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Synthesis, crystal structure, magnetic and electrochemical studies of two copper complexes with carboxylate rich dinucleating ligand

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ABSTRACT

Three new copper compounds of a symmetric dinucleating ligand, *N*,*N*'-bis[2-carboxybenzomethyl]-*N*,*N*'-bis[carboxymethyl]-1,3-diaminopropan-2-ol (H₅ccdp) with diverse coordinating groups, have been synthesized and studied in the solid state as well as in solution. In acetonitrile/H₂O solution, the reaction of stoichiometric amounts of Cu(NO₃)₂·2.5H₂O and the ligand H₅ccdp, in the presence of K₂CO₃, produced a dinuclear copper compound, K₃[Cu₂(ccdp)(μ -CO₃)]·7H₂O·C₃H₆O, K₃[1]·7H₂O·C₃H₆O. Whereas in an alkaline methanol/water solution, the reaction of Cu(ClO₄)₂·6H₂O and the ligand H₅ccdp gave a slightly different dinuclear copper compound, Na₃[Cu₂(ccdp)(μ -CO₃]]·5H₂O, Na₃[1]·5H₂O. The reaction of Cu(ClO₄)₂·6H₂O and the ligand H₅ccdp gave a slightly different dinuclear copper compound, Na₃[Cu₂(ccdp)(μ -CO₃]]·5H₂O, Na₃[1]·5H₂O. The reaction of Cu(ClO₄)₂·6H₂O and the ligand H₅ccdp gave a slightly different dinuclear copper compound, Na₃[Cu₂(ccdp)(μ -CO₃]]·5H₂O, Na₃[1]·5H₂O. The reaction of Cu(ClO₄)₂·6H₂O and the ligand H₅ccdp, in the presence of the alt three complexes compound, Na₂[Cu₂(ccdp)(H₂O)(μ -OH₂)]₂·15H₂O, Na₂[2]·15H₂O. The structures of the all three complexes were determined using single crystal X-ray diffraction analyses. Variable-temperature magnetic susceptibility studies on the powder samples of the complexes showed antiferromagnetic behavior. Electrochemical studies in aqueous solutions of these negatively charged complex ions showed fairly assessable oxidations.

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1. Introduction

Transition metal complexes containing two or more metal ions have gained significant interest over the years due to their diverse properties and reactivity, originating from the magnetic exchange occurring between neighboring metal centers and potential applications in the field of magnetism [1], in catalysis [2], and as structural and functional models of metalloenzymes [3]. Polynuclear systems are ubiquitous in nature, especially in metalloenzymes [4]. The active sites of many of these metal-containing enzymes possess oxygen- and nitrogen-rich donating environments. So far, several copper ions coordinated to oxygen and/or nitrogen atoms as structural and functional models metalloenzymes are reported in the literature [5]. However, when compared to N- and other O- donating groups, there are very few complexes with polycarboxylate ligand systems reported in the literature [6].

Copper is the third most abundant transition metal found in living systems [4c], and it plays an essential role in biological systems. Copper is incorporated in metalloenzymes that are involved mainly in oxygen transport, electron transfer, and catalytic oxidation processes [7]. Synthetic coordination complexes employing copper(II) have proven effective functional models for several classes of metalloenzymes including oxidases (catechol oxidase) [8], oxygenases [9], nucleases [10], and phosphatases [8b,11].

The symmetrical bridging ligand N,N'-bis-[2-carboxybenzomethyl]-N,N'-bis[carboxymethyl]-1,3-diaminopropan-2-ol (H₅ccdp) [12] is used to create three interesting copper compounds exhibiting diverse coordination chemistry. The compounds are either dinuclear, K₃[**1**]·7H₂O·C₃H₆O and Na₃[**1**]·5H₂O, or tetranuclear, Na₂[**2**]·15H₂O, in copper. The ligand, shown in Scheme 1, has two symmetrical tetradentate cavities, each with a NO₃ coordination site able to coordinate a Cu(II) ion. This leaves the copper centers coordinatively unsaturated, and thus room for further coordination by exogenous ligands. This is advantageous in terms of available binding sites for substrates in modeling metalloenzymes. In this paper we wish to report the syntheses, structural, magnetic and electrochemical characterizations of these new multi-copper compounds.

2. Experimental

2.1. Materials and methods

All starting materials were purchased from commercial sources and were used without further purification. Elemental analysis was determined by Galbraith Laboratories, Inc., Knoxville, TN.



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Scheme 1. Schematic representation of the synthesis of N,N'-bis[2-carboxybenzomethyl]-N,N'-bis[carboxymethyl]-1,3-diaminopropan-2-ol, H₅ccdp.

Caution: Although no problems were encountered in this work, perchlorate salts of metal complexes are potentially explosive and should be handled in small quantities with great care.

2.2. Synthesis of metal complexes

2.2.1. Synthesis of $K_3[\mathbf{1}] \cdot 7H_2 O \cdot C_3 H_6 O$

An acetonitrile–H₂O solvent mixture (4:1 by vol) (5 ml) with Cu(NO₃)₂·2.5H₂O (0.1965 g, 0.845 mmol) was slowly added drop wise, at ambient temperature, to a stirring 10 ml acetonitrile–H₂O (4:1 by vol) solution of the ligand H₅ccdp (0.200 g, 0.422 mmol) and K₂CO₃ (0.2512 g, 2.53 mmol) in a period of 15 min. After complete addition, a layer of blue was seen separating in solution. The whole reaction mixture was stirred overnight at room temperature. The solution was filtered using gravity filtration and was setup for crystallization. The X-ray quality single crystals were grown by slow acetone or THF diffusion into the acetonitrile–H₂O solution of the complex. Yield: 0.1724 g (43%). *Anal.* Calc. for C₂₄H₃₉Cu₂N₂K₃O₂₁: C, 30.28; H, 4.2; N, 2.99. Found: C, 29.81; H, 3.28; N, 3.38%. UV–Vis (H₂O) λ_{max}/nm (ε/L mol⁻¹ cm⁻¹): 768 (160).

2.2.2. Synthesis of $Na_3[1] \cdot 5H_2O$

This compound was prepared in a similar manner to complex **1** but methanol and NaOH were used in places of acetonitrile and K₂CO₃, respectively. The X-ray quality single crystals were grown by slow acetone–H₂O (6:1 by vol) diffusion into the methanoic solution of the complex. Yield: 0.1633 g (47%). *Anal.* Calc. for C₂₄₋H₅₁Cu₂N₂Na₃O₂₇: C, 28.94; H, 5.16; N, 2.81. Found: C, 28.02; H, 5.19; N, 2.73%. UV–Vis (H₂O) λ_{max}/nm (ε/L mol⁻¹ cm⁻¹): 756 (143).

2.2.3. Synthesis of Na₂[**2**]·15H₂O

A water solution (3 ml) of Cu(ClO₄)₂·6H₂O (0.313 g, 0.845 mmol) was slowly added drop wise, at ambient temperature, to a stirring 8 ml water solution of the ligand H₅ccdp (0.200 g, 0.422 mmol) and NaOH (0.1014 g, 2.54 mmol) in a period of 15 min. After complete addition, a blue solution was obtained. The whole reaction mixture was stirred overnight at room temperature. The solution was filtered using gravity filtration and was setup for crystallization. The X-ray quality single crystals were grown by slow acetone or THF diffusion into the H₂O solution of the complex. Yield: 0.3465 g (53%). *Anal.* Calc. for C₄₆H₇₆Cu₄N₄Na₂O₃₅: C, 35.74; H, 4.96; N, 3.63. Found: C, 35.01; H, 4.78; N, 3.36%. UV–Vis (H₂O) $\lambda_{max}/$ nm (ϵ/L mol⁻¹ cm⁻¹): 766 (339).

2.3. Physico-chemical measurements

2.3.1. X-ray crystallography and data analysis

The data were collected at 98(2) K using a Rigaku AFC12/Saturn 724 CCD fitted with Mo K α radiation (λ = 0.71073 Å) [13]. Data

collection and unit cell refinement were performed using CRYSTAL CLEAR software. The total number of data were measured in the range 2.20° < θ < 27.5° using ω scans. Data processing and absorption correction, giving minimum and maximum transmission factors, were accomplished with CRYSTAL CLEAR and ABSCOR [14], respectively. The structure, using SHELXL-97, was solved by direct methods and refined (on F^2) using full-matrix, least-squares techniques [15,16]. All non-hydrogen atoms were refined with anisotropic displacement parameters. All carbon bound hydrogen atom positions were determined by geometry and refined by a riding model. Electron density peaks were used to identify oxygen bound hydrogen atoms and the displacement parameters were set to 1.5 times the displacement parameters of the bonded atoms.

2.3.2. Electrochemical analysis

Electrochemical measurements were made on a BAS-CV50 electroanalyzer controlled with a Pentium III computer and utilizing three electrodes: a glassy carbon or platinum working electrode, a platinum wire counter electrode, and a Vycor-tipped Ag/ AgNO₃ reference electrode. Working electrodes were polished to a mirror finish on a microcloth of diamond or alumina (1.0 and 0.05 mm particles, respectively) and were cleaned electrochemically. Cyclic voltammograms were obtained from a 1 to 2.5 mM analyte concentration in H₂O, using 0.2 M KCl supporting electrolyte. Data were analyzed using the software provided with this instrumentation. Solutions were degassed with a purge of N₂ for 10 min, and a blanket of N₂ was maintained over the solution while making the measurements. The *iR* compensation between the working and reference electrodes was accomplished by applying the positive feedback from the BAS-CV50 current follower. All potentials were measured at room temperature and scaled to NHE using methyl viologen as an internal standard (MV²⁺/MV⁺ literature value is $E_{1/2}^{\text{NHE}} = -0.45 \text{ V}$ versus NHE in water) [17].

2.3.3. Magnetic measurement

Magnetic measurements were carried out on polycrystalline powder samples ranging from 2 to 300 K at the applied fields of 5 kOe using a SQUID based sample magnetometer on a QUANTUM Design Model PPMS instrument.

3. Results and discussion

3.1. Syntheses

The reaction of Cu(NO₃)₂ salt with the ligand, H₅ccdp, in 2:1 M ratio in presence of a mild base, such as K₂CO₃, at pH ~8 in an acetonitrile/H₂O solution under ambient conditions overnight afforded a dark blue solution, that was easily crystallized into a blue dinuclear copper compound K₃[**1**]·7H₂O·C₃H₆O. Similarly, reaction of Cu(ClO₄)₂ salt with the H₅ccdp ligand in 2:1 M ratio in presence

of a strong base, such as NaOH, at pH ~10 afforded a blue dinuclear copper compound, Na₃[1]·5H₂O, and a blue tetranuclear copper compound, Na₂[2]·15H₂O, in a methanol/H₂O solution and in water, respectively. The syntheses of the ligand H₅ccdp and the respective metal complexes are depicted in Scheme 1 and Fig. 1, respectively. Molecular structures of the three compounds have been established using single crystal X-ray crystallography.

3.2. Crystal and molecular structures

The solid-state structures were confirmed by their single crystal X-ray diffraction studies. The $K_3[1]$ - $7H_2O$ - C_3H_6O compound crystallizes in a triclinic system, and according to the observed systematic extinction, the structure was solved as $P\bar{1}$ space group. Compound Na₃[1]- $5H_2O$ crystallizes in a monoclinic system, and the structure was solved in the $P2_1/c$ space group. The Na₂[2]- $15H_2O$ compound crystallizes in a triclinic system, and the structure was solved in the $P\bar{1}$ space group. Table 1 summarizes the crystallographic data and refinement details for K₃[1]- $7H_2O$ - C_3H_6O , Na₃[1]- $5H_2O$ and Na₂[2]- $15H_2O$. The packing diagrams for the compounds are given in the Figs. S1, S2 and S3 (Supporting information), respectively. Selected bond distances and bond angles are given in Table 2.

3.2.1. K₃[1]·7H₂O·C₃H₆O

In the crystal structure of $K_3[1]$ · $7H_2O\cdot C_3H_6O$, the complex anion **1** contains a dinucleating ligand ccdp^{5–} and a bridging carbonato group to produce a five-coordinate geometries around the copper ions. The coordination geometry around each copper ion is best described as a distorted square pyramidal geometry formed by an alkoxo oxygen, an aliphatic carboxylate oxygen, an aromatic carboxylate oxygen, and a tertiary amine nitrogen of the ligand, plus one oxygen atom from the bridging carbonato. The structural view of **1** is depicted in Fig. 2. While Cu(1) is coordinated to O(2) and O(3) of aromatic and aliphatic carboxylates of the ligand, respectively, in a *cis* to each other fashion, Cu(2) is coordinated to O(6) and O(8) of aromatic and aliphatic carboxylates of the ligand, respectively, also in a *cis* fashion. The bidentate carbonato ligand oxygens, O(10) and O(11), are bridging the two copper ions in a *syn-syn* coordination mode. The main distortion of the resulting octahedral coordination sphere originates in the large bite angles for $N(1)-Cu(1)-O(10) = 166.74(7)^{\circ}$ and $O(5)-Cu(2)-O(8) = 169.28(6)^\circ$, as well as, in the small bite angles for $N(1)-Cu(1)-O(3) = 82.54(6)^{\circ}, O(5)-Cu(1)-N(1) = 85.10(7)^{\circ},$ $O(10)-Cu(1)-O(3) = 110.72(6)^{\circ}$, $O(5)-Cu(2)-N(2) = 85.76(7)^{\circ}$, $O(5)-Cu(2)-O(6) = 97.70(6)^{\circ}$, $O(11)-Cu(2)-O(6) = 101.25(7)^{\circ}$ and $N(2)-Cu(2)-O(6) = 81.06(6)^{\circ}$ of the complex. Furthermore, the $Cu \cdots Cu$ distance measures 3.4699(4)Å, which is in agreement with previously reported dinuclear copper(II) complexes [18,19], and falls well within the range of metal...metal distances observed in several metallohydrolases [20,21]. The aliphatic carboxylate oxygens, O(3) and O(6), coordinated to each copper ion exhibit significantly longer bond lengths compared to the average copper-oxygen bond length. The Cu(1)-O(3) distance of 2.1898(15) Å and the Cu(2)–O(6) distance of 2.2371(15) Å are markedly longer than the average Cu-O distances (2.0104(30) Å for Cu(1) and 2.0112(31) Å for Cu(2)). The bond distances and bond angles for **1** are reported in Table 2 and are consistent with values reported in the literature [22].

3.2.2. Na₃[1]·5H₂O

A view of the dinuclear copper anion of the compound is depicted in Fig. 3, and selected bond lengths and bond angles are listed in Table 2. The crystal structure of the complex is very similar the structure of $K_3[1]$ · $7H_2O$ · C_3H_6O , except for the three Na⁺ ions, instead of K⁺ ions, and fewer water molecules and no acetone of crystallization. The coordination geometry around each copper ion is best described as a distorted square pyramidal geometry. A structural view of **1** is depicted in Fig. 2. The Cu(1) center is coordinated to O(1) and O(3) of aromatic and aliphatic carboxylates of the ligand, respectively. The Cu(2) center is coordinated to O(6) and O(8) of aromatic and aliphatic carboxylates of the ligand, respectively, which are *cis* to each other. Since the synthesis of the compound uses NaOH, the presence of the carbonato ligand in the structure must have come from the atmospheric carbon dioxide.



Fig. 1. Schematic representation of the synthesis of complexes 1 and 2, shown are only the anioinc complexes.

Summary of crystallographic data for the compounds.

	$K_3[1] \cdot 7H_2O \cdot C_3H_6O$	Na ₃ [1]·5H ₂ O	Na ₂ [2]·15H ₂ O
Empirical formula Formula weight Crystal system Space group	K ₃ Cu ₂ O ₂₀ N ₂ C ₂₇ H ₄₁ 1907.3 Triclinic P1 9.4973(8)	Na ₃ Cu ₂ O ₁₇ N ₂ C ₂₄ H ₃₁ 801.54 Monoclinic P2 ₁ /c 18.322(3)	Na ₂ Cu ₄ O ₃₅ N ₄ C ₄₆ H ₇₆ 3317.01 Triclinic PĪ 14.177(3)
b (Å)	11.6634(11)	7.4425(10)	18.009(4)
$c(\dot{A}) \alpha(^{\circ}) \beta(^{\circ}) \gamma(^{\circ}) V(\dot{A}^{3})$	18.2100(17)	23.236(4)	18.663(5)
	97.910(6)	90	110.287(2)
	100.740(7)	111.293(2)	103.704(3)
	109.900(7)	90	102.243(2)
	1818.8(3)	2952.2(8)	4109.6(17)
Z, Z'	2,1	4,1	2,1
ρ_{calc}	1.741	1.803	1.721
λ	0.71073	0.71073	0.71073
T (K)	98(2)	98(2)	98(2)
F(000)	979	1632	1679
μ (mm ⁻¹)	1.597	1.568	1.120
T _{min} , T _{max}	0.864, 1.000	0.792, 1.000	0.876, 1.000
2 θ range (°)	2.00-27.50	2.44-27.50	$\begin{array}{c} 2.07-26.00\\ 32001\\ 15995[R_{\rm int}=0.0319]\\ 15995/0/1036\\ 0.1933\\ 0.0809\\ 1.14\\ 14191\\ 0.010/0.000\\ 2.235/-0.641 \end{array}$
Reflections collected	14348	21720	
Independent reflections	$8226 [R_{int} = 0.0163]$	$6764 [R_{int} = 0.0285]$	
Data/restraints/parameters	8226/0/530	6746/0/457	
$wR(F^2$ all data)	0.0853	0.0722	
R(F obsd data)	0.0308	0.0312	
GOOF on F^2	1.009	1.019	
Observed data [$I > 2\sigma(I)$]	7985	6284	
Largest and mean shift/s.u.	0.001/0.000	0.006/0.000	
Largest difference in peak and hole (e/Å ³)	0.968/-0.574	0.904/-0.429	

 $wR_2 = \{ \sum [w(F_{\rm o}{}^2 - F_{\rm c}{}^2)^2] / \sum [w(F_{\rm o}{}^2)^2] \}^{1/2}; R_1 = \sum ||F_{\rm o}| - |F_{\rm c}|| / \sum |F_{\rm o}|.$

The main distortion of the resulting octahedral coordination sphere originates in the large bite angles for $O(5)-Cu(1)-O(1) = 165.38(7)^{\circ}$ and $O(5)-Cu(2)-O(8) = 163.84(6)^{\circ}$, as well as, in the small bite angles for $N(1)-Cu(1)-O(3) = 102.85(6)^{\circ}$, $N(1)-Cu(1)-O(3) = 81.87(6)^{\circ}$, $O(5)-Cu(2)-O(6) = 111.01(6)^{\circ}$, $O(11)-Cu(2)-O(6) = 100.28(6)^{\circ}$, $O(8)-Cu(2)-O(6) = 84.38(6)^{\circ}$ and $N(2)-Cu(2)-O(6) = 82.26(6)^{\circ}$ of the complex. Furthermore, the Cu \cdots Cu distance measures 3.4972(7) Å, which is in agreement with synthetic copper(II) complexes [18,19] and some metallohydrolase enzymes reported in the literature [20,21]. The bond distances and bond angles for complex **1** are consistent with values reported in the literature [22].

3.2.3. Na₂[**2**]·15H₂O

A view of the anion of the tetracopper complex **2** is shown in Fig. 4, and selected bond lengths and bond angles are listed in Table 2. The crystal structure of Na₂[2]·15H₂O can be described as two $[Cu_2(ccdp)(\mu-OH_2)]^{2-}$ anion units, two sodium ions as counter cations, bridged with two water molecules, along with fifteen water molecules of crystallization. The metal ions within each [Cu₂]⁻ pair are chelated to one ccdp⁵⁻ ligand. Two water molecules act as bridges between the two anion units through the Cu(1)- $H_2O(19)-Cu(3)$ and $Cu(2)-H_2O(20)-Cu(4)$ links. This arrangement has important characteristic in terms of active nucleophile possibilities that could be influenced by pH changes for purposes of bond hydrolysis [23]. The Cu(1)-H₂O(19)-Cu(3) and Cu(2)-H₂O(20)–Cu(4) bond angles of 123.2(2)° and 128.1(2)°, respectively, are open enough to afford the further coordination by two oxygens of the bridging water molecules in a syn-syn bidentate bridging mode to the pair of copper ions in each dinuclear unit. The dinucleating ligand within each dinuclear unit binds the copper ions through one bridging alkoxo moiety, one aliphatic and one aromatic carboxylates as well as amine groups. While all the four Cu(II) centers are penta-coordinated, they assume two different coordination geometries around the metal ions. Whereas both Cu(1) and Cu(4) adopt a distorted square pyramidal geometry, Cu(2) and Cu(3) centers exhibit a distorted trigonal bipyramidal geometry. This is an interesting occurrence since all four copper ions are surrounded by one bridging alkoxo oxygen, one monodentate aliphatic carboxylate oxygen, one monodentate terminal aromatic carboxylate oxygen, and one tertiary amine nitrogen of the $ccdp^{5-}$ ligand, and one oxygen from the bridging water molecule. The two different geometries observed within each dinuclear unit is due to the different coordination modes adopted between the extremely flexible $ccdp^{5-}$ ligand and the metal ions in response to steric constraints within the complex. Each dinuclear unit produces a twisted conformation with respect to the aromatic rings due to one is coordinated towards the front of the complex, while the other ring is coordinated towards the back. This strain has yielded a concave shaped cluster core illustrated in Fig. 5.

The inter-copper distances in the intraligand unit is 3.6814(14) Å for Cu(1)···Cu(2) and 3.7132(14) Å for Cu(3)···Cu(4). The interligand Cu···Cu separation is 3.3698(12) Å for Cu(1)···Cu(3) and 3.4764(13) Å for Cu(2)···Cu(4). The interligand Cu···Cu separation is slightly shorter than the interaligand distances due to an acute bond angle observed between the two coppers coordinated to the bridging water molecules. These bond distances are in agreement with those reported for metallohydrolase enzymes [20,21,4a].

Furthermore, the flexibility of the H₅ccdp ligand originating from the aromatic and aliphatic carboxylate groups and the bridging capabilities to the metal centers is highlighted in this structure. The aromatic carboxylates experience a greater restriction in conformation with a separation between carboxylate oxygens being 6.108(5) Å, for Cu(1)···Cu(2), and 6.335(8) Å, for Cu(3)···Cu(4); whereas the aliphatic carboxylates are less rotationally hindered showing a carboxylate oxygen separation of 7.187(8) Å for Cu(1)···Cu(2), and 7.381(8) Å for Cu(3)···Cu(4). In comparison to the dinuclear complexes, K₃[1]·7H₂O·C₃H₆O and Na₃[1]·5H₂O, the complex showed a significant change in the distance separating

Table 2

Soloctod	bond	dictancoc	and	bond	angloc	for	compounds	
Selected	Dona	uistances	anu	Dona	angles	101	compounds.	

$K_3[1]$ ·7H ₂ O·C ₃ H ₆ O		Na ₃ [1]·5H ₂ O		Na ₂ [2]·15H ₂ O	
Bond lengths (Å)					
Cu1-05	1.9339(15)	Cu1-05	1.9130(15)	Cu1-N1	2.019(5)
Cu1-010	1.9379(15)	Cu1-010	1.9289(16)	Cu1-01	2.283(5)
Cu1-02	1.9798(15)	Cu1-01	1.9816(15)	Cu1-03	2.009(4)
Cu1-N1	2.0740(18)	Cu1-N1	2.0772(18)	Cu1-019	1.925(4)
Cu1-03	2.1898(15)	Cu1-03	2.1790(15)	Cu1-05	1.955(4)
Cu1–Cu2	3.4699(4)	Cu1–Cu2	3.4972(7)	Cu2-N2	2.040(5)
Cu2-05	1.9067(15)	Cu2-05	1.9129(15)	Cu2-05	2.002(4)
Cu2-011	1.9374(16)	Cu2-011	1.9287(15)	Cu2-06	2.078(5)
Cu2-08	1.9637(15)	Cu2-08	1.9986(15)	Cu2-08	2.096(4)
Cu2-N2	2.0867(17)	Cu2-N2	2.0440(18)	Cu2-020	1.928(4)
Cu2-06	2.2371(15)	Cu2-06	2.2480(15)	Cu3-019	1.906(4)
				Cu3-014	1.994(4)
				Cu3-N3	2.009(5)
				Cu3-012	2.090(4)
				Cu3-010	2.159(4)
				Cu4-020	1.939(4)
				Cu4-014	1.975(4)
				Cu4-015	2.006(4)
				Cu4-N4	2.026(5)
				Cu4-017	2.260(4)
Rond angles (°)					
De Cul 010	02 70(6)	OF C:: 1 010	05 22(6)	010 6:1 05	04 22(17)
05-011-010	95.79(0) 172.71(6)	05-01-010	95.22(0)	019-011-05	94.33(17)
03-011-02	1/3.71(0)	010 Cu1 01	103.36(7)	019-011-03	94.55(17)
OIO-CUI-O2	90.21(6)	OIO-CUI-OI	89.11(0)	019-011-03	94.17(10)
05-CUI-NI	85.10(7)	05-CUI-NI	86.09(7)	05-Cu1-03	104.48(19)
$O_1 O_2 C_{11} N_1$	80.00(7)	O10-Cu1-N1	176.30(7)	019-Cu1-N1	174.2(2) 86.7(2)
02 - Cu1 - N1	02.68(6)	01 - Cu1 - N1	102.85(6)	$O_2 C_{11} N_1$	80.7(2)
03-001-03	110 72(6)	03-001-03	06 77(6)	0.10 Cu1 0.1	03.0(2)
010-cu1-03	20 <i>44</i> (6)	010-011-03	90.77(0)	05 Cu1 01	92.08(17)
N1 Cu1 02	89.44(0)	N1 Cu1 02	90.40(0) 91.97(6)	03 - cu1 - 01	90.11(19) 06.44(10)
NI-CUI-05	62.34(0) 120.22(8)	NI-CUI-05	01.07(0) 122.15(9)	N1 Cu1 O1	90.44(19)
05 012 011	129.23(8)	Cu1 = 03 = Cu2	132.13(6)	Cul OF Cul	92.9(2)
05-012-011	169 28(6)	05-012-011	163.84(6)	020-002-005	137.0(2) 05.00(17)
011_012_08	80.84(7)	03-002-08	87 42(6)	05-012-N2	84 Q(2)
$05_{11} = 002_{11} = 0000000000000000000000000000000000$	85.76(7)	$05_{11} = 002_{11} = 0000000000000000000000000000000000$	85 30(7)	05-012-06	125 5(2)
0.011 - 0.02 - N2	177 /3(7)	0.011 - 0.02 - N2	177 38(7)	020_C112_08	88 /3(17)
$08_{11} = 08_{12}$	91 20(7)	$08_{11} = 08_{12}$	92 21(7)	N2_Cu2_08	92 50(19)
05-012-06	97 70(6)	05-012-06	111.01(6)	020-012-05	95 99(17)
08-012-06	91 97(6)	08-012-06	84 38(6)	05-012-N2	849(2)
N2-Cu2-06	81.06(6)	N2-Cu2-06	82 26(6)	$C_{112} = 0.02 = 0.04$	1281(2)
011-012-06	101 25(7)		02.20(0)	019-Cu3-014	92 10(18)
	101120(7)			019 - Cu3 - N3	1754(2)
				014-Cu3-N3	86.6(2)
				019-Cu3-012	95.16(18)
				014-Cu3-012	132.76(19)
				N3-Cu3-012	82.6(2)
				019-Cu3-010	91.92(17)
				014-Cu3-010	118.60(18)
				N3-Cu3-O10	92.6(2)
				012-Cu3-010	107.74(17)
				Cu3-019-Cu1	123.2(2)
				020-Cu4-014	95.68(17)
				020-Cu4-015	94.80(18)
				014-Cu4-015	162.49(19)
				020-Cu4-N4	175.49(19)
				014-Cu4-N4	85.43(19)
				015-Cu4-N4	83.1(2)
				020-Cu4-017	90.66(17)
				014-Cu4-017	98.38(18)
				015-Cu4-017	95.48(17)
				N4-Cu4-017	93.51(18)
				Cu4-014-Cu3	138.6(2)

the aliphatic carboxylate oxygens. For example, in complex K_{3-} [1]·7H₂O·C₃H₆O, the distance between aromatic carboxylate oxygens and aliphatic carboxylate oxygens is 7.179(3) and 3.450(3) Å, respectively. The degree of flexibility and bridging capabilities of the ligand is also nicely displayed when the dicopper and the tetracopper structures are compared. The distance between the oxygens, O(19)–O(20), of the two bridging waters in

complex Na₂[**2**]·15H₂O measures 2.681(5) Å, which is a much larger separation than the distance between the two oxygens, O(10)–O(11), of the bridging carbonato ligand, measuring 2.268(3) Å in K₃[**1**]·7H₂O·C₃H₆O. The Cu–O bond distances are within range of previously reported alkoxo bridged dinuclear copper systems [22a,b], except for the Cu–O_{carboxylate} (aromatic) which are markedly longer than the average distances. The Cu–O_{carboxylate}



Fig. 2. ORTEP drawing with atomic numbering scheme of the molecular structure of complex ion, **1**, from K_3 [**1**]-7H₂O-C₃H₆O. Hydrogen atoms, counter ions, and solvent molecules of crystallization have been omitted for clarity.



Fig. 3. ORTEP drawing with atomic numbering scheme of the molecular structure of complex ion, **1**, from the Na₃[**1**]·5H₂O. Hydrogen atoms, counter ions, and solvent molecules of crystallization have been omitted for clarity.



Fig. 4. ORTEP drawing with atomic numbering scheme of the molecular structure of complex ion, **2**, from Na₂[**2**].15H₂O. Hydrogen atoms, counter ions, and solvent molecules of crystallization have been omitted for clarity.

and Cu–N_{amine} bond distances are in the range of those previously reported in the literature [22].

3.4. Magnetic studies

Magnetic measurements were carried out on polycrystalline powder samples ranging from 2 to 300 K at the applied fields of 5 kOe. The compounds $K_3[1]$ ·7H₂O·C₃H₆O and Na₂[**2**]·15H₂O (due to structural similarity of $K_3[1]$ ·7H₂O·C₃H₆O and Na₃[1]·5H₂O, we carried out the magnetic study only for $K_3[1]$ ·7H₂O·C₃H₆O) show similar behavior. In Fig. 6 we represent the magnetic behavior of **1** and **2** in the forms of χ_M versus *T* and $\chi_M T$ versus *T* plots.

It is well-known that the magnetic behavior of divalent copper complexes bridged by a pair of hydroxide or alkoxide oxygen atoms is highly dependent on the Cu-O-Cu bridge angle [24,25]. Also it can be influenced, but in smaller measure, by the Cu-O bridge distance, the Cu...Cu separation, the geometry around the copper(II) center, and the geometry around the bridging oxygen atom. Hatfield and Hodgson have found a linear correlation between the experimentally determined exchange coupling constant and the Cu–O–Cu angle (σ). An antiferromagnetic character is found for complexes with σ larger than 97.6°, while ferromagnetic appears for smaller values of σ . An apparent similar linear relationship for alkoxide cases shows that at angles around 95.6° the exchange integral approaches zero, the point of the "accidental orthogonality". The magnetic response of compounds 1 and 2 probably will be dominated by the expected strong antiferromagnetic coupling via the alkoxide bridge with the Cu-O-Cu bond angles range from 123.2° to 138.6°.

Compound **1** shows a $\chi_M T$ value of 0.38 cm³ K mol⁻¹ for the Cu2 unit, smaller than that expected for two uncoupled S = 1/2 ions with g = 2.0 (0.75 cm³ K mol⁻¹). On cooling, the magnetic susceptibility χ_M presents a maximum at 143.8 K, whereas $\chi_M T$ decreases quickly, indicating a very strong antiferromagetic coupling. From $|J|/kT_{\text{max}} = 1.599$, |J| is estimated to be about 159.8 cm⁻¹ [26]. The χ_M value increases below 32 K because of magnetic impurity. The experimental magnetic data were fitted using the Bleaney–Bowers expression (1), based on the following Hamiltonian: $H = -J(S_1S_2)$ [27].

$$\chi_m = \frac{2N\beta^2 g^2}{k(T-\theta)} \frac{1}{[3 + \exp(-J/kT)]} (1-\rho) + \frac{N\beta^2 g^2 S'(S'+1)\rho}{3kT} + \text{TIP}$$
(1)

The parameters *N*, *g*, β , and *k* in the equation have their usual meanings with some applied corrections: paramagnetic impurity (fraction ρ), TIP (temperature independent paramagnetism), and a Weiss-like corrective term (θ). After the best least-squares fit to the experimental data, the parameters are given as: g = 2.01, $J = -169.6 \text{ cm}^{-1}$, $\theta = 0 \text{ K}$, $\rho = 0.08$, and TIP = $6.37 \times 10^{-4} \text{ emu mol}^{-1}$ with a final agreement factor $R = 4.86 \times 10^{-5} [R = \Sigma(\chi_m T^{\text{obsd}} - \chi_m T^{\text{calcd}})^2 / \Sigma(\chi_m T^{\text{obsd}})^2]$ and the correlation coefficient R^2 of 0.9976.

Complex **2** shows a $\chi_M T$ value of 0.55 cm³ K mol⁻¹ for the Cu4 unit, smaller than that expected for tetranuclear uncoupled S = 1/2 ions with g = 2.0 (1.5 cm³ K mol⁻¹). Upon cooling, $\chi_M T$ decreases sharply, while χ_M presents a maximum at 175.7 K, and then decreases quickly reaching a practically diamagnetic behavior below 50 K, indicating a very strong antiferromagnetic coupling. The similar behavior was also observed in a tetranuclear copper compound [28]. In complex **2**, two alkoxide and two water oxygen atoms alternatively bridge the four copper ions to form a Cu₄O₄ ring with the sequential bridging Cu–O–Cu angles of 137.0°, 123.2°, 138.6° and 128.1°. The Hamiltonian to use is $H = -J_1S_1S_2 - J_2S_2S_3 - J_3S_3S_4 - J_4S_1S_4$. Taking into account the compound topology, one can count the four exchange pathways, grouped into two averaged different exchange parameters, J_1 and



Fig. 5. (Left) Representation of the metal core and bridging water molecules (representing by O19 and O20) linking the two dinuclear units in complex ion, 2. (Right) Representation of the metal core emphasizing its concave shape in complex ion, 2.



Fig. 6. (Top) Plot of χ_M vs. *T* for K₃[**1**]·7H₂O·C₃H₆O ($_{\bigcirc}$) and Na₂[**2**]·15H₂O ($_{\square}$). The inset shows the maximum between 50–300 K. (Bottom) Plot of observed $\chi_M T$ vs. *T* for K₃[**1**]·7H₂O·C₃H₆O ($_{\bigcirc}$),Na₂[**2**]·15H₂O per Cu₄ unit ($_{\square}$) or Cu₂ unit ($_{\triangle}$). The solid lines represent the best theoretical fits.

 J_2 , corresponding to the alkoxide and water bridges, respectively. But it is difficult to find the energies and eigenfunctions of a spin Hamiltonian for the two J model with D_{2h} symmetry. On the base of the assumption that $J = J_1 = J_2 = J_3 = J_4$, in order to use the conventional spin–vector coupling model, eigenvalues of the Hamiltonian can be obtained analytically and are given by Eq. (2).

$$E(S', S_{13}, S_{24}) = -\frac{J}{2}[(S'(S'+1) - (S_{13}(S_{13}+1) - (S_{24}(S_{24}+1))]$$
(2)

where $S_{13} = S_1 + S_3$; $S_{24} = S_2 + S_4$; $S' = S_1 + S_2 + S_3 + S_4$. The relative energies of the states are:

Quintet: E(2,1,1) = -JTriplets: E(1,1,1) = J E(1,1,0) = 0 E(1,0,1) = 0Singlets: E(0,1,1) = -2JE(0,0,0) = 0

By substituting the appropriate energy terms into the modified van Vleck Eq. (3) refers to the energy of each spin state defined by *S'*, the susceptibility values can be computed as a function of temperature.

$$\chi_{m} = \frac{N\beta^{2}g^{2}}{3k(T-\theta)} \frac{\sum S'(S'+1)(2S'+1)\exp(-E(S)/kT)}{\sum (2S'+1)\exp(-E(S)/kT)} (1-\rho) + \frac{N\beta^{2}g^{2}S(S+1)\rho}{3kT} + \text{TIP}$$
(3)

After the best least-squares fit to the experimental data above 50 K, the parameters are given as: g = 2.00, $J = -186.4 \text{ cm}^{-1}$, $\theta = 0 \text{ K}$, $\rho = 0.15$, and TIP = $7.82 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1}$ with a final agreement factor $R = 9.85 \times 10^{-5} [R = \Sigma(\chi_m T^{\text{obsd}} - \chi_m T^{\text{calcd}})^2 / \Sigma(\chi_m T^{\text{obsd}})^2]$ and the correlation coefficient R^2 of 0.9972. If considering the exchange coupling J_2 via the water oxygen bridge can be neglected, the magnetic susceptibility will follow the Eq. (1). The best least-squares fit gave the parameters as: g = 2.00, $J_1 = -228.6 \text{ cm}^{-1}$, $\theta = 0 \text{ K}$, $\rho = 0.14$, and TIP = $7.31 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1}$ with a final agreement factor $R = 4.50 \times 10^{-5} [R = \Sigma(\chi_m T^{\text{obsd}} - \chi_m T^{\text{calcd}})^2 / \Sigma(\chi_m T^{\text{obsd}})^2]$ and the correlation coefficient R^2 of 0.9950. Although we cannot employ the irreducible tensor operator formalism (ITO) to fit the two J model with D_{2h} symmetry, the exchange coupling J_1

via the alkoxide bridge in **3** in both cases above is larger than that in **1**, which is reasonable due to the corresponding Cu–O–Cu bridging angles in **2** larger than the one in **1**.

3.5. Electrochemical studies

The redox properties of the complexes in water have been investigated by cyclic voltammetry using a glassy carbon or a platinum working electrode, KCl and platinum wire as supporting electrolyte and auxiliary electrode, respectively. The cathodic scan of solutions of complexes K₃[1]·7H₂O·C₃H₆O, Na₃[1]·5H₂O and $Na_2[2]$ ·15H₂O within 750 to -1000 mV potential window at a rate of 75 mV/s resulted in an electrochemical activity. Whereas the cyclic voltammograms are presented in Fig. 7, the electrochemical data for the complexes are given in Table 3. Additionally, the cyclic voltammograms of the complexes in 20-150 mV/s scan rate range, are presented in Figs. 4S, 5S and 6S (Supporting information). Under similar experimental conditions, the electrochemical studies of the free ligand using cyclic voltammetry revealed no electrochemical activity within the scanned potential window. Hence, the electrochemical waves observed in the cyclic voltammagrams of the complex can be characterized as metal-based electron transfer processes. The electrochemical properties of complex $K_3[1] \cdot 7H_2O \cdot C_{3-}$ H₆O, Na₃[1]·5H₂O and Na₂[2]·15H₂O feature an irreversible one electron reduction and one oxidation peak. On the other hand, complex Na₂[2]·15H₂O showed a more complex electrochemical behavior with two oxidation waves and two reduction waves.



Fig. 7. Cyclic voltammograms in aqueous solutions of (a) Compound $K_3[1]$ - $7H_2$. O·C₃H₆O; (b) compound Na₃[1]- $5H_2O$ and (c) compound Na₂[2]- $15H_2O$ measured at a scan rate of 75 mV/s using Pt (complexes K₃[1]- $7H_2O$ -C₃H₆O and Na₂[2]- $15H_2O$) and GC (complex Na₃[1]- $5H_2O$) working electroles and 0.2 M KCl supporting electrolyte. All potential are scaled to NHE using methyl viologen as a standard (MV²⁺/MV⁺, $E_{1/2}$ ^{NHE} = -0.45 V vs. NHE in water) [25].

Table 3

Electrochemical data for copper complexes K_3 [1]·7H₂O·C₃H₆O, Na₃[1]·5H₂O, and Na₂[2]·15H₂O.

Complex	$E_{1/2}$, V ($\Delta E_{\rm p}$, mV)	$E_{\rm pc}\left({\sf V}\right)$	$E_{\rm pa}\left({\sf V}\right)$	$i_{\rm pc}/i_{\rm pa}$
$K_3[1]$ ·7 H_2 O·C ₃ H_6 O ^a		-0.051	0.050	
			-0.134	
Na ₃ [1]·5H ₂ O ^b	-0.013 (339)	-0.182	0.157	3.7216
Na ₂ [2]·15H ₂ O ^a	-0.021 (60)	-0.127	-0.110	0.650
		-0.419	0.085	

Cyclic voltammograms in aqueous solutions of the compounds were measured at a scan rate of 75 mV/s using ^aPt and ^bGC working electrodes and 0.2 M KCl supporting electrolyte. All potential are scaled to NHE using methyl viologen as a standard $(MV^{2+}/MV^*, E_{1/2})^{NHE} = -0.45$ V vs. NHE in water) [25].

Fig. 7(a) shows the electrochemical response of complex $K_3[1]$ ·7H₂-O·C₃H₆O when initially the potential was scanned towards negative values. The irreversible reduction peak at 0.050 V is assigned to the reduction of $[1]^{3-/4-}$. Further scanning towards more negative potentials resulted only in the reduction of the solvent molecule. Upon reversing the scan towards positive potentials, two separate irreversible oxidations at -0.050 and -0.134 V were observed, and have been assigned to the $[1]^{4-/3-}$ and $[1]^{3-/2-}$ oxidations. Shown in Fig. 7(b) is the electrochemical response of complex 2 under similar experimental conditions. The voltammogram shows a clear irreversible reduction with E_{pc} value at -0.182 V and oxidation with E_{pa} at 0.157 V are assigned to the $[1]^{4-/3-}$ redox couple. Presented in Fig. 7(c) is cyclic voltammogram of complex Na₂[**2**]·15H₂O in aqueous solution. Unlike to the dicopper(II) complexes, the electrochemical response of this tetracopper complex exhibited more complex redox activity. The data indicate one reversible and one quasi reversible redox behavior. While the reversible peak, due to the $[\mathbf{2}]^{2-/3-}$ couple, has $E_{1/2}$ value of -0.021 V, the quasi reversible peak has its E_{pc} and E_{pa} peaks at -0.419 and 0.085 V, respectively. The cathodic peak is assigned to the reduction of $[\mathbf{2}]^{3-/4-}$ and the anodic peak is due to $[\mathbf{2}]^{4-/3-}$. When the values of the first reduction potentials for the dicopper(II) and the tetracopper(II) complex are compared, a positive cathodic shift in the $E_{1/2}$ value of $[\mathbf{2}]^{2-/3-}$ versus $[\mathbf{1}]^{3-/4-}$ is observed. The potential shift is partly attributed to the difference in the overall charge of the complexes, dianionic versus trianionic nature of the complexes in solution. The accessibility of reduction potential values of the complexes are similar when compared to the di- and trianionic copper complexes reported in the literature [29].

4. Conclusions

Three new polynuclear copper complexes with interesting coordination chemistry have been synthesized and fully characterized. The symmetrical dinucleating ligand, H₅ccdp, forms a dinuclear copper complex, $K_3[1]$ ·7H₂O·C₃H₆O, in the presence of a weak base. However, a different di-copper compound, Na₃[1]·5H₂O, and a tetra-copper compound Na₂[2]·15H₂O, was synthesized in the presence of a strong base. In Na₂[2]·15H₂O, the crystal structure comprises a rare topology of eight-membered ring formed by linking four coppers and two bridging water molecules. The coordination environment around the Cu(II) ions of the dinuclear complexes assume a distorted square pyramidal geometry. In the tetranuclear complex, however, the copper centers possess either a distorted square pyramidal or distorted trigonal bipyramidal geometry. As attempts to obtain crystals of compound $Na_3[1] \cdot 5H_2O$ in Argon atmosphere have been unsuccessful, this clearly indicates that atmospheric carbon dioxide plays a role in the formation of the Na₃[1]·5H₂O. Studies are underway to further explore the reactivity of the complex towards carbon dioxide. The variable-temperature magnetic susceptibility studies of K₃[1]·7H₂O·C₃H₆O and Na₂[**2**]·15H₂O reveal the overall strong antiferromagnetic coupling between Cu(II) ions with I values of -169.6 and -186.4 cm⁻¹, respectively. The fairly accessible metal based oxidation of the complexes is partly attributed to the *di*- and *tri*-anionic nature of the complexes in solution. This work demonstrates the versatility of the *penta*-anionic ligand, ccdp^{5–}, in forming different anionic multi-copper complexes, under different reaction conditions, with very accessible Cu^{III/II} reduction potentials and strong antiferromaginc coupling.

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Appendix A. Supplementary material

CCDC CD845591, CD845589, and CD845590 contain the supplecrystallographic data K3[1] 7H2O C3H6O, mentary for Na3[1]·5H2O and Na2[2]·15H₂O, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2012.08.013.

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