Inorganica Chimica Acta, *115* (1986) 1–10

Synthesis and X-ray, Magnetic and Spectroscopic Investigations of Tetrakis [μ-(β-alanine)-O,O']bis(diphenylphosphato)dicopper(II) Di(diphenylphosphate) Dihydrate

TADEUSZ GŁOWIAK, IRENA PODGÓRSKA and JERZY BARANOWSKI

Institute of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland

Received July 22, 1985

Abstract

The crystal structure of the tetrakis [μ-(β-alanine)-O,O']bis(diphenylphosphato)dicopper(II) di(diphenylphosphate) dihydrate, $[Cu_2(\beta\text{-ala})_4(DPhP)_2]\cdot 2DPhP\cdot 2H_2O$ (where $\beta\text{-ala} = {}^-OOC{-}CH_2CH_2NH_3^+$ and $DPhP = (C_6H_5O)_2PO_2^-$, diphenylphosphate monoanion) was determined by single-crystal X-ray diffraction method. The compound crystallizes in the triclinic space group $P\bar{1}$ with one formula weight in a unit cell of dimensions: $a = 9.781(3)$, $b = 14.247(4)$, $c = 13.809(4)$ Å, $\alpha = 94.59(5)$, $\beta = 94.73(5)$ and $\gamma = 114.67(5)°$. The structure was solved by the heavy-atom technique and refined by full-matrix least-squares methods to a final R value of 0.050 based on 3540 non-zero, independent data with $I > 3.8\ \sigma(I)$.

The crystal structure consists of centrosymmetric carboxylatobridged dimeric units, uncoordinated diphenylphosphate monoanions and water molecules of crystallization. The coordination geometry about each copper(II) center is squarepyramidal, with four oxygen atoms from zwitterionic β-alanine molecules in the basal plane and the oxygen diphenylphosphate atom at the apical position.

The magnetic susceptibilitiy and ESR results are compared with those found in the copper(II) glycine polymeric complex.

Introduction

Mixed-ligand complexes of copper(II) with molecules of biological interest, such as amino acids or their N-substituted derivatives, have been studied in considerable detail for their use as models in biological systems [1]. In particular, recent X-ray, magnetic and ESR studies of metal–amino acid systems revealed an interesting coordination mode of some amino acids [2–11]. In these complexes amino acid molecules (or their derivatives) being in the zwitterionic form act as simple carboxylic acids and coordinate to the metal ion via the carboxyl group only, giving a 'cupric-acetate'-like dimeric species. This leads under certain conditions to the strong antiferromagnetic coupling between the M^{2+} centers within the pairs [6, 8, 10–15]. These binuclear complexes are of interest not only in regard to magnetic and redox properties, but also as suitable models for understanding the structure–function relationship of the active site of some metalloproteins. Especially as bridging carboxylate groups of the peptide chains have recently been proposed to explain the antiferromagnetic behaviour of type 3 copper enzymes [15].

Being interested in this field, we describe in this paper the crystal structure determination and spectral and magnetic behaviour of the new binuclear mixed-ligand copper(II) complex with β-alanine and diphenylphosphate.

Experimental

Barium diphenylphosphate was prepared by alkaline hydrolysis (with $BaCO_3$) of diphenyl phosphoryl chloride obtained as described by Freeman and Colver [16]. Equimolar amounts of barium diphenylphosphate, copper sulphate (anhydrous) and β-alanine were dissolved in water. After filtrations ($BaSO_4$), the resultant solution was heated on a water bath for 20 min, filtered while hot and then allowed to stand at room temperature. After few days, dark-green well-developed crystals appeared. *Anal.* Calc. for $C_{30}H_{36}CuN_2O_{13}P_2$: C, 47.52; H, 4.79; N, 3.70. Found: C, 47.45; H, 4.71; N, 3.58%.

The diffuse reflectance spectrum of the undiluted well-powdered sample was measured at room temperature in 300–1000 nm region with a Beckman UV 5240 spectrophotometer. The infrared spectrum was recorded with a Perkin-Elmer 180 Infrared spectrophotometer in KBr pellet (4000–400 cm^{-1} range). The ESR spectra were obtained using Jeol JES-ME-3X spectrometer equipped with MJ-110 R magnetic field marker. The spectra were recorded for powder samples at room and liquid nitrogen temperatures.

0020-1693/86/$3.50

Magnetic susceptibility has been measured in the region 80–300 K with a Gouy balance using $HgCo(SCN)_4$ for calibration [17]. Corrections for diamagnetism of the dimer equal to -830×10^{-6} cm^3 mol^{-1} were calculated from Pascal's table [18, 19]. The *TIP* per copper ion was assumed to be 60×10^{-6} cm^3 mol^{-1}. All calculations have been made on RC-3600 computer system.

X-ray crystallographic measurements of the title compound were taken at room temperature. Preliminary cell parameters and the diffraction group of the crystal were determined from the oscillation and Weissenberg photographs. Precise unit-cell parameters were determined by the least-squares refinement based on 15 independent reflections in the range $22.00° < 2\theta < 34.00°$.

Intensity data were collected on a Syntex $P2_1$ computer-controlled, four-circle diffractometer using graphite monochromated Cu Kα radiation.

A dark-green crystal with dimensions of $0.35 \times 0.20 \times 0.32$ mm was used for X-ray diffraction measurements. The 3697 independent intensities in the range $4.0 < 2\theta < 114.5°$ were collected by the θ–2θ scan technique with a variable scan rate from 2.0 to 29.3° min^{-1} depending on intensity. Two standard reflections were monitored every 100 reflections, and their intensities showed good stability. The intensity data were corrected for Lorentz-polarization effects only. 3540 reflections with $I > 3.8\sigma(I)$ were considered as observed, based on counting statistics, and were used for the structure determination and refinement.

Crystal Data

$C_{60}H_{72}Cu_2O_{26}N_4P_4$, $M = 1516.3$, triclinic, $a = 9.781(3)$, $b = 14.247(4)$, $c = 13.809(4)$ Å, $\alpha = 94.59(5)$, $\beta = 94.73(5)$, $\gamma = 114.67(5)°$, $D_m = 1.46(1)$ g cm^{-3} (by flotation in benzene/ethylene dichloride), $D_c = 1.46$ g cm^{-3}, $Z = 1$, $F(000) = 786$ e, Cu Kα radiation, $\lambda = 1.5419$ Å; μ(Cu Kα) = 23.5 cm^{-1}, $T = 295$ K. Space group $P\bar{1}$ (C_i, No. 2).

Determination and Refinement of the Structure

The centrosymmetric space group $P\bar{1}$ was initially assumed and then confirmed by the subsequent refinement of the structure, which was solved by the conventional heavy-atom (Patterson) method. Isotropic full-matrix least-squares refinement of all 48 non-hydrogen atoms yielded $R_1 = 0.092$. Introduction of anisotropic thermal parameters for all these atoms gave final R-factor values of 0.078 and 0.088 for R_1 and R_2, respectively (where R_2 is the weighted R-factor with the weight $w = 1/\sigma^2(F_o)$).

At this stage of the structure solution, the position of 20 hydrogen atoms (from phenyl rings) were computed using the HPSON program [21]. All these H-atoms (C–H = 1.00 Å, H–C–C angle of 120° and B_{iso} value equal to 5.00 $Å^2$) were added to the model as fixed contributors to the structure factors.

After several cycles of refinement, the last 16 H-atoms (all from the β-alaninate molecules) were found from difference Fourier synthesis. The hydrogen atom positions obtained were not refined; they were however used for the computation of the structure factor value.

Several additional cycles of refinement of a model structure containing 84 atoms with 433 parameters reduced the R_1 and R_2 values to 0.050 and 0.064, respectively. For the last cycle of refinement, all parameter changes for non-hydrogen atoms were within 0.10 σ, while the residual electron density in the final difference Fourier synthesis had values within +0.40 and −0.48 e $Å^{-3}$. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$.

Neutral-atomic scattering factors for all atoms, including the anomalous dispersion corrections for Cu and P, were taken from the International Tables for X-ray Crystallography [20].

All calculations were performed on the Nova 1200 minicomputer with the Syntex (1976) XTL/XTLE Structure Determination System [21] and ORTEP-II program [22].

The final refined coordinates and thermal parameters for all non-hydrogen atoms are given in Table I.

TABLE I. Fractional Atomic Coordinates ($\times 10^4$) and B_{eq} ($Å^2$) Values for Non-Hydrogen Atoms with their Standard Deviations. $B_{eq} = 1/3\Sigma_i B_{ii}$

Atom	x	y	z	B_{eq}
Cu	552(1)	−353(1)	739(1)	3.51(5)
P(1)	981(2)	−2083(1)	1951(1)	3.01(11)
P(2)	4422(2)	4370(1)	1978(1)	2.85(10)
O(1)	656(4)	−1345(3)	−316(3)	3.54(31)
O(2)	−301(4)	−757(3)	−1533(3)	3.37(29)
O(3)	−1638(4)	−1316(3)	674(3)	3.18(29)
O(4)	−2555(4)	−691(3)	−514(3)	3.19(29)
O(11)	−191(5)	−2942(3)	1284(3)	4.65(37)
O(12)	1197(4)	−995(3)	1905(3)	3.30(29)
O(13)	1038(5)	−2285(4)	3070(3)	5.85(43)
O(14)	2493(5)	−2213(3)	1748(4)	5.48(42)
O(21)	3234(4)	4243(3)	1172(3)	3.77(31)
O(22)	6023(4)	4801(3)	1796(3)	4.32(34)
O(23)	3878(4)	3242(3)	2320(3)	3.15(28)
O(24)	4357(4)	5100(3)	2898(3)	3.69(32)
OW	1447(5)	5098(3)	−841(3)	4.75(36)
N(1)	−3(5)	−3537(3)	−781(3)	3.67(38)
N(2)	−3315(5)	−3458(3)	720(3)	2.93(33)
C(1)	185(6)	−1372(4)	−1194(4)	2.88(43)
C(2)	148(7)	−2233(4)	−1917(4)	3.61(46)
C(3)	874(7)	−2898(4)	−1500(5)	4.08(49)
C(4)	−2699(6)	−1333(4)	80(4)	2.89(41)
C(5)	−4229(6)	−2224(4)	49(4)	3.33(44)
C(6)	−4368(6)	−2956(4)	809(4)	3.70(46)
C(11)	−72(8)	−2196(5)	3658(4)	4.15(54)
C(12)	578(8)	−1408(6)	4416(6)	5.76(69)
C(13)	−444(13)	−1333(7)	5107(6)	7.81(95)

(continued on facing page)

TABLE I *(continued)*

Atom	x	y	z	B_{eq}
C(14)	−1971(10)	−2070(7)	4916(6)	6.57(78)
C(15)	−2398(9)	−2773(7)	4130(7)	6.44(77)
C(16)	−1508(9)	−2876(6)	3524(5)	5.40(66)
C(21)	3941(7)	−1451(5)	2132(5)	4.49(55)
C(22)	4615(8)	−654(6)	1607(5)	5.47(64)
C(23)	6097(9)	−18(7)	1871(6)	6.96(82)
C(24)	6900(8)	−145(7)	2651(7)	7.22(86)
C(25)	6212(8)	−902(6)	3212(6)	5.80(68)
C(26)	4711(8)	−1581(5)	2957(5)	4.95(59)
C(31)	4638(6)	2899(4)	3012(4)	3.28(44)
C(32)	5688(7)	3536(5)	3759(5)	4.31(53)
C(33)	6314(8)	3090(6)	4439(5)	5.48(65)
C(34)	5831(10)	2019(7)	4330(6)	6.99(79)
C(35)	4782(10)	1411(6)	3588(5)	6.50(74)
C(36)	4134(8)	1821(5)	2917(5)	4.77(56)
C(41)	2945(6)	4956(4)	3188(4)	3.25(43)
C(42)	2210(7)	5500(4)	2815(4)	4.09(50)
C(43)	843(8)	5366(5)	3133(5)	5.06(58)
C(44)	239(7)	4709(5)	3798(5)	4.84(57)
C(45)	1008(8)	4165(5)	4174(5)	5.28(60)
C(46)	2376(7)	4291(5)	3875(4)	4.45(52)

TABLE Ia. Fractional Atomic Coordinates (×10^3) for H-atoms. For all H-atoms B_{iso} = 5.00 Å^2

	x	y	z
H(1)W	235	529	−118
H(2)W	101	450	−102
H(1)N(1)	13	−319	−16
H(2)N(1)	−107	−390	−98
H(3)N(1)	19	−410	−69
H(1)N(2)	−293	−303	93
H(2)N(2)	−330	−370	7
H(3)N(2)	−363	−399	102
H(1)	69	−192	−247
H(2)	−94	−270	−217
H(3)	192	−242	−117
H(4)	95	−337	−205
H(5)	−449	−264	−61
H(6)	−498	−193	14
H(7)	−543	−352	72
H(8)	−413	−256	148
H(12)	168	−91	450
H(13)	−1	−78	569
H(14)	−270	−203	537
H(15)	−350	−325	400
H(16)	−188	−346	297
H(22)	404	−54	103
H(23)	662	57	148
H(24)	800	32	282
H(25)	680	−97	381
H(26)	419	−215	336
H(32)	601	430	382
H(33)	710	354	499
H(34)	629	170	481
H(35)	447	64	352
H(36)	333	136	237
H(42)	264	598	232
H(43)	29	576	286
H(44)	−75	462	402
H(45)	56	367	466
H(46)	294	390	415

TABLE Ib. Anisotropic Thermal Parameters (×10^2) for Non-hydrogen Atoms with their Standard Deviations. The Anisotropic Thermal Parameters are of the Form: $\exp[(-1/4)(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	384(4)	257(3)	413(4)	164(3)	40(3)	59(2)
P(1)	342(7)	219(6)	341(7)	150(5)	47(5)	84(5)
P(2)	306(6)	238(6)	312(6)	116(5)	87(5)	70(5)
O(1)	462(20)	233(16)	367(19)	224(15)	37(15)	−4(13)
O(2)	409(18)	229(16)	373(17)	179(14)	33(14)	17(13)
O(3)	300(17)	249(16)	406(18)	95(13)	23(15)	89(13)
O(4)	320(17)	258(16)	378(17)	124(14)	28(14)	81(14)
O(11)	498(22)	258(18)	639(24)	139(16)	−67(18)	82(17)
O(12)	416(18)	233(15)	341(17)	166(14)	21(14)	65(13)
O(13)	646(26)	547(24)	562(24)	349(21)	149(20)	214(19)
O(14)	442(22)	352(20)	849(29)	225(18)	14(20)	19(19)
O(21)	392(18)	392(18)	346(17)	236(15)	72(14)	68(14)
O(22)	369(19)	373(19)	553(22)	167(16)	173(16)	193(17)

(continued overleaf)

Results and Discussion

The interatomic bond distances and angles are listed in Table II, while in Tables III–V the geometry of hydrogen bonds, the least-squares planes and some torsion angles are given. A detailed view of the copper atoms environment with atom numbering scheme is shown in Fig. 1.

Description of the Structure

The crystal structure of the title compound is composed of bivalent dimeric centrosymmetric

TABLE Ib *(continued)*

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(23)	317(16)	243(16)	386(18)	90(13)	7(14)	77(13)
O(24)	398(19)	301(17)	410(19)	129(15)	81(15)	7(14)
OW	455(20)	294(18)	676(24)	249(16)	143(18)	71(16)
N(1)	394(23)	228(19)	477(24)	188(18)	31(19)	22(17)
N(2)	300(20)	232(18)	347(20)	101(16)	88(16)	73(16)
C(1)	259(23)	177(22)	427(29)	77(19)	106(21)	14(20)
C(2)	426(28)	224(23)	433(28)	147(21)	117(23)	23(21)
C(3)	390(28)	274(25)	560(32)	188(22)	147(24)	0(23)
C(4)	306(25)	204(22)	356(25)	136(19)	78(21)	−6(20)
C(5)	268(24)	244(23)	486(29)	125(19)	96(21)	57(21)
C(6)	342(26)	313(26)	455(29)	164(22)	148(22)	86(22)
C(11)	566(37)	291(27)	387(29)	180(27)	127(26)	120(23)
C(12)	509(37)	406(34)	812(48)	163(29)	26(34)	148(34)
C(13)	1237(73)	604(47)	503(39)	578(51)	−40(44)	−59(33)
C(14)	677(46)	703(47)	591(42)	483(41)	272(36)	288(37)
C(15)	567(41)	652(45)	714(48)	351(36)	−2(37)	148(38)
C(16)	608(41)	521(38)	491(36)	247(34)	45(32)	99(29)
C(21)	326(28)	327(28)	694(39)	193(24)	30(27)	−35(27)
C(22)	582(40)	518(36)	541(36)	330(32)	104(30)	113(29)
C(23)	496(40)	785(51)	807(50)	242(37)	275(37)	349(41)
C(24)	347(34)	721(49)	1097(63)	112(33)	−35(38)	347(46)
C(25)	456(36)	575(40)	708(43)	193(31)	−105(31)	175(34)
C(26)	436(33)	366(30)	683(39)	176(26)	118(29)	142(28)
C(31)	307(25)	360(27)	318(25)	177(22)	76(21)	79(21)
C(32)	399(30)	394(30)	500(33)	150(25)	−11(26)	65(25)
C(33)	556(37)	649(42)	439(33)	275(33)	−73(28)	61(30)
C(34)	849(50)	684(46)	564(41)	545(42)	59(37)	199(35)
C(35)	974(53)	423(35)	553(38)	443(37)	18(38)	85(30)
C(36)	652(38)	375(30)	405(30)	271(28)	20(27)	27(24)
C(41)	362(27)	274(24)	339(25)	130(21)	62(21)	−41(20)
C(42)	533(33)	289(26)	405(29)	211(24)	80(25)	58(22)
C(43)	600(37)	431(32)	486(33)	361(29)	62(28)	3(26)
C(44)	465(33)	525(34)	462(32)	259(28)	178(26)	2(27)
C(45)	621(38)	470(33)	492(33)	283(30)	256(30)	161(27)
C(46)	560(34)	398(29)	378(28)	298(26)	180(25)	114(23)

TABLE II. Interatomic Distances (Å) and Angles (°) with their Standard Deviations[a]

Copper(II) coordination			
Cu–Cu′	2.688(1)	O(12)–Cu–O(1)	96.1(2)
Cu–O(1)	1.986(4)	O(12)–Cu–O(2)′	96.9(2)
Cu–O(2)′	1.963(4)	O(12)–Cu–O(3)	93.3(2)
Cu–O(3)	1.993(4)	O(12)–Cu–O(4)′	100.2(2)
Cu–O(4)′	1.972(4)	O(1)–Cu–O(2)′	167.0(2)
Cu–O(12)	2.091(4)	O(1)–Cu–O(3)	86.8(2)
		O(1)–Cu–O(4)′	89.7(2)
		O(2)′–Cu–O(3)	92.1(2)
		O(2)′–Cu–O(4)′	88.3(2)
		O(3)–Cu–O(4)′	166.4(2)
β-Alaninate			
O(1)–C(1)	1.252(7)	O(3)–C(4)	1.259(7)
O(2)–C(1)	1.260(7)	O(4)–C(4)	1.249(6)
C(1)–C(2)	1.504(8)	C(4)–C(5)	1.499(8)
C(2)–C(3)	1.521(8)	C(5)–C(6)	1.513(8)
C(3)–N(1)	1.478(8)	C(6)–N(2)	1.487(8)

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TABLE II *(continued)*

O(1)–C(1)–O(2)	126.2(5)	O(3)–C(4)–O(4)	124.3(5)
O(1)–C(1)–C(2)	117.6(5)	O(3)–C(4)–C(5)	117.3(5)
O(2)–C(1)–C(2)	116.2(5)	O(4)–C(4)–C(5)	117.8(5)
C(1)–C(2)–C(3)	114.6(5)	C(4)–C(5)–C(6)	115.9(5)
C(2)–C(3)–N(1)	112.4(5)	C(5)–C(6)–N(2)	112.0(5)
Diphenylphosphate			
P(1)–O(11)	1.461(4)	P(2)–O(21)	1.483(4)
P(1)–O(12)	1.481(4)	P(2)–O(22)	1.477(5)
P(1)–O(13)	1.596(5)	P(2)–O(23)	1.593(4)
P(1)–O(14)	1.609(5)	P(2)–O(24)	1.599(4)
O(13)–C(11)	1.449(9)	O(23)–C(31)	1.401(7)
C(11)–C(12)	1.366(10)	C(31)–C(32)	1.356(9)
C(12)–C(13)	1.467(14)	C(32)–C(33)	1.410(10)
C(13)–C(14)	1.409(15)	C(33)–C(34)	1.387(12)
C(14)–C(15)	1.325(12)	C(34)–C(35)	1.340(12)
C(15)–C(16)	1.300(13)	C(35)–C(36)	1.379(11)
C(16)–C(11)	1.318(11)	C(36)–C(31)	1.394(8)
O(14)–C(21)	1.402(8)	O(24)–C(41)	1.406(8)
C(21)–C(22)	1.354(10)	C(41)–C(42)	1.360(9)
C(22)–C(23)	1.349(13)	C(42)–C(43)	1.384(11)
C(23)–C(24)	1.349(13)	C(43)–C(44)	1.354(9)
C(24)–C(25)	1.354(12)	C(44)–C(45)	1.388(11)
C(25)–C(26)	1.375(11)	C(45)–C(46)	1.377(11)
C(26)–C(21)	1.381(10)	C(46)–C(41)	1.378(8)
O(11)–P(1)–O(12)	121.0(3)	O(21)–P(2)–O(22)	119.1(2)
O(11)–P(1)–O(13)	114.4(3)	O(21)–P(2)–O(23)	104.1(2)
O(11)–P(1)–O(14)	102.2(3)	O(21)–P(2)–O(24)	109.8(2)
O(12)–P(1)–O(13)	108.8(3)	O(22)–P(2)–O(23)	111.9(2)
O(12)–P(1)–O(14)	110.9(2)	O(22)–P(2)–O(24)	105.0(2)
O(13)–P(1)–O(14)	96.4(3)	O(23)–P(2)–O(24)	105.2(2)
P(1)–O(13)–C(11)	120.2(4)	P(2)–O(23)–C(31)	128.4(4)
O(13)–C(11)–C(12)	112.1(6)	O(23)–C(31)–C(32)	123.9(5)
C(11)–C(12)–C(13)	115.5(7)	C(31)–C(32)–C(33)	118.6(6)
C(12)–C(13)–C(14)	117.0(9)	C(32)–C(33)–C(34)	119.3(7)
C(13)–C(14)–C(15)	118.8(9)	C(33)–C(34)–C(35)	120.6(8)
C(14)–C(15)–C(16)	125.5(9)	C(34)–C(35)–C(36)	121.6(8)
C(15)–C(16)–C(11)	118.2(8)	C(35)–C(36)–C(31)	118.0(7)
P(1)–O(14)–C(21)	121.7(4)	P(2)–O(24)–C(41)	119.6(4)
O(14)–C(21)–C(22)	117.6(6)	O(24)–C(41)–C(42)	119.6(5)
C(21)–C(22)–C(23)	118.5(7)	C(41)–C(42)–C(43)	118.5(6)
C(22)–C(23)–C(24)	121.6(9)	C(42)–C(43)–C(44)	121.3(7)
C(23)–C(24)–C(25)	120.2(9)	C(43)–C(44)–C(45)	119.5(7)
C(24)–C(25)–C(26)	120.0(8)	C(44)–C(45)–C46)	120.3(7)
C(25)–C(26)–C(21)	118.1(7)	C(45)–C(46)–C(41)	118.3(6)

[a] The primed atoms are related to the unprimed ones by the centre of inversion within the molecule.

TABLE IIa. Interatomic Distances (Å) and Angles (°) Involving the H-atoms

Water molecule			
OW–H(1)W	0.98	H(1)W–OW–H(2)W	102
OW–H(2)W	0.78		
β-Alaninate			
C(2)–H(1)	1.00	C(5)–H(5)	1.00
C(2)–H(2)	1.00	C(5)–H(6)	1.00

(continued overleaf)

TABLE IIa *(continued)*

C(3)–H(3)	1.01	C(6)–H(7)	1.00
C(3)–H(4)	0.99	C(6)–H(8)	1.00
N(1)–H(1)N(1)	0.93	N(2)–H(1)N(2)	0.86
N(1)–H(2)N(1)	0.96	N(2)–H(2)N(2)	0.94
N(1)–H(3)N(1)	0.91	N(2)–H(3)N(2)	0.85
H(1)–C(2)–H(2)	109	H(5)–C(5)–H(6)	109
C(1)–C(2)–H(1)	108	C(4)–C(5)–H(5)	108
C(1)–C(2)–H(2)	108	C(4)–C(5)–H(6)	108
H(1)–C(2)–C(3)	108	H(5)–C(5)–C(6)	108
H(2)–C(2)–C(3)	108	H(6)–C(5)–C(6)	108
H(3)–C(3)–H(4)	109	H(7)–C(6)–H(8)	109
C(2)–C(3)–H(3)	108	C(5)–C(6)–H(7)	109
C(2)–C(3)–H(4)	109	C(5)–C(6)–H(8)	109
H(3)–C(3)–N(1)	109	H(7)–C(6)–N(2)	108
H(4)–C(3)–N(1)	109	H(8)–C(6)–N(2)	109
C(3)–N(1)H(1)N(1)	116	C(6)–N(2)–H(1)N(2)	112
C(3)–N(1)–H(2)N(1)	115	C(6)–N(2)–H(2)N(2)	113
C(3)–N(1)–H(3)N(1)	114	C(6)–N(2)–H(3)N(2)	108
H(1)N(1)–N(1)–H(2)N(1)	107	H(1)N(2)–N(2)–H(2)N(2)	105
H(1)N(1)–N(1)–H(3)N(1)	105	H(1)N(2)–N(2)–H(3)N(2)	113
H(2)N(1)–N(1)–H(3)N(1)	98	H(2)N(2)–N(2)–H(3)N(2)	106
C(12)–H(12)	1.00	C(32)–H(32)	0.99
C(13)–H(13)	1.01	C(33)–H(33)	1.00
C(14)–H(14)	1.00	C(34)–H(34)	1.00
C(15)–H(15)	0.99	C(35)–H(35)	1.00
C(16)–H(16)	1.00	C(36)–H(36)	1.00
C(22)–H(22)	1.00	C(42)–H(42)	1.00
C(23)–H(23)	1.01	C(43)–H(43)	1.00
C(24)–H(24)	0.99	C(44)–H(44)	1.00
C(25)–H(25)	1.00	C(45)–H(45)	1.00
C(26)–H(26)	1.00	C(46)–H(46)	1.00
C(11)–C(12)–H(12)	123	C(31)–C(32)–H(32)	120
H(12)–C(12)–C(13)	122	H(32)–C(32)–C(33)	121
C(12)–C(13)–H(13)	119	C(32)–C(33)–H(33)	120
H(13)–C(13)–C(14)	124	H(33)–C(33)–C(34)	120
C(13)–C(14)–H(14)	119	C(33)–C(34)–H(34)	119
H(14)–C(14)–C(15)	123	H(34)–C(34)–C(35)	120
C(14)–C(15)–H(15)	116	C(34)–C(35)–H(35)	119
H(15)–C(15)–C(16)	118	H(35)–C(35)–H(36)	120
C(15)–C(16)–H(16)	122	C(35)–C(36)–H(36)	121
H(16)–C(16)–C(11)	120	H(36)–C(36)–C(31)	121
C(21)–C(22)–H(22)	121	C(41)–C(42)–H(42)	121
H(22)–C(22)–C(23)	120	H(42)–C(42)–C(43)	121
C(22)–C(23)–H(23)	119	C(42)–C(43)–H(43)	119
H(23)–C(23)–C(24)	119	H(43)–C(43)–C(44)	119
C(23)–C(24)–H(24)	120	C(43)–C(44)–H(44)	120
H(24)–C(24)–C(25)	120	H(44)–C(44)–C(45)	120
C(24)–C(25)–H(25)	120	C(44)–C(45)–H(45)	120
H(25)–C(25)–C(26)	120	H(45)–C(45)–C(46)	120
C(25)–C(26)–H(26)	121	C(45)–C(46)–H(46)	120
H(26)–C(26)–C(21)	121	H(46)–C(46)–C(41)	121

$[Cu_2(\beta\text{-ala})_4(DPhP)_2]$ cations, non-coordinated diphenylphosphate monoanions (DPhP) and water molecules of crystallization.

The coordination polyhedron around the copper(II) ions shows the 'copper(II) acetate'-like dimeric structure, with four bidentate carboxylate groups (from β-alaninate zwitterionic molecules) forming *syn–syn* bridges between two metal(II) ions related by a center of symmetry. The axial coordination site is occupied by a phosphate oxygen atom from

TABLE III. The Hydrogen Bonds

D–H•••A	Distances (Å)			Angle (°) DHA
	D–H	H•••A	D–A	
N(1)–H(1)N(1)•••O(11)	0.93	2.07	2.952(6)	159
N(1)–H(2)N(1)•••O(21^{i})	0.96	1.95	2.875(7)	162
N(1)–H(3)N(1)•••OW^{ii}	0.91	2.01	2.845(7)	152
N(2)–H(1)N(2)•••O(11)	0.86	2.12	2.851(7)	143
N(2)–H(2)N(2)•••O(21^{i})	0.94	1.84	2.779(6)	176
N(2)–H(3)N(2)•••O(22^{iii})	0.85	2.02	2.861(6)	170
OW–H(1)W•••O(22^{iv})	0.98	1.91	2.856(6)	161
OW–H(2)W•••O(11^{i})	0.78	2.01	2.782(5)	169

Symmetry superscript: none x, y, z; (i) $-x, -y, -z$; (ii) $x, y - 1, z$; (iii) $x - 1, y - 1, z$; (iv) $1 - x, 1 - y, -z$

TABLE IV. Least-squares Planes. Values are Given in the Following Order: Atoms Defining the Plane, Equation of the Plane and Deviations (Å) of Atoms from the Plane with their Standard Deviations

Plane (1): O(1), O(2), C(1), C(2)			$0.7687x + 0.6166y - 0.1700z - 0.1711 = 0$						
O(1)	−0.002(4)	O(2)	−0.002(4)	C(1)	0.010(6)	C(2)	−0.003(6)	C(3)	0.138(6)
Cu	−0.192(1)	N(1)	−1.047(5)						
Plane (2): O(3), O(4), C(4), C(5)			$0.5612x - 0.4661y - 0.6840z + 0.2871 = 0$						
O(3)	0.003(4)	O(4)	0.003(4)	C(4)	−0.019(6)	C(5)	0.006(6)	C(6)	−0.082(6)
Cu	0.243(1)	N(2)	1.048(4)						
Plane (3): O(1), O(2)′, O(3), O(4)′			$-0.4632x + 0.4525y - 0.7620z + 1.1141 = 0$						
O(1)	−0.005(4)	O(2)′	−0.004(4)	O(3)	0.004(4)	O(41)	0.004(4)	Cu	−0.229(1)
Plane (4): Cu, O(1), C(1), O(2), Cu′			$0.7418x + 0.6623y - 0.1054z = 0$						
Cu	−0.001(1)	Cu′	0.001(1)	O(1)	0.025(4)	O(2)	−0.007(4)	C(1)	−0.027(6)
Plane (5): Cu, O(3), O(4), C(4), Cu′			$0.4816x - 0.5811y - 0.6561z = 0$						
Cu	−0.001(1)	Cu′	0.001(1)	O(3)	0.023(4)	O(4)	−0.049(4)	C(4)	0.045(5)
Plane (6): O(1), O(2), Cu′, O(1)′ O(2)′ Cu					$0.7397x + 0.6650y - 0.1029z = 0$				
O(1)	0.016(4)	O(2)	−0.015(4)	Cu′	0.001(1)	O(1)′	−0.016(4)	O(2)′	0.015(4)
Cu	−0.001(1)								
Plane (7): O(3), O(4), Cu′, O(3)′, O(4)′, Cu					$0.4762x - 0.5854y - 0.6561z = 0$				
O(3)	0.035(4)	O(4)	−0.035(4)	Cu′	0.002(1)	O(3)′	−0.035(4)	O(4)′	0.035(4)
Cu	−0.002(1)								
Plane (8): C(11)–C(16)		$-0.4725x + 0.6852y - 0.5543z + 5.5433 = 0$							
C(11)	0.006(6)	C(12)	0.002(8)	C(13)	−0.006(10)	C(14)	−0.005(9)	C(15)	0.018(9)
C(16)	−0.016(8)	O(13)	−0.129(5)						
Plane (9): C(21)–C(26)		$0.6179x - 0.5365y - 0.5748z - 2.2798 = 0$							
C(21)	0.019(7)	C(22)	−0.021(8)	C(23)	−0.001(9)	C(24)	0.025(9)	C(25)	−0.015(8)
C(26)	−0.006(7)	O(14)	0.245(5)						
Plane (10): C(31)–C(36)		$0.8060x + 0.1619y - 0.5694z - 0.1634 = 0$							
C(31)	0.009(6)	C(32)	−0.006(7)	C(33)	−0.002(8)	C(34)	0.004(10)	C(35)	0.007(9)
C(36)	−0.013(8)	O(23)	−0.062(4)						
Plane (11): C(41)–C(46)		$-0.1284x + 0.6632y - 0.7373z + 7.0460 = 0$							
C(41)	0.005(5)	C(42)	−0.001(6)	C(43)	−0.004(7)	C(44)	0.003(7)	C(45)	0.002(7)
C(46)	−0.006(6)	O(24)	−0.032(4)						
Angles between planes (°):			(1), (2)	74.9(5)		(4), (5)		87.6(6)	
			(6), (7)	88.3(6)		(8), (9)		109.9(7)	
			(10), (11)	77.9(5)					

TABLE V. Torsion Angles (°) with their Standard Deviations[a]

O(1)–C(1)–C(2)–C(3)	–6.9(6)
O(2)–C(1)–C(2)–C(3)	174.7(5)
C(1)–C(2)–C(3)–N(1)	68.3(7)
O(3)–C(4)–C(5)–C(6)	5.7(8)
O(4)–C(4)–C(5)–C(6)	–177.5(8)
C(4)–C(5)–C(6)–N(2)	–60.4(7)
O(11)–P(1)–O(13)–C(11)	–77.2(6)
O(11)–P(1)–O(14)–C(21)	170.5(6)
O(12)–P(1)–O(13)–C(11)	61.6(5)
O(12)–P(1)–O(14)–C(21)	40.1(6)
O(13)–P(1)–O(14)–C(21)	–72.8(6)
O(14)–P(1)–O(13)–C(11)	176.3(5)
O(21)–P(2)–O(23)–C(31)	174.7(7)
O(21)–P(2)–O(24)–C(41)	43.4(7)
O(22)–P(2)–O(23)–C(31)	44.8(7)
O(22)–P(2)–O(24)–C(41)	173.2(7)
O(23)–P(2)–O(24)–C(41)	–68.1(6)
O(24)–P(2)–O(23)–C(31)	–69.9(8)

[a]Because of the center of symmetry present in the space group, both + and – values of the corresponding torsion angles are present.

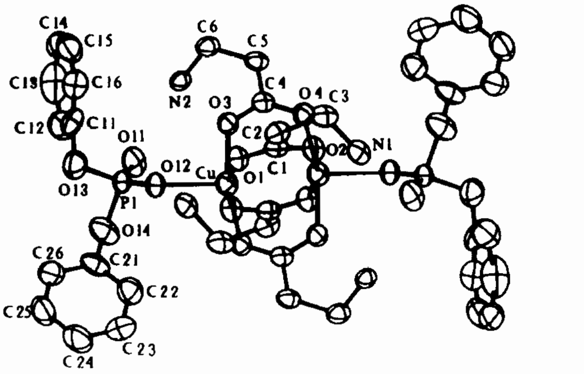

Fig. 1. ORTEP view of the $[Cu_2(\beta\text{-ala})_4(DPhP)_2]$ dimeric unit showing the atom numbering scheme and the thermal motion ellipsoids (50%) for all non-hydrogen atoms. The hydrogen atoms were omitted for clarity.

the diphenylphosphate ligand molecule. Thus the coordination around each copper(II) ion is square-pyramidal (4 + 1).

The structural features of the coordination polyhedron do not significantly differ from those reported for copper(II) acetate monohydrate and normal dimeric carboxylate complexes [23–25]. The Cu–O(carboxylic) bond lengths, ranging from 1.963 to 1.993 Å with the average of 1.979 Å, are comparable to the corresponding distances observed in copper(II) glycine polymeric complex; the average is 1.978 Å [6], which is larger (by ~0.02 Å) than those found in many normal dimeric copper(II) carboxylate complexes (the average length being 1.96 Å). The Cu–O(1)C(1)O(2)–Cu′ and Cu–O(3)C(4)O(4)–Cu′ bridge lengths, 6.461 and 6.473 Å respectively, are in the range of 6.40–6.50 Å observed for many dimeric carboxylate complexes [24, 25]. Coordination planes in the dimer, Cu–O(1)C(1)O(2)–Cu′–O(1)′C(1)′O(2)′–Cu and Cu–O(3)C(4)O(4)–Cu′–O(3)′C(4)′–O(4)′–Cu are nearly perpendicular, the dihedral angle being 88.3° (prime indicates centrosymmetric atoms).

The copper atom is 0.229 Å above the basal plane of four carboxylate oxygen atoms, toward the axial phosphate oxygen atom. This displacement is in good agreement with those observed in most square-pyramidal copper(II) complexes [26].

The Cu–Cu distance of 2.688 Å found in the present compound, though much greater than that (2.565 Å) in copper(II) propionate [27] or 2.577 Å in polymeric *N*-tosylglycine copper(II) complex [10], is comparable with those found in the copper(II) glycine polymeric complex [6] and the copper(II) *N*-acetyloglycinate dimer [4].

One of two crystallographically independent DPhP molecules (molecule **I**) is coordinated through the oxygen atom to the copper(II) atom, with the Cu–O(phosphate)$_{ax}$ bond length of 2.091 Å, which is significantly shorter (by ~0.46 Å) than that found in bis(diphenylphosphato)tetrakis(imidazole)copper(II) [28].

The general features of the phosphate group in both DPhP ligand molecules agree well with those found in glycinium diphenylphosphate and bis(diphenylphosphato)tetrakis(imidazole)copper(II) [28, 29]. The phosphate tetrahedrons are quite distorted, the P–O(C) bond distances being 1.461 and 1.481 Å for the coordinated to copper(II) ion DPhP molecule and 1.477 and 1.483 Å for the uncoordinated DPhP molecule (molecule **II**). The other two P–O distances in both DPhP molecules are essentially equal (considering he experimental uncertainties, see Table II), and are similar to the corresponding lengths found for other copper(II) diphenylphosphate compound [28].

The (C)O–P–O(C) angles involving the esterified oxygen atoms are 96.4 and 105.2° for the molecule **I** and **II**, respectively. It is interesting to note that in the molecule **II** this angle is not the smallest one, as was found in glycinium diphenylphosphate; instead one of the (C)O–P–O angles has the smallest value. In contrast to this, the O–P–O angles in both DPhP molecules are the largest ones.

These two independent DPhP ligand molecules are present in a quite different conformation. The molecule **II** displays the -synclinal, -synclinal conformation about both P–O(C) bonds, while the molecule **I** has the -synclinal, antiperiplanar conformation. Thus drastic conformational changes take place as DPhP ligand molecule coordinates to the copper(II) ion. A similar situation has been observed in the bis(diphenylphosphato)tetrakis(imidazole)copper(II) complex, the structure of which has been previously determined [28].

The two crystallographically independent β-alanine molecules do not display the same conformation. The torsion angles O(1)–C(1)–C(2)–C(3), O(2)–C(1)–C(2)–C(3) and C(1)–C(2)–C(3)–N(1) for the first amino acid molecule and O(3)–C(4)–C(5)–C(6), O(4)–C(4)–C(5)–C(6) and C(4)–C(5)–C(6)–N(2) for the second one being −6.9, 174.7, 68.3° and −177.5, −60.4 and −77.2°, respectively.

The bond lengths and angles within these β-alanine molecules are in good agreement with the values found for other dimeric copper(II) β-alanine complexes [9].

Another interesting aspect of this crystal structure is the hydrogen-bonding pattern, involving a water molecule of crystallization, diphenylphosphate oxygen atoms and ammonium groups of β-alanine moieties. There are eight of these crystallographically independent contacts (two of them being of a intra-, while the other six of a intermolecular character) of different strengths and with parameters in the range: 2.779(6) < N–H···O(phosphate) < 2.952(6) Å, 143 < N–H···O < 176°; N–H···O(water) of 2.845(7) Å and with the angle at hydrogen atom of 152° and two O(water)–H···O(phosphate) hydrogen bonds with the lengths and angles of 2.856(6) Å, 161° and 2.782(5) Å and 169°, respectively.

Spectroscopic Results

The electronic spectrum of the title compound shows two bands at 13 400 cm^{-1} (band I) and 28 200 cm^{-1} (band II), respectively. Band I may be considered to be the 'ordinary copper(II) band', while band II is taken to be diagnostic of a dimeric structure [25].

In the IR spectrum of this complex the bands corresponding to the symmetric and asymmetric vibrations of the bridging carboxyl groups appear (the most probable positions) at 1430 cm^{-1} and 1640 cm^{-1}, respectively. Their positions are in good agreement with those found for other previously examined amino acid copper(II) complexes in which the ligand is coordinated only through the carboxylate group [10, 25].

Magnetic and ESR Results

The ESR spectrum at room temperature (Fig. 2a) exhibits an absorption typical for a randomly orientated triplet state $S = 1$. The lines at 4664 G, 5979 G and about 500 G correspond to the perpendicular ($H_{\perp 2}$) and parallel (H_{z2}, H_{z1}) components. There is no splitting on the line at 4664 G, which shows that the distortion from axial symmetry can be neglected. This spectrum can be adequately described by the effective axial spin Hamiltonian

$$\mathcal{H} = \beta HgS + D[S_z^2 - \frac{1}{3} S(S+1)]$$

The computer simulation procedure based on this Hamiltonian [30] helped us to find the following spin Hamiltonian parameters: $g_\perp = 2.06$, $g_\parallel = 2.29$, $D = 0.3249\ \text{cm}^{-1}$. The 'forbidden' line ($\Delta M_s = 2$) is not present in the spectrum because the zero-field splitting parameter D is greater than the microwave frequency used. The line about 3200 G shows the significant amount of monomeric impurities present in the sample.

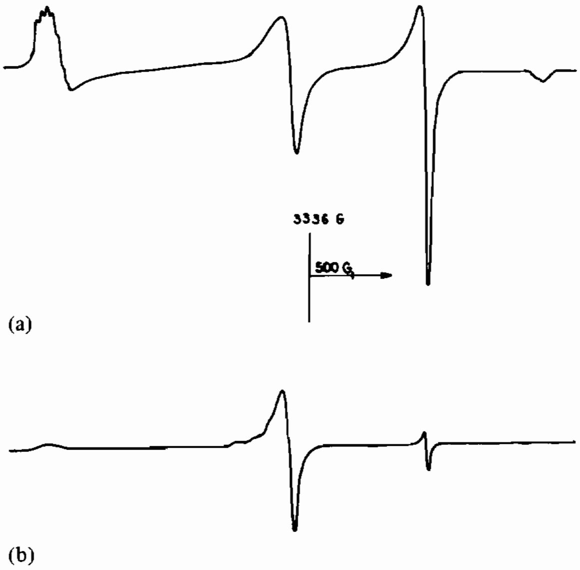

Fig. 2. The X-band of the ESR spectra of $[Cu_2(\beta\text{-ala})_4(DPhP)_2]\cdot 2DPhP\cdot 2H_2O$: (a) at room temperature, and (b) at liquid nitrogen temperature.

TABLE VI. Magnetic Data of $[Cu(\beta\text{-ala})_2DPhP]\cdot DPhP\cdot H_2O$ ($-\Delta \times 10^6 = 415$)

T K	$\chi_{Cu}^{corr} \times 10^6$	μ_{eff} BM
82	241	0.40
102	438	0.60
118	567	0.73
130	598	0.79
140	651	0.85
153	772	0.97
168	787	1.03
180	825	1.09
193	886	1.17
206	878	1.20
219	908	1.26
231	931	1.31
242	916	1.33
252	908	1.35
262	901	1.37
274	901	1.41
285	901	1.43
295	908	1.465

At liquid nitrogen temperature the intensity of the lines caused by transitions between the triplet states decreases (Fig. 2b). This is typical for dimeric systems with the singlet ground state and the thermally accessible triplet excited state. The amount of mononuclear impurities does not change in the sample, and the population of the excited triplet state decreases with the lowering of temperature. As the result, the increase of the relative ratio of monomer to dimer signal is observed (Fig. 2a, b). The monomer signal did not have a well-resolved hyperfine structure, thus gaving us the opportunity to find the monomer spin Hamiltonian parameters.

The title compound has a subnormal magnetic moment at room temperature (1.465 BM), suggesting that some coupling of the copper atoms occurs. The dependence of the magnetic susceptibility on temperature has been studied and the data were fitted by the modified Bleaney–Bowers equation [31] including correction for diamagnetism and correction for temperature independent paramagnetism

$$\chi_{Cu}^{corr} = \frac{N g_{av}^2 \beta^2}{3kT} [1 + 1/3(e^{-2J/kT})]^{-1} (1 - x) + \left(\frac{N g_{imp}^2 \beta^2}{4kT}\right) x$$

(*TIP*), where x is the molar percentage of monomeric impurities (the other symbols have their usual meaning).

The susceptibility–temperature data were fitted using non-linear least-square procedure to two parameters $-2J$ and x. The $g_{av} = [1/3(g_{\parallel}^2 + 2g_{\perp}^2)]^{1/2} = 2.13$ for dimer and $g_{imp} = 2.19$ for mononuclear impurities obtained from the ESR spectra were used as constant parameters. The best fit was found for the following values of the parameters: $-2J = 269$ cm^{-1} and $x = 1.68\%$. This result corresponds well to the conclusions drawn from the ESR spectra.

The exchange integral is much smaller than that found for the copper glycine polymeric complex [6], although the copper-copper ions distance is very similar. It clearly shows that the β-position of the electrophylic NH_3^+ group has little if any influence on the antiferromagnetic Cu^{2+}–Cu^{2+} coupling. The J value obtained for our complex $[Cu_2(\beta\text{-ala})_4(DPhP)_2]\cdot 2DPhP\cdot 2H_2O$, is closer to that found for copper(II)–acetate [23] than to the one found for the copper(II)–glycine dimeric unit in the copper glycine polymeric complex [6].

Acknowledgements

We are grateful to Dr. H. Kozłowski for his helpful discussion of the ESR and magnetic results. This work was supported by the Polish Academy of Sciences (the MR.I.9 problem).

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