



Novel Trinuclear Copper(II) Complex: Crystal Structure at 100 K and Magnetic Properties of (*R,S*)-di[(6,7-dimethoxy-isoquinolin-1-yl)-(3,4-dimethoxy-phenyl)-methanolato]-tetra(2-hydroxybenzoato)-diaqua-tricopper dihydrate, $[\text{Cu}_3(\text{C}_7\text{H}_5\text{O}_3)_4(\text{C}_{20}\text{H}_{20}\text{NO}_5)_2(\text{H}_2\text{O})_2] \cdot 2(\text{H}_2\text{O})$

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Abstract

The crystal structure of $[\text{Cu}_3(\text{C}_7\text{H}_5\text{O}_3)_4(\text{C}_{20}\text{H}_{20}\text{NO}_5)_2(\text{H}_2\text{O})_2] \cdot 2(\text{H}_2\text{O})$ (**1**) and analysis of temperature and field dependence of magnetic susceptibility is reported in this work. The structure of **1** is composed of trinuclear complex units and water molecules. The middle copper atom occupies the center of symmetry. *N*, *O*-bonded (6,7-dimethoxy-isoquinolin-1-yl)-(3,4-dimethoxy-phenyl)-methanolato ligands, 2-hydroxybenzoates with bridging carboxylic groups, and oxo-bridged water molecules connect the middle Cu(II) atom with the terminal copper atoms. Two 2-hydroxybenzoates coordinate the terminal copper atoms *via* one carboxylic oxygen and an O atom of the hydroxyl group. The analysis of copper coordination by bond-valence sum approach and relevant structural correlation is consistent with hexacoordinated Cu(II) centers. Cu...Cu separation is 3.0269(3) Å. The magnetism of **1** shows a strong ferromagnetic interaction between the neighboring metallic centers accompanied by very weak antiferromagnetic intermolecular interactions. The complex units are mutually held by $\pi \cdots \pi$ stack interactions of 2-hydroxybenzoates and hydrogen bonds.

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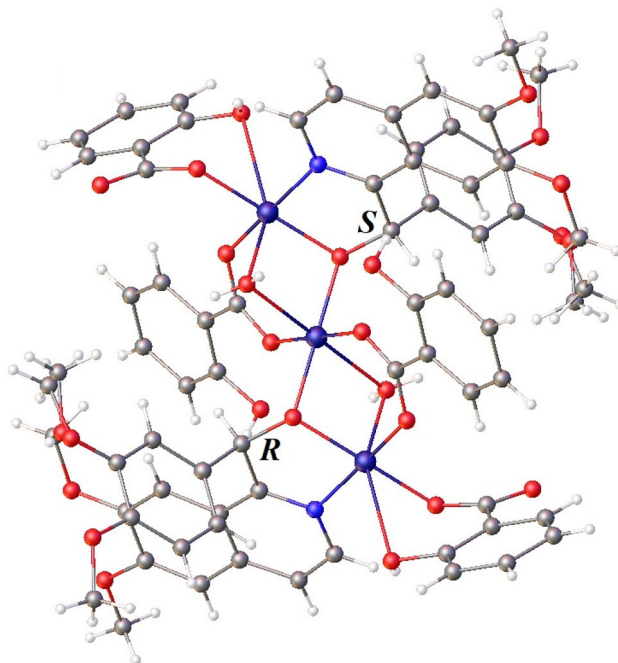
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Graphical Abstract

A new N,O bonded ligands, (*R*, *S*)-[(6,7-dimethoxy-isoquinolin-1-yl)-(3,4-dimethoxy-phenyl)-methanolate] coordinate the terminal atoms of the trinuclear copper(II) complex.

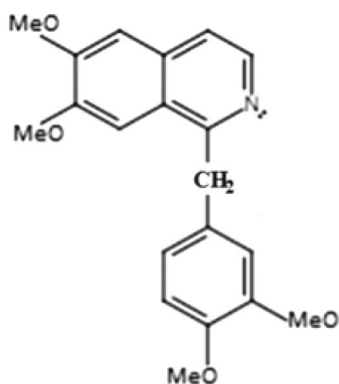


Keywords Trinuclear copper(II) complex · Crystal structure · Carboxylate · Magnetic properties · Structure correlation · Inner coordination

Introduction

Structurally Closely Related Alkaloids to Papaverine

(1-[(3,4-dimethoxyphenyl)methyl]-6,7-dimethoxyisoquinoline) are important pharmacological drugs and biologically active compounds [1–3]. The molecule of papaverine (Scheme 1) is unstable toward oxygen and can be oxidized easily to papaverinol and papaveraldine



Scheme 1 Molecule of papaverine

[4–7]. However, the crystal structure of papaverine hydrochloride [8] is composed of relatively stable nonoxidized papaverine molecules. The formation of copper complexes with the potential ligands contained in human organisms can cause many changes in cells [9]. To our knowledge, until now, with papaverine, only the crystal structure of the binuclear complex $[\text{Zn}_2(\text{C}_6\text{H}_5\text{COO})_4(\text{pap})_2]$ (pap = papaverine) was resolved [10]. Carboxylic copper(II) complexes may be mononuclear, binuclear, tetranuclear, or polynuclear [11–14].

Chemical coordination [15] defined by Werner [16] is an array of atoms surrounding the central atom because of chemical bonding. In transition element complexes, the atoms often interact with the central atom very weakly. In the quantum chemical definition, atomic valence is a measure of the degree of electron sharing of the given atom with the other atoms [17]. According to the residual valency of an atom, the atoms in a molecule may be subvalent, normal, or hypervalent [18]. Such classification deviates from the traditional valence of an atom in the crystal structure. It suggests using the atomic valence approximated by the bond valence sum as a parameter that is as close as possible to the integral value or “formal oxidation number” [19, 20].

The valence of a bond is the measure of interaction between electrons sharing the bonding of atoms. For the amorphous materials, the coordination spheres were limited [21, 22]. Beyond the distance, to the central atom around 6 Å, the refined parameters of dependence bond valence vs. interatomic distance do not change [23, 24]. Introducing chemical considerations, the concept of coordination requires estimating if an atom of a coordination array is bonded to the central atom or not. If such an atom significantly influences the interatomic distances of the remaining atoms of the array, it is primary bonded to the central atom.

For the big family of copper complexes, the concept of coordination sphere plasticity [25] and equatorial-axial influence [26] reflect such influence *via* the central atom. Both effects are manifested in structural correlations of bond distances within the chromophores of transition element compounds. The structural correlations of coordination compounds with CuO₆ and CuN₆ chromophores approach the asymptotical values with the shortest equatorial bond length at around 1.9 Å [25]. Small changes in coordination polyhedra may cause significant changes in a hydrogen-bonding network [27]. In most cases, electronic distortions do not violate the valence sum rule [28, 29]. Importing dynamic features into molecular chemistry requires shifting from “static” to “dynamic” covalent bonds leading from molecular to constitutional dynamic chemistry [30].

As the magnetic properties of linearly arranged trinuclear hydroxy-bridged copper(II) complexes studied by the methods of density functional theory (DFT) showed, the angle Cu–O–Cu and out-of-plane displacement of the hydrogen atoms at the bridge are the key magnet factors that determine their magnetic behavior [31]. The magneto-structural study of binuclear copper(II) benzoates shows the dominance of antiferromagnetic spin interaction between metallic centers through bridging carboxylates over direct Cu...Cu interaction [32, 33]. These facts suggest the crucial structural influence of copper-ligand interactions within the coordination polyhedra of the central and terminal metallic centers. Here we report the crystal structure and magnetic properties of a novel compound consisting of trinuclear copper entities containing the alkaloid derived from papaverine.

Experimental Section

Preparation of Crystals

The light green product of the entitled compound was prepared by heating papaverine (0.01 mol) with Cu(2-HOC₆H₄COO)₂·2H₂O (0.01 mol) in hot water and methanol. The mixture was stirred, filtered, and then left at room temperature. The solid product of the reaction was collected and recrystallized from hot methanol to give air-stable pale

blue-turquoise crystals. The analytical data found/calculated are 12.42/12.54% (Cu), 53.40/53.74% (C), 4.40/4.6% (H), and 1.93/1.84% (N).

Crystal Structure Solution and Refinement

Single crystal data collection was performed on a STOE diffractometer at 100 K. Crystal data and structure refinement details are summarized in Table 1. The structure of **1** was solved by the program SHELXS [34]. The structure was drawn by OLEX2 [35]. The refinements were carried out by SHELXL [36]. OMe group and water molecules disordered in two positions were refined under the constraint of their occupancy sums to unity. Positions of all hydrogen atoms were optimized under the constraint to ride on their parent atoms, with C–H bond length of 0.93 Å and O–H bond length of 0.82 Å.

Magnetic Measurements

Magnetic measurements were performed by a SQUID magnetometer MPMS-XL7 from Quantum Design in the RSO mode of detection. The temperature dependence of magnetic moment was recorded at 0.1 T as an external magnetic field and the temperature sweeping rate was set to 1 K/min. The magnetic susceptibility of the polycrystalline sample was

Table 1 The crystal data and details of crystal structure determination of **1**

Chemical formula	C ₆₈ H ₆₄ Cu ₃ N ₂ O ₂₄ ·2(H ₂ O)
<i>M_r</i>	1519.89
Crystal system, space group	Triclinic, <i>P</i> -1
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.3322(1), 13.4417(2), 13.6606(2)
α, β, γ (°)	104.349(1), 111.855(1), 96.685(1)
<i>V</i> (Å ³)	1659.36(4)
<i>Z</i>	1
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	1.857
Crystal size (mm)	0.48 × 0.16 × 0.15
Absorption correction	Numerical
<i>T</i> _{min} , <i>T</i> _{max}	0.469, 0.768
No. of measured, independent, and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	64,315, 6353, 6328
<i>R</i> _{int}	0.022
(sin Θ/λ) _{max} (Å ⁻¹)	0.654
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.047, 0.131, 1.160
No. of reflections	6356
No. of parameters	510
No. of restraints	28
Δρ _{max} , Δρ _{min} (eÅ ⁻³)	1.44, -0.82

measured by the Faraday method in the temperature range of 77–300 K. The mercury tetracyanato cobalt(II) was used as a calibrant [37].

Calculation Details

Bond Valence Calculations

...For idealized copper hexacoordination of four equidistant equatorial in-plane Cu–N, O₃ bonds and two equidistant out-of-plane Cu–O'₂ bonds (chromophore CuNO₃O'₂) the quantities r_L , r_S were defined. r_S is the length of in-plane (equatorial) bonds and r_L is the length of out-of-plane (axial) bonds. The bond valence sum (BVS) distribution was calculated as the sum of equatorial and axial contributions:

$$BVS(r_S, r_L) = 3s_{Cu-O}(r_S) + s_{Cu-N}(r_S) + 2s_{Cu-O}(r_L) \quad (1)$$

where s_{Cu-O} and s_{Cu-N} are the bond valence functions for Cu–O and Cu–N bonds [38]:

$$s(r) = \frac{\alpha_1}{r} + \frac{\alpha_2}{r^2} + \frac{\alpha_3}{r^3} + \frac{\alpha_4}{r^4} + \frac{\alpha_5}{r^5} \quad (2)$$

If BVS is kept constant, the contour of the function expressed by Eq. (1) with inserted Eq. (2) gives the dependence of r_L vs. r_S . For the idealized copper coordination of the chromophore Cuⁿ⁺NO₃O'₂ this dependence is

$$r_L = R_{o,Cu(n)-O} - b \ln [n - s_{Cu-N}(r_S) - 3s_{Cu(n)-O}(r_S)] + b \ln(2) \quad (3)$$

where parameter n is the formal charge of a copper cation, $R_{o,Cu(n)-O}$ is the bond valence parameter of a copper-oxygen bond, and s_{Cu-N} , $s_{Cu(n)-O}$ are the functions [39]:

$$s(r) = \exp [(R_o - r)/b] \quad (4)$$

The empirical bond-valence parameters R_o and b were used from the latest version of <http://www.iucr.org/resources/data/datasets/bond-valence-parameters>. Equation (4) is appropriate for ionic, covalent, and intermediate ionic-covalent bonding, respectively [40]. The predicted axial Cu–O'(2×) bond length of the copper coordination of Cu²⁺O₄O'₂ chromophore was calculated as a numerical solution of the Eqs. [41, 42]:

$$(BVS_{eq} - 2)r^5 + 2\alpha_1 r^4 + 2\alpha_2 r^3 + 2\alpha_3 r^2 + 2\alpha_4 r + 2\alpha_5 = 0 \quad (5)$$

where BVS_{eq} is the bond valence sum of equatorial Cu–O bonds calculated by Eq. (2). α_i are the parameters of the function (2) for Cu–O bonds.

Magnetic Measurements

The correction for the diamagnetism of the constituent atoms was calculated by Pascal's constants [43]. The effective magnetic moments were calculated using the equation:

$$\mu_{eff} = 2.83(\chi_M^{corr} \cdot T)^{0.5} \quad (6)$$

To assess the values of magnetic exchange parameters the broken-symmetry DFT approach was employed. Major –O–CH₃ (OMe) groups were used in calculations. The magnetic parameters were used in the form $-J_{ij}\hat{S}_i\hat{S}_j$. The final values of magnetic parameters were extracted using the adapted Eq. (7) of Yamaguchi and co-workers, for broken symmetry (BS) and high spin (HS) states [44, 46]:

$$J = (E_{BS} - E_{HS}) / (\langle \hat{S}^2 \rangle_{HS} - \langle \hat{S}^2 \rangle_{BS}) \quad (7)$$

The fitting of the magnetic susceptibility and magnetization in **1** was performed with the program.

PHI 3.1.1 [47]. Before the quantum-chemistry calculations, the positions of all hydrogen atoms were optimized using the method PBEh-3c [48]. All other atoms were kept in their positions as obtained from the crystal structure investigation. Calculation of magnetic exchange parameters was carried out within the program ORCA 4.2.0 [49, 50]. The second-order Douglas–Kroll–Hess correction (DKH2) [51] and the chain-of-spheres approximation (RIJCOSX) [52] were set on. For all atoms, accounting for scalar relativistic effects Ahlrichs's basis set DKH-def2-TZVP [53] was used with an auxiliary basis set def2/J [54]. The magnetic exchange parameters were obtained from DFT calculation utilizing the hybrid functional B3LYP [55–58]. In all calculations, the increased integration and fitting grids were used (grid6 and gridx6 in ORCA convention).

Results and Discussion

Crystal Structure

The crystal structure of compound **1** is composed of the tri copper units [Cu₃(C₇H₅O₃)₄(C₂₀H₂₀NO₅)₂(H₂O)₂] (**2**) presented in Fig. 1 and noncoordinated water molecules.

Selected bond lengths and angles are collected in Table 2. *N*, *O*-bonded(6,7-dimethoxyisoquinolin-1-yl)-(3,4-dimethoxyphenyl)-methanolato ligand in this work is named papaverinyloxy ligand. The trinuclear unit shows chirality at C16. One OMe group attached to the phenyl ring is disordered in two positions of an occupancies ratio of 0.777(3)/0.223(3). The second OMe group is partially stabilized by the hydrogen bond.

OW2–HW4⋯O10, while its relative free methyl group is split in two positions of an occupancies ratio 0.500(3)/0.500(3). The noncoordinated water molecules of oxygens

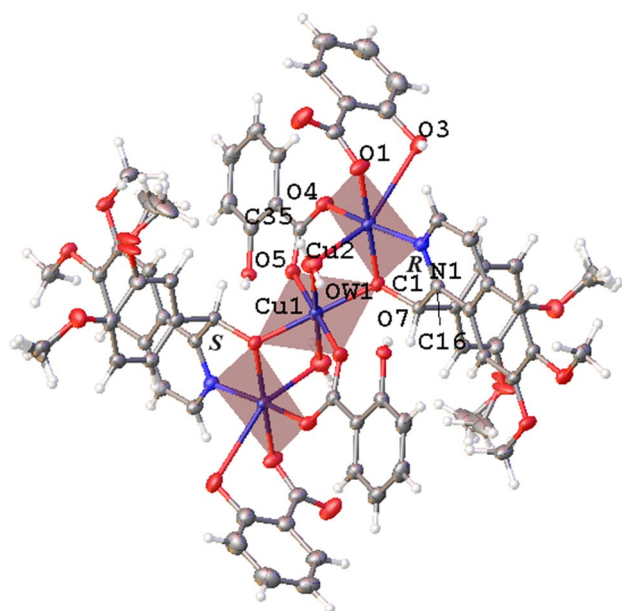


Fig. 1 The structure of complex **2** with the numbering of nonhydrogen atoms. The displacement ellipsoids are drawn at the 50% probability level. The equatorial mean planes of copper coordination polyhedra are shaded. The relative configuration at the C16 centers [59] is mentioned

Table 2 Selected geometric parameters (Å, °) of the complex **2**

Cu1–O5	1.940(2)	Cu2–O4	1.945(2)
Cu1–O7	1.959(2)	Cu2–N1 ⁱ	1.970(2)
Cu1–OW1	2.496(2)	Cu2–OW1	2.442(2)
Cu2–O1	1.925(2)	Cu2–O3	2.873(2)
Cu2–O7 ⁱ	1.930(2)	O5–Cu1–O7	91.43(1)
OW1–Cu1–O5	102.61(1)	O1–Cu2–O4	91.10(1)
N1–Cu2–O7	83.48(1)	O1–Cu2–O3	64.43(1)
N1–Cu2 ⁱ –O3	92.65(1)	Cu1–O7–Cu2 ⁱ –O3 ⁱ	147.6(8)
Cu1–O7–Cu2 ⁱ –O1 ⁱ	–74.8(1)	Cu1–OW1 ⁱ –Cu2 ⁱ –O3 ⁱ	–152.3(6)
Cu1–OW1 ⁱ –Cu2 ⁱ –O1 ⁱ	160.0(6)		

Symmetry code: (i) $-x+1, -y+1, -z+2$.

OW2, and OW3 are disordered in two crystal sites with an occupancy ratio of 0.730(6)/0.270(6). The isoquinoline and phenyl rings of the papaverinyloxy ligand are significantly deviated from planarity. The angle between the least-squares planes of isoquinoline ring and the phenyl ring is 87.19(7)°. In papaverine hydrochloride, the corresponding angle is 80.13(8)°.

In the structure of salicylic acid [60] the corresponding deviation is 0.0012(1) Å. The phenyl rings of 2-hydroxybenzoates do not deviate from planarity. But the atoms O6 of hydroxyl groups deviate from the least-squares planes

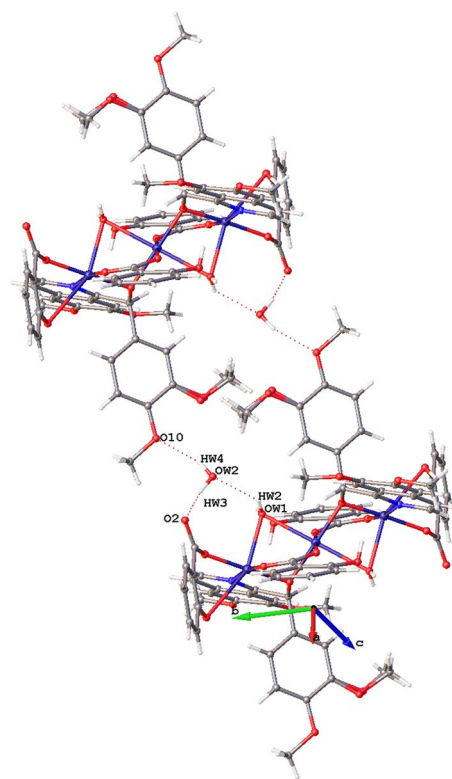


Fig. 2 Schematic drawing of intermolecular hydrogen bonding in the crystal structure of **1**

of phenyl rings by 0.054(2) Å. The complex units **2** are connected *via* hydrogen bonds of OW2 water molecules connected into the infinite chains along [011] direction (Fig. 2). The phenyl rings of adjacent symmetry-related 2-hydroxybenzoates assemble the complex units *via* $\pi\cdots\pi$ stack interactions [61, 62] into the chains along the [010] direction (Fig. 3). The hydrogen bond lengths are presented in Table 3.

The inter-centroid distance and parallel shifts of phenyl rings are 3.7379(1) Å and 1.66901(5) Å. Slightly distorted *trans*-square coordination of Cu1 is created by two in-plane carboxylic O atoms and two oxygens of papaverinyloxy ligands. The five-membered ring containing Cu2 is slightly deviated from the planar geometry. The torsion angle N1–C1–C16–O7 is 18.3(3)°. The Cu2–O3 bond stabilizes the copper coordination of the 2-hydroxybenzoato ligand while the atom O2 remains free.

The coordination polyhedron around Cu2 can be described as a distorted tetragonal bipyramid. The equatorial bonds of its inner coordination are Cu2–N1ⁱ, O1, O4, and O7ⁱ. The greatest deviation from the least-squares plane defined by the donor atoms is shown by atom N1ⁱ [0.079(2) Å]. Atom Cu2 is displaced from the basal plane toward the atom OW1 by 1.1406(1) Å. The hexacoordination of atom Cu2 is completed by the axial bonds Cu2–OW1

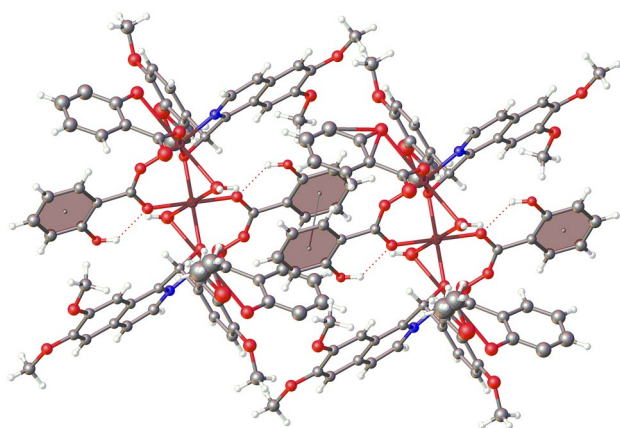


Fig. 3 Schematic drawing of interaromatic $\pi\cdots\pi$ interactions in the crystal structure of **1**. Only the intramolecular hydrogen bonds and OMe groups of major occupancies are presented

Table 3 Hydrogen-bond geometry (\AA , $^\circ$) of **1**

D-H \cdots A	D-H	H \cdots A	D \cdots A	D-H \cdots A
OW1-HW1 \cdots O5 ⁱ	0.771(3)	2.810(4)	2.430(2)	111.8(2)
OW1-HW2 \cdots OW2	0.879(3)	1.827(4)	2.698(5)	170.8(2)
OW2-HW3 \cdots O2	0.849(3)	2.018(3)	2.807(4)	154.2(2)
OW2-HW4 \cdots O10 ⁱⁱ	0.850(3)	2.077(2)	2.840(4)	159.8(2)

Symmetry code: (i) $-x+1, -y+1, -z+2$; (ii) $-x, -y+1, -z+1$

and Cu2-O3 of 2.445(2) \AA and 2.872(2) \AA , respectively. The angle formed by the Cu2-O3 bond and the basal least-squares plane of the coordination polyhedron around Cu2 is 83.56(5) $^\circ$.

Bond Valence Analysis

For copper atom valence 2+, the predicted lengths of Cu1-OW1 bonds calculated by Eq. (5) is 2.50(2) \AA which does not deviate significantly from the experimental bond length of 2.497(2) \AA . The coordination of Cu1 is completed by two out-of-plane water O atoms to an axially distorted tetragonal bipyramid of chromophore CuO₄O'₂. The bond valence sum of Cu1 calculated by formulae (2) is 2.05(2) v. u. Figure 4 shows the contour graph of the copper atom valence (BVS) for idealized copper coordination of CuNO₃O'₂ chromophore. The numeric labels of isolines are the BVS values which are kept constant for relevant r_L vs. r_S dependence. The maximum bond lengths are $r_S(\text{max}) = 2.92(1)$ \AA and $r_L(\text{max}) = 3.07(3)$ \AA .

For those distances, the contributions of equatorial and axial bonds to BVS in Eq. (1) yield zero values. In the regions of distances, the $r_S > r_S(\text{max})$ and $r_L > r_L(\text{max})$ these contributions are negative. The bond lengths $r_S(\text{max})$ and $r_L(\text{max})$ are the supreme limits of bonding

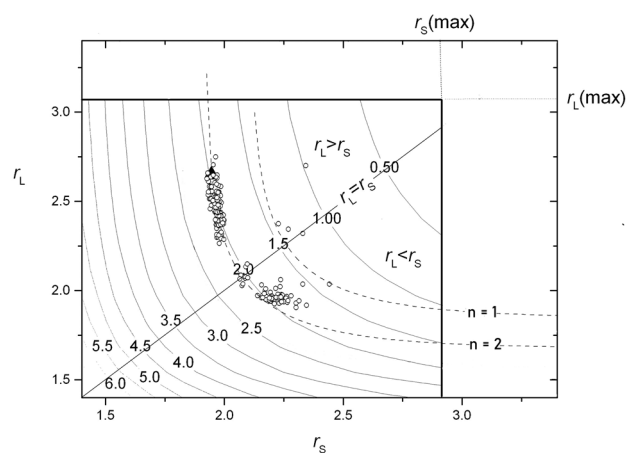
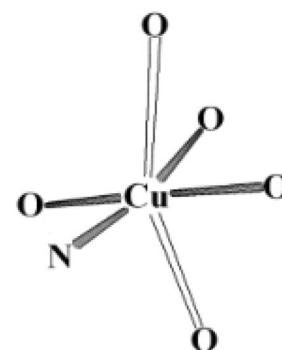


Fig. 4 Diagram r_L vs. r_S (in \AA) for the copper complexes of chromophore CuNO₃O'₂ compared with the calculated r_L vs. r_S dependences. Solid lines - contour graph of the function expressed by the Eqs. (1) and (2). Dashed lines - BVS functions expressed by the Eq. (3). \circ - model structures retrieved in CSD. \blacktriangle - the structure of **1**. Spearman rank-order correlation coefficient [63] is -0.844

distances within the inner copper coordination. If the bond valence sum of a copper atom is kept constant, any increase in the distance r_S causes a decrease of r_L and *vice versa*, i.e. such distortion of the inner coordination is plastic. 293 independent r_S , r_L values of the structures retrieved in CSD [64, 65] were approximated by the means of equatorial bond lengths (R_S) and axial bond lengths (R_L) [66]. The model structures were identified by the connectivity shown in Scheme 2. The standard atomic radii and tolerances of CSD were used. Only the non-disordered structures with an R-factor less than 0.05 were accepted. The structures were inspected by the program ORTEP-3 for Windows [67]. REFCODES of model structures with R_S and R_L values are included in the Supplementary Information. The best approach to the contour line and the graph of Eq. (3) for the copper oxidation state 2.0 show points in the region $r_L \geq r_S$. The weak bonds Cu2-O3 are included in the inner coordination of Cu2. The bond valences of these bonds calculated by Eq. (2)

Scheme 2 The inner coordination of the model structures



are 0.14(1) and 0.030(7) v.u. The bond valence sum of Cu2 is 2.08(1) v. u.

Magnetic Properties

In the trinuclear complex unit, three magnetic exchange pathways are to be considered: Pathways between the metallic centers Cu2...Cu1, Cu1...Cu2ⁱ and the pathway between more distant terminal copper atoms Cu2...Cu2ⁱ (Fig. 1). The resulting parameters of magnetic interaction are $J_{12}=J_{23}=+75.8\text{ cm}^{-1}$, and $J_{13}=+0.4\text{ cm}^{-1}$. The resulting Mullikan spin densities are collected in Table 4.

As apparent, the DFT calculation predicts strong ferromagnetic interaction between adjacent centers in contrast with negligible interaction between the terminal copper centers. The resulting values were used as input for the following analysis of experimental magnetic functions of **1**. The temperature and field dependence of magnetic functions are presented in Fig. 5.

The increase of susceptibility product at low temperatures indicates the presence of ferromagnetic exchange interaction, while the sudden decrease below 10 K can be ascribed to the intermolecular antiferromagnetic interaction

Table 4 Mullikan spin densities for individual broken symmetry spin states of **1**

BS state	$\rho(\text{Cu}2)$	$\rho(\text{Cu}1)$	$\rho(\text{Cu}2^i)$
$\beta\alpha\alpha$	-0.6550	0.6790	0.6570
$\alpha\beta\alpha$	0.6552	-0.6786	0.6552
$\alpha\alpha\beta$	0.6570	0.6790	-0.6550

Symmetry code: (i) $-x+1, -y+1, -z+2$

(molecular field). The magnetic functions were analyzed according to the following spin Hamiltonian [68]:

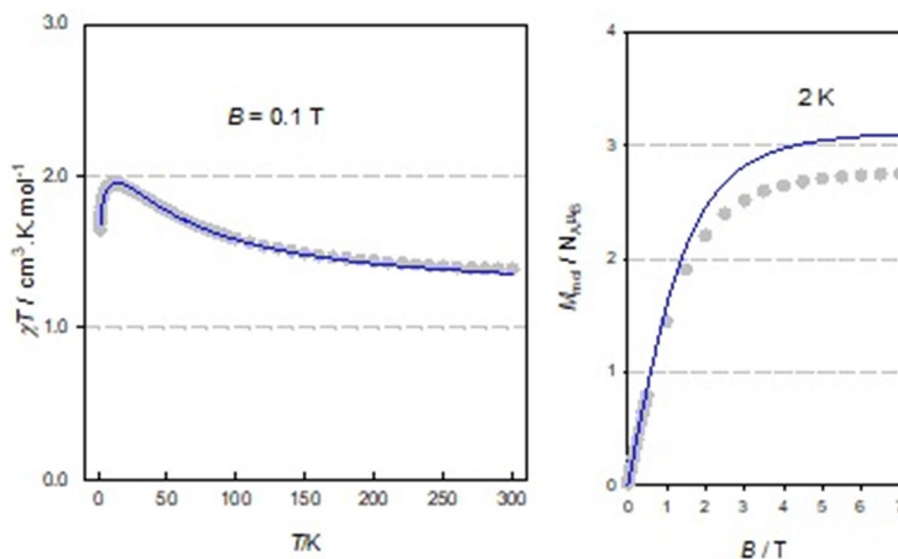
$$\hat{H} = -J_{12}\hat{S}_1\hat{S}_2 - J_{23}\hat{S}_2\hat{S}_3 + m_B g_i \hat{S}_{iz} - zJ\hat{S}_i \quad (8)$$

where m_B is the Bohr magneton, g_i is the average value of the individual g -factors, \hat{S}_{iz} is the projection of the spin operator of the i -th center, and zJ is the parameter of the molecular field. The two parameters of magnetic exchange interaction were fixed equal and the parameter between the terminal copper center Cu2 and Cu2ⁱ was completely omitted based on the DFT assessment (*vide supra*). The constraint $g_1=g_3$ is due to the symmetry of complex **2**. As can be seen, the fitted and calculated values of magnetic exchange interaction are in very good agreement. The g -factors of the magnetic centers gain typical values for copper(II) centers.

Conclusions

The trinuclear 2-hydroxybenzoato copper(II) complex with (6,7-dimethoxy-isoquinolin-1-yl)-(3,4-dimethoxy-phenyl)-methanol has been prepared and characterized. The copper atoms of the centrosymmetric trinuclear complex **2** are hexacoordinated. The novel *N, O*-bonded(6,7-dimethoxyisoquinolin-1-yl)-(3,4-dimethoxyphenyl)-methanolato (papaverinyloxy) ligands are bidentate. One-half of 2-hydroxybenzoates connect atoms Cu1 and Cu2 *via* bridging -COO groups. The remaining 2-hydroxybenzoates are bonded to the atoms Cu2 by the oxygens of nonbridging carboxylate groups. The positions of their phenyl rings are stabilized by the weak bonding of Cu2 atoms with the hydroxyl groups. A significant difference in Cu1 and Cu2 coordination geometries is consistent with the plasticity of the inner copper coordination of

Fig. 5 The optimum fit of magnetic functions (solid lines) of compound **1**. Experimental values are shown by circles



$\text{CuO}_4\text{O}'_2$ and $\text{CuNO}_3\text{O}'_2$ chromophores. The supreme limit for the equidistant equatorial bonds of the last chromophore is 2.92(1) Å. For the equidistant axial bonds, the supreme limit is 3.07(3) Å. If $R_L \geq R_S$, the dependence R_L vs. R_S of copper inner coordination of $\text{Cu}^{n+}\text{NO}_3\text{O}'_2$ chromophore can be approximated by Eq. (3). The magnetism of complex **2** can be well explained by strong ferromagnetic interaction between the neighboring magnetic centers *via* the dominant pathways Cu1–O5–C35–O4–Cu2, Cu1–O7–Cu2¹, and Cu1–OW1–Cu2. The plasticity of inner copper coordination and the papaverinyloxy ligand facilitate the formation of the trinuclear copper complex **2**. By the copper activation of a papaverine methyl C–H bond, the hydrogen atom is replaced with bridging oxygen.

Supplementary Information

X-ray crystallographic data for the title compound (CCDC No.1999284) have been deposited with the Cambridge Crystallographic Data Center (<http://www.ccdc.cam.ac.uk/>). The datasets generated during and/or the current study are available from the corresponding author upon reasonable request.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10870-024-01009-2>.

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Author Contributions FV solved and refined the crystal structure and constructed the structure correlations, JP and IŠ interpreted the data of magnetical measurements and quantum mechanical calculations, MM prepared the single crystal, JK refined the final structure model, FV and JP wrote the manuscript together.

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Data Availability The authors declare that all other data supporting the findings of this study are available within the article and its supplementary information files.

Declarations

Competing Interests The authors declare no competing interests.

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