

References

- BOLDRINI, P., BROWN, I. D., GILLESPIE, R. J., IRELAND, P. R., LUK, W., SLIM, D. R. & VEKRIS, J. E. (1976). *Inorg. Chem.* **15**, 765–770.
- BURNS, R. C., CHAN, W.-L., GILLESPIE, R. J., LUK, W.-C., SAWYER, J. F. & SLIM, D. R. (1980). *Inorg. Chem.* **19**, 1432–1439.
- BURNS, R. C., GRANGER, P. & SCHROBILIGEN, G. J. (1978). *J. Chem. Soc. Chem. Commun.* pp. 957–960.
- CARDINAL, G., GILLESPIE, R. J., SAWYER, J. F. & VEKRIS, J. E. (1982). *J. Chem. Soc. Dalton Trans.* pp. 765–779.
- GILLESPIE, R. J. (1979). *Chem. Soc. Rev.* **8**, 315–352.
- GILLESPIE, R. J., KENT, J. P. & SAWYER, J. F. (1981). *Inorg. Chem.* **20**, 3784–3799.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- LASSIGNE, C. & WELLS, E. J. (1978). *J. Chem. Soc. Chem. Commun.* pp. 956–957.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- XRAY* system (1976). Edited by J. M. STEWART. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

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Crystal Structure Determination of α -Aminoisobutyrate(α -Aib)–Transition-Metal Complexes. I. Structure of Bis(α -Aib)diaquanickel(II) Trihydrate (I) and Refinement of Bis(α -Aib)diaquanickel(II) Dihydrate (II)

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Abstract. (I): $[\text{Ni}(\text{C}_4\text{H}_8\text{NO}_2)_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$, $M_r = 353.01$, triclinic, $P\bar{1}$, $a = 8.262$ (2), $b = 9.717$ (2), $c = 11.441$ (2) Å, $\alpha = 103.36$ (2), $\beta = 110.32$ (1), $\gamma = 103.27$ (2)°, $V = 788.3$ (8) Å³, $Z = 2$, $D_x = 1.49$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 1.197$ mm⁻¹, $F(000) = 372$, $T = 288$ K, $R = 0.045$ for 1838 unique reflections [$I > 3\sigma(I)$] and 182 parameters. (II): $[\text{Ni}(\text{C}_4\text{H}_8\text{NO}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, $M_r = 335.00$, monoclinic, $P2_1/c$, $a = 11.429$ (3), $b = 14.035$ (2), $c = 9.900$ (7) Å, $\beta = 108.67$ (4)°, $V = 1504$ (2) Å³, $Z = 4$, $D_x = 1.48$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 1.248$ mm⁻¹, $F(000) = 704$, $T = 288$ K, $R = 0.085$ for 869 unique reflections [$I > 2\sigma(I)$] and 104 parameters. In both compounds the complex displays approximate local C_2 symmetry with the twofold axis bisecting the angle subtended by the Ni^{2+} ion and the coordination water O atoms. Both structures are built from almost identical layers of molecules in which the Ni^{2+} ions lie on planes containing the two shortest Ni–Ni interatomic distances.

Introduction. Complexes of transition metals with amino acids have been extensively studied as models for the metal-binding sites in proteins (Freeman, 1973; Brill, 1977). The observation of magnetic phase transitions in some of these complexes, believed to be

due to superexchange interactions through the net of hydrogen bonds commonly observed, added considerable interest to the study of new compounds and to the review of earlier data (Castellano, Nascimento & Calvo, 1982).

Attempts to obtain samples of the complex bis(α -Aib)diaquanickel(II) dihydrate (II) suitable for magnetic measurements produced crystals with unit-cell parameters essentially equal to those described by Noguchi (1962) and also others with different unit-cell parameters and crystal symmetry. A crystal structure determination showed this last compound to be $[\text{Ni}(\alpha\text{-Aib})_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ (I). In spite of crystallizing in different space groups the structures turned out to be remarkably similar, displaying almost identical patterns of hydrogen bonds. To show this the structure of (II) was redetermined in order to locate its H atoms. Refinement of compound (II) and the crystal structure determination of (I) are reported below.

Experimental. Crystals obtained from aqueous solutions; cell dimensions from least-squares refinement of 21 reflections (2θ range 18.34 to 51.88°) for (I) and of 18 reflections (2θ range 20.06 to 38.94°) for (II); Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation; ω – 2θ scan; θ_{max}

= 25° ($-9 < h < 9$, $-11 < k < 11$, $l < 13$) for (I), and $\theta_{\max} = 22^\circ$ ($-10 < h < 10$, $k < 14$, $l < 12$) for (II); crystal $0.23 \times 0.20 \times 0.15$ mm for (I), $0.05 \times 0.08 \times 0.25$ mm for (II); 2 standard reflections [$\bar{4}03$, 020 for (I) and 200, 080 for (II)]; mean intensities varied $\pm 1.5\%$ over data collections; 3062 reflections measured, 2774 unique, $R_{\text{int}} = 0.02$, 1840 with $I > 3\sigma(I)$ for (I); 1948 reflections measured, 1842 unique, $R_{\text{int}} = 0.04$, 869 with $I > 2\sigma(I)$ for (II); Lp corrections; no absorption correction; structure solved by heavy-atom method; H atoms located in difference Fourier syntheses; least-squares refinement minimizing $\sum w(|F_o| - |F_c|)^2$ with $w = [\sigma^2(F_o) + 0.004514F_o^2]^{-1}$ for (I) and $w = |\sigma^2(F_o)|^{-1}$ for (II), σ estimated from counting statistics; parameters refined: (I) coordinates and anisotropic thermal parameters for non-H atoms, (II) secondary-extinction correction [$F_{\text{corr}} = F_c \times (1.0 - 10^{-4}\chi F_c^2/\sin\theta)$, χ refined to 0.0005], coordinates and anisotropic thermal parameters for Ni and water O atoms, remaining non-H isotropic; in both cases H atoms were riding on the atom to which they are attached and with a common overall isotropic temperature factor that converged to $B = 6.0$ (4) \AA^2 for (I) and 6 (1) \AA^2 for (II); excluding unobserved reflections [also 100 and 001 in (I)], $R = 0.045$, $wR = 0.05$, max. $\Delta/\sigma = 0.002$ for (I), and $R = 0.085$, $wR = 0.064$, max. $\Delta/\sigma = 0.002$ for (II); final difference Fourier maps for (I) and (II) showed no peaks $> 0.44 \text{ e \AA}^{-3}$; 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. Final fractional coordinates and equivalent B values for the two structures are listed in Tables 1 and 2. The atom-labeling scheme is that used by Freeman (1967). In (II), we chose the standard setting $P2_1/c$ rather than $P2_1/a$ as used by Noguchi (1962). For this compound the crystal was of poor diffracting quality and prevented us from obtaining a good value for the ratio reflections/parameters. This resulted in rather high standard deviations for the refined parameters but fortunately the data were good enough to allow the localization of the H atoms.

The complex has a somewhat distorted octahedral configuration and is essentially identical in both structures. In fact, using the least-squares best orthogonal transformation for one structure on to the other (Kabsch, 1976), a mean deviation distance between equivalent atoms of 0.22 \AA is obtained. If the

* 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 42471 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

methyl C atoms are excluded, this value drops to 0.08 \AA for the 13 atoms remaining. The complex displays approximate local symmetry C_2 , with the twofold axis bisecting the angle subtended by the Ni^{2+} ion and the coordination water O atom. Bond distances and angles are given in Table 3.

A careful comparison of the molecular packing shows that in spite of their different symmetries and water contents, both crystals are built from parallel stacks of almost identical layers containing the two shortest Ni–Ni intermolecular distances. Fig. 1 is a stereoscopic view of (I) down the normal to the ab plane. Owing to the particular values of their fractional coordinates (very close to $0, \frac{1}{4}, 0$), the Ni atoms form an infinite layer in the ab plane with short Ni–Ni distances of 4.872 (1) and 4.851 (1) \AA along the b axis and a unit-cell translation of 8.262 \AA along the a direction.

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

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

	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
Ni	-0.0115 (1)	0.2463 (1)	-0.0034 (1)	1.72 (1)
N(1)	-0.0211 (5)	0.2779 (4)	-0.1777 (3)	2.02 (8)
O(1)	-0.1844 (4)	0.0375 (3)	-0.1348 (3)	2.36 (7)
O(2)	-0.2972 (5)	-0.1133 (4)	-0.3426 (3)	3.63 (9)
C(1)	-0.1676 (6)	0.1520 (5)	-0.2969 (4)	2.3 (1)
C(2)	-0.2199 (6)	0.0133 (5)	-0.2565 (5)	2.3 (1)
C(3)	-0.3396 (7)	0.1955 (6)	-0.3451 (5)	3.5 (1)
C(4)	-0.1013 (9)	0.1168 (7)	-0.4056 (6)	4.3 (2)
N(2)	-0.0507 (5)	0.1908 (5)	0.1532 (4)	2.25 (9)
O(3)	-0.2205 (4)	0.3258 (4)	-0.0048 (3)	2.45 (7)
O(4)	-0.4358 (4)	0.3236 (4)	0.0673 (3)	3.08 (9)
C(5)	-0.1902 (6)	0.2468 (5)	0.1845 (4)	2.2 (1)
C(6)	-0.2906 (6)	0.3003 (5)	0.0734 (4)	2.2 (1)
C(7)	-0.0918 (8)	0.3847 (7)	0.3103 (5)	3.8 (1)
C(8)	-0.3226 (7)	0.1221 (7)	0.2016 (6)	3.7 (1)
O(5W)	0.1803 (4)	0.4571 (3)	0.1204 (3)	2.77 (8)
O(6W)	0.2061 (4)	0.1613 (3)	0.0148 (3)	2.25 (7)
O(7W)	0.6326 (5)	0.6377 (5)	0.1753 (4)	3.8 (1)
O(8W)	0.4144 (6)	0.4075 (5)	0.3222 (4)	5.8 (1)
O(9W)	0.7165 (6)	0.6734 (5)	0.4460 (4)	4.5 (1)

Table 2. Fractional atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses for (II)

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

	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
Ni	0.3268 (2)	0.2531 (2)	0.2843 (2)	1.8 (1)
N(1)	0.150 (1)	0.242 (1)	0.139 (1)	2.5 (3)
O(1)	0.249 (1)	0.1584 (9)	0.389 (1)	2.5 (3)
O(2)	0.076 (1)	0.0921 (9)	0.397 (1)	4.4 (3)
C(1)	0.068 (2)	0.185 (1)	0.191 (2)	2.9 (4)
C(2)	0.135 (2)	0.139 (1)	0.334 (2)	3.5 (4)
C(3)	0.961 (2)	0.255 (2)	0.213 (2)	6.1 (5)
C(4)	0.010 (2)	0.104 (1)	0.084 (2)	6.2 (6)
N(2)	0.498 (1)	0.2358 (9)	0.435 (1)	1.9 (3)
O(3)	0.390 (1)	0.1436 (9)	0.188 (1)	2.2 (3)
O(4)	0.527 (1)	0.2076 (7)	0.227 (1)	2.7 (3)
C(5)	0.577 (2)	0.160 (1)	0.390 (2)	1.9 (3)
C(6)	0.493 (2)	0.108 (1)	0.261 (2)	2.5 (4)
C(7)	0.638 (2)	0.098 (1)	0.516 (2)	3.3 (5)
C(8)	0.666 (2)	0.212 (1)	0.336 (2)	2.6 (4)
O(5W)	0.268 (1)	0.3620 (8)	0.393 (1)	2.8 (4)
O(6W)	0.382 (1)	0.3546 (9)	0.163 (1)	2.6 (4)
O(7W)	0.638 (1)	0.0760 (8)	0.000 (1)	4.1 (5)
O(8W)	0.138 (1)	0.4828 (8)	0.171 (1)	4.3 (5)

The hydrogen bonds are also shown in Fig. 1; we have distinguished those common to both structures from those involving the extra water O atom O(9W) in (I) (dashed and dotted lines respectively). In (II) the local C₂ axis is approximately parallel to the unique crystallographic axis. For this reason two molecules related by the twofold screw axis appear in almost identical orientations. The Ni atom lies nearly on the glide plane *c* in *x*₁/₂, *z*, thus giving rise to a line of Ni atoms along the *c* direction with an intermolecular Ni–Ni distance of *c*/2 [actual value 4.951 (3) Å]. The combined effects of the glide plane (which generates chains of molecules along the *c* direction) and the twofold screw axis (which gives rise to new chains of

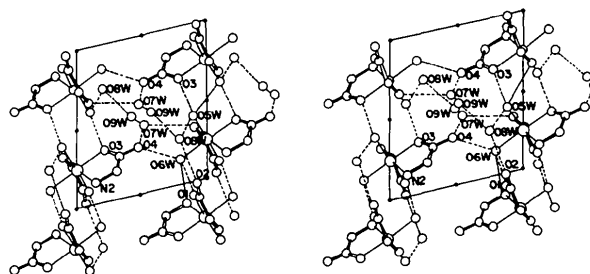


Fig. 1. Stereoscopic view of (I) down the normal to the *ab* plane.

Table 3. Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses for (I) and (II)

Compound (I)			
Ni–N(1)	2.064 (3)	Ni–N(2)	2.092 (4)
Ni–O(1)	2.046 (3)	Ni–O(3)	2.044 (4)
Ni–O(5W)	2.079 (4)	Ni–O(6W)	2.112 (4)
N(1)–C(1)	1.491 (6)	N(2)–C(5)	1.496 (7)
C(1)–C(2)	1.541 (7)	C(5)–C(6)	1.531 (7)
C(1)–C(3)	1.530 (8)	C(5)–C(7)	1.524 (7)
C(1)–C(4)	1.525 (9)	C(5)–C(8)	1.534 (8)
C(2)–O(1)	1.270 (6)	C(6)–O(3)	1.262 (6)
C(2)–O(2)	1.239 (6)	C(6)–O(4)	1.253 (7)

Compound (II)			
Ni–N(1)	2.08 (1)	Ni–N(2)	2.06 (1)
Ni–O(1)	2.05 (1)	Ni–O(3)	2.06 (1)
Ni–O(5W)	2.10 (1)	Ni–O(6W)	2.09 (1)
N(1)–C(1)	1.45 (2)	N(2)–C(5)	1.55 (2)
C(1)–C(2)	1.52 (3)	C(5)–C(6)	1.52 (2)
C(1)–C(3)	1.64 (3)	C(5)–C(7)	1.50 (3)
C(1)–C(4)	1.55 (3)	C(5)–C(8)	1.48 (2)
C(2)–O(1)	1.27 (3)	C(6)–O(3)	1.27 (2)
C(2)–O(2)	1.24 (2)	C(6)–O(4)	1.27 (2)

Compound (I)		Compound (II)	
N(1)–Ni–O(1)	80.6 (1)	N(1)–Ni–O(1)	79.6 (5)
N(1)–Ni–N(2)	169.8 (2)	N(1)–Ni–N(2)	168.6 (5)
N(1)–Ni–O(3)	94.0 (1)	N(1)–Ni–O(3)	91.8 (5)
N(1)–Ni–O(5W)	95.6 (1)	N(1)–Ni–O(5W)	90.5 (5)
N(1)–Ni–O(6W)	91.3 (1)	N(1)–Ni–O(6W)	93.4 (5)
O(1)–Ni–N(2)	91.2 (2)	O(1)–Ni–N(2)	91.3 (5)
O(1)–Ni–O(3)	93.8 (1)	O(1)–Ni–O(3)	91.3 (5)
O(1)–Ni–O(5W)	174.4 (1)	O(1)–Ni–O(5W)	87.2 (5)
O(1)–Ni–O(6W)	87.2 (1)	O(1)–Ni–O(6W)	172.4 (5)
N(2)–Ni–O(3)	80.5 (2)	N(2)–Ni–O(3)	81.6 (5)
N(2)–Ni–O(5W)	93.0 (2)	N(2)–Ni–O(5W)	95.8 (5)
N(2)–Ni–O(6W)	94.3 (1)	N(2)–Ni–O(6W)	96.0 (5)
O(3)–Ni–O(5W)	90.4 (1)	O(3)–Ni–O(5W)	177.0 (5)
O(3)–Ni–O(6W)	174.7 (1)	O(3)–Ni–O(6W)	91.6 (5)
O(5W)–Ni–O(6W)	89.0 (1)	O(5W)–Ni–O(6W)	90.2 (5)
Ni–N(1)–C(1)	112.1 (3)	Ni–N(1)–C(1)	113. (1)
N(1)–C(1)–C(2)	108.8 (4)	N(1)–C(1)–C(2)	112. (1)
N(1)–C(1)–C(3)	109.1 (4)	N(1)–C(1)–C(3)	108. (1)
N(1)–C(1)–C(4)	110.3 (4)	N(1)–C(1)–C(4)	110. (1)
C(2)–C(1)–C(3)	106.8 (4)	C(2)–C(1)–C(3)	108. (1)
C(2)–C(1)–C(4)	110.9 (4)	C(2)–C(1)–C(4)	108. (1)
C(3)–C(1)–C(4)	110.9 (5)	C(3)–C(1)–C(4)	111. (1)
C(1)–C(2)–O(1)	116.9 (4)	C(1)–C(2)–O(1)	117. (1)
C(1)–C(2)–O(2)	119.4 (4)	C(1)–C(2)–O(2)	120. (1)
O(1)–C(2)–O(2)	123.7 (5)	O(1)–C(2)–O(2)	123. (1)
Ni–O(1)–C(2)	117.4 (3)	Ni–O(1)–C(2)	118. (1)
Ni–N(2)–C(5)	112.5 (3)	Ni–N(2)–C(5)	112.2 (9)
N(2)–C(5)–C(6)	108.7 (4)	N(2)–C(5)–C(6)	108. (1)
N(2)–C(5)–C(7)	109.0 (4)	N(2)–C(5)–C(7)	109. (1)
N(2)–C(5)–C(8)	109.8 (4)	N(2)–C(5)–C(8)	107. (1)
C(6)–C(5)–C(7)	106.3 (4)	C(6)–C(5)–C(7)	115. (1)
C(6)–C(5)–C(8)	111.9 (4)	C(6)–C(5)–C(8)	105. (1)
C(7)–C(5)–C(8)	110.9 (5)	C(7)–C(5)–C(8)	113. (1)
C(5)–C(6)–O(3)	119.2 (4)	C(5)–C(6)–O(3)	121. (1)
C(5)–C(6)–O(4)	118.4 (4)	C(5)–C(6)–O(4)	119. (1)
O(3)–C(6)–O(4)	122.3 (5)	O(3)–C(6)–O(4)	120. (1)
Ni–O(3)–C(6)	117.0 (3)	Ni–O(3)–C(6)	115. (1)

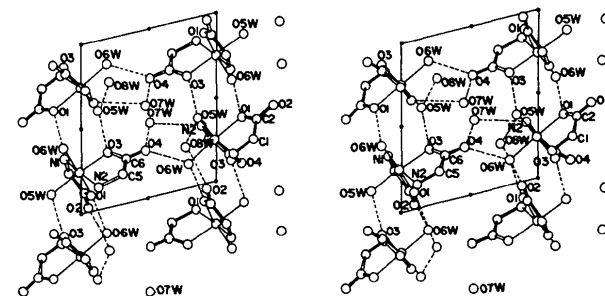


Fig. 2. Stereoscopic projection of (II) perpendicular to the plane defined by the interatomic vectors joining a Ni atom and its equivalents related by the *c* glide and the twofold screw axis. Pseudo centers of symmetry are indicated by double circles. The vertical edges through these centers are parallel to (and of the same length as) *c*.

Table 4. Hydrogen bonds and short intermolecular contacts in (I) and (II)

Hydrogen bonds marked with an asterisk are equivalent in both structures. Distances are in Å and angles in degrees.

<i>a</i>	<i>b</i>	<i>c</i>	<i>ab</i>	<i>ac</i>	<i>bc</i>	∠ <i>abc</i>
Compound (I)						
*O(5W)	H(5W)	O(3 ^h)	0.952 (5)	2.754 (5)	1.871 (5)	153.1 (4)
*O(5W)	H'(5W)	O(8W ^h)	0.945 (5)	2.673 (6)	1.760 (6)	161.4 (4)
*O(6W)	H(6W)	O(4 ^h)	0.938 (5)	2.791 (5)	1.865 (5)	168.2 (4)
*O(6W)	H'(6W)	O(1 ^h)	0.965 (5)	2.624 (5)	1.662 (5)	173.9 (4)
*O(7W)	H(7W)	O(4 ^h)	0.993 (6)	2.849 (5)	1.868 (5)	169.0 (5)
*O(7W)	H'(7W)	O(4 ^h)	1.014 (6)	2.853 (6)	1.860 (6)	166.0 (4)
O(8W)	H(8W)	O(9W ^h)	0.977 (7)	2.794 (7)	1.928 (7)	143.5 (5)
O(8W)	H'(8W)	O(2 ^h)	1.016 (7)	2.891 (6)	1.976 (7)	148.4 (5)
O(9W)	H(9W)	O(7W ^h)	0.968 (6)	2.845 (6)	1.889 (5)	169.0 (5)
O(9W)	H'(9W)	O(2 ^h)	0.838 (7)	2.853 (6)	2.073 (6)	154.7 (5)
*N(1)	H(N1)	O(7W ^h)	1.080 (6)	3.114 (6)	2.068 (6)	162.1 (4)
N(1)	H'(N1)	O(5W ^h)	0.899 (6)	3.188 (6)	2.346 (6)	156.0 (4)
N(2)	H(N2)	O(6W ^h)	1.026 (6)	3.026 (5)	2.303 (5)	146.1 (4)
Compound (II)						
O(5W)	H(5W)	O(3 ^h)	0.99 (2)	2.81 (2)	1.90 (2)	150 (1)
O(5W)	H'(5W)	O(8W ^h)	1.00 (2)	2.80 (2)	2.16 (2)	120 (1)
O(6W)	H(6W)	O(1 ^h)	1.00 (2)	2.66 (2)	1.98 (2)	123 (1)
O(6W)	H'(6W)	O(4 ^h)	1.00 (2)	2.73 (2)	1.81 (2)	151 (1)
O(7W)	H(7W)	O(4 ^h)	1.00 (2)	2.99 (2)	2.04 (2)	158 (1)
O(7W)	H'(7W)	O(4 ^h)	0.99 (2)	2.83 (2)	1.89 (2)	156 (1)
O(8W)	H(8W)	O(2 ^h)	1.00 (2)	2.78 (2)	1.85 (2)	143 (1)
O(8W)	H'(8W)	O(2 ^h)	1.00 (2)	2.78 (2)	1.85 (2)	154 (1)
N(2)	H'(N2)	O(7 ^h)	1.00 (2)	3.05 (2)	2.07 (2)	164 (1)

Symmetry codes

- Compound (I)
 (i) *x*, 1 – *y*, – *z*
 (ii) *x*, *y*, *z*
 (iii) *x* – 1, *y*, *z*
 (iv) –*x*, –*y*, –*z*
 (v) *x*, 1 + *y*, *z* – 1
 (vi) 1 – *x*, 1 – *y*, –*z*

- Compound (II)
 (i) *x*, ½ – *y*, ½ + *z*
 (ii) *x*, *y*, *z*
 (iii) 1 – *x*, ½ + *y*, ½ – *z*
 (iv) 1 – *x*, –*y*, –*z*
 (v) –*x*, ½ + *y*, ½ – *z*
 (vi) *x*, ½ – *y*, *z* – ½

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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References

- BRILL, A. S. (1977). *Transition-Metal Ions in Biochemistry*. Berlin: Springer Verlag.
- CASTELLANO, E. E., NASCIMENTO, O. R. & CALVO, R. (1982). *Acta Cryst.* **B38**, 1303–1305.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- FREEMAN, H. C. (1967). *Adv. Protein Chem.* **22**, 257–424.
- FREEMAN, H. C. (1973). *Inorganic Biochemistry*, edited by G. L. EICHHORN, ch. 4. Amsterdam: Elsevier.
- HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KABSCH, W. (1976). *Acta Cryst.* **A32**, 922–923.
- NOGUCHI, T. (1962). *Bull. Chem. Soc. Jpn*, **35**, 99–104.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1986). **C42**, 19–21

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