

molecules with nearly identical orientation owing to the local C_2 symmetry mentioned above) produce the layer structure shown in Fig. 2 (a stereoscopic projection perpendicular to the plane defined by the net of Ni atoms). It can be seen from Fig. 2 that a pattern of pseudo centers of symmetry is generated and that the layer can be simply described by a two-dimensional lattice defined in terms of this pattern. It is remarkable that this pseudo lattice is almost identical to that of complex (I); the only obvious difference in the layers is the presence of an additional water molecule in the latter.

Distances and angles describing the hydrogen bonds are given in Table 4. In (I) the shortest Ni—Ni distance is slightly shorter than the corresponding one in (II). This is probably due to the bite of the extra hydrogen bonds resulting from the presence of O(9W). This extra water molecule causes an increase in the interlayer distances from 9.547 (4) Å in (II) to 10.101 (1) Å in (I).

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Crystal Structure Determination of α -Aminoisobutyrate(α -Aib)—Transition-Metal Complexes. II. Structure of Bis(α -Aib)copper(II)

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Abstract. $[\text{Cu}(\text{C}_4\text{H}_8\text{NO}_2)_2]$, $M_r = 267.7$, monoclinic, $P2_1/c$, $a = 10.470$ (3), $b = 5.335$ (1), $c = 10.201$ (3) Å, $\beta = 115.6$ (2)°, $V = 513.9$ (5) Å³, $Z = 2$, $D_x = 1.73$ Mg m⁻³, graphite-monochromatized $\text{Cu K}\alpha$, $\lambda = 1.54184$ Å, $\mu = 2.79$ mm⁻¹, $F(000) = 278$, $T = 296$ K, $R = 0.055$, $wR = 0.059$ for 879 observed reflections [$I > 3\sigma(I)$] and 86 refined parameters. The Cu^{2+} ion is at a center of symmetry and is coordinated to the amine N atoms [at 1.981 (3) Å] and carboxylate O [at 1.946 (2) Å] of two α -aminoisobutyrate (α -Aib) groups related by the center of symmetry, in a crystallographically planar arrangement. The carboxyl O atoms of two other α -Aib groups are at 3.045 (3) Å from the Cu atoms completing a rather elongated

coordination octahedron. The crystal is built from layers parallel to the bc plane; within a layer the complexes are linked by a net of hydrogen bonds.

Introduction. The complexes of transition metals with amino acids have been extensively studied as models for the metal-binding sites in proteins (Freeman, 1973; Brill, 1977). Also, it has been pointed out that some Cu—amino acid complexes have a quasi two-dimensional magnetic behavior with exchange interactions much smaller than other two-dimensional magnetic systems reported in the literature (Newman, Imes & Cowen, 1976; Willet, Jardine, Rouse, Wong, Landee & Numata, 1981). As part of a series of EPR, magnetic

and crystallographic studies of metal complexes with α -Aib (Castellano, Oliva, Zukerman-Schpector & Calvo, 1986*a,b*), we report here the crystal and molecular structure of the title compound. Partial details of this work, together with EPR and magnetic-susceptibility studies, have been published elsewhere (Calvo, Mesa, Oliva, Zukerman-Schpector, Nascimento, Tovar & Arce, 1985).

Experimental. Deep-blue crystals, $0.08 \times 0.50 \times 0.80$ mm; Enraf-Nonius CAD-4 diffractometer; cell parameters by least squares on setting angles for 25 reflections with $26 < 2\theta < 63^\circ$; ω - 2θ scans for $\omega = (1.0 + 0.35 \tan\theta)^\circ$ at $6.7^\circ \text{ min}^{-1}$ max.; 3 standard reflections, variations less than 4%; $-13 \leq h \leq 13$, $0 \leq k \leq 6$, $0 \leq l \leq 12$; $2\theta_{\text{max}} = 75^\circ$; 1057 reflections measured, 1001 unique, $R_{\text{int}} = 0.03$, 880 observed above $3\sigma(I)$ level; Lp and absorption corrections (transmission factors 0.8119 to 0.3394); structure solved by direct methods; H(N1) and H'(N1) located in a difference map, those of the methyl groups calculated and refined as rigid groups; anisotropic least-squares refinement (isotropic for H) minimizing $\sum w(|F_o| - |F_c|)^2$, $w = [\sigma^2(F_o) + 0.006644F_o^2]^{-1}$, excluding unobserved reflections and one strong reflection (100); $R = 0.055$, $wR = 0.059$; inspection of F_c and F_o values indicated that a correction for secondary extinction was required [$F_{\text{corr}} = F_c \times (1.0 - 10^{-4}\chi F_c^2/\sin\theta)$; χ refined to 0.1656 in the final run]; max. $\Delta/\sigma = 0.038$; $-0.560 \leq \Delta\rho \leq 0.25 \text{ e } \text{\AA}^{-3}$; scattering factors for Cu, C, N and O from Cromer & Mann (1968) with corrections for anomalous dispersion from Cromer & Liberman (1970), for H from Stewart, Davidson & Simpson (1965); MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and SHELX76 (Sheldrick, 1976) system of programs, and ORTEP (Johnson, 1965).*

Discussion. The final atomic parameters for all atoms except the methyl H atoms are given in Table 1. Fig. 1 is a projection of the molecule, showing the atomic numbering and bond distances. Bond angles are given in Table 2. The Cu^{II} ion is at a center of symmetry and is coordinated to two α -Aib residues related to one another by the inversion center. α -Aib groups act as bidentate ligands bonded to the cation through their amine N atoms and O(1) oxygen atoms of the carboxylate groups, resulting in a crystallographically planar configuration. The Cu^{II} ion is also semi-coordinated to the carboxyl O atoms of two other

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

$$B_{\text{eq}} = \frac{4}{3} \sum_{ij} T_{ij} B_{ij} \text{ (Hamilton, 1959).}$$

	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
Cu	0	0	0	2.35 (3)
O(1)	0.0460 (3)	0.1691 (5)	0.1840 (2)	2.18 (6)
O(2)	0.1751 (3)	0.1251 (5)	0.4214 (3)	2.17 (6)
C(1)	0.1461 (4)	0.0673 (6)	0.2952 (4)	1.70 (7)
C(2)	0.2367 (3)	-0.1261 (5)	0.2594 (3)	1.52 (7)
C(3)	0.3077 (4)	-0.3129 (7)	0.3816 (4)	2.47 (9)
C(4)	0.3470 (4)	0.0223 (7)	0.2317 (5)	2.17 (9)
N(1)	0.1385 (3)	-0.2526 (5)	0.1233 (3)	1.80 (7)
H(N1)	0.176 (5)	-0.357 (9)	0.066 (5)	3.9 (8)
H'(N1)	0.081 (5)	-0.378 (8)	0.149 (6)	3.9 (8)

Table 2. Relevant bond angles ($^\circ$) with e.s.d.'s in parentheses

N(1)-Cu-O(1)	84.0 (1)	C(1)-C(2)-N(1)	106.0 (3)
O(1)-C(1)-O(2)	123.9 (3)	C(3)-C(2)-C(4)	110.6 (3)
O(1)-C(1)-C(2)	115.0 (3)	C(3)-C(2)-N(1)	111.4 (3)
O(2)-C(1)-C(2)	121.0 (3)	C(4)-C(2)-N(1)	109.7 (3)
C(1)-C(2)-C(3)	112.1 (3)	H(N1)-N(1)-H'(N1)	102. (4)
C(1)-C(2)-C(4)	106.7 (2)		

Table 3. Hydrogen bonds and close intermolecular contact distances (\AA) and angles ($^\circ$)

a	b	c	ab	bc	ac	$\angle abc$
N(1)	H(N1)	O(2 ⁱ)	1.00 (1)	2.05 (5)	3.003 (4)	158 (4)
N(1)	H'(N1)	O(1 ⁱⁱ)	1.01 (1)	2.49 (4)	3.370 (4)	145 (4)
N(1)	H'(N1)	O(1 ⁱⁱⁱ)	1.01 (1)	2.59 (6)	3.324 (4)	130 (4)
N(1)	H'(N1)	O(2 ⁱⁱⁱ)	1.01 (1)	2.46 (6)	3.181 (4)	128 (4)

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

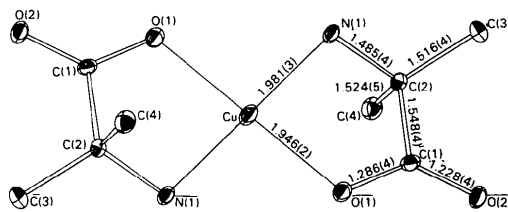


Fig. 1. Projection of the molecule showing the interatomic distances and atom numbering.

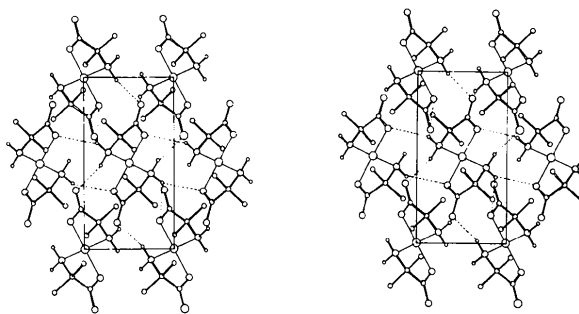


Fig. 2. Stereoscopic projection of the structure on to the bc plane.

* Lists of structure factors, anisotropic thermal parameters and methyl-H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42472 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

centrosymmetrically related α -Aib groups of neighboring complexes, completing a somewhat distorted coordination octahedron around the cation. The semi-coordination Cu^{II}—O distance of 3.045 (3) Å is much longer than the Cu^{II}—O and Cu^{II}—N coordination distances of 1.946 (2) and 1.981 (3) Å. This suggests that the electronic configuration of the Cu^{II} ion is essentially that due to a square-planar crystal field (Hathaway & Billing, 1970), in agreement with the predictions of Graddon & Munday (1961) who proposed this model to explain their solubility data and optical behavior in the visible and the infrared range.

The semi-coordination O—Cu^{II}—O line forms an angle of 14.7° with the normal to the (approximate) square base. The Cu—N and Cu—O distances fall in the rather narrow ranges from 1.97 to 2.02 and from 1.94 to 1.97 Å respectively, reported for several tetragonally coordinated copper(II)—bis(amino acid) complexes (Fawcett, Ushay, Rose, Lalancette, Potenza & Schugar, 1979, and references therein).

The periodic structure is built up from layers of complexes parallel to the *bc* plane. Within a layer, the Cu(α -Aib)₂ units are linked to one another by intermolecular N—H...O hydrogen bonds (Table 3). The intralayer Cu—Cu distances are 5.335 (1) and 5.756 (2) Å; the interlayer Cu—Cu distance is 10.470 (3) Å. Fig. 2 shows a stereoscopic view of one of these layers.

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Crystal Structure Determination of α -Aminoisobutyrate(α -Aib)—Transition-Metal Complexes. III. Crystal Structure of the 1:2 Complex of Bis(α -Aib)diaquazinc(II) and Bis(α -Aib)aquazinc(II)

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Abstract. [Zn(C₄H₈NO₂)₂(H₂O)₂]₂[Zn(C₄H₈NO₂)₂(H₂O)], *M_r* = 880.87, monoclinic, *C2/c*, *a* = 19.928 (2), *b* = 16.460 (2), *c* = 11.509 (2) Å, β = 97.57 (1)°, *V* = 3742 (2) Å³, *Z* = 4, *D_x* = 1.56 Mg m⁻³, graphite-monochromated Cu *K* α , λ = 1.54184 Å, μ = 2.97 mm⁻¹, *F*(000) = 1840, *T* = 296 K, *R* = 0.041 for 2751 observed reflections [*I* > 3 σ (*I*)] and 294 refined parameters. The Zn²⁺ ion is

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