

similar to the early results for tetrakis(pyridine)metal(II) (Ni, Fe, Co) chloride complexes (Long & Clarke, 1978).

The crystal structure is shown in Fig. 2. The structure consists of the host *trans*-diiodotetrakis(pyridine) complexes and the guest pyridine molecules. The host complexes form layers with I—Cd—I bonds parallel to *a*, held together by van der Waals forces between the coordinated pyridine molecules. The guest pyridine molecules are enclathrated in the cavities formed between the host layers. The cavity is surrounded by the ligating pyridine molecules and I atoms. It has a twofold axis of symmetry, and 2:1 is the maximum value for the guest/host molar ratio. The low measured density indicates partial occupancy of the guest pyridine sites, since clathrates are potentially non-stoichiometric. This is consistent with the large thermal parameters of the guest pyridine atoms N(3), C(7), C(8), C(9) in comparison with the complexed pyridine molecules of the host structure. The individual molecules of Cd(py)₄I₂ are remarkably well isolated from each other. No significant shortening of the intermolecular distances compared to the sum of the

van der Waals radii is observed. Only two are less than 3.6 Å: between N(3) of a guest pyridine molecule and C(1) [3.581 (10) Å] and C(2) [3.456 (10) Å] of a coordinated pyridine ligand.

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Structure of Tetrakis[μ -(β -alanine)-*O,O'*]-diaquadicopper(II) Tetranitrate Tetrahydrate, [Cu₂(H₂O)₂(C₃H₇NO₂)₄](NO₃)₄·4H₂O

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Abstract. $M_r = 839.6$, triclinic, $P\bar{1}$, $a = 12.499$ (1), $b = 8.717$ (1), $c = 8.070$ (1) Å, $\alpha = 77.74$ (2), $\beta = 82.44$ (1), $\gamma = 71.48$ (1)°, $V = 812.8$ Å³, $D_x = 1.715$, D_m (floatation) = 1.758 Mg m⁻³, $Z = 1$, $F(000) = 434$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 1.35$ mm⁻¹, room temperature, $R = 0.048$ for 2225 observed reflexions. Four alanine groups form centrosymmetric dimers with two Cu atoms; they are nearly mutually perpendicular and are in *cis* configuration. The Cu—Cu separation is 2.639 (1) Å. The four carboxyl O atoms and an axial water O coordinate with Cu to form a square pyramid. The Cu—O(alanyl) bonds are in the range 1.961 (4)–1.981 (4) Å and Cu—O(water) is 2.124 (3) Å.

Introduction. Alanine residues have been the subject of intensive study because of the variety of conformations in which alanine is found to be bonded in certain peptides, appearing, for instance, repetitively in the form of an Ala-Pro sequence over the light chain of rabbit skeletal muscle myosin (Kamwaya, Oster, Bradaczek, Ponnuswamy, Parthasarathy, Naraj & Balaram, 1982) and because of some interesting physical properties of complexes of metallic salts with amino acids (Griffith, 1943; Blakeslee & Hoard, 1956; Tomita, 1961; Jose, Pant & Biswas, 1964; Jose & Pant, 1965; Rao & Viswamitra, 1972; Herak, Prelesnik, Manojlović-Muir & Muir, 1974). In particular, it has been observed that certain derivatives of β -alanine with Cu(NO₃)₂·3H₂O form a bacteriocidal composition

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against *Bacillus subtilis* (Aeloney, 1982). Hence we have determined the structure of the title compound.

Experimental. Copper nitrate trihydrate and β -alanine in stoichiometric proportion, dissolved in distilled water, filtered and then allowed to evaporate slowly at $T = 297$ K; green, transparent crystals obtained in the form of platelets. Approximate cell parameters determined from oscillation and Weissenberg photographs. Infrared spectra in KBr pellet using Perkin Elmer model 577 spectrometer at USIC, Madurai Kamaraj University, confirmed the presence of water molecules (broad peak at 3755 cm⁻¹). Final unit-cell parameters and intensity data measured from a crystal 0.25 × 0.30 × 0.55 mm in the range 1.4 < θ < 26° on a Syntex P2₁ diffractometer (Nicolet, 1975) of the School of Physics, USM. Total of 3211 reflexions collected, of which 2225 considered observed with $I > 2.5 \sigma(I)$; index range $h -14/15$, $k -10/10$, $l 0/9$; standard reflexions showed no significant variation; Mo K α radiation, graphite monochromator. No absorption corrections. Structure solved by the heavy-atom method using *SHELX76* (Sheldrick, 1976). Refinement (on F) favoured $P\bar{1}$ rather than $P1$. H atoms were fixed at ideal positions with bond lengths of 1.08 Å. Introduction of anisotropic temperature factors for non-H atoms and isotropic temperature factors for H atoms reduced R to a final value of 0.048 ($R_w = 0.047$). Final max. and min. difference electron densities 0.45 and -0.33 e Å⁻³, respectively. $(\Delta/\sigma)_{\max} = 0.0005$. The weighting scheme $w = 1.2615/[\sigma^2(F) + 0.000659F^2]$ was used; atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Discussion. Positional and equivalent isotropic thermal parameters are given in Table 1,* bond angles and lengths in Table 2; Fig. 1 is a view of the complex along c .

Four alanil residues bridge two Cu atoms, forming a centrosymmetric dimer. Adjacent pairs of alanil residues are mutually perpendicular and, therefore, the alanil residues about Cu are in *cis* configuration, while their N atoms are in *trans* configuration. The centre of inversion of the dimers lies between the two Cu atoms. The Cu—Cu separation is 2.639 (1) Å.

The alanil, nitro and carboxyl groups are involved in intermolecular hydrogen bonds, forming a network of hydrogen bonds of type N—H...O—N, O...H—O(*W*) and O(*W*)—H...O—N. The closest contact distances between nitrate ions are N(3)...O(24) 3.048 (6) and

N(4)...O(23) 3.325 Å. The nearest Cu—O(water) contact is the Cu—O(5) normal covalent distance of 2.12 (3) Å. The four carboxyl O atoms and this axial water O coordinate with Cu to form a square pyramid (bond angles at Cu are listed in Table 2).

The Cu—O bond distances (see Table 2) are longer than the mean value of 1.96 Å found in similar

Table 1. Atomic coordinates and equivalent isotropic temperature factors (Willis & Pryor, 1975)

$$B_{eq} = \frac{1}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}(\text{Å}^2)$
Cu	0.0741 (1)	-0.1198 (1)	0.0924 (1)	2.4 (9)
O(1)	-0.0155 (3)	-0.2596 (4)	0.0641 (5)	3.5 (3)
C(1A)	-0.1031 (5)	-0.2027 (6)	-0.0187 (7)	2.9 (9)
C(2A)	-0.1662 (5)	-0.3231 (7)	-0.0275 (8)	3.4 (11)
C(3A)	-0.2587 (5)	-0.2564 (7)	-0.1506 (7)	3.4 (4)
N(1A)	-0.3515 (4)	-0.1195 (5)	-0.0941 (6)	3.3 (3)
O(2)	-0.0316 (3)	-0.0511 (4)	0.2871 (4)	3.1 (4)
C(1B)	-0.1231 (4)	0.0662 (7)	0.2698 (6)	2.8 (4)
C(2B)	-0.1977 (4)	0.1006 (7)	0.4275 (7)	3.3 (4)
C(3B)	-0.2909 (5)	0.2655 (7)	0.4035 (8)	3.7 (11)
N(1B)	-0.3794 (4)	0.2600 (6)	0.2991 (6)	3.5 (8)
O(3)	0.1425 (3)	0.0563 (4)	0.0915 (5)	3.2 (11)
O(4)	0.1576 (3)	-0.1526 (5)	-0.1298 (5)	3.3 (9)
O(5)	0.1940 (3)	-0.3124 (5)	0.2405 (5)	4.0 (11)
N(3)	-0.4251 (5)	-0.1491 (7)	0.3851 (7)	4.1 (8)
O(13)	-0.3581 (5)	-0.0981 (6)	0.2772 (6)	6.1 (11)
O(23)	-0.5291 (4)	-0.0882 (6)	0.3758 (6)	5.6 (6)
O(33)	-0.3903 (4)	-0.2626 (6)	0.5045 (6)	6.5 (5)
N(4)	-0.5229 (5)	-0.3490 (6)	0.1254 (7)	3.8 (11)
O(14)	-0.5741 (4)	-0.2181 (5)	0.0356 (6)	5.2 (6)
O(24)	-0.4209 (4)	-0.3796 (6)	0.1466 (6)	5.2 (5)
O(34)	-0.5715 (4)	-0.4526 (6)	0.1943 (7)	6.3 (4)
O(1W)	-0.0209 (4)	-0.2936 (6)	-0.4092 (6)	6.2 (6)
O(2W)	-0.1617 (4)	-0.4435 (5)	-0.5041 (6)	5.7 (7)

Table 2. Bond lengths (Å), angles (°) and selected torsion angles (°)

O(1)—Cu	1.961 (4)	O(1)—Cu—O(2)	89.1 (2)
O(2)—Cu	1.981 (4)	O(1)—Cu—O(3)	168.5 (1)
O(3)—Cu	1.978 (4)	O(2)—Cu—O(3)	90.2 (2)
O(4)—Cu	1.980 (4)	O(1)—Cu—O(4)	90.1 (2)
O(5)—Cu	2.124 (3)	O(2)—Cu—O(4)	168.6 (1)
Cu...Cu	2.639 (1)	O(3)—Cu—O(4)	88.4 (2)
		O(1)—Cu—O(5)	94.6 (2)
O(1)—C(1A)	1.264 (6)	O(2)—Cu—O(5)	95.7 (1)
C(1A)—O(3*)	1.255 (6)	O(3)—Cu—O(5)	96.9 (1)
C(1A)—C(2A)	1.518 (7)	O(4)—Cu—O(5)	95.7 (2)
C(2A)—C(3A)	1.513 (7)		
C(3A)—N(1A)	1.480 (6)	Cu—O(1)—C(1A)	121.6 (3)
		O(1)—C(1A)—C(2A)	116.4 (4)
O(2)—C(1B)	1.269 (6)	C(1A)—C(2A)—C(3A)	114.1 (5)
C(1B)—O(4*)	1.261 (6)	C(2A)—C(3A)—N(1A)	111.4 (4)
C(1B)—C(2B)	1.501 (7)		
C(2B)—C(3B)	1.529 (7)	Cu—O(2)—C(1B)	122.9 (3)
C(3B)—N(1B)	1.494 (6)	O(2)—C(1B)—C(2B)	117.4 (4)
		C(1B)—C(2B)—C(3B)	114.2 (5)
N(3)—O(13)	1.240 (6)	C(2B)—C(3B)—N(1B)	110.4 (4)
N(3)—O(23)	1.243 (6)		
N(3)—O(33)	1.236 (6)	O(13)—N(3)—O(23)	121.0 (6)
		O(13)—N(3)—O(33)	120.8 (6)
N(4)—O(14)	1.242 (6)	O(23)—N(3)—O(33)	118.2 (6)
N(4)—O(24)	1.245 (6)		
N(4)—O(34)	1.241 (6)	O(14)—N(4)—O(24)	120.4 (6)
		O(14)—N(4)—O(34)	121.1 (5)
		O(24)—N(4)—O(34)	118.5 (5)
		O(1)—Cu—O(2)—C(1B)	-85.5 (1)
		C(1A)—O(1)—Cu—O(2)	83.9 (4)

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, selected torsion angles and the results of mean-plane calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39601 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

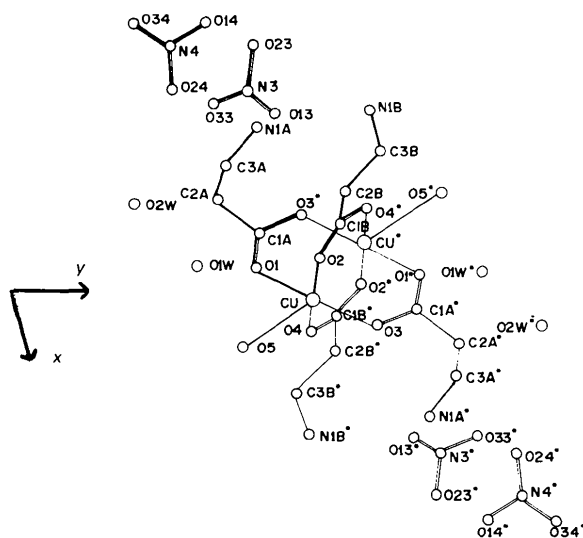


Fig. 1. Schematic drawing of the dimer (projection along *c*). Adjacent pairs of alanyl moieties are mutually perpendicular and are in *cis* configuration, while the alanyl N atoms are in *trans* configuration. The centre of inversion lies between the two Cu atoms. The four carboxyl O atoms and an axial water O coordinate with Cu to form a square pyramid.

complexes (Ueki, Ashida, Sasada & Kakudo, 1968), and references cited therein), but comparable to the value of 1.975 Å in bis(β -alanine)copper(II) tetrahydrate (Kamwaya & Teoh, 1984). The angles O(1)—Cu—O(2), O(2)—Cu—O(3), O(3)—Cu—O(4) and O(4)—Cu—O(1) fall within the range 82–96° as reported for Cu compounds by Ueki *et al.* (1968), while O(1)—Cu—O(3) and O(2)—Cu—O(4) are in the range 160–174° as summarized for Ag compounds (Rao &

Viswamitra, 1972, and references cited therein). Angles O(1)—C(1A)—O(3*) [125.8 (1)°] and O(2)—C(1B)—O(4*) [125.0 (1)°] are larger than the values of 122.5 and 122.2° for analogous angles previously reported by us (Kamwaya & Teoh, 1984).

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Structure of Bis(μ_3 -phenylimido)-tris(tricarbonyliron)(2Fe—Fe), [Fe₃(C₆H₅N)₂(CO)₉]

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Abstract. $M_r = 601.9$, monoclinic, $P2_1/n$, $a = 11.282$ (2), $b = 13.658$ (1), $c = 15.379$ (4) Å, $\beta = 99.81$ (2)°, $V = 2335.1$ Å³, $Z = 4$, $D_x = 1.712$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 1.89$ mm⁻¹,

$F(000) = 1200$, $T = 291$ K, $R = 0.029$ for 3495 observed reflections. The three Fe atoms form an approximately isosceles triangle, with Fe—Fe 2.484 (1) and 2.421 (1) Å, Fe...Fe 3.044 (1) Å, Fe—Fe—Fe 76.7 (1)°. All carbonyl groups are terminal. The NPh ligands are triply bridging, with Fe—N 1.926 (2) to 1.969 (2) Å, N...N 2.301 (6) Å.

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