European Journal of Chemistry

View Journal Online
View Article Online

Synthesis and crystal structure of the copper (II) carboxylate with 2,2-bipyridine, [Cu(4-mba)$_2$(bipy)(H$_2$O)]

Sibel Demir Kanmazalp [1,*], Adnan Qadir [2] and Necmi Dege [3]

[1] *Naci Topçuoğlu Vocational School, Biomedical Device Technology Program, Gaziantep University, Gaziantep, 27600, Turkey*
[2] *Department of Chemistry, College of Science, Salahaddin University, Erbil, 44001, Iraq*
[3] *Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayis University, 55139, Samsun, Turkey*

* *Corresponding author at: Naci Topçuoğlu Vocational School, Biomedical Device Technology Program, Gaziantep University, Gaziantep, 27600, Turkey.*
e-mail: sibeld@gantep.edu.tr (S.D. Kanmazalp).

RESEARCH ARTICLE

10.5155/eurjchem.14.1.109-113.2390

Received: 22 December 2022
Received in revised form: 11 January 2023
Accepted: 25 January 2023
Published online: 31 March 2023
Printed: 31 March 2023

KEYWORDS

Synthesis
Carboxylate
Cu(II) complex
Crystal structure
Single-crystal XRD
Hydrogen bonding

ABSTRACT

The new Cu(II) carboxylate complex, aqua(2,2'-bipyridine-κ^2*N,N'*)bis(4-methylbenzoato-κ*O*)copper(II) [Cu(4-mba)$_2$(bipy)(H$_2$O)] (4-mba: 4-methylbenzoate, bipy: 2,2'-bipyridine) was synthesized, and the molecular structure of the complex was characterized by the single crystal X-ray diffraction technique. The X-ray diffraction analysis indicated that the asymmetric unit comprises an independent molecule. Crystal data for [Cu(4-meb)$_2$(2,2-bipy)(H$_2$O)]: Triclinic, space group *P*-1 (no. 2), a = 7.0452(13) Å, b = 11.260(2) Å, c = 16.635(3) Å, α = 103.543(7)°, β = 91.002(7)°, γ = 104.106(6)°, V = 1240.4(4) Å^3, Z = 2, T = 296 K, μ(MoKα) = 0.918 mm^{-1}, *Dcalc* = 1.360 g/cm^3, 51364 reflections measured (5.054° ≤ 2Θ ≤ 57.38°), 6258 unique (R_{int} = 0.0398, R_{sigma} = 0.0284) which were used in all calculations. The final R_1 was 0.0392 (I > 2σ(I)) and wR_2 was 0.1021 (all data). The Cu(II) ion was found to be coordinated with two nitrogen atoms of the 2,2'-bipyridine ligand, two oxygen atoms of the 4-methyl benzoate molecule, and one oxygen atom of the aqua ligand. In the three-dimensional supramolecular architecture, molecules are connected through pairs of O-H···O and C-H···O intermolecular interactions, consisting of chains. The molecule also demonstrates Cg···Cg intermolecular interactions between six-membered rings of 2,2'-bipyridine.

Cite this: *Eur. J. Chem.* **2023**, *14(1)*, 109-113 **Journal website**: www.eurjchem.com

1. Introduction

To coordinate compound formation, 2,2'-bipyridine (bipy) and phenanthroline are used due to their effectiveness in catalysis, electrochemistry, analytical chemistry and biochemistry [1]. These ligands have extended π-systems and their complexes show various π-π interactions that participate in the supramolecular architecture [2]. Generally, the substituents have steric effects on the 2,2'-bipyridine rings, which affect the bond distance between the metal and nitrogen atoms. For example, in the two complexes of type [Cu(L)Cl(NO$_3$)]$_2$ (L = 2,2'-Bipyridine (1A), L = 4,4-Dimethyl-2,2-bipyridine (2A)), the Cu-N bond distances (2.004-2.008 Å) in complex 2A are longer than those (1.993-1.994 Å) in complex 1A due to the steric effect of the methyl groups on 4,4-dimethyl-2,2-bipyridine rings [3].

Cu(II) complexes with the d^9 configuration exhibit four, five, and six coordinates that adopt tetrahedral, square planar, square pyramidal, and distorted octahedral coordinates due to the Jahn-Teller effect [4]. In our previous work, we synthesized a Cu(II) complex {bisaqua-bis(3-methylbenzoato-κ*O*)(*N,N,N',N'*-tetramethylethylenediamine-κ^2*N,N'*)copper(II), [Cu(3-mba)$_2$(tmeda)(H$_2$O)$_2$]} involving 3-methyl benzoate (3-mba) and *N,N,N',N'*-tetramethylethylenediamine (tmeda) [5]. The [Cu(3-mba)$_2$(tmeda)(H$_2$O)$_2$] was characterized by X-ray diffraction analysis and showed a distorted octahedral geometry with carboxylate ligands acting as monodentate.

The Cu(II) ion exists in many enzymes including; such as cytochrome C oxidase [6], dopamine hydroxylase [7], tyrosinate [8], superoxide dismutase [9] and ceruloplasmin [10]. Furthermore, the Cu (II) carboxylate complexes showed different biological activities, such as antibacterial [11], antifungal [12], antiviral [13], and antitumor activities [14]. Given the biological importance of Cu(II) carboxylate complexes, a new Cu(II) complex with 4-methyl benzoate and 2,2'-bipyridine has been synthesized and characterized by single crystal X-ray diffraction analysis.

2. Experimental

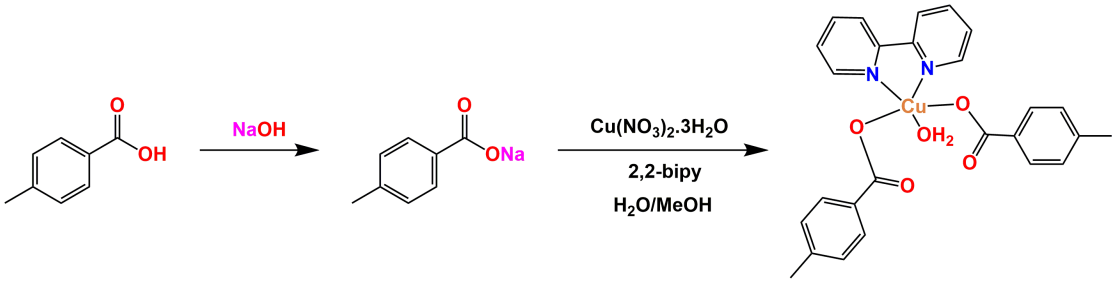
2.1. Synthesis of [Cu(4-mba)$_2$(bipy)(H$_2$O)]

4-Methylbenzoic acid (4 mmol, 0.54 g) and sodium hydroxide (4 mmol, 0.16 g) were dissolved in water (20 mL). Then, a solution of Cu(NO$_3$)$_2$·3H$_2$O (2 mmol, 0.48 g) in water (20 mL) was added with stirring to the prepared solution. Subsequently, a solution of 2,2'-bipyridine (2 mmol, 0.3 g) in MeOH (25 mL) was added and blue sediment was formed.

ISSN 2153-2249 (Print) / ISSN 2153-2257 (Online)
https://dx.doi.org/10.5155/eurjchem.14.1.109-113.2390

Table 1. Crystal data and structure refinement for [Cu(4-mba)$_2$(bipy)(H$_2$O)].

Empirical formula	$C_{26}H_{24}CuN_2O_5$
Formula weight (g/mol)	508.01
Temperature (K)	296
Crystal system	Triclinic
Space group	*P*-1
a, (Å)	7.0452(13)
b, (Å)	11.260(2)
c, (Å)	16.635(3)
α (°)	103.543(7)
β (°)	91.002(7)
γ (°)	104.106(6)
Volume (Å^3)	1240.4(4)
Z	2
ρ_{calc} (g/cm^3)	1.360
μ (mm^{-1})	0.918
F(000)	526.0
Crystal size (mm^3)	0.11 × 0.07 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection (°)	5.054 to 57.38
Index ranges	$-9 \le h \le 9$, $-15 \le k \le 15$, $-22 \le l \le 22$
Reflections collected	51364
Independent reflections	6258 [R_{int} = 0.0398, R_{sigma} = 0.0284]
Data/restraints/parameters	6258/2/317
Goodness-of-fit on F^2	1.082
Final R indexes [I≥2σ (I)]	R_1 = 0.0392, wR_2 = 0.0933
Final R indexes [all data]	R_1 = 0.0545, wR_2 = 0.1021
Largest diff. peak/hole (e.Å^{-3})	0.32/-0.28



Scheme 1. The synthesis scheme of [Cu(4-mba)$_2$(bipy)(H$_2$O)].

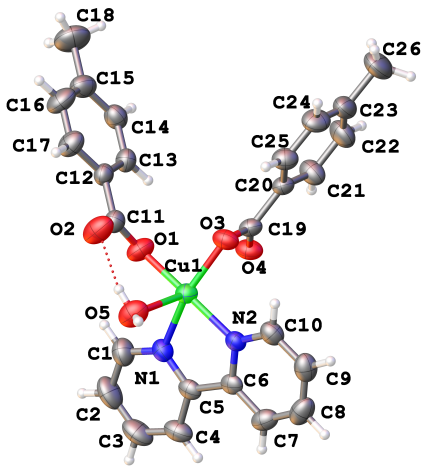


Figure 1. Crystal structure of [Cu(4-mba)$_2$(bipy)(H$_2$O)], indicating the atom numbering scheme.

The sediment was filtered, washed with water, and dried at room temperature. The obtained product was recrystallised from ethanol (Scheme 1).

2.2. Crystal structure analysis

XRD measurements for [Cu(4-mba)$_2$(bipy)(H$_2$O)] were taken on a Bruker D8 QUEST diffractometer (MoKα radiation, λ = 0.71073 Å; graphite monochromator) at 296 K. WinGX software [15] was used to solve the molecular structure. The structure was refined by the full-matrix least squares method using SHELXL-97 [16]. All non-H atoms were first refined isotropically and then with anisotropic displacement parameters. The residual electron density was a troublesome model and therefore the SQUEEZE routine [17] in PLATON [18] was used to subtract the contribution of the electron density in the solvent zone from the intensity data and the solvent-free model was used for the final refinement. The details of the structure refinement for [Cu(4-mba)$_2$(bipy)(H$_2$O)] are given in Table 1.

Table 2. Bond lengths and bond angles for [Cu(4-mba)$_2$(bipy)(H$_2$O)].

Atom	Atom	Length (Å)	Atom	Atom	Length (Å)
Cu1	O3	1.9824(14)	C5	C6	1.480(3)
Cu1	O1	1.9484(15)	C5	C4	1.388(3)
Cu1	O5	2.3532(18)	C12	C11	1.505(3)
Cu1	N1	2.0183(17)	C12	C17	1.388(3)
Cu1	N2	2.0066(16)	C6	C7	1.385(3)
O3	C19	1.273(2)	C14	C15	1.383(3)
O4	C19	1.251(2)	C10	C9	1.374(3)
O1	C11	1.272(2)	C21	C22	1.378(3)
O2	C11	1.228(3)	C23	C24	1.374(4)
N1	C5	1.341(3)	C23	C22	1.379(4)
N1	C1	1.339(3)	C23	C26	1.516(3)
N2	C6	1.352(2)	C17	C16	1.381(3)
N2	C10	1.336(3)	C9	C8	1.375(4)
C20	C19	1.498(3)	C15	C16	1.379(4)
C20	C25	1.386(3)	C15	C18	1.516(3)
C20	C21	1.385(3)	C4	C3	1.375(4)
C13	C12	1.384(3)	C1	C2	1.382(4)
C13	C14	1.378(3)	C2	C3	1.359(4)
C25	C24	1.391(3)	C8	C7	1.378(3)

Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)
O3	Cu1	O5	107.36(6)	C13	C12	C11	121.90(18)
O3	Cu1	N1	163.22(6)	C13	C12	C17	118.35(19)
O3	Cu1	N2	92.31(6)	C17	C12	C11	119.74(19)
O1	Cu1	O3	90.88(7)	N2	C6	C5	114.49(17)
O1	Cu1	O5	91.48(7)	N2	C6	C7	121.21(19)
O1	Cu1	N1	94.56(7)	C7	C6	C5	124.30(18)
O1	Cu1	N2	172.36(6)	O1	C11	C12	115.67(18)
N1	Cu1	O5	88.38(7)	O2	C11	O1	125.1(2)
N2	Cu1	O5	94.19(6)	O2	C11	C12	119.21(19)
N2	Cu1	N1	80.50(7)	C13	C14	C15	121.1(2)
C19	O3	Cu1	104.67(12)	N2	C10	C9	122.5(2)
C11	O1	Cu1	124.17(13)	C22	C21	C20	121.2(2)
C5	N1	Cu1	115.07(13)	C24	C23	C22	117.7(2)
C1	N1	Cu1	125.91(16)	C24	C23	C26	122.2(3)
C1	N1	C5	119.02(19)	C22	C23	C26	120.1(3)
C6	N2	Cu1	115.11(13)	C16	C17	C12	120.2(2)
C10	N2	Cu1	125.95(14)	C10	C9	C8	118.9(2)
C10	N2	C6	118.88(18)	C14	C15	C18	120.6(3)
C25	C20	C19	121.62(18)	C16	C15	C14	117.9(2)
C21	C20	C19	120.11(18)	C16	C15	C18	121.5(3)
C21	C20	C25	118.27(19)	C3	C4	C5	118.6(2)
O3	C19	C20	118.35(17)	C23	C24	C25	122.1(2)
O4	C19	O3	122.35(18)	N1	C1	C2	121.8(2)
O4	C19	C20	119.29(17)	C3	C2	C1	119.1(2)
C14	C13	C12	120.9(2)	C21	C22	C23	121.1(2)
C20	C25	C24	119.6(2)	C15	C16	C17	121.6(2)
N1	C5	C6	114.68(16)	C9	C8	C7	119.4(2)
N1	C5	C4	121.5(2)	C8	C7	C6	119.1(2)
C4	C5	C6	123.77(19)	C2	C3	C4	119.9(2)

The PLATON program [18] was used for structure analysis. Molecular structure illustrations have been drawn with MERCURY [19] and the OLEX program [20] for publication.

3. Results and discussion

The crystallographic data for [Cu(4-mba)$_2$(bipy)(H$_2$O)] are indicated in Table 1 and the essential geometrical parameters are shown in Table 2. The single-crystal structure of [Cu(4-meb)$_2$(bipy)(H$_2$O)] crystallises in the triclinic crystal system with the space group *P*-1, as indicated in Figure 1.

The Cu(II) ion is coordinated with the two nitrogen donors of the 2,2'-bipyridine ligand, two oxygen atoms of 4-methyl benzoate molecules, and one oxygen atom of the aqua ligand. As shown in Figure 1, the Cu1 atom is five-coordinated in a slightly distorted square pyramidal configuration (τ_5 = 0.15; τ_5 = (β-α)/60, where β = O1-Cu1-N2 172.36(6)° and α = O3-Cu1-N1 163.22(6)°, Table 2). The τ_5 parameter is 0 and 1 for perfect square pyramidal and trigonal bipyramidal geometries, respectively [21-23], by two nitrogen atoms from a 2,2'-bipyridine (N1 and N2 are in the equatorial position) and two oxygen atoms from 4-methyl benzoate molecules (O1 and O3 are in the equatorial position) and an oxygen atom from the aqua ligand (O5 in the axial position) [24].

The bond lengths of Cu1-O1 (1.9484(15) Å) and Cu1-O3 (1.9824(14) Å) in the equatorial position are found to be shorter than Cu1-O5 (2.3532(18) Å) in the axial position, for the square pyramidal complex. Furthermore, at the axial position, the Cu1-O5 bond length in the aqua ligand is shorter in five-coordinated aqua complexes (on average 2.25 Å [24] than in the six-coordinated ones (on average 2.56 Å [24]).

The bond lengths of Cu-N$_{bipy}$, 2.0066(16) and 2.0183(17) Å, are slightly shorter than those obtained in [Cu(bpdc)(dap)(H$_2$O)]·2H$_2$O, 2.075(6) and 2.036(5) Å [24] and agree well with the complex [tetra-azido-tris(2-pyridyl)amine]dicopper(II) [25]. As a result, the bond length variation can be clarified by the effect of the neighbouring functional group. The bond angle of N1-Cu1-N2 (80.50(7)°) is closer to that found in [Cu(bp5dc)(en)(H$_2$O)$_2$]$_2$·5H$_2$O (80.87(2)°) [26].

In the 2,2'-bipyridine ring, the C-C and C-N bond lengths are in good agreement in the literature for 2-substituted pyridine derivatives [27-30]. The lengths of the C-O bonds in 4-methyl benzoate molecules range from 1.251(2) to 1.273(2) Å, due to all C-O bonds showing a single-bond character (Table 2). Furthermore, the bond angles of O2-C11-O1 (125.1(2)°) and O4-C19-O3 (122.35(18)°) in the 4-methyl benzoate molecules conform which is close to those notified in the similar structure 123.28(10)° [31].

Table 3. Hydrogen bonds for [Cu(4-mba)$_2$(bipy)(H$_2$O)] *.

D	H	A	d(D-H) (Å)	d(H-A) (Å)	d(D-A) (Å)	∠ D-H-A (°)
C10	H10	O3	0.93	2.54	3.035(3)	113.5
C4	H4	O4^1	0.93	2.48	3.367(3)	159.0
C2	H2	O2^2	0.93	2.64	3.448(3)	146.3
C7	H7	O4^1	0.93	2.46	3.348(3)	160.6
O5	H5A	O2	0.792(17)	1.904(19)	2.658(3)	159(3)
O5	H5B	O4^3	0.809(17)	1.975(18)	2.774(2)	170(3)

* Symmtery codes: [1] 1-*x*, 1-*y*, 1-*z*, [2] 2-*x*, 2-*y*, 1-*z*, [3] 1+*x*, +*y*, +*z*

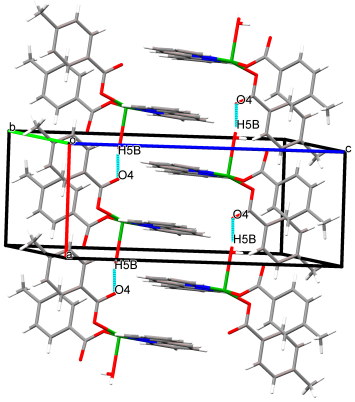


Figure 2. A packing view of the molecules along with the *b*-axis.

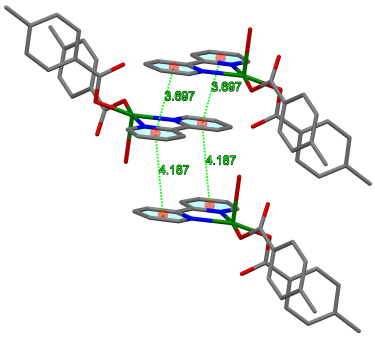


Figure 3. The *Cg*···*Cg* intermolecular interactions are shown as green dashed lines.

In this molecular conformation, two O5-H5A···O2 and C10-H10···O3 are stabilised by intramolecular contacts. As shown in Figure 1, O5-H5A···O2 intramolecular hydrogen bond interaction forms a pseudo-five-membered ring with the *S*(5) graph set motif [32]. The crystal packing diagram for [Cu(4-mba)$_2$(bipy)(H$_2$O)] consists of intramolecular and intermolecular O5-H5A···O2, O5-H5B···O4 hydrogen bonds, respectively, in the crystal packing as detailed in Table 3 and shown in Figure 2. These intramolecular and intermolecular interactions are influential in stabilising the molecular crystal structure and the creation of the 3-D chain supramolecular combination. There are also *Cg*···*Cg* interactions in the molecular system between 2,2'-bipyridine rings belonging to different symmetry codes, *Cg*3···*Cg*4. The distances are 3.6973(15) and 4.1869(15) Å, symmetry codes are −*x*+1, −*y*+1, −*z*+1, and *x*, *y*, *z*; and *Cg*3 and *Cg*4 are the center mass of the rings (*Cg*3: N1/C1/C2/C3/C4/C5) and (*Cg*4: N2/C6/C7/C8/C9/C10), as indicated in Figure 3.

4. Conclusions

In this work, the [Cu(4-meb)$_2$(bipy)(H$_2$O)]) complex was synthesized and characterized by the single crystal X-ray diffraction method. The molecular structure and coordination properties comprising the geometrical parameters of the prepared complex were designated. The obtained molecular geometry showed a square pyramidal configuration with the carboxylate ligand acting as a monodentate ligand. X-ray crystallographic studies of [Cu(4-mba)$_2$(bipy)(H$_2$O)] show that the molecular structure has two intramolecular interactions and four intermolecular interactions.

Acknowledgments

The authors acknowledge the Scientific and Technological Research Application and Research Center, Sinop University, Turkey, for the use of the Bruker D8 QUEST diffractometer.

Supporting information

CCDC-2141370 contains the supplementary crystallographic data for this article. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Disclosure statement

Conflict of interest: The authors declare that they have no conflict of interest.
Ethical approval: All ethical guidelines have adhered.
Sample availability: Sample of the compound is available from the author.

CRediT authorship contribution statement

Conceptualization: Sibel Demir Kanmazalp; Methodology: Sibel Demir Kanmazalp, Adnan Qadir; Software: Sibel Demir Kanmazalp, Necmi Dege; Validation: Adnan Qadir, Necmi Dege; Formal Analysis: Adnan Qadir, Necmi Dege; Investigation: Sibel Demir Kanmazalp; Resources: Sibel Demir Kanmazalp, Adnan Qadir; Data Curation: Necmi Dege; Writing - Original Draft: Sibel Demir Kanmazalp, Adnan Qadir; Writing - Review and Editing:

Sibel Demir Kanmazalp; Visualization: Sibel Demir Kanmazalp; Project Administration: Sibel Demir Kanmazalp.

ORCID and Email

Sibel Demir Kanmazalp
sibeld@gantep.edu.tr
ssibdemir@gmail.com
https://orcid.org/0000-0002-5896-0966
Adnan Qadir
adnan.qadir@su.edu.krd
https://orcid.org/0000-0002-9286-0344
Necmi Dege
necmid@omu.edu.tr
https://orcid.org/0000-0003-0660-4721

References

[1]. Jennifer, S. J.; Muthiah, P. T. Synthesis, crystal structures and supramolecular architectures of square pyramidal Cu(II) complexes containing aromatic chelating N,N'-donor ligands. *Chemistry Central Journal* **2014**, *8*, 42.
[2]. Liu, F.-Y.; Zhang, M.-H.; Kou, J.-F. (2,2'-Bi-pyridine-κ(2) N,N')bis-(nitrato-κ(2) O,O')copper(II). *Acta Crystallogr. Sect. E Struct. Rep. Online* **2013**, *69*, m609.
[3]. Atria, A. M.; Cortés, P.; Acevedo, L.; Trujillo, R.; Manzur, J.; Peña, O.; Baggio, R. PREPARATION, STRUCTURE AND PROPERTIES OF BIS (M2-CHLORO)-(NITRATO-O)-(2,2'-BIPYRIDINE-N.n')-COPPER(II):[cu(2,2'-BP)cl NO3]2. *J. Chil. Chem. Soc.* **2004**, *49*, 341–344.
[4]. Cody, C. C.; Kelly, H. R.; Mercado, B. Q.; Batista, V. S.; Crabtree, R. H.; Brudvig, G. W. Distorted copper(II) complex with unusually short CF···Cu distances. *Inorg. Chem.* **2021**, *60*, 14759–14764.
[5]. Kansız, S.; Qadir, A. M.; Dege, N.; Faizi, S. H. Two new copper (II) carboxylate complexes based on N,N,N',N'-tetramethylethyleneamine: Synthesis, crystal structures, spectral properties, dft studies and hirshfeld surface analysis. *J. Mol. Struct.* **2021**, *1230*, 129916.
[6]. Llases, M.-E.; Morgada, M. N.; Vila, A. J. Biochemistry of copper site assembly in heme-copper oxidases: A theme with variations. *Int. J. Mol. Sci.* **2019**, *20*, 3830–3848.
[7]. Abdul-Ghani, A.-S.; Abu-Hijleh, A. L.; Qazzaz, M. Effect of bis(acetato)tetrakis(imidazole) copper(II) in delaying the onset and reducing the mortality rate of strychnine- and thiosemicarbazide-induced convulsions. *Biol. Trace Elem. Res.* **2004**, *101*, 87–95.
[8]. Gawlig, C.; Jung, J.; Mollenhauer, D.; Schindler, S. Synthesis and characterization of copper complexes with tripodal ligands bearing amino acid groups. *Z. Anorg. Allg. Chem.* **2021**, *647*, 951–959.
[9]. Valentine, J. S.; Mota de Freitas, D. Copper-zinc superoxide dismutase: A unique biological "ligand" for bioinorganic studies. *J. Chem. Educ.* **1985**, *62*, 990–997.
[10]. Batool, S. S.; Ahmad, S.; Khan, I. U.; Ejaz; Harrison, W. T. A. Structural characterization of a new copper(II) complex of 1,10-phenanthroline and benzoate [Cu(phen)(C6H5CO 2 –)2]. *J. Struct. Chem.* **2015**, *56*, 387–391.
[11]. Mojumdar, S. C.; Madgurambal, G.; Saleh, M. T. A study on synthesis and thermal, spectral and biological properties of carboxylato-Mg(II) and carboxylato-Cu(II) complexes with bioactive ligands. *J. Therm. Anal. Calorim.* **2005**, *81*, 205–210.
[12]. Kozlevčar, B.; Leban, I.; Turel, I.; Šegedin, P.; Petric, M.; Pohleven, F.; White, A. J. P.; Williams, D. J.; Sieler, J. Complexes of copper (II) acetate with nicotinamide: preparation, characterization and fungicidal activity; crystal structures of [Cu2 (O2CCH3)4 (nia)] and [Cu2 (O2CCH3)4 (nia)2]. *Polyhedron* **1999**, *18*, 755–762.
[13]. Ranford, J. D.; Sadler, P. J.; Tocher, D. A. Cytotoxicity and antiviral activity of transition-metal salicylato complexes and crystal structure of Bis(diisopropylsalicylato)(1,10-phenanthroline)copper(II). *J. Chem. Soc., Dalton Trans.* **1993**, 3393.
[14]. Devereux, M.; O'Shea, D.; O'Connor, M.; Grehan, H.; Connor, G.; McCann, M.; Rosair, G.; Lyng, F.; Kellett, A.; Walsh, M.; Egan, D.; Thati, B. Synthesis, catalase, superoxide dismutase and antitumour activities of copper(II) carboxylate complexes incorporating benzimidazole, 1,10-phenanthroline and bipyridine ligands: X-ray crystal structures of [Cu(BZA)2(bipy)(H2O)], [Cu(SalH)2(BZDH)2] and [Cu(CH3COO)2 (5,6-DMBZDH)2] (SalH2=salicylic acid; BZAH=benzoic acid; BZDH = benzimidazole and 5,6-DMBZDH=5,6-dimethyl benzimidazole). *Polyhedron* **2007**, *26*, 4073–4084.
[15]. Farrugia, L. J. WinGXsuite for small-molecule single-crystal crystallography. *J. Appl. Crystallogr.* **1999**, *32*, 837–838.
[16]. Sheldrick, G. M. (1996). SHELXS97 and SHELXL97. University of Göttingen, Germany.
[17]. Spek, A. L. PLATON SQUEEZE: a tool for the calculation of the disordered solvent contribution to the calculated structure factors. *Acta Crystallogr. C Struct. Chem.* **2015**, *71*, 9–18.
[18]. Spek, A. L. checkCIF validation ALERTS: what they mean and how to respond. *Acta Crystallogr. E Crystallogr. Commun.* **2020**, *76*, 1–11.
[19]. Macrae, C. F.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Shields, G. P.; Taylor, R.; Towler, M.; van de Streek, J. *Mercury*: visualization and analysis of crystal structures. *J. Appl. Crystallogr.* **2006**, *39*, 453–457.
[20]. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
[21]. Abedi, A.; Mehri-Lighvan, Z.; Yasan, M.; Amani, V. Novel Cu(II) complexes of bithiazole: structure and biological study. *J. Iran. Chem. Soc.* **2017**, *14*, 491–502.
[22]. Su, C.-C.; Lin, Y.-L.; Liu, S.-J.; Chang, T.-H.; Wang, S.-L.; Liao, F.-L. Bonding properties of copper(II)—N chromophores: Molecular and electronic structures of copper(II) complexes containing ethylenediamine and heterocyclic diimine ligands. *Polyhedron* **1993**, *12*, 2687–2696.
[23]. Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. Synthesis, structure, and spectroscopic properties of copper(II) compounds containing nitrogen–sulphur donor ligands; the crystal and molecular structure of aqua[1,7-bis(N-methylbenzimidazol-2'-yl)-2,6-dithiaheptane]copper(II) perchlorate. *J. Chem. Soc., Dalton Trans.* **1984**, 1349–1356.
[24]. Pirsiavash, F.; Amani, V.; Abedi, A. Coordination number in copper(II) complexes with bipyridine-dicarboxylate anion and diamine derivatives. *Res. Chem. Intermed.* **2018**, *44*, 7411–7426.
[25]. Merabet, L.; Setifi, Z.; Ferjani, H.; Geiger, D. K.; Glidewell, C.; Kanmazalp, S. D.; Setifi, F.; Kaboub, L. Dinuclear azide-bridged copper(II) polymer with azido···π(pyridiyl) interaction: Synthesis, crystal structure and Hirshfeld surface analysis. *J. Chem. Crystallogr.* **2022**, https://doi.org/10.1007/s10870-022-00960-2.
[26]. Yousefi, M.; Khalighi, A.; Tadayon Pour, N.; Amani, V.; Khavasi, H. R. Diaqua(2,2'-bipyridine-5,5'-dicarboxylato-κ2N,N')(ethylenediamine-κ2N,N')copper(II) 2.5-hydrate. *Acta Crystallogr. Sect. E Struct. Rep. Online* **2008**, *64*, m1284–m1285.
[27]. Strotmeyer, K. P.; Fritsky, I. O.; Ott, R.; Pritzkow, H.; Krämer, R. Evaluating the conformational role of an allosteric CuII ion in anion recognition and catalysis by a tricopper complex. *Supramol. Chem.* **2003**, *15*, 529–547.
[28]. Iskenderov, T. S.; Golenya, I. A.; Gumienna-Kontecka, E.; Fritsky, I. O.; Prisyazhnaya, E. V. (2RS)-3-Hydr-oxy-2-methyl-2-(2-pyrid-yl) imidazolidine-4-one. *Acta Crystallogr. Sect. E Struct. Rep. Online* **2009**, *65*, o2123-4.
[29]. Golenya, I. A.; Gumienna-Kontecka, E.; Boyko, A. N.; Haukka, M.; Fritsky, I. O. Collapsed Cu(II)-hydroxamate metallacrowns. *Inorg. Chem.* **2012**, *51*, 6221–6227.
[30]. Qadir, A. M.; Kansiz, S.; Rosair, G. M.; Dege, N.; Safyanova, I. S. Crystal structure and Hirshfeld surface analysis of a zinc xanthate complex containing the 2,2'-bi-pyridine ligand. *Acta Crystallogr. E Crystallogr. Commun.* **2019**, *75*, 1857–1860.
[31]. Saeed, A.; Rafique, H.; Flörke, U. Methyl 4-methyl-benzoate. *Acta Crystallogr. Sect. E Struct. Rep. Online* **2008**, *64*, o821.
[32]. Demir, S.; Cakmak, S.; Dege, N.; Kutuk, H.; Odabasoglu, M.; Kepekci, R. A. A novel 3-acetoxy-2-methyl-N-(4-methoxyphenyl)benzamide: Molecular structural describe, antioxidant activity with use X-ray diffractions and DFT calculations. *J. Mol. Struct.* **2015**, *1100*, 582–591.