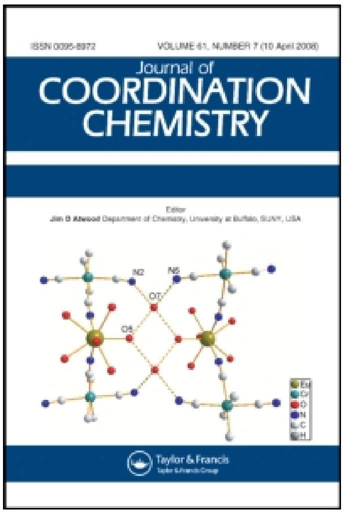

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Synthesis, crystal structure and magnetic properties of a novel tripeptide Schiff base heterotrinuclear complex with 1D supramolecular structure

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Synthesis, crystal structure and magnetic properties of a novel tripeptide Schiff base heterotrinuclear complex with 1D supramolecular structure

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A novel tripeptide Schiff-base heterotrinuclear complex, $[Co(H_2O)_4(CuL)_2]\cdot 4H_2O$ (**1**) ($H_3L = $ N-5-bromosalicylideneglycylglycylglycine) has been synthesized and characterized by elemental analyses, IR and electronic spectra. Single-crystal X-ray diffraction analysis showed that the molecular structure is made up of centrosymmetrical trinuclear units with the Co atom lying on an inversion center. Through $Cu\cdots O$ and $Cu\cdots Br$ weak interactions and hydrogen bonds, the 1D supramolecular chain structure is formed. The magnetic susceptibility data (2–300 K) revealed antiferromagnetic interactions between copper(II) ions and the central metal cobalt(II) ions. The magnetic susceptibility data were quantitatively analyzed using the theoretical expressions deduced from the spin Hamiltonian for a symmetrical three-spin system $\hat{H} = -2J\hat{S}_{Co}(\hat{S}_{Cu(1)} + \hat{S}_{Cu(2)})$ to give the coupling $J_{CuCo} = -2.26\,cm^{-1}$.

Keywords: Heterotrinuclear complex; Tripeptide; Weak interactions; Crystal structure; Magnetic properties

1. Introduction

Rational design of supramolecular polymeric architectures has attracted considerable interest due to their potential applications in the fields of catalysis, conductivity, non-linear optical and molecular magnetic materials and host–guest chemistry [1–6]. The most useful strategy to assemble such systems is employing appropriate multidentate bridging ligands capable of binding metal ions either by strong covalent interactions or supramolecular interactions, including hydrogen bonding, π–π stacking, and $M\cdots X$ ($X = S$, O, Br, I) contacts [7–14]. We are exploring Schiff-base complexes derived from simple peptides, which may act as ligands to bind other metal ions *via* carboxylate groups and capable of forming hydrogen bonds and $M\cdots O$ interactions to give heteropolymetallic supramolecular extended frameworks. The present article

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contributes to the synthesis, crystal structure, and variable-temperature magnetic behavior of the heterotrinuclear copper(II)–cobalt(II)–copper(II) complex with $[CuL]^-$ as ligands, namely $[Co(H_2O)_4(CuL)_2]\cdot 4H_2O$ (**1**) (H_3L = N-5-bromosalicylideneglycylglycylglycine).

2. Experimental

2.1. *Materials and synthesis*

The tripeptide, glycylglycylglycine was purchased from Sigma and used without further purification. All other reagents and solvents were purchased from commercial sources and were analytical grade.

2.1.1. Synthesis of mononuclear Cu(II) complexes ($K[CuL]\cdot H_2O$). The mononuclear precursor $[CuL]^-$ was obtained as described [15] by replacing salicylaldehyde with 5-bromosalicylaldehyde. Anal. Calcd for $K[Cu(C_{13}H_{11}N_3O_5Br)]\cdot H_2O$ (%): C, 31.88; H, 2.68; N, 8.58. Found: C, 31.42; H, 2.80; N, 8.40. IR (KBr, cm^{-1}): 3425s, 1643s, 1591s, 1378m, 1302m. ESI-MS: m/z 432.9 for $[CuL]^-$.

2.1.2. Synthesis of the trinuclear complex $[Co(H_2O)_4(CuL)_2]\cdot 4H_2O$ (1). An aqueous solution (5 mL) of $Co(NO_3)_2\cdot 6H_2O$ (1 mmol, 291 mg) was added to a solution of K[CuL] H_2O (2 mmol, 980 mg) in 20 mL of water with constant stirring at 25°C for 30 min and then filtered. The filtrate was allowed to evaporate slowly at room temperature. After several days violet red crystals, suitable for X-ray diffraction, were obtained. Anal. Calcd for $C_{26}H_{38}N_6O_{18}BrCoCu_2$ (**1**) (%): C, 31.59; H, 3.87; N, 8.50. Found: C, 31.52; H, 3.95; N, 8.44. FTIR (KBr; cm^{-1}): 3423s, 1642s, 1620s, 1376m, 1537m, 1292m. UV-Vis (in H_2O) λ_{max} nm ($\varepsilon/L\,mol^{-1}\,cm^{-1}$): 364 ($5.3\times10^3$), 591 ($2.6\times10^2$).

2.2. *Physical measurements*

The IR spectra were recorded on KBr discs on a Bruker Vector 22 spectrophotometer in the 400–4000 cm^{-1} region. The UV-Vis spectra were recorded with a Shimadzu UV-3100 spectrophotometer. Elemental analyses (C, H, N) were obtained using a Perkin-Elmer 240C elemental analysis instrument. Electrospray mass spectra were recorded on a LCQ system (Finnigan MAT, USA) using methanol/water as the mobile phase. Variable-temperature magnetic susceptibilities were performed on a Quantum Design MPMS SQUID magnetometer down to 2 K. Diamagnetic corrections for the constituent atoms were made using Pascal's constants.

2.3. *X-ray structure determination*

The diffraction experiments were carried out on a Bruker AXS SMART APEX CCD diffractometer. Data were collected with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using SMART and SAINT programs [16]. Absorption corrections were calculated and applied for the structure by using SADABS [17]. The structure was solved by direct methods and non-hydrogen atoms were anisotropically refined

Table 1. Crystal data and structure refinement for $[Co(H_2O)_4(CuL)_2]\cdot 4H_2O$ (**1**).

Empirical formula	$C_{26}H_{38}N_6O_{18}BrCoCu_2$
Formula weight	1068.45
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	8.885(1)
b (Å)	9.524(2)
c (Å)	11.175(2)
α (°)	85.650(10)
β (°)	81.730(10)
γ (°)	82.180(10)
V (Å^3)	925.6(3)
Z	1
D_{Calcd} (Mg m^{-3})	1.917
μ (Mo-Kα) (cm^{-1})	3.824
T/K	293(2)
F(000)	535.0
Crystal size (mm^3)	0.30 × 0.20 × 0.20
Theta range for data collection	2.7–25.0
Index ranges	$-10 \le h \le 8$, $-11 \le k \le 11$, $-11 \le l \le 13$
Reflections collected	4645
Independent reflections	3212
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3212/0/250
R_{int}	0.0456
R_1 [$I > 2\sigma(I)$]	0.0532
wR_2	0.0909
Goodness-of-fit on F^2	0.955
Largest difference: peak and hole (e Å^{-3})	0.85 and −0.78

by full-matrix least-squares based on F^2 using SHELXTL [18]. All hydrogen atoms were included in the refinement in calculated positions riding on their carrier atoms. The hydrogen thermal displacement parameters were fixed at 1.2 and 1.5 times the equivalent isotropic thermal displacement parameters of their internal and terminal carrier atoms, respectively. A summary of the data collection and structure refinement is listed in table 1.

3. Results and discussion

3.1. *Description of the crystal structure*

The complex is a centrosymmetric trinuclear unit with the L ligand bound to Cu(II). An ORTEP diagram of **1** with numbering scheme is shown in figure 1. Selected bond lengths and angles are listed in table 2.

The compound crystallizes in the centrosymmetric space group $P\bar{1}$ with the cobalt(II) atom located on the center of symmetry. The Schiff-base ligand acts as a triple negatively charged quadridentate ONNO chelate and coordinated to the Cu(II) atom *via* one phenolic oxygen (Cu(1)–O(1) = 1.875(4) Å), one imino nitrogen atom

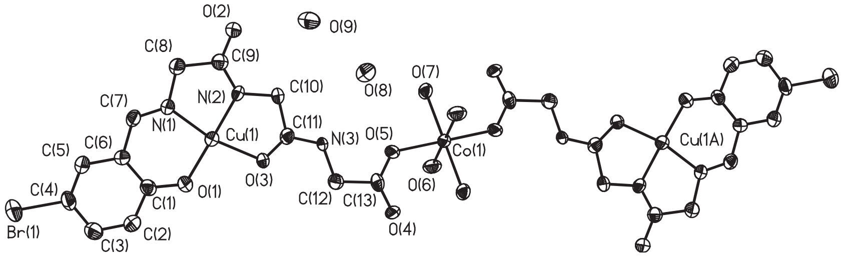

Figure 1. ORTEP view of the trinuclear molecule in **1**. The thermal ellipsoids are drawn at the 30% probability level.

Table 2. Selected bond distances [Å] and angles [°] for **1**.

Co1–O5	2.035(5)	Cu1–O3	2.007(4)
Co1–O6	2.098(4)	Cu1–N2	1.899(5)
Co1–O7	2.131(4)	Cu1–N1	1.940(5)
Cu1–O1	1.875(4)	Cu1 $\cdots$ O7^a	2.590(4)
Cu1 $\cdots$ Br1^b	3.795(2)		
O6–Co1–O7	92.1(2)	O1–Cu1–N2	175.8(2)
O5–Co1–O7	88.6(2)	O1–Cu1–O7^a	86.8(2)
O6–Co1–O7^c	88.0(2)	O3–Cu1–N1	166.4(2)
O5–Co1–O7^c	91.4(2)	O3–Cu1–N2	83.2(2)
O5–Co1–O6	87.7(2)	O3–Cu1–O7^a	87.0(2)
O5–Co1–O6^c	92.3(2)	N1–Cu1–N2	83.6(2)
Cu1^b–O7–Co1	123.8(2)	O7^a–Cu1–N1	97.9(2)
O1–Cu1–O3	97.0(2)	O7^a–Cu1–N2	97.4(2)
O1–Cu1–N1	95.9(2)		

Symmetry transformations used to generate equivalent atoms: ^{a} $-1+x, y, z$; ^{b} $1+x, y, z$; ^{c} $2-x, -y, 1-z$).

(Cu(1)–N(1) = 1.940(5) Å), one deprotonated amide nitrogen atom (Cu(1)–N(2) = 1.899(5) Å) and one carbonyl oxygen atom (Cu(1)–O(3) = 2.007(4) Å). The carbonyl oxygen atoms O(3) are preferred to the peptide nitrogen atoms N(3) as metal binding sites at pHs where the amide proton of the peptide is not dissociated, are reported in the tripeptide complexes of Cu(gly-gly-gly)$^+$ [19], Cu(gly-leu-tyr)$^+$ [20], [Ru(glyglyglyH$_{-1}$)(PPh$_3$)]$_2$ [21].

The copper(II) atom is in a slightly distorted square-planar environment with four donor atoms deviating from their mean plane by +0.0028 Å (N(1)), −0.0031 Å (N(2)), −0.0024 Å (O(1)) and +0.0027 Å (O(3)) (observed bond angles vary from 83.2(2) and 97.2(2)°). The values 1.468(8) Å for the C(8)–N(1) bond, shorter than the usual C–N single bond, and 1.265(8) Å for the double bonds C(7)–N(1) are in good agreement with the values of Schiff-base type I [22]. The phenyl ring [C(1)–C(6)] and the chelate ring O(1), C(1), C(6), C(7), N(1), Cu(1) make a small dihedral angle of 1.7°, suggesting a large π-electron delocalization.

The cobalt is in a distorted octahedral environment, ligated by two carboxylate oxygen atoms (O(5)) arising from two [CuL]$^-$ units and four aqua ligands. The cobalt cation connects the two [CuL]$^-$ groups together *via* two monodentate carboxylate ligands in a syn-anti mode to form a trinuclear Cu(II)–Co(II)–Cu(II) unit with Cu $\cdots$ Co distances of 8.545 Å.

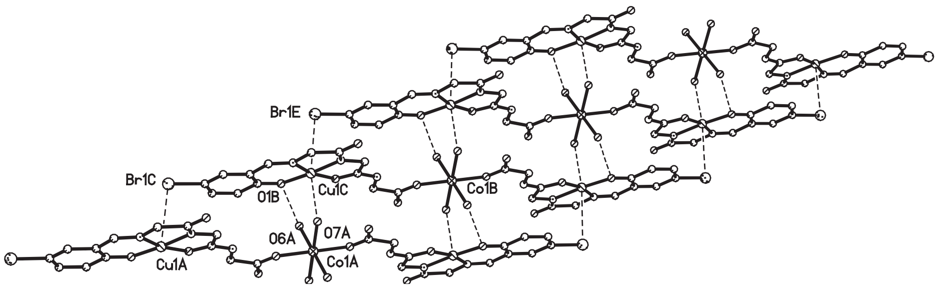

Figure 2. View of the 1D infinite chain jointed together *via* Cu···O, Cu···Br weak interactions and H-bonds.

Table 3. Selected Hydrogen-bond distances [Å] and angles [°] for **1**.

D–H···A	*r*(D–H) (Å)	*r*(H···A) (Å)	*r*(D···A) (Å)	α(D–H···A) (Å)	Symmetry operation
N3–H3A···O5	0.860	2.200	2.577(7)	106.00	
N3–H3A···O8	0.860	2.230	3.072(7)	166.00	
O6–H6C···O1	0.850	2.744	2.802(6)	77.34	$1+x, y, z$
O6–H6A···O2	0.850	2.140	2.818(6)	136.00	$1+x, -1+y, z$
O6–H6C···O3	0.850	2.510	3.232(6)	144.00	$1+x, y, z$
O7–H7B···O4	0.850	2.320	2.688(6)	106.00	$2-x, -y, 1-z$
O7–H7C···O8	0.850	2.250	2.678(6)	112.00	
O8–H8D···O9	0.850	2.160	2.887(6)	144.00	
O8–H8E···O2	0.850	2.060	2.770(6)	141.00	$1-x, 1-y, 1-z$
O9–H9C···O4	0.850	2.010	2.652(7)	132.00	$x, 1+y, z$
O9–H9D···Br1	0.850	2.890	3.414(6)	122.00	$-x, 1-y, -z$
C10–H10B···O9	0.970	2.540	3.161(8)	122.00	

Comparing with a Cu(II)–Cd(II)–Cu(II) heterotrinuclear complex previously published [15], the structures are similar in the coordination modes of Cu(II) and Co(II) or Cd(II) atoms. Because of the effect of the substituent –Br, the Cu(II)–Co(II)–Cu(II) complex packs in a different manner. Adjacent trinuclear units are linked together through two weak bonds (Cu···O(7), 2.590(4) Å; Cu···Br(1), 3.795(2) Å) at the axial sites of Cu(II), complemented by O(6)–H···O(1) hydrogen bonds, resulting in a 1D polymeric chain with the intrachain Cu···Co distances of 4.170 Å in the solid as depicted in figure 2. The adjacent chains are further linked together through O(6)–H···O(2) hydrogen bonds and supported by other O–H···O and N–H···O hydrogen bonds in the crystal structure (table 3). The amide N(3)–H of the ligand forms hydrogen bonds to O(5) of carboxylate group and O(8) of the lattice water. The ligand water and the lattice water molecules also participate in hydrogen bonding with carbonyl oxygen, carboxylate oxygen, other water molecules, or phenolic oxygen atoms, which allows the compound to form a 3D network structure.

3.2. *IR and electronic spectra*

The IR absorption of **1** at 3423 cm^{-1} confirms the presence of lattice or coordinated water for the compounds [23, 24]. The sharp band at 1642 cm^{-1} is characteristic of the ν(C=N) Schiff base imino group. The band at 1620 cm^{-1} is assigned to the asymmetric vibration of coordinated carboxylate group [$\nu_{as}(COO^-)$] and the band at $1376\,cm^{-1}$ is attributed the symmetric stretching vibration of carboxylate group [$\nu_s(COO^-)$]. The large difference between [$\nu_{as}(COO^-)$] and [$\nu_s(COO^-)$] in frequencies ($\Delta\nu > 200\,cm^{-1}$) is indicative of monodentade coordination of the carboxylate [25–27]. The band around $1292\,cm^{-1}$ can be assigned to ν(C–O) of phenolic group in the complex [24]. A medium band at $1537\,cm^{-1}$, present in the compound, may originate from the vibration of the ν(Ph–)C–C(=N) bond.

Electronic absorption spectra of complex 1 were measured in aqueous solutions. The complex exhibits a very intense band at 364 nm, assignable to charge-transfer transitions (CT) in the Cu(II) chromophores [28]. The d–d transition spectra of the complex show a broad band centered at 591 nm more consistent with square-planar geometries about Cu(II) complexes [29, 30].

The d–d transitions of octahedral [CoO_6] should also be observed in the above ranges. In the present case, the spectrum in the visible range is dominated by the d–d bands of [CuN_2O_2] and the bands arising from Co(II) cannot be assigned.

3.3. *Magnetic properties*

The magnetic behavior of complex **1** is shown in figure 3 in the form a $\chi_M T$ versus T plot. At 300 K, $\chi_M T$ is equal to $3.38\,cm^3\,mol^{-1}\,K$, which is higher than the sum of the contributions of the isolated Cu(II)Co(II)Cu(II) trinuclear ions ($2.63\,cm^3\,mol^{-1}\,K$). On lowering the temperature $\chi_M T$ gradually decreases, reaches a minimum around 2 K with $\chi_M T$ of $1.68\,cm^3\,mol^{-1}\,K$. These features are typical of Cu(II)–Co(II)–Cu(II) systems with an antiferromagnetic interaction, and indicates that $S = 3/2$ state of cobalt(II) is antiferromagnetically coupled to the terminal $S = 1/2$ state of copper(II) ion.

The magnetic analysis was then carried out by using the theoretical expression of the magnetic susceptibility deduced from the spin Hamiltonian: $\hat{H} = -2J\hat{S}_{Co}(\hat{S}_{Cu(1)} + \hat{S}_{Cu(2)})$. The expression of the magnetic susceptibility for the

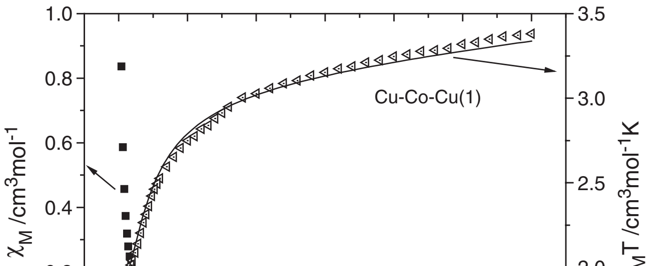

Figure 3. χ_M *vs.* T and $\chi_M T$ *vs.* T plots for the complex **1**. The solid line represents the best fit (see text for the parameters).

Cu(II)–Co(II)–Cu(II) system is

$$\chi_{\rm M} = \frac{Ng^2\beta^2}{4k(T-\theta)}\left[\frac{10\exp(-5J/kT)+10\exp(-2J/kT)+35\exp(3J/kT)}{\exp(-5J/kT)+2\exp(-2J/kT)+2\exp(3J/kT)+2}\right]+N_\alpha$$

where J is the exchange integral between Co(II) and Cu(II) ions; N_α is the temperature-independent paramagnetism. The best-fit parameters are $J=-2.26\,\mathrm{cm}^{-1}$, $g=2.06$, $\theta=-3.86$, and $N_\alpha=0.0009\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$. The agreement factor $R=\sum(\chi_{\rm obsd}-\chi_{\rm cacld})^2/\sum\chi_{\rm obsd}^2$ is 3.7×10^{-3}.

The negative J value suggests the interaction between the central Co^{2+} ion and the outer Cu^{2+} ions is weak antiferromagnetic. $\theta < 0$, indicates a weak antiferromagnetic perhaps through the Cu $\cdots$ O(7)–Co–O(7A) $\cdots$ Cu weak interactions and hydrogen bonds [31–33].

Supplementary material

Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 267144. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk) or also from the author.

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