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-Aminoisobutyrato(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. $[Zn(C_4H_8NO_2)_2(H_2O)_2].2[Zn(C_4H_8NO_2)_2(H_2O)]$, $M_r = 880.87$, monoclinic, $C2/c$, $a = 19.928$ (2), $b = 16.460$ (2), $c = 11.509$ (2) Å, $\beta = 97.57$ (1)°, $V = 3742$ (2) Å^3, $Z = 4$, $D_x = 1.56$ Mg m^{-3}, graphite-monochromated Cu $K\alpha$, $\lambda = 1.54184$ Å, $\mu = 2.97$ mm^{-1}, $F(000) = 1840$, $T = 296$ K, $R = 0.041$ for 2751 observed reflections [$I > 3\sigma(I)$] and 294 refined parameters. The Zn^{2+} ion is

coordinated to two bidentate α-Aib residues and two water molecules in one case, in a very distorted octahedral configuration, and to two α-Aib residues and only one water molecule in the other case, in a somewhat distorted trigonal-bipyramidal configuration. All water molecules are involved in hydrogen bonding.

Introduction. In the preceding papers (Castellano, Oliva, Zukerman-Schpector & Calvo, 1986; Oliva, Castellano, Zukerman-Schpector & Calvo, 1986) the structures of Ni(α-Aib)$_2$(H$_2$O)$_2$.3H$_2$O, Ni(α-Aib)$_2$-(H$_2$O)$_2$.2H$_2$O and Cu(α-Aib)$_2$ were described. Following the series of crystallographic studies of complexes of transition-metal ions with amino acids, the crystal structure of the title compound, in which Zn^{2+} appears with coordination numbers five and six, has been determined by three-dimensional X-ray analysis.

Experimental. Prismatic colorless crystals, 0·45 × 0·33 × 0·18 mm; Nonius CAD-4 diffractometer; cell parameters by least squares on setting angles for 25 reflections, 19° < θ < 34°; ω–2θ scans for ω = (1·0 + 0·14 tanθ)° at ω speed of 6·7° min^{-1} max.; θ < 75°; range of hkl: −24 < h < 24, k < 20, l < 14; standards 463, 537 varied ±1·5% from mean intensities over data collection; 4567 reflections measured, 3656 unique, R_{int} = 0·039, 2752 above 3σ(I); Lp and absorption corrections (transmission factors 0·52–0·75); structure solved by direct methods; H atoms located in a difference map, those of the methyl groups refined as rigid groups; anisotropic least-squares refinement (isotropic for H) minimizing $\sum w(|F_o| - |F_c|)^2$, $w = [\sigma^2(F_o) + 0·002124F_o^2]^{-1}$, excluding unobserved and one strong reflection (110); R = 0·041, wR = 0·047; inspection of F_c and F_o values indicated that a correction for secondary extinction was required [$F_{corr} = F_c \times (1·0 - 10^{-4}\chi F_c^2/\sin\theta)$, where χ refined to 0·0063 in the final run]; max. Δ/σ = 0·02; $\Delta\rho$ excursions within −0·49 and 0·40 e Å^{-3}; scattering factors for non-H atoms from Cromer & Mann (1968) with corrections for anomalous dispersion from Cromer & Liberman (1970), for H from Stewart, Davidson & Simpson (1965); SHELX76 (Sheldrick, 1976) system of programs and ORTEP (Johnson, 1965).*

Discussion. The final atomic parameters for non-hydrogen atoms are given in Table 1. Distances and angles are given in Table 2. The system of nomenclature is that of Freeman (1967). The structure is particularly interesting in that the two independent Zn^{2+} ions appear with different coordination numbers.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42473 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic coordinates and equivalent isotropic thermal parameters for the non-H atoms with e.s.d.'s in parentheses*

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

	x	y	z	B_{eq}(Å^2)
Zn(1)	0·2101 (1)	0·0793 (1)	0·5601 (1)	2·22 (1)
N(1)	0·1831 (2)	0·1964 (2)	0·5903 (3)	2·12 (8)
C(1)	0·1207 (2)	0·1989 (2)	0·6479 (3)	1·87 (9)
C(2)	0·0773 (2)	0·1243 (2)	0·6079 (3)	1·93 (9)
O(1)	0·1081 (1)	0·0613 (2)	0·5775 (2)	2·39 (7)
O(2)	0·0155 (1)	0·1272 (2)	0·6109 (2)	2·56 (8)
C(3)	0·1412 (2)	0·1892 (3)	0·7806 (3)	3·1 (1)
C(4)	0·0814 (2)	0·2774 (2)	0·6221 (4)	3·0 (1)
N(2)	0·3126 (2)	0·0801 (2)	0·5451 (3)	2·25 (9)
C(5)	0·3466 (2)	0·0140 (3)	0·6166 (3)	2·8 (1)
C(6)	0·3062 (2)	−0·0070 (3)	0·7178 (4)	3·2 (1)
O(3)	0·2447 (2)	0·0169 (2)	0·7071 (3)	3·56 (9)
O(4)	0·3340 (2)	−0·0463 (3)	0·8009 (3)	5·4 (1)
C(7)	0·3449 (3)	−0·0632 (3)	0·5405 (5)	4·5 (2)
C(8)	0·4200 (3)	0·0368 (5)	0·6644 (6)	5·7 (2)
O(5W)	0·1872 (2)	0·0241 (3)	0·3997 (3)	4·5 (1)
Zn(2)	0	0·1127 (1)	0·25	1·87 (2)
N(3)	0·0723 (2)	0·1239 (2)	0·1345 (3)	2·08 (8)
C(9)	0·1155 (2)	0·1960 (2)	0·1631 (3)	2·04 (9)
C(10)	0·1206 (2)	0·2122 (2)	0·2958 (3)	2·03 (9)
O(6)	0·0734 (1)	0·1850 (2)	0·3491 (2)	2·37 (7)
O(7)	0·1693 (1)	0·2534 (2)	0·3428 (2)	2·87 (8)
C(11)	0·0790 (2)	0·2698 (3)	0·1017 (4)	3·4 (1)
C(12)	0·1851 (2)	0·1842 (3)	0·1242 (4)	3·6 (1)
O(8W)	0·0481 (1)	0·0118 (2)	0·3587 (2)	2·14 (7)

One is on a special position of point symmetry C_2 and is coordinated to two α-Aib residues and two water molecules, each equivalent moiety being related by the twofold axis. The other Zn^{2+} ion is in a general position and is coordinated to two independent α-Aib residues and only one water molecule. In both cases the residues act as bidentate ligands bonded to the cation through their amine N atoms and one O of their carboxylate groups. The resulting coordination numbers are, therefore, six and five respectively. In the first case the coordination polyhedron is a very distorted octahedron; in the second it is a somewhat distorted trigonal bipyramid. Fig. 1 is a projection of the structure down the unique axis. Both configurations are known to exist for Zn^{2+} although the first is far more common than the second. In fact, to the best of our knowledge, the present one is the first report of a trigonal-bipyramidal configuration for Zn^{2+} with non-tridentate ligands. The fact that the two polyhedra appear together in the same crystal structure indicates that, for this case, the energies associated with each configuration are very similar. Since the Zn^{2+} ion has all its d shells saturated, ligand-field stabilization effects are not expected. The stereochemistry of its complexes will therefore be dominated by size factors, electrostatic interactions and covalent bonding (Cotton & Wilkinson, 1972). On this basis a perfect octahedron is expected to be more favorable in terms of energy than a trigonal bipyramid. In the present case, however, the six-coordination polyhedron is very distorted from the

ideal octahedral point symmetry O_h, due to the steric constraints imposed by the bites of the residues. This can be appreciated in Fig. 2, which shows a projection of the polyhedron on to the plane defined by O(6), O(8W) and the twofold-axis equivalent of N(3). Bite distances of 2·66 Å are much shorter than the value of about 2·90 Å that would be expected for a ligand—Zn²⁺—ligand angle of 90°.

Fig. 3 is a projection of the five-coordination polyhedron on to the plane defined by atoms N(1), O(3) and O(5W).

The r.m.s. deviation of atoms Zn(1), N(1), O(3) and O(5W) (which define the base of the bipyramid) from the best least-squares plane through them is 0·05 (2) Å. The normal to this plane and the lines through Zn(1)—O(1) and Zn(1)—N(2) form angles of 8 (1) and
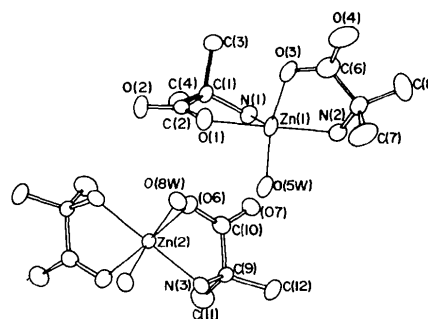

Fig. 1. A projection of the structure down the unique axis.

Table 2. *Interatomic distances (Å) and bond angles (°) with e.s.d.'s in parentheses*

Zn(1)—N(1)	2·043 (3)		Zn(1)—N(2)	2·072 (3)	
Zn(1)—O(1)	2·090 (3)		Zn(1)—O(3)	2·021 (3)	
Zn(1)—O(5W)	2·054 (4)				
N(1)—C(1)	1·485 (4)		N(2)—C(5)	1·474 (5)	
C(1)—C(2)	1·537 (5)		C(5)—C(6)	1·540 (6)	
C(1)—C(3)	1·536 (5)		C(5)—C(7)	1·541 (7)	
C(1)—C(4)	1·520 (5)		C(5)—C(8)	1·540 (7)	
C(2)—O(1)	1·277 (4)		C(6)—O(3)	1·278 (6)	
C(2)—O(2)	1·237 (4)		C(6)—O(4)	1·225 (6)	
Zn(2)—N(3)	2·093 (3)		C(9)—C(11)	1·539 (5)	
Zn(2)—O(6)	2·102 (3)		C(9)—C(12)	1·525 (5)	
Zn(2)—O(8W)	2·220 (3)		C(10)—O(6)	1·270 (4)	
N(3)—C(9)	1·478 (5)		C(10)—O(7)	1·247 (4)	
C(9)—C(10)	1·540 (5)				

		80·6 (1)	90*	101·7†
N(1)—Zn(1)—O(1)		80·6 (1)	90*	101·7†
N(1)—Zn(1)—N(2)		107·0 (1)	90	101·7
N(1)—Zn(1)—O(3)		113·9 (1)	120	101·7
N(1)—Zn(1)—O(5W)		122·5 (1)	120	101·7
O(1)—Zn(1)—N(2)		172·2 (1)	180	156·7
O(1)—Zn(1)—O(3)		94·4 (1)	90	87·8
O(1)—Zn(1)—O(5W)		85·4 (1)	90	87·8
N(2)—Zn(1)—O(3)		80·9 (1)	90	87·8
N(2)—Zn(1)—O(5W)		91·9 (1)	90	87·8
O(3)—Zn(1)—O(5W)		122·6 (1)	120	156·7

Zn(1)—N(1)—C(1)	110·9 (2)	C(2)—O(1)—O(2)	27·7 (2)
N(1)—C(1)—C(2)	108·4 (3)	C(2)—O(2)—O(1)	28·6 (2)
N(1)—C(1)—C(3)	108·2 (3)	N(2)—C(5)—C(6)	109·9 (3)
N(1)—C(1)—C(4)	112·1 (3)	N(2)—C(5)—C(7)	108·5 (4)
C(2)—C(1)—C(3)	106·3 (3)	N(2)—C(5)—C(8)	111·4 (4)
C(2)—C(1)—C(4)	111·4 (3)	C(6)—C(5)—C(7)	105·7 (4)
C(3)—C(1)—C(4)	110·2 (3)	C(6)—C(5)—C(8)	110·6 (4)
C(1)—C(2)—O(1)	117·3 (3)	C(7)—C(5)—C(8)	110·7 (4)
C(1)—C(2)—O(2)	118·9 (3)	C(5)—C(6)—O(3)	116·6 (4)
O(1)—C(2)—O(2)	123·7 (3)	C(5)—C(6)—O(4)	118·8 (4)
Zn(1)—O(1)—C(2)	114·8 (2)	O(3)—C(6)—O(4)	124·6 (4)
Zn(1)—N(2)—C(5)	109·5 (2)	Zn(1)—O(3)—C(6)	117·0 (3)
N(3)—Zn(2)—O(6)	78·9 (1)	C(10)—C(9)—C(11)	106·5 (3)
N(3)—Zn(2)—O(8W)	98·1 (1)	C(10)—C(9)—C(12)	111·7 (3)
O(6)—Zn(2)—O(8W)	84·25 (9)	C(11)—C(9)—C(12)	111·0 (3)
Zn(2)—N(3)—C(9)	111·0 (2)	C(9)—C(10)—O(6)	117·5 (3)
N(3)—C(9)—C(10)	108·7 (3)	C(9)—C(10)—O(7)	118·0 (3)
N(3)—C(9)—C(11)	107·8 (3)	O(6)—C(10)—O(7)	124·4 (3)
N(3)—C(9)—C(12)	111·0 (3)	Zn(2)—O(6)—C(10)	116·4 (2)

* Theoretical values for trigonal-bipyramidal configuration.
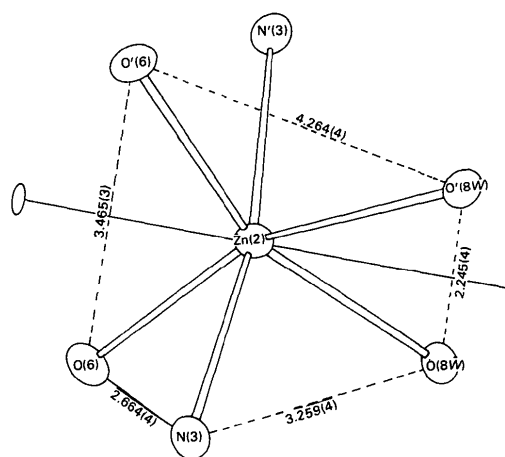† Theoretical values for tetragonal-pyramidal configuration.

Fig. 2. Projection of the six-coordination polyhedron on to the plane defined by atoms O(6), O(8W) and N'(3).
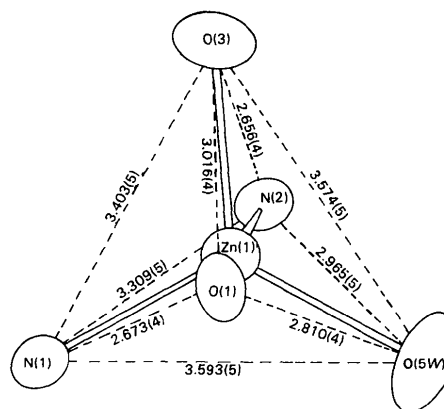

Fig. 3. Projection of the five-coordination polyhedron on to the plane defined by atoms N(1), O(3) and O(5W).

15 (1)° respectively. Since small distortions from the trigonal-bipyramid configuration may produce a tetragonal pyramid (Cotton & Wilkinson, 1972), we tested the possibility of this second configuration by looking for a planar square base. The 'most planar' arrangement was that of atoms N(2), O(1), O(3), O(5W) for which the r.m.s. deviation from the best least-squares plane through them was 0·42 (2) Å These figures and the comparison of actual angles with the theoretical values for the two models (Table 3) show that the observed five-coordination polyhedron is much closer to the ideal trigonal-bipyramid (C_{3h}) configuration than to that of the tetragonal pyramid (C_{4v}). We conclude that the distortions from the ideal O_h configuration imposed by the bites of the bidentate α-Aib groups raise the energy of the resulting six-coordination polyhedron to a value similar to that of the trigonal-bipyramid configuration, therefore making possible the simultaneous occurrence of five- and six-coordination.

All water molecules are involved in hydrogen bonding to carboxylate groups or to other water molecules. Table 3 is a list of these hydrogen bonds and some intermolecular short contacts.

Table 3. *Hydrogen bonds and short intermolecular distances (distances in Å, angles in °)*

a	b	c	ab	ac	bc	∠abc
N(1)	H(N1)	O(7^i)	0·83 (4)	3·055 (4)	2·28 (4)	155 (1)
N(1)	H'(N1)	O(7^{ii})	0·72 (5)	2·977 (4)	2·27 (5)	168 (1)
N(2)	H(N2)	O(7^i)	0·92 (4)	3·030 (4)	2·16 (4)	158 (1)
N(2)	H'(N2)	O(4^{iii})	0·96 (4)	2·951 (5)	2·01 (4)	165 (1)
N(3)	H(N3)	O(1^{iii})	0·86 (5)	3·218 (4)	2·45 (5)	149 (1)
N(3)	H'(N3)	O(2^{iv})	0·89 (5)	3·121 (4)	2·24 (5)	171 (1)
O(5W)	H(5W)	O(3^{iii})	0·65 (6)	2·711 (5)	2·11 (6)	155 (1)
O(5W)	H'(5W)	O(8W^{ii})	1·01 (6)	2·757 (4)	1·80 (6)	155 (1)
O(8W)	H(8W)	O(2^v)	0·75 (4)	2·661 (4)	1·94 (4)	161 (1)
O(8W)	H'(8W)	O(1^{ii})	0·96 (4)	2·764 (4)	1·83 (4)	163 (1)

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

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Structure of Caesium 3,3'-*commo*-Bis(8,9,12-tribromooctahydro-1,2-dicarba-3-cobalta-*closo*-dodecaborate)(1−)

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Abstract. $Cs[Co(C_2H_8B_9Br_3)_2]$, $M_r = 930·0$, monoclinic, $C2/c$, $a = 15·145$ (2), $b = 14·953$ (2), $c = 11·855$ (1) Å, $\beta = 113·850$ (9)°, $V = 2455·5$ Å^3, $Z = 4$, $D_m = 2·51$, $D_x = 2·52$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 11·63$ mm^{-1}, $F(000) = 1688$, $T = 293$ K. Final $R = 0·044$ for 1736 observed reflections.