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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

Soumavo Ghosh, Sanjib Giri, Ashutosh Ghosh*

Department of Chemistry, University College of Science, University of Calcutta, 92, A.P.C. Road, Kolkata 700009, India

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ABSTRACT

A new trinuclear complex $[(CuL^{\alpha-Me})_2Co(bnz)_2]$ (1) has been synthesized by using a metalloligand $[CuL^{\alpha-Me}]$ (H₂L^{$\alpha-Me$} = N,N'-bis(α -methylsalicylidene)-1,3-propanediamine, bnz = benzoate) with *trans*-coordinated syn-syn bridging benzoate group (1 κ O:2 κ 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 $[(CuL^{\alpha-Me})_2\dot{M}]^{n+}$ 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



^{*} Corresponding author. Fax: +91 33 2351 9755. *E-mail address:* ghosh_59@yahoo.com (A. Ghosh).



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

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 [$(CuL^{\alpha-Me})_2Co(bnz)_2$] (**1**) and [$(CuL^{\alpha-Me})_2Co(tph)$]_n·2nH₂O (**2**) [H₂L^{α -Me} = N,N'-bis(α -methylsalicylidene)-1,3-propanediamine; bnz⁻ and tph²⁻ 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 (1 κ O:2 κ O'). The variable-temperature magnetic susceptibility measurement reveals that both compounds show very similar magnetic properties with antiferromagnetic 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_2CO_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 $H_2L^{\alpha-Me}$ and the metalloligand $[CuL^{\alpha-Me}]$

The di-Schiff base ligand $H_2L^{\alpha-Me}$ and the metalloligand [CuL^{$\alpha-Me$}] were prepared by the reported method described earlier [11].

2.3. Synthesis of $[(CuL^{\alpha-Me})_2Co(bnz)_2]$ (1) and $[(CuL^{\alpha-Me})_2Co(tph)]_n \cdot 2nH_2O$ (2)

To a solution (10 mL) of the precursor metalloligand $[CuL^{\alpha-Me}]$ (0.038 g, 0.1 mmol) in methanol, a solution of $Co(ClO_4)_2 \cdot 6H_2O$ (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 $C_{52}H_{50}N_4O_8Cu_2$ -Co (1044.99): C 59.77, H 4.82, N 5.36. Found: C 59.67, H 4.91, N 5.28%. IR (KBr): $v_{s+as}(COO^-) = 1578$, 1566, 1400 cm⁻¹, v(C=N) = 1603 cm⁻¹.

Compound **2**: Yield 0.028 g, (56%) *Anal.* Calc. for $C_{46}H_{48}N_4O_{10}$ -Cu₂Co (1002.92): C 55.09, H 4.82, N 5.59. Found: C 55.18, H 4.72, N 5.51%. IR (KBr): $v_{s+as}(COO^-) = 1579$, 1539, 1368 cm⁻¹, v(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 K α (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.

Table 1

Crystal data and structure refinement of complexes 1 and 2.

Compound	1	2
Formula Formula weight Space group	C ₅₂ H ₅₀ N4O ₈ Cu ₂ Co 1044.99 monoclinic	C ₄₆ H ₄₈ N ₄ O ₁₀ Cu ₂ Co 1002.92 triclinic
Crystal system	$P2_1/n$	ΡĪ
a (Å)	11.346(5)	11.644(5)
b (Å)	10.808(5)	11.787(5)
c (Å)	19.288(5)	18.098(7)
α (°)	90	91.579(9)
β(°)	105.944(5)	90.987(8)
γ (°)	90	113.674(8)
V (Å ³)	2274.3(16)	2272.9(16)
Ζ	2	2
$D_{\rm calc}$ (g cm ⁻³⁾	1.526	1.459
μ (mm ⁻¹)	1.349	1.349
F(000)	1078	1026
R _{int}	0.0318	0.0776
θ (°)	1.9-25.6	1.1-25.0
Total reflections	15480	10874
Unique reflections	4213	7254
Data with $I > 2\sigma(I)$	3461	3052
R_1^a on $I > 2\sigma(I)$	0.0296	0.0936
wR_2^{b} ($I > 2\sigma(I)$)	0.0720	0.2358
GOF^c on F^2	1.037	1.002
T (K)	296	296

 $\begin{array}{l} ^{a} \ R_{1} = \Sigma ||F_{o}| - |F_{c}||/\Sigma|F_{o}|. \\ ^{b} \ wR_{2} = [\Sigma w(F_{o}^{2} - F_{c}^{2})^{2}/\Sigma w(F_{o}^{2})^{2}]^{1/2}. \\ ^{c} \ \text{GOF} = [\Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}/(N_{obs} - N_{params})]^{1/2}. \end{array}$

2.6. Computational methodology

To calculate the coupling constant (*I*) for complexes **1** and **2**, we have performed DFT calculation and the energies of high spin (E_{hs}) and broken symmetry (E_{bs}) states. The hybrid B3LYP functional [18-20] and def2-TZVP [21] basis set has been applied in all calculations as implemented in the ORCA package [22]. We have incorporated zeroth-order regular approximation (ZORA) to describe scalar relativistic effects along with tight SCF convergence criteria (Grid4) [23]. To speed up the calculations, we have used RI approximation by considering auxiliary def2-TZVP/I coulomb fitting basis sets [24]. Finally, the *I* values have been obtained from the Eq. (1) as proposed by Ruiz et al. [25].

$$2J = \frac{E_{bs} - E_{hs}}{2S_1 S_2 + S_1} \tag{1}$$

where $S_1 \ge S_2$

3. Result and discussions

3.1. Syntheses and spectroscopic characterizations of complexes 1 and **2**

Previously, we have synthesized quite a few trinuclear complexes using [CuL] and [CuL $^{\alpha-Me}$] as metalloligands [H₂L = N,N'bis(salicylidene)-1,3-propanediamine] (Scheme S1, ESI) [4-6]. Several trinuclear complexes derived from [CuL] were connected successfully by N-donor linker to produce oligo-/polymeric complexes. In contrast, every attempt of joining the metallatecton derived from $[CuL^{\alpha-Me}]$ metalloligands with the same linkers failed and only discrete trinuclear complexes were formed [6.26]. In the present study, we chose O-donor ligands benzoate and terephthalate that can potentially coordinate to the metal centers in a stronger way (one coordination bond for N-donor linker vs. two coordination bonds for O-donor carboxylate linker). Both the complexes were obtained as dark green crystals upon mixing the required precursors in methanol at room temperature and subsequent slow evaporation of the solvent (Scheme 2). As expected, benzoate produces discrete trinuclear linear coordination cluster whereas terephthalate yields a rare one-dimensional chain comprising of the same bimetallic trinuclear core.

Besides elemental analyses, both compounds 1 and 2 were initially characterized by IR spectra (Fig. S1, ESI). The precursor metalloligand $[CuL^{\alpha-Me}]$ is neutral and does not have any counter anion, whereas both the complexes include IR active carboxylato coligands. The carboxylato anion shows its characteristic bands for bidentate chelation for each compound [5]. In both complexes, a strong and sharp band due to the azomethine v(C=N) group of the Schiff base appears at 1600–1603 cm⁻¹ for $[CuL^{\alpha-Me}]$ as observed before [5].

3.2. Structure descriptions

Both complexes 1 and 2 consist of linear trinuclear $(Cu^{II}L^{\alpha-Me})_{2}$ - $Co^{"}$ units [5a] of formulae [$(CuL^{\alpha-Me})_2Co(bnz)_2$] and [$(CuL^{\alpha-Me})_2Co$ $(tph)]_n 2nH_2O$, respectively where Co^{II} resides at the center of inversion. The asymmetric unit of complex 2 possesses crystallographically two different halves of $(CuL^{\alpha-Me})_2$ Co units with slightly different bond parameters, which are connected by two carboxylate $(1\kappa O: 2\kappa O')$ groups from one tph linker. The corresponding molecular structures are depicted in Figs. 1 and 2, and selected bond lengths and angles are listed in Table S1, ESI.

The trinuclear units in both structures contain a hexacoordinate central cobalt atom in a CoO₆ octahedral geometry together with two pentacoordinate square-pyramidal copper atoms. The four μ_2 -bridging phenoxido oxygen atoms around Co^{II} from two $(CuL^{\alpha-Me})$ metalloligands are in a planar arrangement. These are O(1) and O(2) and their symmetry related ones (O(1a) and O(2a)) for Co(1) in complex **1**. For complex **2**, these atoms are O(1), O(2)and O(5), O(6) and their symmetry related ones (O(1a), O(2a) and O(5a), O(6a)) for Co(1) and Co(2) respectively. The Co-O distances for 1 are 2.093(2) and 2.208(2) Å whereas those for 2 ranges 2.115(8)–2.184(9) Å. These are comparable to the reported high spin octahedral Co^{II}–O bond distances [5a]. A pair of O atoms from two syn-syn bridging $(1\kappa O: 2\kappa O')$ carboxylato donors coordinate *trans*- to the central Co atom to complete the octahedral coordination sphere of Co^{II}. These atoms for complex 1; O(3) and O(3a) are distances at 2.023(2) Å and for complex 2; O(3), O(3a) and O(7), O(7a) (for Co(1) and Co(2) respectively) are distances at 2.009(8) and 2.035(8) Å respectively. In each of the Co centers for both complexes, the *cis* angles involving the carboxylato oxygen atoms [in the ranges of 87.7(1)°-92.3(1)° for **1** and $88.6(3)^\circ - 91.4(3)^\circ$ for **2**] are close to the ideal values (90°) but the *cis* angles in the plane of phenoxido O atoms [range between 73.8(1)°-106.2(1)° for **1** and 76.2(3)°-103.8(3)° for **2**] deviate considerably indicating a distorted octahedral geometry.

The symmetrically related Cu atoms from each metalloligand of these centrosymmetric linear $(Cu^{II}L^{\alpha-Me})_2Co^{II}$ units take up a five coordinated square pyramidal geometry in both complexes. Each of these square pyramids is comprised of a N₂O₂ basal plane belonging to two phenoxido O atoms and two imine N atoms (O(1), O(2), N(1) and N(2) for Cu(1) in 1; O(1), O(2), N(1), N(2) and O(5), O(6), N(3), N(4) for Cu(1) and Cu(2) respectively in 2) from doubly deprotonated $H_2L^{\alpha-Me}$ ligand. The axial positions are occupied by coordinated oxygen atoms (O(4) for Cu(1) in 1; O(4)and O(8) for Cu(1) and Cu(2) respectively in 2) of the syn-syn bridging carboxylato groups. The Cu-O and Cu-N bond lengths at the N₂O₂ basal planes in **1** are 1.932(2), 1.955(2) and 1.990(2), 1.996(2) Å, respectively and the axial Cu-O bond distance is 2.257(2) Å. Whereas the Cu-O and Cu-N bond lengths at the N₂O₂ basal planes in **2** are ranges between 1.943(8)–1.973(9)Å and 1.949(16)-1.999(13) Å, respectively and axial Cu-O bond distances are 2.199(11) and 2.221(10) Å. The r.m.s. deviation of the four basal atoms from the mean plane for complex **1** is 0.016



Scheme 2. Syntheses of complexes 1 and 2.



Fig. 1. Molecular structure of complex **1** along with atomic numbering scheme (H atoms are omitted for clarity; color scheme Co pink, Cu green, O red, N blue, C white; symmetry operation a = 2 - x, -y, 2 - z). (Color online.)

(4) Å with the metal atom 0.180(1) Å from this plane toward the axially coordinated O(4) atom of Cu(1). The same deviations for Cu(1) and Cu(2) centers in complex **2** are 0.054(23) and 0.026 (23) Å with the metal atoms 0.233(2) and 0.191(2) Å from the plane toward the axially coordinated O(4) and O(8) atoms, respectively. The Addison parameters of Cu(1) atom in complex **1** as well as of Cu(1) and Cu(2) atoms in complex **2** are 0.013, 0.103 and 0.055 respectively indicating negligible amount of distortion toward trigonal bipyramid geometry [27].

The structural characterizations of complexes 1 and 2 reveal that the basic structural unit, $(Cu^{II}L^{\alpha-Me})_2Co^{II}$ metallatecton has an intriguing ability to distinguish a carboxylato functionality only at its *trans*-positions in a particular coordinating (*syn-syn* bridging) mode that makes it useful for programmed supramolecular system (Fig. 3) [5a,b]. It arises due to formation of a typical linear Cu₂Co coordination cluster comprising of a central Co-octahedron and two terminal Cu-square pyramids in an edge-sharing manner where the apical coordination sites of two Cu centers are mutually trans and aligned with the axial sites of Co atom to accommodate two carboxylato groups. Such coordinative selectivity of the trinuclear unit towards carboxylate (coordinative adaptability) would not allow any coordination mismatch. As a result, it leads to the formation of a discrete trinuclear complex, **1** with benzoate (a mono-carboxylate donor) whereas with terephthalate (a di-carboxylate: ditopic linker) the trinuclear metallatectons are connected to form a heterometallic one-dimensional quasi-linear chain 2. The results indicate that the fidelity of the $(Cu^{II}L^{\alpha-Me})_2Co^{II}$ metallatecton in forming precisely designed architectures with carboxylato based



Fig. 2. Molecular structure of complex **2** with atomic numbering scheme (H atoms and solvent molecules are omitted for clarity; color scheme unchanged; symmetry operation a = 3 - x, 3 - y, 1 - z and 2 - x, 2 - y, 2 - z for Co(1) and Co(2) respectively). (Color online.)



Fig. 3. Supramolecular growth from discrete linear complex 1 to 1D quasi-linear chain of 2 with identical coordination cluster substituting benzoate by terephthalate.

functionalities is good enough to use them as reliable supramolecular synthon for crystal engineering and molecular tectonics.

It is to be noted that a large number of bimetallic Cu(II)-M tecton (M = Mn(II), Co(II), Ni(II), Zn(II), Cd(II), Hg(II), Na(I), K(I), Ln(III)) consisting of Schiff base ligands derived from the reaction of amines with aldehydes have been used to prepare coordination polymers [4d,6c,9,26,28]. Such example with Schiff bases derived from ketone is extremely rare. Complex 2 represents only the second coordination polymer where the Schiff base moiety of the bimetallic tecton is made by 2+1 condensation of a ketone (2-hydroxyacetophenone) and 1,3-propanediamine [29]. Moreover, the previously used bimetallic tectons are mostly dinuclear, derived from bicompartmental Schiff base ligands. Compared to them fewer bimetallic trinuclear tectons had been joined with N-donor linkers (dicyanamide, cyanometallates, 4,4'-bipridine etc.) to form coordination polymers [4d,6c,9a,26,28c,28d,29,30]. There are some examples where very similar trinuclear units have been joined with dicarboxylates but the used carbonyls are aldehyde [9d,28e,31]. Complex 2 is the first example where a keto-carbonyl derived bimetallic trinuclear tecton has been connected with a dicarboxylate to form a rationally designed 1Dcoordination polymer.

3.3. Description of supramolecular interactions

The packing of the molecules in both complexes **1** and **2** is controlled by $C-H\cdots\pi$ and $C-H\cdots0$ interactions. There are two types of $C-H\cdots\pi$ interactions, namely, $C-H\cdots\pi$ (side chain) and $C-H\cdots\pi$ (phenyl), between the neighboring molecules of **1** and **2** to generate a three-dimensional (3D) supramolecular architecture (Fig. 4).

In case of **1**, C–H··· π (phenyl) interaction is established between the hydrogen atoms H(3) of a phenyl ring of one molecule and the phenyl ring of the Schiff base of another molecule and vice versa, forming a one-dimensional (1D) supramolecular column parallel to crystallographic *b*-axis at $C(3)-H(3)\cdots C_g(1)$ and $C(3)\cdots C_g(1)$ $(C_g = centroid of the phenyl ring) distances of 2.61 and 3.47(1) Å,$ respectively with $\angle C(3)-H(3)\cdots C_g(1)$ angles of 155° (symmetry code: x, -1 + y, z). These supramolecular columns are closely packed to form a two dimensional layer parallel to $10\overline{1}$ plane by another C–H··· π (phenyl) interaction through H(15) at C(15)–H $(15) \cdots C_g(2)$ and $C(15) \cdots C_g(2)$ with the distances of 2.97 and 3.82 (1) Å, respectively and $\angle C(15)$ -H(15)···C_g(2) angles of 154° (symmetry code: 5/2 - x, 1/2 + y, 5/2 - z). These layers are stacked to form three dimensional architecture by $C-H\cdots\pi$ (side chain) interaction through H(9A) of the methylene chain of the Schiff base. The C(9)–H(9A)···C_g(2) and C(9)···C_g(2) distances are 2.99 and 3.91(1)Å, respectively with $\angle C(9)-H(9A)\cdots C_g(2)$ angle of 157° (symmetry code: 3 - x, -y, 2 - z). These stacking is further reinforced by a non-classical C-H···O interaction occurring through C(8)–H(8B)···O(4) of the α -methyl group of the Schiff base and carboxylato oxygen at $H(8B) \cdots O(4)$ and $C(8) \cdots O(4)$ distances of 2.67 and 3.51(1) Å, respectively with $\angle C(8) - H(8B) \cdots O(4)$ angles of 146° (symmetry code: 3 - x, -y, 2 - z).

In case of **2**, the 1D-quasilinear chains being parallel to each other (no supramolecular entanglement) mutually interact to form a two dimensional supramolecular sheet like architecture through a C-H···O interaction parallel to 011 plane. It takes place through α -methyl group of the Schiff base with the carboxylate functions of terephthalate linkers at C(8)–H(8B)···O(8) and C(8)···O(8) distances of 2.71 and 3.61(3) Å, respectively with \angle C(8)–H(8B)···O(8) angles of 157° (symmetry code: -1 + x, -1 + y, z). These sheets further interact to form 3D-supramoleclar network by

2D-Sheet (left) to 3D architecture (right)



Fig. 4. 3D supramolecular packing (right panel) of trinuclear complexes 1 (upper panel) and 2 (lower panel) formed by stacking of 2D layers (highlighted as red boxes) which are assembled (left panel) from interaction between 1D columns/chains (highlighted as gray shading). See text for details. (Colour online.)

C-H··· π (side chain) interaction through H(31A) of the α -methyl group of the Schiff base at C(31)–H(31A)···C_g(1) and C(31)··· C_g(1) distances of 2.99 and 3.81(2) Å, respectively with \angle C(9)–H (9A)···C_g(2) angles of 144° (symmetry code: 1 – *x*, 2 – *y*, 2 – *z*). The introduction of the tph in **2** is likely to form structural voids that are occupied by guest water molecules which are not observed in **1**.

3.4. Magnetic properties

Powdered polycrystalline samples of 1 and 2 were used for the molar paramagnetic susceptibility (χ_M) measurements in the temperature (T) range of 2–300 K under a constant magnetic field of 0.05 T. The compounds exhibited very similar magnetic properties as expected from their analogous bond parameters (Fig. 5). The resultant of the molar magnetic susceptibility times the temperature ($\chi_{\rm M}T$) shows the values of ca. 3.47 and 3.55 cm³ K mol⁻¹ at room temperature for compounds 1 and 2 respectively which are within the usual range expected for two non-interacting Cu(II) ions and a Co(II) ion i.e. per Cu₂Co trimer. The values of ca. 2.67 and 2.75 cm³ K mol⁻¹ for the Co(II) contribution of compounds **1** and 2, respectively are found by subtracting the expected room temperature contribution for two Cu(II) ions (ca. $0.80 \text{ cm}^3 \text{ K mol}^{-1}$, $g_{Cu(II)}$ = 2.00) for each trimeric units (within the normal range of 2.5–3.1 cm³ K mol⁻¹ observed in isolated high-spin octahedral Co (II) complexes, $g_{Co(II)} = 2.1-7.0$ [32]. These values are way above the expected ones for an S = 3/2 spin ground state (1.875 cm³ -K mol⁻¹) that signifies the presence of an orbital contribution arising from the ${}^{4}T_{1}$ ground state of high-spin octahedral Co(II) complexes. The $\gamma_{\rm M}T$ values exhibit a constant decrease by lowering the temperature to reach a smooth plateau of ca. 0.1 cm³ K mol⁻¹

at low temperature (a small bump in compound **1**, ascribed to the occurrence of a small portion of a paramagnetic impurity). The decrease in the observed $\chi_M T$ may be account for two possible reasons: firstly, it may be an outcome of the first-order spin–orbit coupling present in Co(II) complexes; secondly, it may be because of an antiferromagnetic coupling between the central Co(II) ion and the terminal Cu(II) ones per Cu₂Co unit. Since the spin–orbit coupling in isolated Co(II) complexes normally led to $\chi_M T$ values at 2 K in the range of 1.0–2.0 cm³ K mol⁻¹ which is well above the observed value of ca. 0.1 cm³ K mol⁻¹ on an average for both compounds [33]. This indicates that both compounds present an antiferromagnetic coupling between the central Co(II) and the terminal Cu(II) ions.

The presence of antiferromagnetic couplings in both compounds are further confirmed from the temperature dependence of the molar susceptibility $\chi_{\rm M}$ that shows maxima at ca. 53 and 31 K for **1** and **2**, respectively, which are slightly masked by the paramagnetic contribution (Curie tail) of the *S* = 1/2 ground state at low temperatures. This contribution of the *S* = 1/2 ground state is clearly seen in the isothermal magnetization measurements of **1** and **2** at 2 K that show saturation values almost of 1 $\mu_{\rm B}$ (0.93 and 1.04 $\mu_{\rm B}$ for **1** and **2** respectively) which is the projected value for a *S* = 1/2 spin ground state with *g* = 2 (Figs. S3 and S4, ESI).

Both compounds possess a centrosymmetric linear trinuclear unit with a central Co(II) ion connected to two terminal Cu(II) ions through a double phenoxido bridge and single carboxylato bridged. As there is a negligible difference present between two Cu₂Co trimers in one asymmetric unit of compound **2** they can be considered as equivalent units like **1**. We have considered a model that ascribed for a ground state of ⁴*T*₁ for the octahedral Co(II) ion with *S* = 3/2 spin state with angular momentum *L* = 1. The Hamiltonian



Fig. 5. $\chi_{M}T$ vs. *T* plots for complexes **1** (left) and **2** (right) at an applied dc field of 0.05 T.

for this trinuclear system comprises of three part: (a) an isotropic exchange interaction between Cu(II) and Co(II) real spins (*S*) that based on the Lines model [6c,34], (b) a spin–orbit interaction term in the Co(II) ion, and (c) a term considering the effect of axial distortions [35]:

$$\dot{H} = -2J(S_{\text{Cu}1}S_{\text{Co}} + S_{\text{Cu}2}S_{\text{Co}}) + A\sigma\lambda S_{\text{Co}}L + D(L_z^2 + L(L+1))$$

In this Hamiltonian *J* is the exchange coupling constant between Co and Cu, σ is the orbital reduction factor and λ is the spin–orbit coupling constant. The *A* factor, described in the perspective of *T* and *P* term isomorphism that allows differentiation between the matrix elements of the orbital angular momentum operator, calculated with the employment of the *P* term basis from those calculated with the wave functions of the ⁴T₁ term [36]. The Zeeman interaction is supposed to be isotropic and can be demonstrated as:

$$H = \beta (g_e S_{Co} + A\sigma L)H + \beta g_{Cu} (S_{Cu1} + S_{Cu2})H$$

where the first part illustrates the interaction of an octahedral Co(II) ion with an external magnetic field together with both spin and orbital Zeeman contributions (g_e is the electronic g factor) and the second term only tells about the spin Zeeman contribution of the Cu(II) ions.

Since, the problem does not allow for an analytical solution for fitting the magnetic properties to the wave equation from the resulting Hamiltonian [37]; therefore, to simulate the magnetic properties in these systems, it is necessary to employ matrix diagonalization procedures [38] and the program PHI [39] was employed for the diagonalization of the matrix arising from this Hamiltonian and to obtain the parameters that best fit the experimental data. A very reasonable fit of the $\chi_M T$ product is obtained for both compounds with the parameters displayed in (solid lines in Fig. 5). The data could only be fitted satisfactorily if the contribution of a small amount of a Cu(II) paramagnetic impurity (unreacted metalloligand) was considered (amounting to molar fractions of 1.5% and 2.5% in 1 and 2, respectively). The best solutions obtained for J, for compounds 1 and 2 were, -17.3 and -9.2 cm⁻¹ respectively. Very weak coupling shall take place across the terephthalate linkers which is negligible compared to phenoxido bridges thus cannot be quantified. The solutions were acquired for g, λ , and σ values of (in the 1/2 format) 2.02/2.08, -180/-179 cm⁻¹, and -1.25/-1.10, respectively, and the consequent simulations are represented as solid lines in Fig. 5.

The antiferromagnetic coupling observed in these two compounds can be explained from their structures. They both present double 1,1-phenoxido and single 1,3-carboxylato bridges connecting the central Co(II) ion with the two terminal Cu(II) ones which are known to be active as magnetic couplers [40]. However, as the carboxylato functionalities are bound to the square pyramidal Cu(II) ions through the long axial positions, their interaction with the $d_{x^2-y^2}$ magnetic orbitals of the Cu(II) ions and, thus, their contribution to the magnetic coupling is expected to be negligible [41]. Thus in the present system, Cu–O–Co bridges are only active for magnetic couplings which is mainly controlled by the Cu–O–Co bond angle and bond distances. Correlations show that for such cases the coupling is antiferromagnetic (even average bond angle as low as 91.5°) and increases (in absolute value) as the Cu–O–Co angle increases [5a].

In compounds **1** and **2** the Cu–O–Co bond angles are $97.0(1)^{\circ}$ and $100.2(1)^{\circ}$ (in **1**) and $96.2(3)^{\circ}$, $95.3(3)^{\circ}$, $97.3(3)^{\circ}$, and $96.5(4)^{\circ}$ (in **2**). We can conclude that for the angles present in compounds **1** and **2** the Cu–Co coupling is expected to be antiferromagnetic and moderate, in agreement with the experimental results. Furthermore, since the average Cu–O–Co bond angles are significantly larger in compound **1** ($98.6(1)^{\circ}$) than in **2** ($96.3(8)^{\circ}$), compound **2** is expected to show a smaller antiferromagnetic coupling which is in agreement with the observed *J* values.

The antiferromagnetic interaction observed in compounds **1** and **2** are of the same order as those of the only two reported discrete linear triply bridged Cu_2Co complexes with similar double oxido bridges [5a]. The present study thus allows investigating any strong magnetic exchange taking place between the connected units. However such complexes behaved similar as discrete magnetic unit while linking them with such a long spacer as terephthalate due to very small exchange taking place through linker compared to that through phenoxido bridges. In order to increase the magnetic communication between two consecutive trinuclear units the linker better be much shorter albeit, one cannot establish any comparison.

3.5. DFT calculations

To obtain further insight into the magneto-structural phenomena along with exchange mechanism, we adopted DFT calculations using broken symmetry approach and calculated *J* values theoretically. The DFT calculation gives the following values of J = -19.01and -8.75 cm⁻¹ for complexes **1** and **2**, which agree well with the

Table 2

Calculated and experimentally obtained coupling constant (J) parameters of complexes 1 and 2.

Complex	Average Cu-O-Co	Coupling constant (J)	Coupling constant
	bond angles (°)	Ruiz method (cm ⁻¹)	(J) Exp (cm ⁻¹)
1	98.6(1)	-19.01	-17.26
2	96.3(8)	-8.75	-9.2



Fig. 6. Spin density plot corresponds to the low spin state (S = 1/2) for **1** (left) and **2** (right). Positive and negative values are represented as white and blue surfaces with isosurface cutoff value 0.004 e/Å³. (Colour online.)

experimentally obtained values of J = -17.26 and -9.2 cm⁻¹, respectively (Table 2). The spin density plots (Fig. 6) show that the $d_{x^2-y^2}$ orbitals of the Cu(II) centers combined with the hybrid p-orbitals of the bridging phenoxy ligands and Co(II) d-orbital are playing main role in the hetero exchange coupling.

It is clear from the Mulliken atomic spin distributions (Table S2, ESI) that both of the complexes at high spin state support direct spin delocalization mechanism in which Co atoms carry ~80% of net spin and the remaining part is delocalized over coordinating and bridging atoms of the ligands. The spin delocalization is strong as it is found that \sim 20% of the spins for the unpaired electrons on the Cu(II) and Co(II) centers are delocalized onto the ligand atoms. It is also seen that the phenoxo-bridged oxygen are carrying a moderate amount of (0.10-0.11 au) positive spin density. This indicates a weak to moderate antiferromagnetic exchange through direct spin delocalization mechanism. It is worth to note that with increase in positive spin density at bridging phenoxo oxygen causes more delocalization which in turn is responsible for stronger antiferromagnetic interaction [42]. Considering µ-1,3-carboxylate bridges, it is seen that noticeable spin densities are delocalized on the carboxylate oxygen connecting to cobalt center; however, spin densities on carboxylate oxygen connecting to copper center is negligible. The central carbon atoms of carboxylates group also show a very small spin density in both of the cases implying a very weak antiferromagnetic interaction through the carboxylate linker.

4. Conclusions

Herein, we synthesized two bimetallic $Cu_{\perp}^{II}Co^{II}$ complexes, derived from a N₂O₂-donor salen-type Schiff base metalloligand [CuL^{α -Me}], from keto precursor that has been very rarely used to synthesize coordination polymer. This metalloligand usually produces discrete bent trinuclear complexes even in the presence of bridging anions. However, utilizing the coordinative selectivity of the flexible trinuclear [(CuL^{α -Me})₂Co]²⁺ coordination cluster towards carboxylate donors, we succeed to steer its geometry into linear form as is found in the discrete complex with benzoate (**1**). Our attempt in joining these linear nodes by dicarboxylate to generate 1D-polymeric architecture is successful with terephthalate yielding complex **2**. Magnetic susceptibility measurement reveals that both compounds are antiferromagnetically coupled with exchange coupling (*J*) of -17.3 and -9.2 cm⁻¹ for **1** and **2** respectively. The difference in values of *J* can be correlated with phenoxido bridging angles of such compounds. The nature and magnitude of exchange interactions were further supported from density functional calculations. These discrete and polymeric systems with structural similarities give an excellent platform for comparative study of magnetic properties. It suggests that the phenoxido bridging atoms act as the significant spin carriers in these systems whereas possible contribution of magnetic exchange through μ -1,3-carboxylate bridges or along terephthalate is negligible. This DFT-based theoretical perspective of magnetic interaction pathways of the heterometallic nodes is presented in this study which has rarely been evaluated previously.

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Appendix A. Supplementary data

The electronic supplementary information file contains the IR spectra, the synthetic scheme for trinuclear tecton, the plots for molar paramagnetic susceptibility (χ_M) measurements in the temperature (*T*) range of 2–300 K and field dependant molar magnetization plots at 2 K (Figs. S1–S3) as well as tables for bond parameters and Mulliken atomic spin densities of the complexes (Tables S1 and S2). CCDC 1055823 (for 1) and 1055824 (for 2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac. uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@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.poly.2015.10.014.

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