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An adaptable heterometallic trinuclear coordination cluster in the synthesis of tailored one-dimensional architecture: Structural characterization, magnetic analysis and theoretical calculations

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ABSTRACT

A new trinuclear complex $[(CuL^{\alpha-Me})_2Co(bnz)_2]$ (1) has been synthesized by using a metalloligand $[CuL^{\alpha-Me}]$ ($H_2L^{\alpha-Me}$ = N,N′-bis(α-methylsalicylidene)-1,3-propanediamine, bnz = benzoate) with *trans*-coordinated *syn–syn* bridging benzoate group ($1\kappa O{:}2\kappa O'$). The *syn–syn* coordinative selectivity of carboxylate towards this trinuclear unit leads exclusively to the formation of linear coordination cluster. Such coordinative adaptability is exploited for supramolecular assembly using a dicarboxylate linker, terephthalate (tph, 1,4-benzenedicarboxylate) which yielded a tailored one-dimensional quasi-linear coordination polymer $[(CuL^{\alpha-Me})_2Co(tph)]_n{\cdot}2nH_2O$ (2) having the linear trinuclear node. Isothermal magnetization measurement at 2 K suggests that both 1 and 2 posses $S = 1/2$ ground spin state indicating the presence of antiferromagnetic coupling at low temperature. The variable-temperature magnetic susceptibility measurements also reveal that both compounds are antiferromagnetically coupled with exchange coupling constants (J) of -17.3 and -9.2 cm^{-1} for 1 and 2, respectively. The nature and magnitude of exchange interactions are further corroborated by density functional calculations.

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1. Introduction

The chemistry of self organization process through non-covalent interactions has evolved to the idea of chemical programming i.e., systems capable of spontaneously generating precise supramolecular architectures by combinatorial self-assembly from reliable supramolecular synthons, thus behaving as programmed systems [1]. The program is molecular, where the information is stored in the covalent structural framework of the individual components and its operation is supramolecular, making use of recognition algorithms based on specific interaction patterns [2]. When the structural instructions are sufficiently strong, the system is narrowed down to singularity. This strategy is widely adopted in synthetic design of coordination polymers where mononuclear or polynuclear (homo-/heterometallic) complexes containing replaceable or available coordination sites (regarded as metallatecton) are combined with exodentate organic/inorganic ligands (anionic or neutral) as complementary tecton [3]. Recently, we had been intrigued by the robustness and adaptability of a family of bimetallic trinuclear Cu₂M (s, p, d and f metal ions) complexes derived from N₂O₂ donor Salen type di-Schiff base ligands obtained

from 2 + 1 condensation of a 2-phonolic carbonyl and a primary diamine (Scheme 1) [4]. Previous reports indicate that, when the carbonyl is an aldehyde (salicyldehyde), the trinuclear complex $[(CuL)_2M]^{n+}$ can desirably be transformed to linear or bent tecton to form discrete or infinite architectures with judicial choice of coligands [4d,5]. On the other hand, use of 2-hydroxyacetophenone invariably yields discrete bent complexes $[(CuL^{\alpha-Me})_2M]^{n+}$ that act very inertly in the attempt of joining them to form coordination polymer [6]. The preference for discrete bent trinuclear species may arise as the α-methyl group modulates (less $-R$ effect of keto-carbonyl group) the property of phenoxido donor atoms in a way that the interactions between two terminal metalloligands are sufficiently strong through axial site of the Cu centers which could not be perturbed by N-donor coligands. However, polyatomic O-donor ligands e.g. carboxylates are known to bind strongly with this type clusters to form discrete linear complexes [5a,7]. Therefore, a mono-carboxylate is expected to subdue the Cu–O axial interactions from phenoxido atoms and to form a discrete trinuclear complex whereas a di-carboxylate should join the linear cluster to generate a one dimensional (1D) coordination polymer [8]. Such endeavor with polycarboxylates has been pursued frequently to generate various oxido-bridged 1D-heterodinuclear systems while there is only one report that deals with heterometallic coordination polymer comprised of

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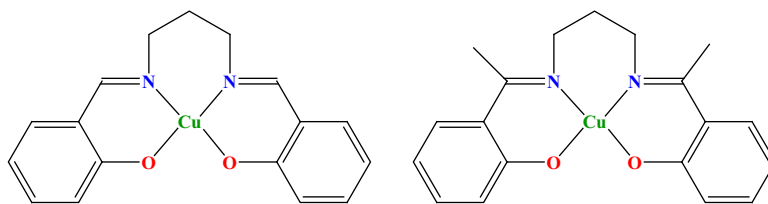
Scheme 1. Metalloligands [CuL] and [CuL$^{\alpha\text{-Me}}$].

oxido-bridged 3d–3d′ trinuclear node [9]. Moreover, theoretical DFT based evaluation of the magnetic exchange couplings between such heterometallic spin centers of 3d-block ions through single atom bridges or a long spacer (if any) are still considered to be very rare [10].

Herein we report synthesis, crystal structure and magnetic properties of two new heterometallic coordination complexes of formulae [(CuL$^{\alpha\text{-Me}}$)$_2$Co(bnz)$_2$] (**1**) and [(CuL$^{\alpha\text{-Me}}$)$_2$Co(tph)]$_n$·2nH$_2$O (**2**) [H$_2$L$^{\alpha\text{-Me}}$ = N,N′-bis(α-methylsalicylidene)-1,3-propanediamine; bnz$^-$ and tph^{2-} are benzoate and terephthalate, respectively]. As is expected, the monocarboxylate (benzoate) and dicarboxylate (terephthalate) groups resulted in the linear coordination cluster and one-dimensional quasi-linear coordination polymer, respectively, through *syn–syn* bridging mode (1κO:2κO′). The variable-temperature magnetic susceptibility measurement reveals that both compounds show very similar magnetic properties with anti-ferromagnetic exchange coupling (J) of −17.3 and −9.2 cm^{-1} for **1** and **2**, respectively. A magneto-structural correlation along with density functional theory based calculations and spin density plot successfully validate the magnetic behavior of these complexes.

2. Experimental

2.1. Starting materials

Reagent grade 2-hydroxyacetophenone and 1,3-propanediamine was obtained from Spectrochem, India and used as received. The sodium salts were prepared by reacting the corresponding carboxylic acid (10 mmol) with Na$_2$CO$_3$ (10 mmol) in water (100 ml). The solid product is collected through filtration and recrystallized from hot water. Other reagents and solvents used were of commercially available reagent quality, unless otherwise stated.

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Though not encountered throughout the experiment, only a small amount of material should be prepared and it should be handled with care.

2.2. Synthesis of the Schiff base ligand H$_2$L$^{\alpha\text{-Me}}$ and the metalloligand [CuL$^{\alpha\text{-Me}}$]

The di-Schiff base ligand H$_2$L$^{\alpha\text{-Me}}$ and the metalloligand [CuL$^{\alpha\text{-Me}}$] were prepared by the reported method described earlier [11].

2.3. Synthesis of [(CuL$^{\alpha\text{-Me}}$)$_2$Co(bnz)$_2$] (**1**) and [(CuL$^{\alpha\text{-Me}}$)$_2$Co (tph)]$_n$·2nH$_2$O (**2**)

To a solution (10 mL) of the precursor metalloligand [CuL$^{\alpha\text{-Me}}$] (0.038 g, 0.1 mmol) in methanol, a solution of Co(ClO$_4$)$_2$·6H$_2$O (0.018 g, 0.05 mmol, 5 mL methanol) was added and stirred for five minutes. To it an aqueous solution (5 mL) of sodium salt of bnz (benzoate) and tph (terephthalate) (0.014 g 0.1 mmol and 0.010 g, 0.05 mmol) for **1** and **2** respectively was slowly added drop wise with stirring. A green precipitate appeared in case of **2**. The mixtures were stirred for 2.5 h and then filtered. The clear filtrate was allowed to stand overnight at room temperature, and single

crystals of X-ray quality appeared at the bottom of the vessel of each solution.

Compound **1**: Yield 0.031 g (59%) *Anal.* Calc. for C$_{52}$H$_{50}$N$_4$O$_8$Cu$_2$-Co (1044.99): C 59.77, H 4.82, N 5.36. Found: C 59.67, H 4.91, N 5.28%. IR (KBr): ν_{s+as}(COO$^-$) = 1578, 1566, 1400 cm^{-1}, ν(C=N) = 1603 cm^{-1}.

Compound **2**: Yield 0.028 g, (56%) *Anal.* Calc. for C$_{46}$H$_{48}$N$_4$O$_{10}$-Cu$_2$Co (1002.92): C 55.09, H 4.82, N 5.59. Found: C 55.18, H 4.72, N 5.51%. IR (KBr): ν_{s+as}(COO$^-$) = 1579, 1539, 1368 cm^{-1}, ν(C=N) = 1600 cm^{-1}.

2.4. Physical measurements

Elemental analyses (C, H and N) were carried out using a Perkin-Elmer 2400 series II CHN analyzer. IR spectra (4000–500 cm^{-1}) were recorded by a Perkin-Elmer RXI FT-IR spectrophotometer in KBr pellets. All solutions were prepared in spectroscopic grade methanol. Variable-temperature magnetic-susceptibility data were collected on crystalline samples of **1** and **2** with a Quantum Design SQUID VSM magnetometer housed at the Center for Research in Nanoscience and Nanotechnology (CRNN) of the University of Calcutta. Pascal's constants were used to quantify diamagnetic corrections to the molar paramagnetic susceptibility, and a correction was applied for the sample holder.

2.5. Crystallographic data collection and refinement

Suitable single crystals of each of the two complexes were mounted on a Bruker-AXS SMART APEX II diffractometer ready with a graphite monochromator and Mo Kα (λ = 0.71073 Å) radiation. The crystals were placed at 60 mm from the CCD. 360 frames were measured with a counting time of 5 s. The structures were solved using Patterson method by using the SHELXS 97. Subsequent difference Fourier synthesis and least-square refinement revealed the positions of the remaining non-hydrogen atoms that were refined with independent anisotropic displacement parameters. However for complex **2**, the disordered oxygen atom O(11) of water molecule was refined isotropically in three positions. Hydrogen atoms were placed in idealized positions and their displacement parameters were fixed to be 1.2 times larger than those of the attached non-hydrogen atom except the interstitial solvent water molecules in **2** in which H atoms could not be located in the Fourier map. Successful convergence was indicated by the maximum shift/error of 0.001 for the last cycle of the least squares refinement. The non-ideal data obtained for complex **2** are due to the intrinsic nature of the crystal which on removal from mother liquor readily releases lattice solvent and disintegrate during data collection. The data set presented here is the best collected. Absorption corrections were carried out using the SADABS program [12]. All calculations were carried out using SHELXS 97 [13], SHELXL 97 [14], PLATON 99 [15], ORTEP-32 [16] and WINGX system ver-1.64 [17]. Data collection with selected structure refinement parameters and selected bond parameters for both the complexes are given in Table 1 and Table S1, ESI respectively.