Inorganica Chimica Acta 413 (2014) 194-202

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Phenoxo bridged tetranuclear copper(II) and dinuclear zinc(II) complexes of 2,6-diformyl-4-methylphenol-di(benzoylhydrazone): Synthesis, structure, spectra and magnetism



Inorganica Chimica Acta



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ARTICLE INFO

Article history: Received 9 September 2013 Received in revised form 4 January 2014 Accepted 6 January 2014 Available online 23 January 2014

Keywords: Cu(II) and Zn(II) 2,6-DiformyI-4methylphenol-benzhydrazide Tetranuclear copper(II) X-ray structure Fluorescence VTM and EPR

ABSTRACT

Phenoxo bridged tetranuclear Cu(II) and dinuclear Zn(II) complexes are synhesized namely, Cu₄[(L)₂ (OCH₃)₂] (**1**) and Zn₂(HL)₂ (**2**) (H₃L = [(HOC₆H₂CH₃){2,6-(CH=N-N=C(OH)(C₆H₅))(CH=N-N=C(OH)(C₆H₅))]) and characterized by FTIR, UV–Vis, ¹H NMR, fluorescence and mass spectrometry. Single crystal X-ray diffraction analysis of **1** shows that the Cu atom possesses a square pyramid environment *via* bridging of 'phenolato'-O and 'enolato'-O of the ligand, additional bridging of 'methanolato'-O of coordinated CH₃OH and monodentate coordination of imine-N. The EPR spectrum of **1** are characterized by $g_{\parallel} = 2.286$, $A_{\parallel} = 169 \times 10^{-4}$ cm⁻¹, $g_{\perp} = 2.068$, $A_{\perp} = 17 \times 10^{-4}$ cm⁻¹ (298 K) and $g_{\parallel} = 2.283$, $A_{\parallel} = 178 \times 10^{-4}$ cm⁻¹, $g_{\perp} = 2.072$, $A_{\perp} = 15 \times 10^{-4}$ cm⁻¹ (77 K). The study of the variable temperature magnetic properties agrees with a predominant intramolecular antiferromagnetic coupling (2J = -186.5 cm⁻¹), rendering a ground state of *S* = 0.

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1. Introduction

Schiff base ligands have been extensively studied in coordination chemistry mainly due to their facile syntheses, easily tuneable steric, electronic properties and good solubility in common solvents [1–5]. Transition metal complexes with oxygen and nitrogen donor Schiff bases are of particular interest [6,7] because of their ability to possess unusual configurations, be structurally labile and their sensitivity to molecular environments [8]. Considerable effort has been devoted to the design, synthesis and modification of such complexes, obtained by the appropriate choice of metal ions and ligands and a detailed examination of their structure– function correlation helps to develop new synthetic routes to molecular magnetism [9–11]. Especially, Cu(II) complexes are of particular interest from both structural and functional points of view. Multinuclear Cu(II) complexes are useful from the standpoint of magneto-structural correlations [12,13]. The coordination sphere around the Cu(II) ion can be modulated relatively easily, and the stereochemical diversity has led to the isolation of a number of copper(II)-phenolato complexes [14-18]. A phenolato ion bridges two Cu(II) centers providing an exchange pathway that results in strong antiferromagnetic coupling. The Cu(II)-phenolato complexes exhibit coordination numbers ranging from 4 to 6, as is typical for the coordination chemistry of Cu(II). The phenolates in most of these compounds are usually incorporated as a part of multidentate ligand systems [19-21]. In this regard, the discrete tetranuclear clusters, cubane like oxygen-bridged Cu₄O₄ polynuclear complexes (Scheme 1, [2+4], [4+2], [6+0]) received special attention. Correlations between the structural parameters and magnetic properties for oxygen-bridged copper binuclear complexes or pseudodimeric copper cubanes ([2+4]) are well established [22–25]. In the case of dinuclear complexes containing a Cu₂O₂ core from alcoxo or hydroxo bridges, Hatfield, Hodgson and co-workers [22] established that the primary geometric factor determining the magnitude of exchange coupling was the Cu–O–Cu bridging angle (θ). The larger the θ angle, the stronger the antiferromagnetic coupling between the copper(II) ions.



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Scheme 1. Tetranuclear copper cubane.

Accordingly, double-open cubane containing a Cu_4O_6 core (4 in Scheme 1) are scarcely described in literature [26–28] and, therefore, their magnetic properties are even less known.

The ability to simply and independently vary the steric and electronic properties of a given ligand may provide a wealth of opportunities to influence reactivity, stability, structural and other important properties at the metal center. Hence, following our continuous interest in the development on transition metal derivatives incorporating Schiff base precursors, we have selected 2,6-diformyl-4-methylphenol-di(benzoylhydrazone) (H₃L), first developed by Robson [29,30] and the corresponding copper complexes of this ligand were reported by Sakamoto et al. [31]. On CSD search, we have observed that some copper and lanthanide complexes with same or related ligand have been published [32–35]. Phenoxo-bridged Zn complexes are still very less reported [36,37].

In this work, the ligand 2,6-diformyl-4-methylphenol-di(benzoylhydrazone) (H₃L), a multidentate ONONO donor [31,33] was used in order to synthesize the double-open cubane $Cu_4[(L)_2$ (OCH₃)₂] (**1**). In addition, the coordination ability of the ligand towards zinc was also tested, allowing to isolate the dinuclear $Zn_2(HL)_2$ (**2**) complex. The results achieved are described herein.

2. Experimental

2.1. Materials

All chemicals and solvents used here were of reagent grade and used as received. $Cu(NO_3)_2 \cdot 3H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ were purchased from Merck, India. Benzhydrazide, 4-methylphenol and formaldehyde were purchased from Aldrich Chemicals, India. 2,6-Diformyl-4-methylphenol-di(benzoylhydrazone) (H₃L) (see Scheme 2) synthesized following published procedure [31].

2.2. Physical measurements

Microanalytical data (C, H, and N) were collected on Perkin– Elmer 2400 CHNS/O elemental analyzer. FTIR spectra were recorded on a Perkin-Elmer RX-1 spectrophotometer in the range 4000–400 cm⁻¹ as KBr pellets. Electronic spectra were measured on a Lambda 25 (UV–Vis–NIR) spectrophotometer in methanol. Thermal analysis was carried out at a heating rate of 10 °C/min with a Mettler-Toledo Star TGA/SDTA-851e thermal analyzer system in a dynamic atmosphere of N₂ (flow rate 30 ml/min) in an alumina crucible for the range 25–350 °C. Emission spectra were examined by LS 55 Perkin–Elmer spectrofluorometer at room temperature (298 K) in different solution under degassed condition. The fluorescence quantum yield of the complexes was determined using carbazole as a reference with known ϕ_R of 0.42 in benzene [38]. The complex and the reference dye were excited at same wavelength, maintaining nearly equal absorbance (~0.1), and the emission spectra were recorded. The area of the emission spectrum was integrated using the software available in the instrument and the quantum yield is calculated according to the following equation:

$$\frac{\phi_{\rm S}}{\phi_{\rm R}} = \left[\frac{{\rm A}_{\rm S}}{{\rm A}_{\rm R}}\right] \times \left[\frac{({\rm Abs})_{\rm R}}{({\rm Abs})_{\rm S}}\right] \times \left[\frac{\eta_{\rm S}^2}{\eta_{\rm R}^2}\right]$$

Here, $\phi_{\rm S}$ and $\phi_{\rm R}$ are the fluorescence quantum yield of the sample and reference, respectively. A_S and A_R are the area under the fluorescence spectra of the sample and the reference, respectively, $(Abs)_{S}$ and $(Abs)_{R}$ are the respective optical densities of the sample and the reference solution at the wavelength of excitation, and η_{s} and $\eta_{\rm R}$ are the values of refractive index for the respective solvent used for the sample and reference. Fluorescence lifetimes were measured using a time-resolved spectrofluorometer from IBH. UK. The instrument uses a picoseconds diode laser (NanoLed-03, 370 nm) as the excitation source and works on the principle of time-correlated single photon counting [39]. The goodness of fit was evaluated by γ^2 criterion and visual inspection of the residuals of the fitted function to the data. EPR spectra were recorded from 0 to 10000 Gauss in the temperature range 77–298 K with an X-band (9.15 GHz) Varian E-9 spectrometer. EPR parameters reported in the text for the solid polycrystalline compound were obtained by simulating the spectra with the computer program Bruker WinEPR SimFonia [40]. In all the simulations, second-order effects were taken into account and the ratio Lorentzian/Gaussian, affecting the line shape, was set to 1. Magnetic susceptibility measurements of a powder crystalline sample of **1** were carried out at the Unitat de Mesures Magnètiques of the Universitat de Barcelona, with a Quantum Design SQUID MPMS-XL susceptometer. The magnetic susceptibility data were recorded in the 2-300 K temperature range under a magnetic field of 10000 G. Diamagnetic corrections were estimated from Pascal's Tables [41]. The agreement factor is based on the function $R = \sum (\chi_M T_{exp} - \chi_M T_{cal})^2 / \sum (\chi_M T_{exp})^2$. ESI mass spectra were recorded on a micro mass Q-TOF mass spectrometer (serial No. YA 263). The estimation of Cu and Zn are performed by titrimetric and complexometric assay, respectively.

2.3. Preparation of the complexes

2.3.1. Synthesis of $Cu_4[(L)_2(OCH_3)_2]$ (1)

To a methanol solution (10 ml) of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.482 g, 2 mmol), the ligand H₃L (0.400 g, 1 mmol) was added with constant stirring. The resulting green solution was kept undisturbed at room temperature. Dark-green square-shaped single crystals of **1** were generated after one week. These were separated over filtration and air-dried before X-ray diffraction analysis. Yield: 0.183 g (66%). *Anal.* Calc. for C₄₈H₄₀Cu₄N₈O₈: C, 51.84; H, 3.63; N, 10.08; Cu, 22.86. Found: C, 52.38; H, 3.43; N, 10.49; Cu, 22.31%.

2.3.2. Synthesis of Zn₂(HL)₂ (2)

Similar procedure was applied as mentioned in **1**, using $Zn(NO_3)_2 \cdot 6H_2O$. A yellow colored precipitate was afforded. Yield: 67%. *Anal.* Calc. for $C_{46}H_{36}Zn_2N_8O_6$: C, 59.54; H, 3.91; N, 12.08; Zn, 14.11. Found: C, 58.67; H, 3.82; N, 12.20; Zn, 13.73%. ¹H NMR, 300 MHz, d_6 -DMSO: 11.71 ((O=C-)NH^s); 8.94 (8'-H s); 8.51



Scheme 2. The syntheses of H₃L and its complexes.

(8-H s); 8.06 (13, 17-H d, J = 4.5); 7.91 (13'-Hd, J = 8.37); 7.76 (17'-Hd, J = 7.56); 7.60 (4-H s); 7.55 (6-H s). 14,14'-16,16H protons appear as multiplate at δ 7.1–7.53 ppm; 2.2 (5-CH₃,s) (s = singlet; d = doublet; e = multiplet).

2.4. X-ray crystallography

X-ray quality single crystals of **1** were isolated from slow evaporation of reaction mixture. The crystals of **2** were unstable to X-ray diffraction. Details concerning crystal data, data collection characteristics and structure refinement are summarized in Table 1. Single crystal of **1** ($0.25 \times 0.18 \times 0.15 \text{ mm}^3$) was mounted on glass fibers with epoxy cement. The crystal data collection was performed at room temperature with an automated Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo K α radiation. The ω :2 θ scan technique was applied within a θ range of 2.23–27.54°. A total of 17881 reflections were collected of which 5018 were independent [R_{int} = 0.022]. Structure wqs solved by direct methods [42], full-matrix least squares refinement [43] based on F^2 and 307 parameters. Hydrogen atoms were constrained to ride on the respective carbon or nitrogen atoms with isotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement of their parent atom in all cases. The largest difference Peak and hole are 0.499 and $-0.377 \text{ e} \text{ Å}^{-3}$, respectively and C–H varies 0.93–0.96 Å. All calculations were carried out using SHELXS 97 [42], SHELXL 97 [43] and PLATON 99 [44] program.

3. Results and discussion

3.1. Synthesis and characterization

The reaction between 2,6-diformyl-4-methylphenolato-di-(benzoylhydrazone) (H₃L) and Cu(NO₃)₂·3H₂O yielded green crystals of tetranuclear Cu₄[{(μ_2 -OC₆H₂C₃H₃)(2,6-CH=N-N=C(O)(C₆H₅)₂)}₂ (μ_3 -OCH₃)₂] (**1**) while using Zn(NO₃)₂·6H₂O, a dinuclear complex Zn₂[(μ -OC₆H₂CH₃){2,6-(CH=N-N=C(O)(C₆H₅))(CH=N-NH-C(O)(C₆ H₅))}]₂ (**2**) was isolated. In the mass spectrum of **1** the most abundant ion is 555.03, attributable to [Cu₂L.OMe]⁺ (calculated *m/z*: 555.4) and the next abundant ions are 462 ([CuH₂L]⁺ calculated *m/z*: 460.9), 862.2, ([Cu(H₂L)₂]⁺ calculated *m/z*: 862.3), 925.15 ([Cu₂(HL)₂]⁺ calculated *m/z*: 923.8), 1079 ([Cu₄L₂.OMe]⁺ calculated

Table 1Crystallographic data of **1**.

5 6 1	
Empirical formula	$C_{48}H_{40}Cu_4N_8O_8$
Formula weight	1111.04
Temperature	293(2)
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	ΡĪ
a (Å)	8.317(5)
b (Å)	9.357(5)
c (Å)	14.734(5)
α (°)	79.394(5)
β (°)	80.992(5)
γ (°)	81.651(5)
Volume (Å ³)	1105.1(10)
Ζ	1
$D_{\text{calc}} (\text{mg m}^{-3})$	1.669
μ (Mo K α) (mm ⁻¹)	1.965
F(000)	564
Reflections collected	17881
Independent reflections $[R_{int} = 0.022]$	5018
Final R indices $[I > 2\sigma(I)]^{a,b}$	$R_1 = 0.0286, wR_2 = 0.0806$
Goodness-of-fit on F ²	1.047

 $_{1}^{a} R_{1} = \sum ||F_{0}| - |F_{c}|| / \sum |F_{0}|.$

^b $wR_2 = \left[\sum_{v} w(F_0^2 - F_c^2)^2 \right]^{1/2} \le w(F_0^2)^{2}$, $w = 1/\left[\sum_{v} 2(F_0)^2 + (0.0439P)^2 + (0.5317P)\right]$ where $P = (F_0^2 + 2F_c^2)/3$.

m/z: 1079.8), and 1109.6 corresponding to molecular ion $[Cu_2(L) (OMe)]_2^+$ (calculated *m/z*: 1111). The complex **2** is detected through the ion peak *m/z* 465.1 corresponds to $[Zn(HL)]^+$ (calculated *m/z*, 463.8); and next ions are *m/z* 929.1, 401.2 corresponding to the molecular ion $[Zn(HL)]_2^+$ (calculated *m/z*, 927.6) and H₃L (calculated *m/z*, 400.4) respectively. The ¹H NMR spectrum of H₃L shows singlet signals at δ 12.31 and 12.13 ppm for –OH and –NH protons,

respectively; singlet at δ 7.55 ppm refer to 4-H and 6-H protons. In addition, one singlet signal at δ 8.70 ppm is assigned to -CH=Nproton. Furthermore, one doublet and two multiplets appear for the protons of $-C(0)-C_6H_5$ group at δ 7.93 (having coupling constant, J = 7.2 Hz), 7.59 and 7.51 ppm, respectively. The NMR spectrum of **2**, does not exhibit resonance corresponding to $\delta(OH)$; this suggests deprotonation on phnolato-O and coordination to Zn(II). Phenolato aromatic-Hs, 4- and 6-H, are not equivalent (as it is observed in H_3L) and assign at δ 7.60 and 7.55 ppm, respectively which indicates unsymmetrical binding. The resonance of $\delta(NH)$ is drastically shifted to up field region (8.94 ppm), in comparing with H₃L. The protons in **2** show resonance comparable with free ligand. The single crystal X-ray diffraction analysis confirms the tetranuclear derivative of Cu(II) (1). Based upon Mass and NMR data, the expected structure of compound 2 is shown in Scheme S1. The IR spectrum of H₃L shows two sharp vibrations at 1650 and 1547 cm⁻¹ which may be assigned for (C=O) and (C=N) stretchings, respectively. In both the complexes, the v(C=0) band shifts to 1620 cm⁻¹ whereas v(C=N) band switches to 1559 and 1562 cm⁻¹ for **1** and **2**, respectively [45]. The free ligand shows sharp band at 3400, 3237 and 3059 cm⁻¹ that can be designated to the stretching frequencies of v(OH) for phenol, v(NH) for hydrazone and v(=C-H), respectively. The electronic spectrum is recorded in HPLC grade dimethyl formamide. For H₃L, the absorption bands at 302, 363 and 447 nm are attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions [46]. In the copper(II) complex, **1**, the $\pi \rightarrow \pi^*$ band is shifted to 333 from 302 nm whereas $n \rightarrow \pi^*$ band is moved to 400 nm. Furthermore, the d-d transitions are appeared at 427 and 700 nm [47]. We have ascertained two intense absorption peaks in complex 2; the band at 303 nm corresponds intra-ligand charge transfer and another intense band at 407 nm, may be assigned to MLCT [37] transition.



Fig. 1. Molecular structure of complex 1. Ellipsoids are drawn at the 40% probability label.

Table 2
Selected bond lengths (Å) and angles (°) for 1.

Cu(1)-O(1)	1.9400(15)	Cu(1)-O(2)	1.9329(15)
Cu(1) - O(4)	1.9369(16)	Cu(1) - N(1)	1.9061(19)
Cu(2) - O(1)	1.9163(16)	Cu(2) - O(4)	1.9331(15)
Cu(2)-O(3)	1.8996(17)	Cu(2)-N(3)	1.9067(18)
O(1)-Cu(1)-O(2)	O(1)-Cu(1)-O(4)	O(1)-Cu(1)-N(1)	
174.15(7)	80.00(6)	91.55(7)	
O(1)-Cu(1)-O(4)	O(2)-Cu(1)-O(4)	O(2)-Cu(1)-N(1)	
93.13(6)	105.55(6)	82.72(7)	
O(2)-Cu(1)-O(4)	O(4)-Cu(1)-N(1)	O(4)-Cu(1)-O(4)	
89.31(6)	169.37(7)	84.51(6)	
N(1)-Cu(1)-O(4)	O(1)-Cu(2)-O(4)	O(1)-Cu(2)-O(3)	
102.52(6)	80.69(7)	173.53(7)	
O(1)-Cu(2)-N(3)	O(1)-Cu(2)-O(2)	O(4)-Cu(2)-O(3)	
92.66(7)	95.08(6)	103.80(7)	
O(4)-Cu(2)-N(3)	O(4)-Cu(2)-O(2)	O(3)-Cu(2)-N(3)	
173.33(7)	82.61(6)	82.81(7)	
O(3)-Cu(2)-O(2)	N(3)-Cu(2)-O(2)	Cu(1)-O(1)-Cu(2)	
90.17(6)	98.47(6)	99.73(7)	
Cu(1)-O(1)-C(1)	Cu(2)-O(1)-C(1)	Cu(1)-O(2)-C(9)	
130.2(1)	129.4(1)	108.3(1)	
Cu(1)-O(2)-Cu(2)	Cu(1)-O(4)-Cu(2)	Cu(1)-O(4)-Cu(1)	
90.15(6)	99.24(7)	95.49(6)	
Cu(2)-O(4)-Cu(1)	Cu(1)-N(1)-N(2)	Cu(2)-N(3)-N(4)	
97.57(6)	114.2(1)	113.9(1)	

3.2. Crystal structure of 1

The molecular structure of the tetranuclear copper compound is shown in Fig. 1. Relevant bond lengths and angles are given in Table 2. The geometric center of the molecule lies on a crystallographic inversion center. The coordination environment around each copper is distorted square pyramidal with NO₄ donor sites. This square-pyramid geometry is evident from the τ value (an index parameter of the degree of trigonality, $\tau = 1$ for an ideal trigonal bipyramid, $\tau = 0$ for an ideal square pyramid) [48] of 0.08. The dimer is assembled via μ_2 -phenolato oxygen of L³⁻ with two adjacent copper centers and a bridging methanolato-O; thus overall charge of dimer is balanced. Two dimeric units are then combined by μ_2 -O atoms of adjacent deprotonated enolato form of two units of ligands and also *via* deprotonated μ_3 -O methanol. There are five Cu₂O₂ "squares" formed in the structure. In the molecule, the Cu(1)–Cu(2) distance (μ_2 -phenolato) is 3.3169(10) Å which is lower than similar complexes found in the literature [31-33,49].



Fig. 3. Emission spectra of (a) H₃L (in DMF) and (b) complex 2 (in CH₂Cl₂).

Noticeably, $[Cu(\mu_3-OCH_3)_2Cu]$ forms a square with Cu(1)— Cu(1A) separation of 3.2676(17) Å. The μ_2 -enolato O atom bridged Cu(1)—-Cu(2) distance is 2.9481(9) Å which is well comparable with previously reported doubly phenolato-bridged copper complexes [50], where Cu–Cu separation lies in the range, 2.901–3.345 Å. The Cu–O–Cu angle is 99.73(7)°, disposing Cu–O distances 1.940(15) and 1.916(16) Å which are comparable with similar bond distances, [1.922(4) and 1.941(4) Å] of literature report [31]. The Cu-O-Cu angle lies in the range of 90.15-99.73° which shows relatively lower in comparing with literature data [31,49,51], where θ lies in the range of 95.7–107.5° [52,53]. The Cu–O–Cu angles of the Cu_2O_2 core consisting of Cu(1), Cu(2), O(1), and O(4) are 99.73(7)° (phenolic) and 99.24(7)° (methoxide) which is comparable with similar phenoxo-bridged copper complex, 99.3(2)° (phenolato) and 101.8(2)° (methoxide) [31]. The packing view (Fig. 2) shows π - π interactions between two almost parallel (dihedral angle, 7.24(11)°) pendant phenyl rings of two neighboring tetrameric units namely, C(18)-C(19)-C(20)-C(21) C(22)-C(23) (Cg(19) and C(1)-C(2)-C(3)-C(4)-C(6)-C(7) (Cg(17)) at 3.835(3) Å (symmetry, x, -1 + y, z) to constitute an infinite 1-D supramolecular chain.



Fig. 2. Packing diagram of complex 1.

Table 3
Fluorescence and lifetime data of H ₃ L and 2.

Compounds	Fluorescence data			Lifetime decay data				
	λ_{ex} (nm)	$\lambda_{\rm em} ({\rm nm})$	ф	χ^2	τ (ns)	$k_{ m r} imes 10^{-9}$	$k_{ m nr} imes 10^{-9}$	
H ₃ L	302 363	504 412 531	0.06	1.112	0.09	0.630	9.873	
2	302	489	0.08	1.157	21.67	0.004	0.042	



Fig. 4. Exponential decay profile (
) and fitting curve (–) of (a) H₃L and (b) complex 2 (in CH₂Cl₂). Excitation is carried out at 370 nm.



Fig. 5. X-band EPR spectra of the solid polycrystalline complex **1** at RT (a) and 77 K (b), and of the complex dissolved in DMF (c and d) and DMSO (e). The trace (d) is the low-field region of the spectrum in DMF (trace c) amplified 5 times. The broken lines indicates the resonances of the complex **1**. Diphenylpicrylhydrazyl (dpph) is the standard field marker (g = 2.0036).



Fig. 6. Temperature dependence of $\chi_M T$ vs. *T* of **1**. The solid line represents the best fit of the experimental data with a 2*J* model without restrictions (see text). •, represents the best fit with a 2*J* model with $J_2 = 0$.



Table 4

Com	naricon of como n	agrantostrustural	naramatara for	dinucloar com	playar containing	c a Cull	ODLY	OMA	Cu coro an	d for totrapucl	00r 1
COIII	parison or some n	lagiletosti ucturar	parameters ion	unnuclear com	ιριέλες τοπταππη	ς α τυ(μ	ι-ΟΓΠ μ	i-Oivie)	Cu core an	u ioi tetranuci	Cdi I.

Complex ^a	Cu-O _{Me} -Cu (°)	Cu-O _{Ph} -Cu (°)	$2J^{\rm b}~({\rm cm}^{-1})$	Geometry type ^c	Refs.
$[Cu_2(L^1)(CH_3O)]$	101.8	99.3	-630	Ι	[31]
$[Cu_2(L^2)(CH_3O)](ClO_4)_2$	105.4	98.7	-94	II	[67]
$[Cu_2(L^3)(CH_3O)(CH_3OH)_2]$	103.3	99.2	-336	I	[68]
$[Cu_2(L^4)(CH_3O)]$	105.2	100.1	-299	I	[69]
[Cu ₂ (L ⁵)(CH ₃ O)](ClO ₄) ₂	102.4	93.4	-312	II	[70]
$[Cu_2(L^6)(CH_3O)(THF)_2]$	102.4	99.4	-384.2	I	[71]
$[Cu_2(L^7)(CH_3O)](ClO_4)_2$	104.0	95.8	-38.3	III	[72]
$[Cu_2(L^8)(CH_3O)](BPh_4)_2$	127.9	99.7	-2.0	IV	[72]
$[Cu_2(L^9)(CH_3O)(CH_3OH)]$	104.0	100.2	-352	I	[73]
1	99.2	99.7	-186.5	Ι	This work

^a Ligands L^{x} (x = 1-9) are 2,6-R-phenol derivatives, with different R' pendant arms.

^b J values referred to Hamiltonian $H = -2JS_1S_2$.

^c See Scheme 4.

3.3. Emission spectroscopy

The emission spectroscopy of the ligand and the complexes. 1 and **2** are carried out at room temperature in DMF. MeOH and CH₂Cl₂, respectively (Fig. 3). The ligand exhibits fluorescence when it is excited at π - π * (302 nm) and n- π * (363 nm) (Table 3). It displays emission at 504 nm at 298 K upon excitation at 302 nm whereas; excitation at 363 nm gives emission maxima at 412 and 531 nm with a lower intensity than the former. The complex, 1 does not show significant emission, may be due to paramagnetic quenching of d⁹ configuration. The complex **2** exhibits higher fluorescence quantum yield (ϕ = 0.08) than that of H₃L (ϕ = 0.06). It is known that the metal ions of d^{10} configuration (Zn^{2+} , Cd^{2+} and Hg^{2+}) can efficiently enhance the emission behavior, though Hg^{2+} is well known as a typically quenching metal ion [54] because of heavy atom effect. Other metal ions such as Cr³⁺, Mn²⁺, Fe³⁺, Co²⁺, Ni²⁺ and Cu²⁺ quench the fluorescence emission intensities. The decay profiles are shown in Fig. 4. Life time data is taken on excitation at 370 nm. The fluoroscence decay fits with bi-exponential nature. Mean fluorescence life time ($\tau_f = a_1 \tau_1 + a_2 \tau_2$ where a_1 and a_2 are relative amplitudes of decay process) is used to compare excited state stability of the complexes. While calculating the radiative and non-radiative rate constants (k_r and k_{nr}), data show usual

higher $k_{\rm nr}$ value than $k_{\rm r}$ (Table 3). The complex shows much higher life time (τ , 21 ns) than the free ligand (τ , 0.09 ns). This implies that the excited state stability of the complex is much better than the ligand. Radiative decay constant is usually lower that nonradiative decay which refers to quick deactivation of the excited state through collision and dynamic pathways [55].

3.4. EPR spectroscopy

The complex **1** is EPR active while **2** is EPR inactive. The EPR spectra of polycrystalline powder of **1** were recorded at room (298 K) or liquid nitrogen (77 K) temperature (Fig. 5, traces a and b). For solid Cu(II) complex, the intramolecular spin exchange, due to the spin coupling among the paramagnetic ions, usually broadens the lines which collapse in very large absorptions. This precludes the resolution of the hyperfine interaction between the unpaired electron and 63,65 Cu nuclei; in most cases of solid Cu(II) compounds only an isotropic band or two/three bands corresponding to the g values can be detected. Instead, for **1** such interaction between the unpaired electron and 63,65 Cu nucleus is observed; this is rare, but not unique case [56–58]. This experimental evidence denotes weak magnetic interaction between the Cu(II) centers.



Scheme 4. The geometrical arrangements for crystallographically characterized dinuclear complexes containing a Cu(µ-OPh)(µ-OMe)Cu core. X = heteroatom.

The spectra are characterized by g_{\parallel} = 2.286, A_{\parallel} = 169 × 10⁻⁴ cm⁻¹, g_{\perp} = 2.068, A_{\perp} = 17 × 10⁻⁴ cm⁻¹ (298 K) and g_{\parallel} = 2.283, $A_{\parallel} = 178 \times 10^{-4} \,\mathrm{cm}^{-1}, \quad g_{\perp} = 2.072, \quad A_{\perp} = 15 \times 10^{-4} \,\mathrm{cm}^{-1}$ (77 K). These values are in agreement with those reported in the literature for dinuclear Cu(II) complexes formed by 2,6-diformyl-4-methylphenol-di(benzoylhydrazone) and a bridging X⁻, such as Br⁻, Cl⁻, N_3^- , $CH_3CH_2O^-$ and OH^- , if the structural differences with compound **1** are taken into account [59]. The order $g_{\parallel} > g_{\perp} > g_{e}$ indicates an axial symmetry, consistent with the square pyramidal geometry around Cu(II) centers established by X-ray structure [60]. The spectrum is typical of the species in which the unpaired electron occupies d_{x2-y2} orbital [61]. It can be observed that the linewidth is rather high (92.0 and 92.4 Gauss for the low-field parallel hyperfine transitions for the traces a and b) and the resonances are unsymmetrical: this may suggest that the experimental spectrum is the overlap of the signals of two structurally distorted Cu(II) ions (Cu(1) and Cu(2)), in agreement with the X-ray structure reported in Fig. 1 (in fact, the axial distance of O(4) and O(2)from Cu(1) and Cu(2) centers is 2.453(2) and 2.691(2) Å, respectively). Thus, g_{\parallel} and A_{\parallel} are compatible with the coordination environment of Cu(II) [62].

The EPR spectra of **1** dissolved in DMF (Fig. 5, traces c and d), DMSO (Fig. 5, trace e) and CH₃CN (not reported) indicate that one part of the complex retains its polynuclear nature and another part dissociates as a species characterized by $g_{\parallel} = 2.400$ and $A_{\parallel} = 136 \times 10^{-4} \text{ cm}^{-1}$ (in DMF), $g_{\parallel} = 2.399$ and $A_{\parallel} = 135 \times 10^{-4} \text{ cm}^{-1}$ (in DMSO) and $g_{\parallel} = 2.399$ and $A_{\parallel} = 136 \times 10^{-4} \text{ cm}^{-1}$ (in CH₃CN). The presence of more than one species in solution precludes in this case the measurement of g_{\perp} and A_{\perp} value. This parameters are comparable with those of solvated Cu(II) ion [63]. This suggest that when the ligand binds Cu(II) only the tetranuclear structure of **1** can be formed. The partial dissociation of a polynuclear species into monomeric centers has been noticed for other Cu(II) complexes [64–66].

3.5. Magnetic properties

The magnetic properties of **1** have been investigated in the 2-300 K temperature range. The plot of $\gamma_{\rm M}T$ versus T for **1** is shown in Fig. 6, where it can be seen that $\chi_{\rm M}T$ is 1.14 cm³ K mol⁻¹ at 300 K and that this product constantly decreases with lowering temperature, reaching a value of ca. 0 at 30 K. This value remains practically constant between 30 and 2 K. This behavior agrees with antiferromagnetic coupling, with a ground state of *S* = 0. The structural analysis of the double half-cubane 1, where all Cu(II) ions are in square pyramidal environments, reveals three different superexchange pathways (Scheme S2): one magnetic pathway (between Cu(1)...Cu(2)) corresponds to a double μ -oxo bridge (phenoxo/ methoxo), where both oxygen atoms are in the equatorial plane (J_1) ; the second superexchange way (between Cu(1)…Cu(2') and vice versa) corresponds to a double oxo bridge (methoxo/carbonyl), where the oxygen bridges occupy a basal–apical position (J_2) , with two short [Cu(1)-O(2)] and Cu(2')-O(4') and two long [Cu(1)-O(4')]and Cu(2')-O(2)] bonds. The third magnetic pathway (between Cu(1)···Cu(1'), J_3) is a double oxo-methoxo bridge, occupying a basal-apical position with two short and two long Cu-O bond distances. Thus, J_2 and J_3 define the coupling between two copper centers mediated by a double oxo bridge, in apical-basal disposition. Therefore, the three different magnetic pathways (Scheme 3) can be reduced to two, in order to avoid over parameterization, with $I_2 = I_3$.

Accordingly, the susceptibility curve was treated with the MAGPACK program [67], where the exchange spin Hamiltonian is expressed as $H = -2\sum J_{ij}S_iS_j$. Thus, a 2*J* model, with a fixed *TIP* of 2.4 × 10⁻⁴ cm³ mol⁻¹, was chosen (Scheme 3) in order to try to reproduce the magnetic data. The best fit with this model renders an *S* = 0 calculated ground state and the following parameters: $2J_1 = -191.6$ cm⁻¹, $2J_2 = 2J_3 = -93.4$ cm⁻¹, g = 2.12 (*R* = 2.5 × 10⁻⁴).

The reliability of the parameters was checked by comparison with literature. Thus, J_1 reflects the magnetic interaction between two Cu(II) ions mediated by an O_{methoxo} and an O_{phenoxo} bridge (Scheme 3). The structurally and magnetically characterized reported dinuclear copper(II) complexes containing a phenoxo/ methoxo bridge are recorded in Table 4, with the geometry of the copper cores represented in Scheme 4. As it can be seen, this kind of mixed phenoxo/methoxo complex is scarcely described in literature [31,68–74], but most of these complexes show similar polyhedra arrangement (Type I, Scheme 4), usually displaying an important antiferromagnetic coupling. In this geometry, the two d_{x2-y2} orbitals are coplanar and the magnetic interaction depends, among other factors, on the Cu–O–Cu angle [75]. For angles close to 97° it is possible to found accidental orthogonality and consequently, positive *J* values (or $J \sim 0$) [75].

In this complex, respect to I_1 , a Type I geometry is recommended with the Cu(1)-O(1)-Cu(2) (99.73(7)°) and Cu(1)-O(4)-Cu(2) (99.24(7)°). Therefore, an antiferromagnetic coupling is expected. The I_1 value of -191.6 cm⁻¹ could seem quite low in view of the data of Table 4. However, it should be noted that the variation of the J value with the Cu-O-Cu angle is not linear, as this is not the only factor affecting the magnetic interaction. Thus, other factors such as the roof shape of the Cu_2O_2 core and the angle between the C atom of the methanolate group and the molecular plane or the co-planarity between basal donor planes [76] also play an important role in the super exchange magnetic strength. In this way, values close to -100 cm^{-1} were found for phenolate/hydroxy bridged complexes with Type I geometry and average Cu-O-Cu angles close to 99° [77]. Besides, Tercero et al. [78] demonstrated for [2+4] cubane Cu₄O₄ compounds that, for the same superexchange pathway, the antiferromagnetic coupling is higher in dinuclear entities that in tetranuclear ones, what is in agreement with the obtained results. In fact, the J_1 value is not exceptional as there are reported values so low as $2J = -120 \text{ cm}^{-1}$ for the magnetic exchange in a basal-basal Cu₂O₂ core of a cubane like complex with Cu–O–Cu angles close to 100° [79].

The $J_2 = J_3$ represent the magnetic exchange between two copper atoms mediated by a double oxygen bridge, in an apical-basal disposition, with two short and two long Cu–O distances (one of each type per bridge). Thus, this superexchange pathway should transmit a very weak or null exchange interaction. Besides, this magnetic superexchange pathway is comparable to one for the two magnetic pathways for [2+4] cubanes. In this latter case, this *J* value is always small, usually close to zero, with reported exceptions maybe due to multiple sets of values of the coupling constants [78].

Accordingly, the value of J_2 obtained in this study does not seem a reasonable result. Therefore, in a new attempt to fit the data, taking into account the expected relatively low J_2 value in contrast to J_1 , J_2 was set to zero, in agreement with a quite common practice for complexes of this kind [27,78,80,81]. In this case, the best fir of the data gives the parameters $2J_1 = -186.5$ cm⁻¹ and g = 2.03($R = 7.3 \times 10^{-4}$), with a nearly superimposed curve (Fig. 6, solid circle). These values are consistent with those found in the first fit and, besides, also render an S = 0 ground state. Thus, this second approximation seems to be more realistic to explain the magnetic situation.

4. Conclusion

Phenoxo-bridged tetranuclear Cu(II) and dinuclear Zn(II) complexes incorporating 2,6-diformyl-4-methylphenol-di(benzoylhydrazone) are afforded and spectroscopically characterized. In addition, the X-ray structure of the Cu(II) complex could be solved, contributing to swell the scarce number of double-half cubane copper compounds crystallographically and magnetically studied. In this way, the temperature variable magnetic behavior of **1** agrees with a predominant intramolecular antiferromagnetic coupling, with $J = -186.5 \text{ cm}^{-1}$, which renders a ground state S = 0. Furthermore, it is noticeable that the Zn(II) complex shows a high fluorescence quantum yield in solution. Future work will explore the mechanistic pathway and modification that corresponds to several applications among metal complexes of newly designed organic precursors.

Acknowledgements

K.D. and C.S. would like to thank to DST (Department of Science and Technology, New Delhi, India) for the grant (SR/S1/IC-31/2008) to carry out the present study.

Appendix A. Supplementary data

Crystallographic data for structural analysis has been deposited to the Cambridge Crystallographic Data Center, bearing CCDC 874021. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (fax: +44 1223 336 033; e-mail deposit@ccdc.cam.ac.uk or http:// www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/ 10.1016/j.ica.2014.01.013.

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