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Synthesis, structural characterization and magnetic properties of new tripeptide Schiff base heterotrinuclear Cu(II)–M(II)–Cu(II) (M = Ni and Mn) complexes

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Abstract

Two novel heterotrinuclear Cu(II)-M(II)-Cu(II) (M = Ni and Mn) complexes, $[Ni(H_2O)_4(CuL)_2]\cdot 7H_2O$ (**1**), $[Mn(H_2O)_4(CuL)_2]\cdot 8H_2O$ (**2**), have been obtained by the self-assembly of the mononuclear tripeptide Schiff base complexes $[CuL]^-$ with bivalent metal ion M^{2+}, where H_3L = *N*-salicylideneglycylglycylglycine. Single crystal X-ray diffraction experiments indicate that the structures both **1** and **2**, are made up of centrosymmetric trinuclear units with the M atom lying on an inversion center, formed the 1D supramolecular chain structures via hydrogen bondings and M···O weak interactions. The magnetic susceptibility data (2–300 K) revealed antiferromagnetic interactions between copper(II) ions and the central metal. The magnetic susceptibility data were quantitatively analyzed using the theoretical expressions deduced from the spin Hamiltonian for a symmetrical three-spin system $\hat{H} = -2J\hat{S}_M(\hat{S}_{Cu(1)} + \hat{S}_{Cu(2)})$ to give the coupling parameters $J_{CuNi} = -0.46\ cm^{-1}$ and $J_{CuMn} = -0.15\ cm^{-1}$.

Keywords: Heterotrinuclear complexes; Tripeptide; Schiff base complexes; Magnetic properties

1. Introduction

Heteropolymetallic complexes are of current interest due to their importance in the study of magnetic exchange and charge transfer between metal ions, in the designing of new magnetic materials, such as molecular-based magnets and in the area of the bioinorganic chemistry for their potential use as models for the active site of many metalloproteins [1–9], especially when the bridging group between the metal ions is of biological relevance, such as imidazolate, carboxylate, etc. One of the best strategies to design heteropolymetallic species is the 'complex as ligand' approach [10–14], that is to say, metal complexes containing potential donor atoms for another metal ion or metal complex with empty coordination sites.

Recently, we have designed several tetradentate tripeptide Schiff base ligands [15], which is able to accommodate a copper(II) ion at the inner ONNO coordination site, leading to the mononuclear complexes $[CuL]^-$. It is noteworthy that these complexes contain unbridged carboxylate groups so that they can act as potential 'ligands' to bind other metal ions to give the heterometallic trinuclear complexes. Here we report the synthesis, structures, and magnetic properties of two novel heterotrinuclear copper(II)–M(II)–copper(II) complexes where M are Ni(II) and Mn(II) ions. Their formulas are $[Ni(H_2O)_4(CuL)_2]\cdot 7H_2O$ (**1**) and $[Mn(H_2O)_4(CuL)_2]\cdot 8H_2O$ (**2**), (H_3L = *N*-salicylideneglycylglycylglycine).

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. The mononuclear

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precursor K[CuL]$\cdot$2H_2O was prepared as described elsewhere [15].

2.1.1. Caution

Although we have not encountered any problems, it should be kept in mind that perchlorate salts of metal complexes are potentially explosive and should be handled with care.

2.1.2. Synthesis of trinuclear complex [Ni(H_2O)$_4$(CuL)$_2$]$\cdot$7H_2O (**1**)

An aqueous solution (5 ml) of Ni(ClO_4)$_2\cdot$6H_2O (1 mmol, 366 mg) was added to a solution of K[CuL]$\cdot$2H_2O (2 mmol, 858 mg) in 20 ml of water with constant stirring at 25 °C for half an hour and then filtered.. The filtrate was allowed to evaporate slowly at room temperature. After several days violet red crystals, which were suitable for X-ray diffraction, were obtained. *Anal.* Calculated. for $C_{26}H_{46}N_6O_{21}NiCu_2$ (**1**): C, 32.38; H, 4.81; N, 8.71%. Found: C, 32.58; H, 4.80; N, 8.81%. *IR* (KBr cm^{-1}): 3339 s, 1652 s, 1597 s, 1546 m, 1387 m, 1292 m. UV–Vis (in H_2O, λ_{max}): 366 nm, 587 nm.

2.1.3. Synthesis of trinuclear complex [Mn(H_2O)$_4$(CuL)$_2$]$\cdot$8H_2O (**2**)

The complex **2** was prepared in the same way as **1**, using Mn(ClO_4)$_2\cdot$6H_2O instead of Ni(ClO_4)$_2\times$6H_2O. Violet red crystals were obtained by slow evaporation of the resulting solution at room temperature. Anal. Calcualted for $C_{26}H_{48}N_6O_{22}MnCu_2$ (**2**): C, 31.91; H, 4.94; N, 8.59. Found: C, 31.40; H, 4.85; N, 8.73%. FTIR (KBr cm^{-1}): 3417 s, 1649 s, 1625 s, 1396 m, 1543 m, 1283 m. UV–Vis (in H_2O, λ_{max}): 352 nm, 588 nm.

2.2. Physical measurements

The IR spectra were recorded as KBr discs on a Bruker Vector 22 spectrophotometer in the 400–4000 cm^{-1} region. The UV–Vis spectra were measured 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 carried out using 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 was 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 K_α radiation (λ=0.71073 Å) using SMART and SAINT program [16]. Absorption corrections were calculated and applied for each structure by using SADABS [17]. The structures were solved by direct methods and non-hydrogen atoms were anisotropically refined 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.

Table 1
Crystal data and structure refinement

	[Ni(H_2O)$_4$(CuL)$_2$]$\times$ 7H_2O (**1**)	[Mn(H_2O)$_4$ (CuL)$_2$]$\cdot$8H_2O (**2**)
Empirical formula	$C_{26}H_{46}N_6O_{21}NiCu_2$	$C_{26}H_{48}N_6O_{22}MnCu_2$
Formula weight	964.48	978.74
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	8.911(2)	8.916(2)
b (Å)	9.609(2)	9.685(2)
c (Å)	12.552(2)	12.676(3)
α (°)	70.240(10)	70.320(10)
β (°)	76.250(10)	75.490(10)
γ (°)	78.170(10)	77.270(10)
V(Å^3)	973.3(3)	986.6(4)
Z	1	1
D_{calc} (Mg m^{-3})	1.645	1.647
μ (Mo Kα) (cm^{-1})	1.650	1.474
T/K	293(2)	293(2)
F(000)	498.0	505.0
Crystal size (mm^3)	0.3$\times$0.15$\times$0.10	0.30$\times$0.20$\times$0.10
Theta range for data collection	2.3 to 25.0	2.3 to 25.0
Index ranges	$-10\leq h\leq 8$, $-10\leq k\leq 11$, $-12\leq l\leq 14$	$-10\leq h\leq 10$, $-10\leq k\leq 11$, $0\leq l\leq 15$
Reflections collected	4903	4965
Independent reflections	3374	3424
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	3374/0/259	3424/0/259
R_{int}	0.0418	0.0248
R_1 [I>2sigma(I)]	0.0521	0.0527
wR_2	0.1175	0.1196
Goodness-of-fit on F^2	1.028	1.016
Largest difference: peak and hole (e Å^{-3})	0.50 to $-$0.38	0.32 and $-$0.28

3. Results and discussion

3.1. Description of the crystal structures

3.1.1. Structure of the complex **1**

The structure of **1** consists of a neutral centrosymmetric trinuclear [Ni(H_2O)$_4$(CuL)$_2$] unit and water molecules. A perspective view is given in Fig. 1 and selected bond lengths and angles are listed in Table 2.