxal or salicylaldehyde) have been isolated in the solid state (Eichhorn & Dawes, 1954; Christensen, 1957; Kishita, Nakahara & Kubo, 1964; Burrows & Bailar, 1966; Theriot, Carlisle & Hu, 1969; Carlisle & Theriot, 1973; Wroblewski & Long, 1977; Fujii, Shiono, Ezuka & Isago, 1980). Several room-temperature X-ray structural studies have also been performed (Willstadter, Hamor & Hoard, 1963; Brander cited by Freeman, 1967; Cutfield, Hall & Waters, 1967; Bentley, Waters & Waters, 1968; Ueki, Ashida, Sasada & Kakudo, 1968, 1969; Fujimaki, Oonishi, Muto, Nakahara & Komiyama, 1971; Capasso, Giordano, Mattia, Mazzarella & Ripamonti, 1974; Nassimbeni, Percy & Rodgers, 1976; Belokon *et al.*, 1977; Darriet, Cas-saigne, Darriet & Neuzil, 1978; Hämäläinen, Turpeinen, Ahlgren & Rentala, 1978; Korhonen & Hämäläinen, 1979, 1981; Aoki & Yamazaki, 1980, 1984; Dawes & Waters, 1982; Dawes, Waters & Waters, 1982; Davies, 1984; Rao, Manohar & Bau, 1984, 1985).

These structure determinations have, however, not achieved the level of precision necessary for a detailed understanding of the catalytic processes. In particular, more precise data on the stereochemistry at the α -C

center, including the H atoms, are needed in order to relate structure and reactivity of the catalytically active, inactive and related complexes.

In this paper, we report the precise determination by neutron diffraction of the structure for a metal chelate of salicylaldehyde, a model for amino-acid vitamin B₆ metal derivatives.

In order to study a proposed intermediate step in the catalysis, the salicylaldehyde chelate was chosen over pyridoxal chelates for which it is difficult to grow large crystals, and Cu^{II} was chosen over other metals because of the high reaction rate for some Cu^{II}-catalyzed reactions (reviewed by Martell, 1982). The salicylaldehyde chelate readily produces large crystals of a monomeric complex. A lower precision structure of this compound has been determined earlier by X-ray diffraction at room temperature (Ueki, Ashida, Sasada & Kakudo, 1967).

Chemical synthesis

The title compound was prepared according to the method reported by Kishita *et al.* (1964).

An aqueous solution (50 ml) of glycine (0.04 mol, 3 g) and salicylaldehyde (0.04 mol, 4.8 g) was kept at 353 K with stirring for 30 min. Copper(II) acetate monohydrate (0.04 mol, 7.8 g) was then added and the temperature of the solution was readjusted to 353 K and kept constant for 30 min. The mixture was cooled to 273 K and the precipitate was filtered and washed with water. The crude product was recrystallized from an aqueous solution maintained above 303 K for 80 h. Dark blue-green crystals were obtained.

Analysis for C₉H₁₀NO_{4.5}Cu. Calculated: C 40.38, H 3.76, N 5.23, Cu 23.73%. Found: C 40.10, H 3.73, N 5.12, Cu 23.69%.

Experimental

A crystal coated with a thin film of polystyrene (*i.e.*, quickly dipped in a solution of polystyrene in CH₂Cl) to prevent hydration was sealed under helium atmosphere in an Al can and mounted with the $\langle 100 \rangle$ direction approximately parallel to the ϕ axis of a four-circle diffractometer at the Brookhaven National Laboratory High Flux Beam Reactor. The neutron diffraction experiment was carried out with conditions given in Table 1. Cell parameters were determined by least-squares fit to $\sin^2\theta$ values of 32 reflections with $45 < 2\theta < 56^\circ$. The C-lattice extinctions were verified by intensity scans. Reference reflections monitored every 50 measurements showed no significant intensity variation. Intensities were measured with scans adjusted between 59 and 90 steps per scan, assuming background as the first and last tenths of the total scan. Each step was counted for about 2 s until a preset number of counts was accumulated in the direct-beam

Table 1. *Experimental and refinement conditions*

Neutron source	Brookhaven High Flux Beam Reactor	
Monochromator	Be(002), reflection geometry	
Wavelength	1.0505 (1) Å	
Wavelength calibration: KBr crystal	$a_0 = 6.6000$ Å at 295 K	
Low-temperature device	Closed-cycle helium refrigerator*	
Temperature	130 ± 0.5 K	
Space group	Monoclinic, $C2/c$, $Z = 8$	
Formula weight (g mol ⁻¹)	267.717	
Cell parameters	Neutron,	X-ray, room temperature†
	130 ± 0.5 K	
a (Å)	17.030 (3)	17.16 (3)
b (Å)	6.665 (1)	6.84 (2)
c (Å)	17.469 (5)	17.57 (1)
β (°)	111.13 (1)	111.29 (5)
V (Å ³)	1849.50	1920.20
Crystal: weight	6.51 mg	
volume	3.45 mm ³	
boundary faces	(100), (100), (110), (110), (401), (101)	
Reciprocal space	$\pm h, \pm k, \pm l$	
hkl range	$h -26$ – 26 , $k 0$ – 10 , $l 0$ – 27	
Scan mode	$\theta/2\theta$	
Scan range	3.0° for $2\theta < 60^\circ$ $(1.0 + 3.5 \tan\theta)^\circ$ for $2\theta > 60^\circ$	
Reference reflections	1408, 738	
($\sin\theta/\lambda$) _{max}	0.786 Å ⁻¹	
Linear absorption coefficient	1.775 cm ⁻¹	
Transmission factors	0.74–0.87	
g (isotropic extinction)	0.35 (1) $\times 10^4$	
No. of reflections measured (including those for primitive cell)	4584	
No. of reflections used in final refinement (m)	3800	
No. of parameters varied (n)	232	
Agreement factors		
$R(F^2) = \sum F_m^2 - k^2 F_c^2 / \sum F_m^2$	0.045	
$wR(F^2) = [\sum w(F_m^2 - k^2 F_c^2)^2 / \sum w F_m^4]^{1/2}$	0.053	
$S = [\sum w(F_m^2 - k^2 F_c^2)^2 / (m - n)]^{1/2}$	1.14	

* Air Products and Chemicals, Inc., Displex Model CS-202.

† Ueki *et al.* (1967).

monitor. Data were corrected for Lorentz and absorption effects (Gaussian grid $8 \times 8 \times 10$). The atomic neutron-scattering lengths used were: $b_{Cu} = 7.718$, $b_O = 5.805$, $b_N = 9.300$, $b_C = 6.648$ and $b_H = -3.741$ fm.

Initial coordinates of non-H atoms were taken from the room-temperature X-ray model (Ueki *et al.*, 1967). All H atoms were located from a difference Fourier synthesis. Full-matrix least-squares refinement was carried out with weights $w^{-1}(F_m^2) = \sigma_{\text{count}}^2(F_m^2) + (0.015F_m^2)^2$. Final agreement factors are given in Table 1. Isotropic type I extinction correction with Lorentzian mosaic distribution was applied. An anisotropic type I correction with Lorentzian mosaic distribution according to Thornley & Nelmes (1974) did not show any significant improvement. The number of reflections with $|\Delta F/\sigma| > 4.0$ is 35. Zero weight was given to 33 reflections with final $F_m^2/F_c^2 < 0.60\sigma$ or $> 1.40\sigma$. The final difference Fourier synthesis showed no significant features, with the largest residual scattering density corresponding to less than 2% of that of the Cu atom. The computer programs used are locally modified versions of the Uppsala package (Lundgren, 1983).

Results and discussion

A stereoscopic illustration of the crystal structure is given in Fig. 1. The atomic notation and selected bond distances and angles are illustrated in Fig. 2. The final

atomic coordinates and thermal parameters are given in Table 2.* Interatomic distances and angles are listed in Tables 3 and 4.

The Schiff base complexes are linked *via* weak Cu–O(3) interactions to form chains along the b axis. These chains are linked by hydrogen bonding *via* water molecules to form the three-dimensional structure. The geometry of the water molecules and their bonding is summarized in Fig. 3. The structure is in essential agreement with the previous determination (Ueki *et al.*, 1967), but the precision in non-hydrogen-bond distances and angles is improved in the range 6–20 σ (joint e.s.d.'s). Precise information on the H atoms is also obtained in the present study.

The general mechanism for B_6 -catalyzed reactions in non-enzymatic systems proposed by Metzler *et al.* (1954) assumes electron displacement from the α -C region of the amino-acid residue. The electrons are transported *via* the conjugated systems of double bonds down to the electron-accepting pyridine N atom. The metal atom serves as a catalyst in promoting the formation of a Schiff base and maintaining the planarity of the conjugated system through chelate formation. The metal ion further enhances the withdrawal of electrons from the α -C region. In the present study we concentrate on the role of the metal ion.

Coordination around the Cu atom

The chelate is stabilized by the Cu^{II} ion, which has a pyramidal coordination. The four basal atoms are O(1),

* Lists of structure factors, bond lengths and bond angles, anisotropic thermal parameters, r.m.s. components of thermal parameters and equations of least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51025 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

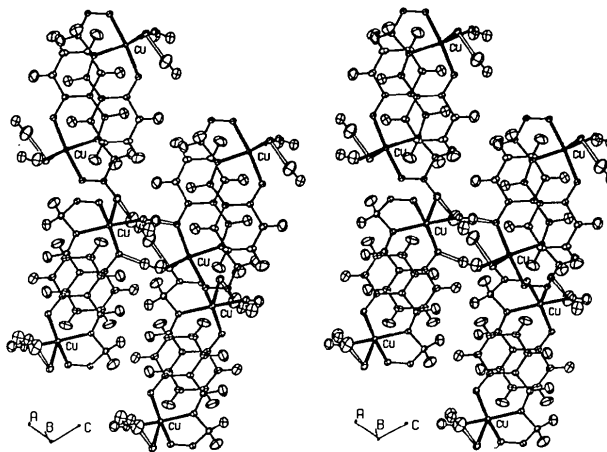


Fig. 1. Stereoview of the molecules held together by the shortest hydrogen bonds (open bonds) through the water molecules; thermal ellipsoids enclose 70% probability.

O(2) and N of the Schiff base and a water OW(1) atom. A neighboring chelate provides the apical O atom O(3) to complete the coordination. The four basal atoms deviate less than 0.0149 (8) Å from their least-squares plane. The Cu coordination to O(3) [Cu...O(3) = 2.308 (1) Å] pulls the Cu ion 0.2228 (6) Å out of the basal plane.

The Cu–O(1) distance of 1.918 (1) Å is considerably shorter than the Cu–O(2) distance of 1.959 (1) Å, as is the case in related compounds (Capasso *et al.*, 1974), suggesting that more negative charge is localized on the phenolic O(1) atom than on the carboxy O(2) atom. This conclusion is corroborated by the short hydrogen-bond distance [O(1)...H(2) = 1.611 (2) Å] to water molecule W(1). This hydrogen bond [O(1)...OW(1) = 2.616 (1) Å] is considerably shorter than the mean distance of 2.805 Å calculated from several water-containing structures (Chiari & Ferraris, 1982). To a first approximation hydrogen bonds may be considered to be electrostatic in nature (Kvick, 1974).

Effects of the Cu coordination on the C–O bond character are evident in bond lengths: the C(9)–O(1) bond [1.325 (1) Å] is shortened and the C(1)–O(2) bond [1.269 (1) Å] is lengthened compared with the expected values for single and double C–O bonds.

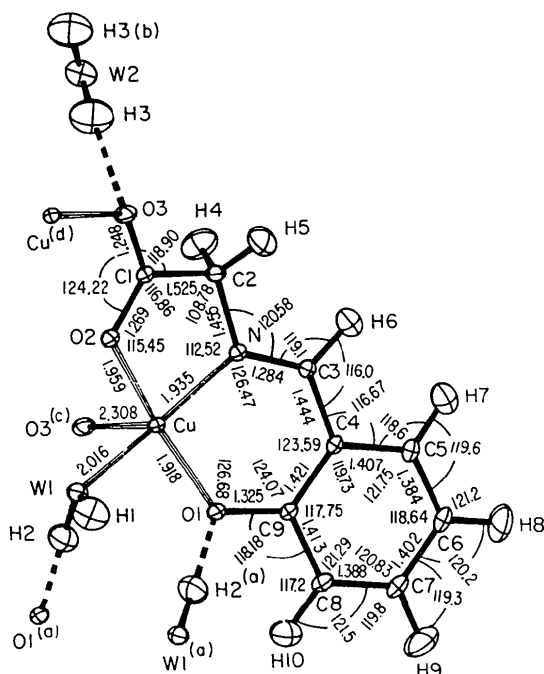


Fig. 2. Bond lengths (Å) and angles (°) in the aqua(*N*-salicylidene-glycinato)copper(II) molecule, with water molecules and hydrogen bonds [dashed lines; for water molecule W(1)H(1)H(2), only the shortest hydrogen bonding through H(2) is represented]; thermal ellipsoids enclose 60% probability. The e.s.d.'s for the angles involving H atoms are 0.1°. For the other angles and distances e.s.d.'s are given in Table 4. Symmetry operations: (a) $-x, y, \frac{1}{2}-z$; (b) $1-x, y, \frac{1}{2}-z$; (c) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (d) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$.

Table 2. Fractional atomic coordinates ($\times 10^5$) and isotropic thermal parameters (Å²), with e.s.d.'s in parentheses

	x	y	z	B_{iso}^*
Cu	12177 (3)	9233 (9)	20431 (3)	0.60 (1)
O(1)	669 (4)	17006 (12)	14914 (5)	0.81 (2)
O(2)	22996 (4)	-4832 (12)	24576 (5)	0.82 (20)
O(3)	34358 (5)	-12088 (12)	21653 (5)	0.94 (2)
W(1)	9484 (5)	-3166 (12)	29722 (5)	0.87 (2)
W(2)	50000	9434 (19)	25000	1.39 (3)
N	15266 (3)	14282 (7)	10974 (3)	0.67 (1)
C(1)	27431 (4)	-3560 (10)	20111 (4)	0.67 (1)
C(2)	24067 (4)	9799 (10)	12535 (4)	0.75 (1)
C(3)	10235 (4)	18757 (10)	3717 (4)	0.70 (1)
C(4)	1418 (4)	23492 (10)	1529 (4)	0.66 (1)
C(5)	-2954 (4)	29369 (10)	-6641 (4)	0.84 (1)
C(6)	-11364 (4)	34745 (11)	-9378 (4)	0.99 (1)
C(7)	-15571 (4)	34333 (11)	-3801 (4)	1.01 (1)
C(8)	-11435 (4)	28401 (11)	4274 (4)	0.91 (1)
C(9)	-2865 (4)	22758 (10)	7162 (4)	0.67 (1)
H(1)	6770 (11)	-16090 (25)	28527 (12)	2.20 (4)
H(2)	5742 (10)	5339 (25)	31749 (10)	1.79 (4)
H(3)	45317 (12)	578 (29)	24289 (14)	2.77 (5)
H(4)	24936 (11)	2549 (28)	7276 (10)	2.11 (4)
H(5)	27722 (10)	23817 (26)	13999 (12)	2.14 (4)
H(6)	12675 (10)	19285 (28)	-1305 (10)	2.03 (4)
H(7)	473 (11)	30197 (28)	-10824 (10)	2.10 (4)
H(8)	-14606 (11)	39756 (30)	-15610 (10)	2.40 (4)
H(9)	-22169 (10)	38834 (31)	-5853 (12)	2.44 (4)
H(10)	-14596 (10)	28313 (29)	8689 (11)	2.21 (4)

$$* B_{iso} = \frac{1}{3} \sum_i \sum_j \beta_{ij} (a_i^* a_j^*)$$

Table 3. Selected bond lengths (Å) and angles (°) involving H atoms, with e.s.d.'s in parentheses

(a) Uncorrected distances, (b) distances corrected for thermal riding motion, (c) root-mean-square component of thermal displacement of H atom in H→C direction, (d) of C atom in C→H direction, and (e) angles around C(2) atom.

	(a)	(b)	(c)	(d)
C(2)–H(4)	1.094 (2)	1.115	0.125 (3)	0.103 (1)
C(2)–H(5)	1.100 (2)	1.121	0.133 (2)	0.104 (1)
C(3)–H(6)	1.098 (2)	1.118	0.125 (3)	0.093 (1)
C(5)–H(7)	1.089 (2)	1.108	0.139 (2)	0.117 (1)
C(6)–H(8)	1.081 (2)	1.103	0.113 (3)	0.090 (1)
C(7)–H(9)	1.091 (2)	1.114	0.117 (2)	0.092 (1)
C(8)–H(10)	1.088 (2)	1.108	0.139 (3)	0.115 (1)

(e)	
C(1)–C(2)–H(4)	110.4 (1)
C(1)–C(2)–H(5)	106.9 (1)
N–C(2)–H(4)	112.1 (1)
N–C(2)–H(5)	109.1 (1)
H(4)–C(2)–H(5)	109.5 (1)

Table 4. Distances (Å) and angles (°) for intermolecular interactions

$\Delta d = v(H) + v(Y) - d(H...Y)$, where $v(H)$ and $v(Y)$ are van der Waals radii from Taylor & Kennard (1982). $\Delta(X...Y)$ is the shortening of the $X...Y$ distance from room temperature.

X–H...Y	Δd	$d(H...Y)$	X...Y	$\angle X-H...Y$	$\Delta(X...Y)$
C(2)–H(5)...O(2 ^a)	-0.210	2.490 (2)	3.172 (9)	119.0 (1)	0.068 (10)
C(6)–H(8)...O(2 ^b)	-0.292	2.408 (2)	3.371 (1)	147.6 (1)	0.027 (10)
C(8)–H(10)...O(3 ^c)	-0.279	2.421 (2)	3.421 (1)	152.1 (1)	0.027 (10)
C(5)–H(7)...OW(2 ^d)	-0.156	2.544 (2)	3.501 (1)	146.2 (1)	0.042 (11)
C(6)–H(8)...C(1 ^a)	-0.407	2.543 (2)	3.623 (1)	176.2 (1)	0.045 (13)
C(8)–H(10)...H(9 ^d)	0.014	2.414 (2)	3.122 (2)	121.4 (1)	—
C(7)–H(9)...H(10 ^d)	—	—	3.282 (2)	135.4 (2)	—
OW(1)–H(2)...O(3 ^c)	-0.438	2.938 (2)	2.972 (1)	82.1 (1)	0.049 (10)

Symmetry operations: (a) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (b) $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$; (c) $-\frac{1}{2}+x, \frac{1}{2}+y, z$; (d) $-\frac{1}{2}-x, \frac{1}{2}-y, -z$.

The Cu coordination produces a planar conformation of the conjugated system: C(2), N, C(3) and the C atoms of the benzene ring are all coplanar within 0.04 Å. The entire chelate may be described by two planes (1) the Cu–salicylaldiminato plane and (2) the Cu–glycinato plane, which intersect with a dihedral angle of 14.5°.

Salicylidenglycinato moiety

The geometry around the α -C atom. Since the catalytic activity of these Schiff base complexes has been proposed to be related to the labilization of the bonds around the α -C atom, it is particularly interesting to compare these bond lengths with those of glycine itself.

The high-precision, low-temperature neutron diffraction studies (Legros & Kvik, 1980; Kvik, Canning, Koetzle & Williams, 1980) of α -glycine and γ -glycine

(at 120 and 83 K) give mean C_α – C_β , C_α –H and C_α –N distances of 1.525, 1.094 and 1.478 Å respectively as compared to 1.525 (1), 1.097 (1) and 1.455 (1) Å in the present compound. As expected there is a marked shortening in the C–N bond distance but the mean C–H distance is only marginally different while the C(1)–C(2) distances are identical. However, in the α and γ forms of glycine the independent C–H distances (1.095, 1.094, 1.094 and 1.092 Å) are equal within their e.s.d.'s, whereas in the present molecule they differ by 3σ [1.094 (2) vs 1.100 (2) Å] suggesting that one of the bonds may be weakened. The difference of 0.006 Å is retained after correction for thermal riding motion (Table 3). The longer C–H(5) bond is also involved in a short contact with an O atom in a neighboring molecule [C–H(5)···O(2) = 2.490 (2) Å] suggesting the possibility of an electrostatic interaction causing enhanced positive charge on this H atom. The most significant observed difference in the two H atoms H(4) and H(5) is found in their respective distances to the plane defined by atoms C(1), C(2) and N [+0.857 (2) and –0.933 (2) Å] and to the aldimine plane [C(2), N, C(3), H(6)] [+0.546 (2) and –1.039 (2) Å]. According to a current hypothesis (Dunathan, 1966) the bond to be cleaved in the catalytic reaction should tend to become perpendicular to the plane of the extended π -system to optimize the σ – π overlap, resulting in an increase in delocalization energy. For the present complex the angles observed between the C–H bond vectors and the plane of the π -system are 29.9 and 70.8° for C–H(4) and C–H(5), respectively. Dunathan's hypothesis of the direction of the C–H bonds has earlier provided a basis for an understanding of the reactivities of pyridoxylidene-*O*-phosphate-DL-threonine complexes of Ni^{II} and Cu^{II} (Aoki & Yamazaki, 1980). In the present compound our observations seem to show a difference between the two C–H bonds. A comparison of bond lengths may however not be a sensitive enough probe for understanding the rather subtle electronic redistributions responsible for the catalytic processes. A further discussion of the α -C bond labilization will be provided in a charge-density study which is in progress (Bkouche-Waksman & Kvik, to be published).

The geometry around the N atom. The N–C(2) distance [1.455 (1) Å] is shorter than the value of 1.479 (1) Å found in α -glycine as a consequence of the condensation with the *N*-salicyloylaldehyde group, but is close to the value found in *N*-salicyloylglycine [1.435 (9) Å] (Smeets, Kanters & Venkatasubramanian, 1985) and in α -glycylglycine [1.453 (1) Å] (Kvik, Al-Karghouli & Koetzle, 1977). The bond has partial double-bond character, which has been suggested to be related to the reactivity in transamination processes (Darriet *et al.*, 1978).

The N–C(3) bond formed by the condensation reaction has a length [1.284 (1) Å] in the normal

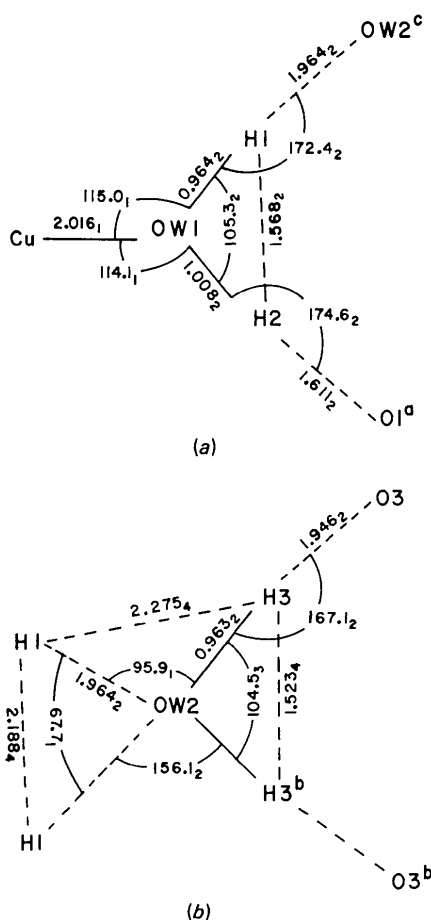


Fig. 3. Description of the two water molecules present in the structure, showing distances (Å) and angles (°) with e.s.d.'s given as subscripts. (a) Water molecule *W*(1) coordinated to Cu with hydrogen bonds $OW(1)\cdots O(1^a) = 2.616$ (1) and $OW(1)\cdots O(2^c) = 2.923$ (1) Å. Same symmetry operations as in Fig. 2. (b) Water molecule *W*(2) not coordinated to Cu, with hydrogen bonds $OW(2)–H(3)\cdots O(3) = 2.894$ (1) Å.

double-bond range, and is considerably shorter than the peptide link in α -glycylglycine [1.3333 (5) Å] and in *N*-salicyloylglycine [1.330 (8) Å]. The shortening is similar to those found in other related imine-type bonds in systems with extended conjugated π -systems (Darriet *et al.*, 1978). The C(2)–N–C(3) angle [120.58 (5)°] is smaller than that found in *N*-salicyloylglycine [122.4 (5)°]; this is most likely due to the Cu–N interaction.

Thus one of the N–C bonds is normal, while the other is shorter than normal. This observation is consistent with kinetic studies by solution NMR of Al^{III}–alanine and Al^{III}–pyruvate chelates showing conjugation between these bonds (Martell & Taylor, 1984).

The carboxylate group. The carboxylate group [C(1), C(2), O(2), O(3)] is planar, with a maximum deviation of 0.079 (7) Å for the C(1) atom from the best least-squares plane. This plane makes a dihedral angle of 23.85° with the aldimine plane [C(2), N, C(3), H(6)], and an angle of 20.41° with the Cu–salicylaldiminato plane. The two O atoms are coordinated to Cu atoms in different complexes; O(3) is also hydrogen bonded to water *W*(2). The long C(1)–O(2) bond [1.269 (1) Å] corresponds to the shorter Cu–O bond and the shorter C(1)–O(3) bond [1.248 (1) Å] is associated with the longer Cu–O interaction. The difference in C–O distances of 0.021 Å is considerably larger than in α -glycine [0.002 (1) Å] (Legros & Kvik, 1980), γ -glycine [0.008 (1) Å] (Kvik *et al.*, 1980) and in α -glycylglycine [0.009 (1) Å] (Kvik *et al.*, 1977), where the carboxylate ends are also in the ionized carboxylate form.

The C(1)–C(2)–N angle [108.78 (5)°] is significantly different from the angles found in γ -glycine [111.3 (1)°] and α -glycylglycine [112.49 (3)°] because of the chelating effect, but is similar to the value found in *N*-salicyloylglycine [109.4 (5)°].

The benzene ring. The C–C bond lengths and angles range from 1.384 (1) to 1.421 (1) Å and from 117.75 (6) to 121.75 (6)° respectively. The C–H bond lengths and angles involving H atoms (Table 5) range from 1.081 (2) to 1.098 (2) Å (1.103–1.114 Å after correction for thermal motion) and from 116.0 (1) to 121.5 (1)°.

The shorter C(5)–C(6) and C(7)–C(8) bonds indicate a contribution from a quinoid form. This was also found in free salicylic acid by Bacon & Jude (1973). The internal angles of the ring depart slightly from 120°; greater deviations are seen for the angles from the ring to O(1) and to C(3).

The displacement of C(4) and C(7) [–0.006 (1) Å] from the least-squares plane based on the ring C atoms, is opposite to those of the remaining four C atoms [+0.002 (1), +0.004 (1), +0.000 (1), +0.005 (1) Å] resulting in a slightly distorted boat configuration.

All four H atoms in the ring are displaced, in the same direction as C(4) and C(7), by distances ranging

from –0.024 (2) to –0.032 (2) Å while the Cu atom is effectively in the plane [–0.002 (1) Å].

With respect to the Cu–salicylaldiminato plane, the displacements of the C atoms are also smaller [0.007 (1)–0.035 (1) Å] than those of the H atoms [–0.024 (2) to –0.076 (2) Å], and they are generally in the opposite direction of that of the Cu atom [0.040 (1) Å].

Conclusions

This work is the first precise structure determination for a model of a vitamin B₆–amino-acid complex. The precise determination of the hydrogen positions makes it possible to characterize molecular interactions, the water molecules, and the benzene ring.

The catalytically interesting part of the chelate is stabilized by the Cu ion to form a planar conjugated system. The lack of a strong electron-attracting group *ortho* or *para* to the aldimine group in salicylaldehyde, which is one of the structural requirements for the catalytic process, reduces the effects of the electron redistribution. In fact, the proposed withdrawal of electrons from the bonds around the α -C atom by the Cu ion cannot be detected in the bond distances.

The observations for the two α -C–H bonds, characterized by slightly different bond lengths and σ – π overlap positions of these with respect to the π -system plane, seem to indicate differences in the α -C–H bonds. These results are consistent with the kinetic studies by NMR showing two different rates for the glycine moiety's α -proton exchange in a Co^{III} complex (Fischer & Abbott, 1979).

When the corresponding bond-length values from very accurate structure determinations are compared, it is clear that the electron redistribution does not extend to the glycine C–C bond in the studied compound. Such an electron redistribution has earlier been suggested for a valine complex by Dawes, Waters & Waters (1982). However, this bond in α -glycine was shown to have partial π -bond character (Legros & Kvik, 1980) and its contribution to the extended π -system in the complex molecule should therefore not be excluded.

Since the transamination does not occur with salicylaldehyde derivatives, the difference between the α -C–H bonds alone cannot be sufficient for this process to be completed. More subtle details may be revealed in a subsequent charge-density study. Attempts to crystallize a compound with an 'electron sink' attached to the aromatic ring are also underway.

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Structural and Strain-Energy-Minimization Study of the Geometric and Configurational Isomers of Bis(L-methioninato)cobalt(III)

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Abstract

The crystal structures of the three geometric isomers of bis(L-methioninato)cobalt(III) have been determined by

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X-ray analysis. (1) *trans*-S-[Co^{III}(L-met)₂]⁺: Na-[Co(C₅H₁₀NO₂S)₂](ClO₄)₂, *M_r* = 577.2, orthorhombic, *P*2₂1, *a* = 5.4951 (5), *b* = 11.1890 (9), *c* = 16.604 (2) Å, *V* = 1020.9 (2) Å³, *Z* = 2, *D_x* =

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