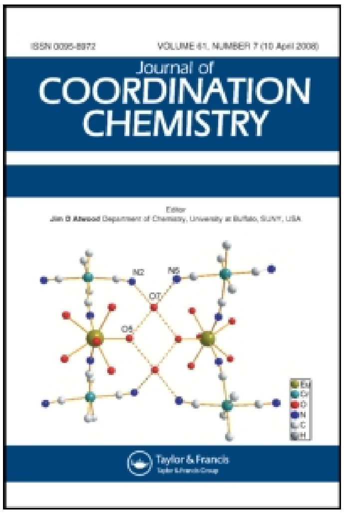

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Synthesis, crystal structure and properties of a one-dimensional L-valinate bridged coordination polymer: $[Cu_2(L\text{-}val)_2(bpy)_2]$_n$\cdot 2n ClO_4 \cdot 2n H_2O$

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Synthesis, crystal structure and properties of a one-dimensional L-valinate bridged coordination polymer: $[Cu_2(\text{L-val})_2(bpy)_2]_n \cdot 2nClO_4 \cdot 2nH_2O$

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The complex $[Cu_2(\text{L-val})_2(bpy)_2]_n \cdot 2nClO_4 \cdot 2nH_2O$ (L-val = L-valinate, bpy = 2,2′-bipyridine) has been synthesized and investigated by elemental analysis, IR and UV spectroscopy, DTA–TG analysis and X-ray diffraction methods. The complex crystallizes in the monoclinic space group $P2_1$ with two molecules in a unit cell of dimensions $a = 10.0954(12)$, $b = 8.1245(9)$, $c = 23.297(3)$ Å, $\beta = 102.447(2)°$, $V = 1865.9(4)$ Å^3, $D_c = 1.614$ g/cm^3, $\mu = 1.357$ mm^{-1}, $F(000) = 932$, $R = 0.0337$, $wR = 0.0847$ for 7024 unique reflections. Single-crystal structure analysis reveals that $[Cu_2(\text{L-val})_2(bpy)_2]_n^{2n+}$ cations have a one-dimensional polymeric structure, with two $Cu(bpy)^{2+}$ units bridged by a carboxylate group of L-valinate. Each Cu^{2+} ion is in a slightly distorted square-pyramidal geometry, with the bpy(N,N′) and L-val(N,O) acting as bidentate ligands in the equatorial plane and another carboxylate oxygen atom from a symmetry-related neighboring L-valinate ion in the apical position. IR and UV spectra and thermal analysis are in agreement with the crystal structure.

Keywords: Copper(II) complex; L-Valine; 2,2′-Bipyridine; One-dimensional chain; Crystal structure

1. Introduction

Mixed-ligand metal complexes with an aromatic amine as the primary ligand and biomolecules, such as amino acids, peptides or nucleotides, as secondary ligands serve as useful models for gaining a better understanding of enzyme–metal ion–substrate or metalloenzyme–inhibitor complexes, which play an important role in metalloenzyme-catalyzed biochemical processes [1,2]. We have reported a series of crystal structures of mixed-ligand metal complexes involving an aromatic diamine and an L-α-amino acid, in which the L-α-amino acid is generally coordinated to the metal ion as a bidentate N,O-ligand through its α-glycinate portion [3–9]. Here we report a new coordination polymer, $[Cu_2(\text{L-val})_2(bpy)_2]_n \cdot 2nClO_4 \cdot 2nH_2O$ (L-val = L-valinate, bpy = 2,2′-bipyridine), in which L-valinate chelates Cu^{2+} through its glycinate-N,O portion and

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bridges a second Cu center through the remaining carboxylate-O. This unusual coordination behavior has been found only in the similar complex [Cu(L-trp)(phen)] $\cdot$ $ClO_4 \cdot 2.5H_2O$ (L-trp = L-tryptophanate, phen = 1,10-phenanthroline) [10].

2. Experimental

2.1. *Materials*

All chemicals and solvents were commercial reagent grade or better and were used without further purification; $Cu(ClO_4)_2 \cdot 6H_2O$ was prepared as described in the literature [11].

2.2. *Physical measurements*

Elemental analysis (carbon, nitrogen and hydrogen contents) was performed on a Perkin-Elmer 240 micro analyzer. Molar conductivity was measured in acetronitrile using a DDS-11A conductivity gauge. Infrared absorption spectra in KBr disks were recorded in the 400–4000 cm^{-1} range on a Nicolet 170SX spectrophotometer. Electronic absorption spectra were measured in water on a Shimadzu UV-260 spectrophotometer at room temperature. A TG–DTA study was performed on a Shimadzu DTG-60 simultaneous DTA–TG instrument. The sample was contained within alumina crucibles and heated at a rate of 10°C min^{-1} from room temperature to 700°C in air.

2.3. *Synthesis*

The title complex was prepared by dissolving $Cu(ClO_4)_2 \cdot 6H_2O$ (0.19 g, 0.5 mmol) and 2,2′-bipyridine (0.08 g, 0.5 mmol) in 25 mL of 30% (v/v) methanol–water with stirring, followed by addition of an aqueous solution of L-valine (0.13 g, 1 mmol). After filtration, the filtrate was kept in a refrigerator (4°C) for several weeks, yielding dark blue crystals (60% yield). Anal. Calcd. for $C_{20}H_{26.67}Cl_{1.33}N_4O_{9.33}Cu_{1.33}$(%): C, 39.71; H, 4.41; N, 9.26. Found: C, 39.97; H, 4.36; N, 9.32.

2.4. *X-ray crystal structure determination*

A single crystal of the title complex with dimensions $0.43 \times 0.41 \times 0.38\ mm^3$ was selected for data collection at 273(2) K, using a Bruker Smart 1 K CCD system diffractometer with graphite-monochromated Mo Kα radiation at $\lambda = 0.71073$ Å. The SMART program was applied to search for diffraction peaks to determine cell parameters, and the collected data were reduced by using the SAINT + program [12]. Absorption correction was carried out using the Siemens Area Detector ABSorption (SADABS) program [13]. The structure was solved by direct and Fourier methods using SHELXS-97 [14]; refinement on F^2 was performed using SHELXS-97 [15] by full-matrix least-squares with positional and anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were placed in calculated positions. Atomic scattering factors were taken from the *International Tables for X-ray Crystallography* [16]. Crystal data and some experimental details of data collection and refinement for the complex are listed in table 1.

Table 1. Crystal data and structure refinement details for $[Cu_2(\text{L-val})_2(bpy)_2]_n \cdot 2nClO_4 \cdot 2nH_2O$.

Empirical formula	$C_{30}H_{40}Cl_2Cu_2N_6O_{14}$
Formula weight	906.66
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	$a = 10.0954(12)$ Å; $\alpha = 90°$ $b = 8.1245(9)$ Å; $\beta = 102.447(2)°$ $c = 23.297(3)$ Å; $\gamma = 90°$
Volume	1865.9(4) $Å^3$
Z	2
Density (calculated)	1.614 Mg/m^3
Absorption coefficient	1.357 mm^{-1}
$F(000)$	932
Crystal size	$0.43 \times 0.41 \times 0.38$ mm^3
Theta range for data collection	1.79 to 26.98°
Index ranges	$-12 \le h \le 12$, $-8 \le k \le 10$, $-29 \le l \le 26$
Reflections collected	11 681
Independent reflections	7024 [$R(\text{int}) = 0.0123$]
Completeness to theta = 26.98°	99.5%
Absorption correction	Semiempirical from equivalents
Max. and min. transmission	0.5953 and 0.5453
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7024/61/516
Goodness-of-fit on F^2	1.020
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0304$, $wR_2 = 0.0826$
R indices (all data)	$R_1 = 0.0337$, $wR_2 = 0.0847$
Absolute structure parameter	0.042(11)
Largest diff. peak and hole	0.401 and –0.521 e $Å^{-3}$

3. Results and discussion

Elemental analysis of the complex is in agreement with the formula $[Cu_2(\text{L-val})_2(bpy)_2]_n \cdot 2nClO_4 \cdot 2nH_2O$. The complex is stable in air and soluble in water, methanol, ethanol and acetronitrile, but not in ether and other weak-polarity organic solvents. The molar conductivity for the complex in acetronitrile at 10^{-3} M, $\Lambda_m = 329.7\ S\,cm^2\,mol^{-1}$, indicates a 1 : 2 electrolyte [17].

3.1. *Crystal structure*

The crystal structure consists of one-dimensional polymeric chain cations $\{[Cu_2(\text{L-val})_2(bpy)_2]^{2+}\}_n$, counter anions ClO_4^- and crystallized water. In the long chain the Cu atom is ligated in a slightly distorted square-pyramidal geometry by the bidentate ligand bpy [Cu–N 1.998 Å (mean)] and one carboxylate oxygen [Cu–O 1.940 Å (mean)] and amino nitrogen [Cu–N 1.996 Å (mean)] of the L-val ligand; the axial position is occupied by another carboxylate oxygen belonging to the symmetrically-related neighboring L-val molecule [Cu–O 2.346 Å (mean)]. Each carboxylate group of L-val links two Cu atoms along the *b* axis, thereby producing an infinite $(OCO–Cu–OCO)_n$ chain configuration from which bpy rings and L-val residues project outwards and stack with each other in the form ··· ABAB ···. Selected bond lengths and angles of the complex are presented in table 2.

Table 2. Selected bond lengths (including H-bonds) [Å] and angles [°] for the complex.

Cu(1)–O(9)	1.943(2)	Cu(2)–O(11)	1.936(2)
Cu(1)–N(2)	1.990(2)	Cu(2)–N(4)	1.994(2)
Cu(1)–N(3)	1.998(2)	Cu(2)–N(6)	1.994(2)
Cu(1)–N(1)	2.011(3)	Cu(2)–N(5)	1.998(3)
Cu(1)–O(10)#1	2.318(2)	Cu(2)–O(12)#2	2.375(2)
C(11)–O(10)	1.231(4)	C(26)–O(11)	1.265(3)
C(11)–O(9)	1.274(3)	O(10)–Cu(1)#3	2.318(2)
O(12)–Cu(2)#4	2.375(2)	Cl(1)–O(1)	1.399(7)
Cl(1)–O(2)	1.472(4)	Cl(1)–O(3)	1.384(6)
Cl(1)–O(4)	1.435(4)	Cl(2)–O(5)	1.386(3)
Cl(2)–O(6)	1.406(3)	Cl(2)–O(7)	1.370(4)
Cl(2)–O(8)	1.418(5)	C(11)–O(10)	1.231(4)
C(11)–O(9)	1.274(3)	C(26)–O(12)	1.250(4)
C(26)–O(11)	1.265(3)		
O(9)–Cu(1)–N(2)	95.06(10)	N(4)–Cu(2)–O(12)#2	92.34(9)
O(9)–Cu(1)–N(1)	176.17(9)	N(6)–Cu(2)–O(12)#2	91.23(10)
N(2)–Cu(1)–N(3)	159.23(10)	N(5)–Cu(2)–O(12)#2	93.14(9)
O(9)–Cu(1)–N(3)	84.35(10)	O(12)–C26–O(11)	123.5(3)
N(2)–Cu(1)–N(1)	81.31(10)	O(3)–Cl(1)–O(1)	110.8(5)
N(3)–Cu(1)–N(1)	99.47(11)	O(3)–Cl(1)–O(4)	110.6(5)
O(9)–Cu(1)–O(10)#1	88.58(9)	O(1)–Cl(1)–O(4)	109.8(4)
N(2)–Cu(1)–O(10)#1	88.91(9)	O(3)–Cl(1)–O(2)	107.4(4)
N(3)–Cu(1)–O(10)#1	111.81(9)	O(1)–Cl(1)–O(2)	115.4(4)
O(10)–C(11)–O(9)	123.2(3)	O(4)–Cl(1)–O(2)	102.5(3)
O(10)–C(11)–C(12)	119.9(2)	O(7)–Cl(2)–O(5)	114.7(3)
O(11)–Cu(2)–N(6)	83.86(10)	O(7)–Cl(2)–O(6)	109.9(3)
N(4)–Cu(2)–N(6)	175.64(13)	O(5)–Cl(2)–O(6)	110.2(2)
O(11)–Cu(2)–N(5)	172.45(10)	O(7)–Cl(2)–O(8)	106.3(4)
N(4)–Cu(2)–N(5)	81.41(11)	O(5)–Cl(2)–O(8)	105.7(3)
N(6)–Cu(2)–N(5)	100.90(11)	O(6)–Cl(2)–O(8)	109.8(3)
O(11)–Cu(2)–N(4)	93.47(10)		
O(11)–Cu(2)–O(12)#2	92.60(9)		
O(2W)···O(10)#5	2.916(4)	O(2W)···O(8)#6	3.288(6)
O(1W)···O(12)#7	2.887(4)	O(1W)···O(1)#8	3.212(9)
N(6)···O(3)	3.224(8)	N(6)···O(1W)#9	2.995(4)
N(3)···O(2W)#3	3.048(4)	N(3)···O(7)	3.081(5)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, y+1/2, -z+1$; #2 $-x+1, y-1/2, -z$; #3 $-x+1, y-1/2, -z+1$; #4 $-x+1, y+1/2, -z$; #5 $-x+1, y+3/2, -z+1$; #6 $x-1, y+1, z$; #7 $x, y-1, z+1$; #8 $-x, y-1/2, -z+1$; #9 $x, y, z-1$.

In each long chain there are two repetitive units, shown in figure 1. The coordination bond lengths and angles around Cu(I) and Cu(II), which are similar to each other, are compared with the literature values, and the details are presented in table 3. The results show that the complex resembles reported amino acid–Cu^{2+}–bpy (phen) complexes with square-pyramidal geometry, which is a usual configuration for this kind of complex. In addition, the related coordination bond lengths and angles in the complexes are similar to each other, showing that Cu–N(O) bond lengths and N–Cu–N(O) bond angles are not changed with different coordination geometry around the central Cu atom.

It is interesting to compare the structural features of the L-α-amino acid of the title complex with other reported complexes [3–10,18,19] in which L-α-amino acids act as simple bidentate –N,O ligands bonding to the same Cu^{2+} ions, and the remaining O atoms of the carboxylate groups are free, whereas in the title complex the carboxylate groups act as μ_2-carboxylate-O–O bridging two Cu^{2+} ions to form one-dimensional

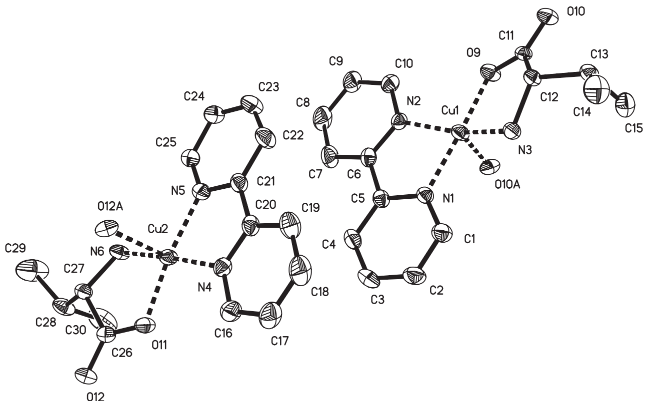


Figure 1. The two repetitive units in the long chain of $[Cu_2(\text{L–val})_2(bpy)_2]_n^{2n+}$ and the atom numbering scheme.

chains along the crystallographic *b* axis through the Cu–O bond in the apical direction. This is an unusual coordination mode, which has been found only in one similar complex containing an aromatic amino acid: $[Cu(\text{L-trp})(phen)] \cdot ClO_4 \cdot 2.5H_2O$ (L-trp = L-tryptophanate) [10].

The crystal packing is mainly determined by electrostatic and H-bonding interactions between the perchlorate oxygen atoms and crystallized waters; the H-bond distances are given in table 2. The ClO_4^- ions have a slightly distorted tetrahedral configuration: Cl(1)–O 1.384(6)–1.472(4) Å; Cl(2)–O 1.370(4)–1.418(5) Å; O–Cl(1)–O 102.5(3)–115.4(4)°; O–Cl(2)–O 105.7(3)–114.7(3)°. Crystal packing views of the complex are presented in figures 2 and 3.

3.2. *Infrared absorption spectra*

The IR spectrum reflects the structural features found by X-ray analysis. The very strong and broad bands at $3439\,\text{cm}^{-1}$ indicate the existence of H_2O and coordinated α-NH_2 of L-val [3–9]. The bands at 1627 and $1394\,\text{cm}^{-1}$ can be attributed, respectively, to the antisymmetric ($\upsilon_{\text{as,COO}}$) and symmetric ($\upsilon_{\text{s,COO}}$) stretching vibrations of the coordinated carboxylate group. The $\Delta\upsilon_{\text{COO}}$ ($\upsilon_{\text{as,COO}} - \upsilon_{\text{s,COO}} = 230\,\text{cm}^{-1}$) value is less than that reported in complexes in which carboxylates of amino acids are monodentate, showing that the carboxylate is bidentate [20]. Bands at 1580(m), 770(m) and 630(m) cm^{-1} can be assigned to the framework vibration and the $\delta_{\text{C–H}}$ of bpy ligand, respectively.

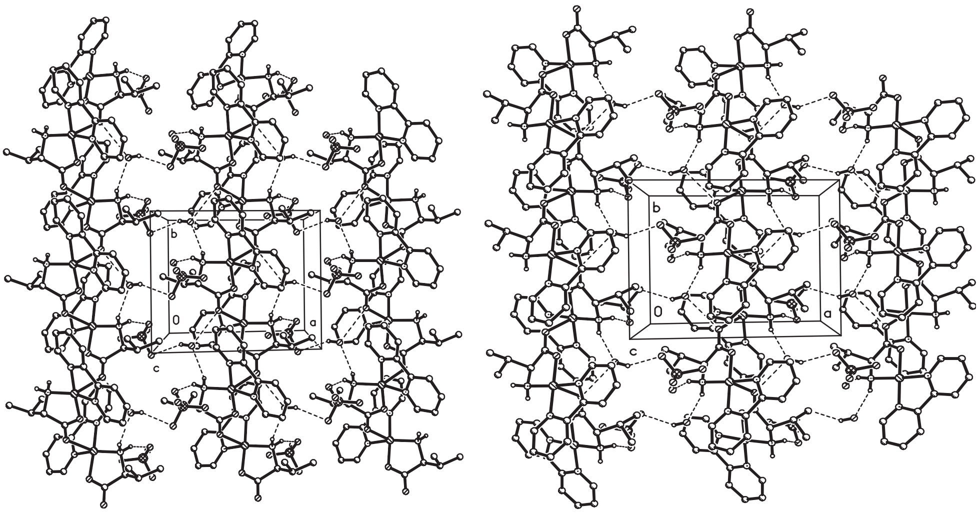
3.3. *Electronic absorption spectra*

The electronic absorption spectrum of the complex in aqueous solution presents four important absorption bands, in which the bands [205.0 nm ($\varepsilon = 16\,180\,\text{L}\,\text{mol}^{-1}\,\text{cm}^{-1}$), 242.7 nm ($\varepsilon = 27\,060\,\text{L}\,\text{mol}^{-1}\,\text{cm}^{-1}$) and 299.0 nm ($\varepsilon = 26\,600\,\text{L}\,\text{mol}^{-1}\,\text{cm}^{-1}$)] can be attributed to the $\pi \rightarrow \pi^*$ transitions of the bpy ligand, and the broad weak absorption band at 640 nm ($\varepsilon = 186\,\text{L}\,\text{mol}^{-1}\,\text{cm}^{-1}$) to the $d \rightarrow d$ transition of the central copper ion, consistent with related aromatic diamine–Cu^{2+}–amino acid complexes [3–9,18,19].

Table 3. Comparison of bond lengths (Å) and angles (°) in similar complexes.

Complex	Ref.	Cu–O	Cu–N	Phen(N_a)–Cu–phen(N_b)	AA(N_c)–Cu–AA(O)	Geometry
$[Cu_2(\text{L-arg})_2(bpy)_2(ClO_4)_2] \cdot 2ClO_4 \cdot 4H_2O$	[3]	1.922, 2.593, 1.929, 2.503	2.005, 2.001, 1.998, 2.009, 1.989, 2.001	81.3, 81.0	84.5, 84.4	Octahedral
$[Cu(\text{L-leu})(phen)(H_2O)] \cdot NO_3$	[4]	1.935, 2.233	2.024, 1.996, 1.984	81.76	83.98	Square-pyramidal
$[Cu(\text{L-his})(phen)] \cdot 2ClO_4 \cdot H_2O$	[5]	1.927	2.003, 1.994, 1.998	82.66	83.70	Square-planar
$[Cu(gly)(phen)(H_2O)] \cdot ClO_4 \cdot 2.5H_2O$	[6]	1.956, 2.254	2.023, 1.992, 1.996	82.34	83.63	Square-pyramidal
$[Cu(\text{L-met})(phen)(H_2O)] \cdot NO_3 \cdot H_2O$	[7]	1.938, 2.352	2.003, 1.987, 2.017	82.51	85.13	Square-pyramidal
$[Cu(\text{L-ile})(phen)(H_2O)ClO_4]$	[8]	1.926, 2.371, 1.937, 2.285, 2.811, 2.854	2.002, 2.019, 2.007 2.022, 2.000, 1.996	82.44, 82.23	83.59, 84.39	Octahedral
$[Cu(\text{L-met})(bpy)(H_2O)] \cdot ClO_4 \cdot 3/8H_2O$	[9]	1.933, 1.924, 1.945, 1.938, 2.330, 2.326, 2.404, 2.375	2.013, 1.998, 1.988, 1.999, 1.990, 1.993, 2.011, 1.982, 1.965, 2.011, 1.994, 1.987	81.3, 84.0, 81.0, 82.3	84.1, 84.0, 83.5, 84.9	Square-pyramidal
$[Cu(\text{L-trp})(bpy)] \cdot ClO_4 \cdot 2.5H_2O$	[10]	1.93, 2.29	2.02, 1.99, 2.00	83.0	84.0	Square-pyramidal
$[Cu(\text{L-glu})(bpy)]$	[18]	1.960, 2.245, 1.926, 2.160	2.026, 2.011, 1.987, 2.010, 2.008, 1.999	81.2, 80.8	83.4, 85.5	Square-pyramidal
$[Cu(\text{L-glu})(phen)(H_2O)] \cdot 3H_2O$	[18]	1.913, 2.294, 1.926, 2.225	2.015, 2.018, 2.020, 2.027, 2.003, 1.997	82.4, 82.2	84.7, 83.7	Square-pyramidal
$[Cu(\text{L-tyr})(phen)(H_2O)] \cdot ClO_4 \cdot 2.5H_2O$	[19]	1.94, 2.24, 1.95, 2.25	1.99, 1.88, 1.98, 2.01, 2.03, 2.00	84, 84.8	83.5, 82.2	Square-pyramidal
$[Cu(\text{L-phe})(bpy)(H_2O)] \cdot ClO_4 \cdot H_2O$	[19]	1.94, 2.50, 1.92, 2.27	2.01, 2.00, 1.96, 2.06, 2.00, 1.99	83.6, 80.1	82.2, 86.9	Square-pyramidal
$[Cu_2(\text{L-val})_2(bpy)_2]_n \cdot 2nClO_4 \cdot 2nH_2O$	This work	1.943, 2.318, 1.936, 2.375	2.011, 1.998, 1.990, 1.998, 1.994, 1.994	81.31, 81.41	84.35, 83.36	Square-pyramidal

AA, amino acid; arg, argininate; leu, leucinate; his, histidinate; gly, glycinate; met, methioninate; ile, isoleucinate; glu, glutamic acid; tyr, tyrosinate; phe, phenylalaninate.



(a) (b)

Figure 2. Crystal packing diagram along the *b* axis showing long chains of the complex $[Cu_2(\text{L-val})_2(bpy)_2]_n \cdot 2nClO_4 \cdot 2nH_2O$: (a) the long chains for Cu(1) and the H-bonds between $H_2O(2)$ and $ClO_4(2)$; (b) the long chains for Cu(2) and the H-bonds between $H_2O(1)$ and $ClO_4(1)$.

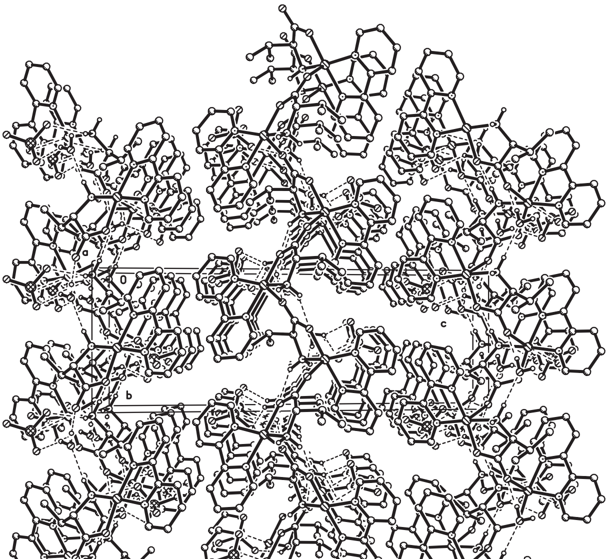


Figure 3. Crystal packing diagram along the *a* axis of the complex $[Cu_2(\text{L-val})_2\ (bpy)_2]_n \cdot 2nClO_4 \cdot 2nH_2O$.

3.4. *TG analysis*

The TGA–DTA study of the title complex shows four weight-loss stages. The first weight loss (3.56%) occurs between 60.2 and 145.7°C (broad endothermal peak observed at 112.1°C in DTA), corresponding to the loss of one lattice water molecule. The second weight loss (24.19%) occurs between 195.7 and 224.3°C (two strong exothermal peaks observed at 203.5 and 220.0°C, respectively, in DTA), corresponding to the loss of one L-val molecule. The third weight loss (28.15%) occurs between 225.7 and 371.0°C (two strong exothermal peaks observed at 251.0 and 316.2°C, respectively, in DTA), corresponding to the combustion of bipyridine. The fourth weight loss (26.18%) occurs from 372.1°C to the temperature of constant weight (sharp endothermal peak observed at 546.0°C in DTA), corresponding to the decomposition of ClO_4^- and the destruction of the bone structure. The residues were copper oxides.

The results indicate that the experimental value of the gross weight loss of the compound is in agreement with the calculated, and the decomposition temperature of the title complex is similar to that of $[Sm_2(gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$ [21].

Supplementary data

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 231773. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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