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Self-assembly of three new coordination complexes: Formation of 2-D square grid, 1-D chain and tape structures

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ABSTRACT

Three distinct coordination complexes, viz, $[Co(imi)_2(tmb)_2]$ (1) [where imi = imidazole], {[Ni(tmb)_2 $(H_2O)_3$ $\cdot 2H_2O_{n}$ (2) and $[Cu_2(\mu-tmb)_4(CH_3OH)_2]$ (3), have been synthesized hydrothermally by the reactions of metal acetates, 2,4,6-trimethylbenzoic acid (Htmb) and with or without appropriate amine. The Ni analogue of **1** and the Co analogue of **2** have also been synthesized. X-ray single-crystal diffraction suggests that complex 1 represents discrete mononuclear species and complex 2 represents a 1D chain coordination polymer in which the Ni(II) ions are connected by the bridging water molecules. Complex 3 represents a neutral dinuclear complex. In 1, the central metal ions are associated by the carboxylate moiety and imidazole ligands, whereas the central metal atom is coordinated to the carboxylate moiety and the respective solvent molecules in 2 and 3. In 3, the four 2,4,6-trimethylbenzoate moieties act as a bridge connecting two copper (II) ions and the O atoms of methanol coordinate in an anti arrangement to form a square pyramidal geometry, with the methanol molecule at the apical position. In all the three structures the central metal atom sits on a crystallographic inversion centre. In all the cases, the coordination entities are further organized via hydrogen bonding interactions to generate multifarious supramolecular networks. Complexes 1, 2 and 3 have also been characterized by spectroscopic (UV/Vis and IR) and thermal analysis (TGA). In addition, the complexes were found to exhibit antimicrobial activity.The magnetic susceptibility measurements, measured from 8 to 300 K, revealed antiferromagnetic interactions between the Co(II) ions in compound 1 and the Ni(II) ions in 1a, respectively.

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1. Introduction

The exercise of small molecule replica complexes to study more complex organic or life systems has long been appreciated by chemists [1], especially given the reality that structural geometries of model complexes are often quite comparable to those in the proteins [2]. Nitrogen containing heterocyclic ligands are a subject of much interest to those who wish to model biological systems including histidine and its imidazole-1 type bonding [3–9]. Many proteins and enzymes are known to contain active sites with multiple histidine residues bound to a metal center, including, among others, the long studied carbonic anhydrase [7,10], nitrite reductase [6], dopamine β hydroxylase [11,12], superoxide dismutase [13–17], cytochrome *c* oxidase [4,18,19], pirin [20], and acireductone dioxygenases [21]. These enzymes have been shown to contain three histidine residues bound to a metal center in a

distorted tetrahedral or facial octahedral geometry, conducive for model complexes with a tridentate ligand system.

The role of imidazole as a complexing agent has been studied for years, mainly because imidazole is involved in important biological processes [22–26]. The tertiary nitrogen atom in imidazole is a good resource to coordinate with a metal ion and a good number of compounds based on imidazole and different metal ions have been reported [27–33]. On the other hand, the secondary nitrogen atom is a good hydrogen bonding donor and, multidimensional supramolecular assembly can be obtained *via* hydrogen bonding interactions [34–41].

The deliberate construction of extended metal–organic network systems is an area of active research in recent years [42] and variety of organic–inorganic compounds containing benzene-substituted-carboxylic acid and or N-donor ligands as the organic part have been structurally characterized. The structures of these compounds are held together by strong metal–ligand bonding and further stabilized by weaker bonding forces such as hydrogen bonding and π – π interactions. The importance of

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H-bonding interactions for the assembly of supramolecular structures is well documented in the literature [43,44]. A convenient way to build unbounded polymeric structures is by using a multi-functional ligand to link metal ions to form an infinite configuration. In this perspective, substituted benzenecarboxylic acids have been exposed to be very constructive reagents by numerous research groups, as evidenced by the exciting array of interesting metal-organic molecular architectures synthesized from this category of ligands [45-49]. The benefit of using benzene based ligand systems is due to the fact that donor groups like -COOH, -SH, -NH₂, etc. can be anchored onto the rigid six-membered benzene ring and the resulting supramolecular structures will largely depend on the positioning of the donor groups on the six membered ring. Besides, the donor groups can also participate in H-bonding interactions as well to the formation of a metal-ligand bond. As part of an ongoing programme, we are investigating the chemistry of metal complexes of 2.4.6-trimethylbenzoic acid (Htmb). In continuation of this theme, we wish to present the synthesis, spectroscopic, thermal, and structural characterization of three new transition metal 2,4,6-trimethylbenzoates with or without an amine [50].

2. Experimental

2.1. Materials and methods

All chemicals purchased were of analytical grade and used without further purification. IR spectra were recorded on a JASCO FTIR-410 spectrometer using KBr pellets. UV/Vis spectra were recorded on a Perkin-Elmer Lambda 25 UV/Vis spectrophotometer. Thermogravimetric analysis was performed on a Mettler Toledo Star system from room temperature to 700 °C with a heating rate of 10 °C/min. Elemental analysis was carried out using a Perkin-Elmer 1400C analyzer. Magnetic susceptibility measurements were performed on a George Associate Faraday Force Magnetometer.

2.2. Synthesis

A mixture of cobalt acetate tetrahydrate (0.0311 g, 0.125 mmol), 2,4,6-trimethylbenzoic acid (0.041 g, 0.250 mmol), imidazole (0.017 g, 0.250 mmol), and water (2.5 mL) was homogenized for 30 min. It was then sealed in a 23 mL polyfluoroethylene-lined stainless steel bomb, and kept at 150 °C under autogenous



pressure for 72 h. After cooling at a ramp of 10 °C per hour to room temperature, magenta coloured crystals of $Co(tmb)_2(imi)_2$ were collected by filtration, washed with de-ionized water followed by diethyl ether, and then dried (0.0442 g, 68%). Anal. Calc. for $C_{26}H_{30}N_4O_4Co$: C, 59.88; H, 5.80; N, 10.74%: Found: C, 60.40; H, 5.45; N, 10.93%.

Similar procedure was adopted for the synthesis of **1a** with nickel acetate tetrahydrate used in place of cobalt acetate tetrahy-

drate. Anal. Calc. for $C_{26}H_{30}N_4O_4Co$: C, 59.88; H, 5.80; N, 10.74%: Found: C, 60.80; H, 5.77; N, 10.94%.

Nickel acetate tetrahydrate (0.0311 g, 0.125 mmol), and 2,4,6-trimethylbenzoic acid (0.041 g, 0.250 mmol) were dissolved in aqueous medium (2.5 mL). The mixture was sealed in a 23 mL Teflon-lined stainless steel bomb, and held at 70 °C for 72 h. The bomb was cooled naturally to room temperature and pale green coloured crystals of $\{[Ni(tmb)_2(H_2O)_3]\cdot 2H_2O\}_n$ were

Table 1

Crystal data and structure refinement summary for compounds 1-3.

Complex	1	1a	2
Empirical formula	C26H30N4O4C0	C26H30N4O4Ni	C20H32OaNi
Formula weight	521.47	521.25	475.15
Temperature (K)	90	90(2)	90(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Triclinic
Space group	Pbcn	Pbcn	ΡĪ
Unit cell dimensions			
a (Å)	12.2516(12)	12.1888(14)	7.8642(10)
b (Å)	13.0111(14)	13.0080(15)	9.9520(15)
c (Å)	16.842(2)	16.8167(16)	15.398(3)
Volume (Å ³)	2684.7(5)	2666.3(5)	1158.2(3)
Ζ	4	4	2
D_{calc} (Mgm ⁻³)	1.290	1.299	1.363
Absorption coefficient (mm ⁻¹)	0.676	0.765	0.883
F(000)	1092	1096	504
Crystal size (mm)	$0.20\times0.17\times0.10$	$0.10\times0.08\times0.07$	$0.22\times0.20\times0.03$
θ Range for data collection (°)	2.9–27.9	2.59-28.26	2.75-27.86
Limiting indices	$-16 \leqslant h \leqslant 16$	$-16 \leqslant h \leqslant 16$	$-10\leqslant h\leqslant 10$
	$-17\leqslant k\leqslant 17$	$-17 \leqslant k \leqslant 17$	$-13 \leqslant k \leqslant 13$
	$-22 \leqslant l \leqslant 22$	$-22 \leqslant l \leqslant 22$	$-20 \leqslant l \leqslant 20$
Reflections collected/unique	46420/3201	6216/3307	10453/5467
R _{int}	0.018	0.0439	0.0336
Completeness to θ (%)	99.9	99.9	99.1
Absorption correction	0.0024(4)	None	None
Refinement method	Full-matrix least-squares on	F ²	5 4 6 7 10 10 00
Data/restraints/parameters	3201/0/166	3307/0/165	5467/0/298
Goodness-of-fit on F	1.017	1.026	1.074
$R_1 \text{ dill } WR_2 [I > 2\sigma(I)]$	0.028, 0.070	0.0366, 0.0709	0.0349, 0.0802
K_1 difference peak and help ($a^{\Lambda-3}$)	0.039, 0.074	0.0629, 0.0805	0.0530, 0.0869
Largest difference peak and note (e.k.)	0.55 and -0.52	0.200 and -0.571	0.500 dilu -0.455
Complex	2a		3
Empirical formula	C ₂₀ H ₃₂ O ₉ Co		$C_{42}H_{52}O_{10}Cu_2$
Formula weight	475.39		843.92
Temperature (K)	90		298(2)
Wavelength (A)	0.71073		0.71073
Crystal system	Triclinic		Monoclinic
Space group	P1		P121/c1
Unit cell dimensions	0.02(2)		7 56 42(7)
a(A)	8.036(3)		/.5642(/)
$D(\mathbf{A})$	9.962(3)		15.2818(14)
C(A)	1176.9(6)		17.4881(16)
volume (A ²)	11/6.8(6)		2017.7(3)
L (Mam ⁻³)	2		2
D_{calc} (MgIII)	1.342		1.389
	0.774		1.110
(000) (rustal size (mm)		0.10	004 024 × 020 × 019
A Range for data collection (°)	0.23 × 0.20 × 1 85–28 31	0.10	0.34 × 0.20 × 0.18 1 77_25 38
Limiting indices	1.03-20.51 11 < h < 11		0 < h < 0
Limiting mulces	$-11 \le n \le 11$ -13 < k < 13		$-5 \le n \le 5$ -18 < k < 18
			-21 < l < 20
Reflections collected/unique	21743/11380		16420/3690
R _{int}	0.070		0.0476
Completeness to θ (%)	99.0		99.8
Absorption correction	Semi-empiric	al from equivalents	None
Refinement method	Full-matrix le	ast-squares on F^2	
Data/restraints/parameters	11380/0/281	•	3690/1/254
Goodness-of-fit on F^2	1.029		0.947
R_1 and wR_2 [$I > 2\sigma(I)$]	0.046, 0.106		0.0359, 0.0861
R_1 and wR_2 (all data)	0.084, 0.121		0.0475, 0.0897
Largest difference peak and hole ($e Å^{-3}$)	0.51 and -0.4	18	0.408 and -0.295

Table 2

Selected bond lengths and angles for 1-3.

Compound	Bond lengths (A	Å)	Bond angles (deg)	
1	Co(1)-N(1) Co(1)-O(1) Co(1)-O(2) O(1)-C(1) O(2)-C(1) N(1)-C(13)	2.0525(11) 2.1295(10) 2.2145(9) 1.2574(16) 1.2661(16) 1.3799(18)	$\begin{array}{c} N(1)-Co(1)-N(1)^{a}\\ N(1)-Co(1)-O(1)^{a}\\ O(2)-Co(1)-O(2)^{a}\\ N(1)-Co(1)-O(1)\\ O(1)-Co(1)-O(1)^{a}\\ N(1)-Co(1)-O(2)\\ O(2)-Co(1)-O(2)\\ O(2)-Co(1)-O(2)\\ \end{array}$	101.81(6) 97.05(4) 81.62(5) 97.82(4) 156.33(5) 92.74(4) 100.38(4) 120.74(12)
1a	Ni(1)-N(1) Ni(1)-O(1) Ni(1)-O(2) O(1)-C(1) O(2)-C(1) N(1)-C(11) N(1)-C(13) N(2)-C(11) N(2)-C(12)	2.0135(15) 2.0743(13) 2.1910(12) 1.263(2) 1.319(2) 1.382(2) 1.344(2) 1.370(2)	$\begin{array}{l} N(1)-Ni(1)-N(1)^{a}\\ N(1)-Ni(1)-O(1)\\ O(2)-Ni(1)-O(2)^{a}\\ O(1)-Ni(1)-O(1)^{a}\\ O(1)-C(1)-O(2)\\ N(1)-Ni(1)-O(2)^{a}\\ O(1)-Ni(1)-O(2)^{a}\\ O(2)-Ni(1)-N(1)^{a}\\ O(1)-Ni(1)-O(2) \end{array}$	98.51(8) 98.06(6) 83.37(7) 156.94(7) 120.72(17 157.38(5) 99.83(5) 157.38(5) 62.02(5)
2	$\begin{array}{c} Ni(1)-O(3)\\ Ni(1)-O(1)\\ Ni(1)-O(4)\\ Ni(2)-O(7)\\ Ni(2)-O(5)\\ Ni(2)-O(4)\\ O(1)-C(1)\\ O(2)-C(1) \end{array}$	2.0337(15) 2.0485(13) 2.1316(13) 2.0344(15) 2.0464(14) 2.1299(13) 1.270(2) 1.250(2)	$\begin{array}{l} O(3)-Ni(1)-O(1)\\ O(3)-Ni(1)-O(4)\\ O(1)-Ni(1)-O(4)\\ O(7)-Ni(2)-O(5)\\ O(2)-C(1)-O(1)\\ O(6)-C(11)-O(5)\\ O(7)-Ni(2)-O(4)\\ O(5)-Ni(2)-O(4) \end{array}$	89.18(6) 91.45(6) 92.52(5) 88.82(6) 124.29(18) 124.33(18) 91.19(6) 93.15(5)
2a	$\begin{array}{c} Co(1)-O(3)\\ Co(1)-O(1)\\ Co(1)-O(4)\\ Co(2)-O(7)\\ O(5)-C(11)\\ Co(2)-O(5)\\ Co(2)-O(4)\\ O(1)-C(1)\\ O(2)-C(1)\\ O(6)-C(11)\\ \end{array}$	2.0349(13) 2.0813(14) 2.0410(14) 1.271(2) 2.0795(13) 2.1883(14) 1.275(2) 1.250(2) 1.256(2)	$\begin{array}{l} O(3)-Co(1)-O(1)\\ O(1)-Co(1)-O(4)\\ O(1)-Co(1)-O(1)^{\rm b}\\ O(3)-Co(1)-O(4)\\ O(7)-Co(2)-O(5)\\ O(3)-Co(1)-O(3)^{\rm b}\\ O(5)-Co(2)-O(4)\\ O(2)-C(1)-O(1)\\ O(6)-C(1)-O(1)\\ O(6)-C(1)-O(5)\\ O(5)-Co(2)-O(5)^{\rm c}\\ \end{array}$	90.13(6) 92.01(5) 180.00(7) 93.08(5) 89.26(6) 180.00(1) 93.28(5) 123.94(18 124.19(16) 180.0
3	$\begin{array}{c} Cu(1)-O(1)\\ Cu(1)-O(2)^d\\ Cu(1)-O(3)\\ Cu(1)-O(4)^d\\ Cu(1)-O(5)\\ Cu(1)-Cu(1)^d\\ O(1)-C(7)\\ O(2)-C(7)\\ O(3)-C(17)\\ O(4)-C(17)\\ O(5)-C(21) \end{array}$	$\begin{array}{c} 1.9514(17)\\ 1.9699(17)\\ 1.9787(17)\\ 1.9789(16)\\ 2.1550(19)\\ 2.6041(6)\\ 1.262(3)\\ 1.263(3)\\ 1.257(3)\\ 1.270(3)\\ 1.406(4)\\ \end{array}$	$\begin{array}{c} O(1)-Cu(1)-O(2)^d\\ O(1)-Cu(1)-O(3)\\ O(3)-Cu(1)-O(2)^d\\ O(1)-Cu(1)-O(4)^d\\ O(3)-Cu(1)-O(4)^d\\ O(1)-Cu(1)-O(5)\\ O(5)-Cu(1)-O(2)^d\\ O(3)-Cu(1)-O(5)\\ O(5)-Cu(1)-O(4)^d\\ O(1)-C(7)-O(2)\\ O(3)-C(17)-O(4) \end{array}$	$\begin{array}{c} 168.80(7)\\ 87.98(8)\\ 92.87(8)\\ 88.55(7)\\ 168.84(7)\\ 94.52(7)\\ 94.52(7)\\ 94.24(8)\\ 96.60(8)\\ 124.6(2)\\ 124.3(2)\\ \end{array}$

Symmetry transformations used to generate equivalent atoms: a - x + 1, y, $-z + \frac{1}{2}$. b - x + 1, -y + 1, -z + 1. c - x, -y + 1, -z + 1. d - x + 1, -y, -z.

obtained. Then the crystals were collected by filtration, washed with de-ionized water followed by diethyl ether, and then dried (0.048 g, 81.2%). Anal. Calc. for $C_{20}H_{32}O_9Ni$: C, 50.56; H, 6.79%; Found: C, 51.61; H, 6.48%.

The procedure used for the synthesis of **2** was exactly followed for the synthesis of **2a** with cobalt acetate tetrahydrate used in place of nickel acetate tetrahydrate. Anal. Calc. for $C_{20}H_{32}O_9Ni$: C, 50.53; H, 6.78%; Found: C, 51.50; H, 6.46%.

For the synthesis of **3**, copper acetate tetrahydrate (0.0311 g, 0.125 mmol), 2,4,6-trimethylbenzoic acid (0.0205 g, 0.125 mmol), and caffeine (0.0242 g, 0.125 mmol) were mixed in deionised water (3 mL). After stirring for half an hour, the mixtures were placed in a 23 mL Teflon-lined reactor and heated at 85 °C in an oven for three days. Then the reactor was cooled slowly to room temperature; dark green coloured crystals of $[Cu_2(\mu-tmb)_4(CH_3OH)_2]$) were collected by filtration, washed with de-ionized water followed by diethyl ether, and then dried (0.0460 g, 87.7%). In this synthesis caffeine serves as a mineralizer. In the ab-

able 3	
ossible hydrogen bond geometries in the crystal structures of 1-3.	

Compound	D-H…A	D…A (Å)	H…A (Å)	D–H…A (°)
1	$N(2)-H(2 N)\cdots O(2)^{a}$	2.7853(15)	1.905(18)	166.2(1)
	$C(9)-H(9C)\cdots O1^{b}$	3.4310	2.621	140.08(1)
1a	$N(2)-H(2 N)\cdots O(2)^{a}$	2.796(2)	1.91(2)	170(1)
	$C(9)-H(9C)\cdots O1^{b}$	3.471(2)	2.668	139.41(1)
2	$\begin{array}{l} O(3)-H(31)\cdots O(5)^c\\ O(3)-H(32)\cdots O(8)\\ O(4)-H(41)\cdots O(2)\\ O(4)-H(42)\cdots O(6)\\ O(7)-H(71)\cdots O(9)\\ O(7)-H(72)\cdots O(1)^d\\ O(8)-H(81)\cdots O(6)\\ O(9)-H(91)\cdots O(2)\\ \end{array}$	1.84(3) 1.97(3) 1.75(3) 1.71(3) 1.96(3) 1.93(3) 1.83 1.86	2.686(2) 2.762(2) 2.586(2) 2.595(2) 2.753(2) 2.694(2) 2.700(2) 2.693(2)	176(3) 166(3) 172(2) 166(2) 166(3) 176(3) 150.8 144.6
2a	$\begin{array}{l} O(3)-H(31)\cdots O(5)^c\\ O(3)-H(32)\cdots O(8)\\ O(4)-H(41)\cdots O(2)\\ O(4)-H(42)\cdots O(6)\\ O(7)-H(71)\cdots O(9)\\ O(7)-H(72)\cdots O(1)^d\\ O(8)-H(81)\cdots O(6)\\ O(9)-H(91)\cdots O(2)\\ \end{array}$	1.85 1.9 1.78 1.81 1.91 1.86 1.94 1.98	2.6738(19) 2.736(2) 2.616(2) 2.6288(18) 2.735(2) 2.6834(19) 2.715(2) 2.725(2)	167.8 177.4 172.7 163.5 168.9 168.5 153 147.7
3	O(5)−H(5A)…O(4) ^d	1.991(10)	2.830(3)	178(3)
	C18−H18A…O2	2.902(2)	3.729(3)	144.9(2)
	C19−H19C…O2 ^e	2.594(2)	3.554(4)	179.02(2)

Symmetry transformations used to generate equivalent atoms: $a_x + 1/2$, y - 1/2, z. $b_x + 1/2$, y + 1/2, z. $c_x + 1$, y, z. $d_x - 1$, y, z. e_x , -y - 1/2, z + 1/2.



Fig. 1. Molecular structure of 1 with atom labeling of the asymmetric unit and metal coordination. Symmetry code for A: -x + 1, y, -z + 1/2.



Fig. 2. A perspective view of square grid network in 1.

sence of caffeine, no crystals were obtained. Anal. Calc. for $C_{42}H_{52}O_{10}Cu_2$: C, 59.77; H, 6.21%: Found: C, 59.68; H, 6.13%. The syntheses of all the five complexes were schematically represented in Scheme 1.

2.3. X-ray crystallography

Diffraction data for the compounds **1** and **2**, were collected at 90 K on a Nonius Kappa CCD diffractometer fitted with an Oxford Cryostream cooler and graphite-monochromated MoK α ($\lambda = 0.71073$ Å) radiation. Data reduction, including multi-scan absorption corrections, was carried out using DENZO and HKL SCALEPACK [51]. The structures were solved by direct methods and refined by full-matrix least squares techniques using SHEL-XL97 [52]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were visible in difference maps, but were placed in idealized positions, except for N–H and H₂O hydrogen atoms, for which coordinates were typically refined. In cases where H₂O hydrogen atom positions did not refine well, they were placed by difference maps and allowed to ride on the O atoms.

Diffraction data for the compound **3**, was collected at 298 K on a Bruker Smart APEX AXS CCD diffractometer fitted with graphitemonochromated MoK α (λ = 0.71073 Å) radiation. The data was collected by using SMART [53]. Cell refinement and data reduction, including multi-scan absorption corrections, were carried out using SAINT [53]. The structures were solved by direct methods and refined by full-matrix least squares techniques using SHELXTL [54]. All H atoms bonded to C were found in a difference Fourier map and refined using a riding model, with C–H = 0.93–0.97 Å and U_{iso}(H) = 1.2Ueq(C). H atom bonded to N was refined, giving N–H distances of 0.69–0.97 Å and U_{iso}(H) = 1.2U_{eq}(N).

All H atoms other than those of water molecules in **1**, **2**, and **3** were positioned geometrically (C–H = 0.93–0.97 Å) and refined as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$. The H atoms of water molecules were located in a difference map and refined as riding in their as-found relative positions, with $U_{iso}(H) = 1.5U_{eq}(O)$. Crystal data and details of measurements are summarized in Table 1. Selected bond distances and angles are listed in Table 2, and the hydrogen bonding geometric details are summarized in Table 3.

3. Results and discussion

3.1. Structure descriptions

Compound **1** crystallizes in the orthorhombic space group *Pbcn*. The Co(II) atom sits on an inversion centre. The asymmetric unit in **1** (Fig. 1) consists of one cobalt, two carboxylate and two imidazole ligands. The cobalt centre is coordinated by two nitrogens from two imidazole groups and four oxygens from two carboxylates to form $[Co(imi)_2(tmb)_2]$ monomers with distorted octahedral geometry.

The molecule can be viewed as a four-bladed paddle wheel (Fig. 1), when viewed with the Co–O1 bond as axis and the four ligands, each nearly planar, as paddles. The bond lengths involving imidazole and 2,4,6-trimethylbenzoate ligands Co(1)-N(1) [2.0525(11)Å], Co(1)-O(1) [2.1295(10)Å] and Co(1)-O(2) [2.2145(9)Å] are comparable to those found in similar reported cobalt complexes. The difference in the bond lengths of Co–O is probably due to the effect of the chelating coordination of the carboxylate group in the cobalt complex. The O–Co–O angles are in the range $60.62(4)^\circ$ –156.33(5)° [average = 99.73°]. The O–C–O angle is $120.74(12)^\circ$. The N–Co–N angle is $101.81(6)^\circ$. The average angles of O–Co–N and Co–O–C are 103.41° and 89.23° , respectively.

A view of the crystal packing of complex (1) is shown in Fig. 2. The packing results from an extended 2D network of inter-molecular interactions. Each [Ni(imi)₂(tmb)₂] complex molecule is involved in N-H···O $[d_{N2-H2N\cdots O2(-x+1/2, y-1/2, z)} = 2.785 \text{ Å}, \angle = 166.25(1)^{\circ}]$ hydrogen bonds with its four nearest neighbours. The hydrogen bonds from the four nearest neighbours when extended forms infinite square grid. It is noteworthy that two Co^{ll} atoms, two imidazole molecules and two tmb anions produce a 24 membered grid, with a Co…Co distance of 8.935(1)Å (through ligand), and 12.252Å (through space), via coordination covalent bonds and hydrogen bonds. These grids, by sharing Co^{II} atoms, extend to form a molecular-sieve type structure (Fig. 2). The frame work has large, 2-dimensionally inter-connected voids. The ring shaped hydrogen bonded motif can be described by Etter's hydrogen bond notation [55] as $R_4^4(24)$. Also the C9-H9C-01 interaction present in the structure $[d_{C9-H9C\dotsO1(-x+1/2, y+1/2, z)} = 3.431 \text{ Å}, \angle = 140.08(1)^{\circ}]$ plays a significant role in stabilizing the structure (Fig. 3).



Fig. 3. Packing diagram of 1 showing the arrangement of the mononuclear molecules.

The mean plane through C2–C10 shows that C8 has a higher deviation from the plane (0.0486 Å). The puckering parameters (ϕ_2 , θ and Q) [56,57] indicate that the six membered ring C2–C7 is between envelope ²E and sofa ²S₁ conformations, and the five membered ring N1, N2/C11–C13 adopts a deformed envelope conformation. The ϕ_2 = 100.40(56.71) is close to the value of envelope with 108° for ϕ_2 .

The least square plane calculations to find the dihedral angles present in complex **1** and **1a** show that the dihedral angle between the phenyl rings of two 2,4,6-trimethylbenzoate anions is 72.92° (for **1**) and 73.50° (for **1a**) for the planes containing [C2, C3, C4, C5, C6, C7] and [C2A, C3A, C4A, C5A, C6A, C7A; symmetry code: (A) -x + 1, y, -z + 1/2], and the dihedral angle between the two imidazole rings is 87.10° (**1**) and 86.44° (**1a**) for the planes containing [C11, N2, C12, N1, C13] and [C11A, N2A, C12A, N1A, C13A, symmetry code: (A) -x + 1, y, -z + 1/2], and the dihedral angle between the imidazole ring and a phenyl ring of 2,4,6-trimethylbenzoate anion is 47.77° (for **1**) and 48.54° (for **1a**) for the planes containing (C11, N2, C12, N1, C13) and (C2, C3, C4, C5, C6, C7). The nickel complex **1a** is isomorphic in structure with the cobalt analogue (**1**) described above.

{ $[Ni(tmb)_2(H_2O)_3]\cdot 2H_2O_{n}$, (2) crystallizes in the triclinic space group $P\bar{1}$. In 2 the coordination sphere of Ni^{2+} ion includes six oxygen atoms two of these belonging to the carboxylate group of 2,4,6-trimethylbenzoic acid moieties, and the other four to the water molecules. Each nickel(II) metal ion is bridged to the neighbouring nickel(II) ions by a water molecule on either side of the



Fig. 4. A portion view of 2 showing the coordination spheres of Nill. Symmetry codes for A: -x + 1, -y + 1, -z + 1 and B: -x, -y + 1, -z + 1.

polymeric chain in the crystal. Two water molecules are left uncoordinated in the crystal. The coordinated geometry of nickel(II) ions can be well described as a distorted octahedron (Fig. 4).

The Ni…Ni distance across the chain is 3.932 Å. Ni–O bond lengths in the complex are in the range 2.0337(15)-2.1316(13) Å which are consistent with the similar reported structure. [58] Among the Ni–O coordinations, the Ni(1)–O(3) bond [2.0337(15)Å] is the shortest and the Ni(1)–O(4) bond [2.1316(13) Å] is the longest in the structure. This difference may be attributed to the large bidentate binding of O(4) of the bridged water molecule. The bridging O(4) atom is almost equidistant from the two nickel atoms. The aqua ligands and the 2,4,6-trimethylbenzoate ligands are at *trans* disposition in each metal center. The O(2)–C(1)–O(1) and O(6)–C(11)–O(5) angles are 124.29(18)° and 124.33(18)°, respectively. These values seem to be slightly increased than that present in a free acid (122.2)°. This deviation in the bond angle is attributed to the coordination of oxygen atoms [O(1) and O(5)] to the metal atom. The C–O bond lengths in the carboxylic acid moiety indicate delocalization of charge [C(1)-O(1) = 1.270(2) Å and C(1)-O(2) = 1.250(2) Å] as they are intermediate between single and double bond lengths. The C(1)-O(1) = 1.270(2)Å and C(11)-O(5) = 1.270(2)Å are quite greater than the C(1)-O(2) = 1.250(2) Å and C(11)-O(6) = 1.251(2) Å. This difference shows that only O(1) and O(5) are coordinated to the metal.

Each monomer unit in the coordination polymer **2** is held together by O–H···O type hydrogen bonds between the carbonyl groups of the 2,4,6-trimethylbenzoate of one unit with the terminal and bridging water molecules of the adjacent unit, thereby forming an indefinite chain along *a*-axis (Fig. 5).

An unligated carboxylate oxygen atom O(6) makes two hydrogen bonds, one from the oxygen atom O(4) of bridged water molecule and another from the uncoordinated water molecule O(8)present in the lattice which in turn accepts a hydrogen bond from the oxygen atom of a water molecule O(3) coordinated to the neighbouring metal atom. The oxygen atom O(7) of coordinated water molecule donates two hydrogen bonds, one to the lattice water O(9) and the other to the ligated carboxylate oxygen atom O(1). This hydrogen bond $[O(7)-H(72)\cdots O(1)]$ bridges the two metal ions Ni(1) and Ni(2). The five oxygen atoms except O(9) form a ring shaped hydrogen bonding pattern with the graph symbol



Fig. 5. The polymeric chain of **2** extended by water bridges along [1 0 0]. The different H-bonds are shown in red (within the chain) and green (between the chain and lattice water) broken lines, respectively, and irrelevant H atoms are omitted for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

 $R_3^3(12)$. This large ring consists of three smaller rings namely $R_3^2(8)$, $R_1^1(6)$, and $R_1^1(5)$.

All of the bridging and terminal H_2O molecules are involved in hydrogen-bonding interactions. The H_2O molecules coordinating to the terminal nickel ions of the dinuclear clusters form "moderate" hydrogen bonds with the oxygen atoms of the carboxylate groups in the nearest-neighbour lying in the polymeric chain. The bridging H_2O molecules afford intracluster hydrogen bonding interactions with the oxygen atoms of the carboxylate groups. The bond distances of 2.586(2) and 2.595(2) Å are very short, indicating the formation of "strong" hydrogen bonds. The bond angles of O–H…O are close to 180° [166(2)° and 172(2)°].

In the dinuclear cluster, neighbouring nickel ions are bridged by the H₂O molecule. The Lewis basicity of a H₂O molecule is weaker than that of a 2,4,6-trimethylbenzoic acid ligand. Therefore, to stabilize the dinuclear cluster, it is necessary to improve the Lewis basicity of the bridged H₂O molecule. Each nickel ion is coordinated to the monodentate carboxylate groups in addition to the bridged H₂O molecules. Coordination-free oxygen atoms of such carboxylate groups can interact with bridged H₂O molecules *via* "strong" hydrogen bonds. As the protons of the bridged H₂O molecules are attracted to the oxygen atoms of the carboxylate groups, the Lewis basicity of the bridged H₂O molecule increases. Hence, it is presumed that formation of 'strong' hydrogen bonds stabilize the dinuclear clusters. The cobalt complex **2a** is found isomorphic in structure with the nickel analogue (**2**) described above.

Compound **3** consists of centrosymmetric dinuclear paddlewheel units in which four 2,4,6-trimethylbenzoato groups are bridging the two copper atoms, in a *syn–syn* disposition, and a methanol molecule occupies the axial position of each copper atom, coordinated to them through the oxygen atom. Fig. 6 shows the ORTEP view of the dimer **3** with the atomic numbering scheme (35% probability ellipsoids).

Compound **3**, is a dimeric copper(II) complex $[Cu_2(\mu-tmb)_4(CH_3OH)_2]$). Since the copper(II) ion is located on a crystallographic inversion centre, the asymmetric unit is composed of half of the complex $[Cu_2(\mu-tmb)_4(CH_3OH)_2]$. Each Cu^{II} atom has a (regular within experimental error) five-coordinate square-pyramidal environment, with the basal plane defined by the O atoms of four bridging bidentate carboxylate groups of 2,4,6-trimethylbenzoate ligands. The apical position is occupied by the O atom of methanol, coordinating in an *anti* arrangement. The Cu^{II} atom deviates out of

cal O(5) atom by 0.188 Å. The four oxygen atoms which are coplanar, lie at an average distance of 1.9697 Å and the fifth oxygen atom, O(5), of a molecule of methanol, at 2.1550(19) Å. The Cu(1)^a...Cu(1)–O(5) [symmetry code: (a) -x + 1, -y, -z] angle of 174.03° indicates a slight deviation from the expected value of 180° for idealized D_{4h} symmetry [59].

the mean plane formed by the four basal O atoms towards the api-

The adjacent $[Cu_2(\mu-tmb)_4(CH_3OH)_2]$ units are linked by the axial methanol group through an intermolecular O–H…O hydrogen bond. The linkage forms eight-membered rings described by the $R_2^2(8)$ graph-set motif. This linkage which associates the adjacent units can also be represented as $C_2^2(8)$ chains. The combination of these motifs results in the formation of a one-dimensional ribbon structure lying in *ab*-plane and running along the a-axis, as shown in Fig. 7.

The C–O distances in all the 2,4,6-trimethylbenzoate groups are approximately equal ranging from 1.257(3) to 1.270(3) Å, indicating the distinct delocalization of their π electrons [60]. The planes of the two independent bridging 2,4,6-trimethylbenzoate groups are orthogonal within experimental error. Due the presence of mutual O–H···O interaction between the Cu₂(µ-tmb)₄ neighbours, the rotation of the Cu₂(µ-tmb)₄ core is sterically restricted by the adjacent unit. The methanol ligands form strong intermolecular hydrogen bond to the coordinating carboxylate oxygen atom (O4) with d_{05–H5A···O4} (*x*–1, *y*, *z*) = 2.830(3) Å and \angle = 178(3)°. Also, there are C–H···O interactions present in the structure [d_{C19–H19C··O2} (*x*, *y*–*y*–1/2, *z*+1/2) = 2.594 Å and \angle = 179.02°, d_{C18–H18A···O2} (*x*, *y*, *z*) = 2.902 Å and \angle = 144.98°], which play a significant role in stabilizing the overall 3-D structure. The Cu···Cu distance of 2.604 Å is comparable to those found in other dimeric copper(II) carboxylates. [59] The vibrational frequencies [61] for **1–3** are given in Table 4.

3.2. Electronic absorption spectra

The electronic spectrum for complexes **1–3** is shown in Fig. 11. In the electronic spectrum for complex **1**, the imidazole and 2,4,6-trimethylbenzoate ligands exhibit energy bands at 284 nm region, which is generally assigned to $\pi - \pi^*$ transition of the benzenoid and/or (C=N) chromophore of the ligands. As a rule, the longer wavelength bands in the spectra of metal complexes may be considered as evidence for the complex formation. The absorption band at 533 nm due to the ${}^4T_{1g} \rightarrow {}^4T_{1g}$ (P) transition, suggests a high-spin octahedral sphere [62].

The electronic spectrum of the Ni(II) complex **1a** shows two absorption bands at 284 and 398 nm due to π - π * transition caused by the ligands and another band at 685 nm appears due to the MLCT transitions, as generally observed for octahedral Ni(II) complexes.

The electronic spectra of the nickel(II) complex **2** exhibits absorption peaks at 287 nm, 410 nm, and 712 nm showing three spin-allowed transitions in ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{2g}(F)$, ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$ and ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$ regions, which clearly indicated the octahedral stereochemistry of the complexes. The cobalt(II) complex **2a** shows absorption peaks at 287 nm and 534 nm respectively corresponding to $\pi - \pi^{*}$ transition effected by the ligand and d–d transitions (${}^{4}T_{1g} \rightarrow {}^{4}T_{1g}(P)$).

The copper(II) complex **3** shows absorption peaks at 303 nm and 725 nm, respectively, subsequent to π - π ^{*} transition resulted by the ligand and d-d transitions.

3.3. Thermogravimetric analysis

Thermal analysis (TGA) of complex **1** was performed between room temperature and 700 °C under the nitrogen atmosphere. The TGA results indicate that **1** (Fig. 8) undergoes a weight loss of 24.2% due to the decomposition of two imidazole moieties



Fig. 6. Molecular structure 3 with atom labeling of the asymmetric unit and coordination spheres of Cull. Symmetry code for A: -x + 1, -y, -z.



Fig. 7. A perspective view of 3 exhibiting the 1-D hydrogen-bonded chain extended along the [0 1 0] direction. A portion of trimethylphenyl groups of the ligands are omitted for clarity.

(calculated 26.1%) in the temperature range of 246–290 °C. The second stage occurs with the gradual decomposition of the two 2,4,6-trimethylbenzoate moieties leading to the formation of co-balt oxide. There is no apparent weight loss beyond 575 °C.

The TGA curve of the nickel analogue (1a) exhibits similar weight loss stages compared with 1.

The TGA results indicate that complex **2** (Fig. 8) loses 19.2% (calculated 18.9%) of its mass in the temperature range of 98–121 °C, corresponding to the loss of three coordinated and two lattice water molecules. The second stage occurs with the gradual decomposition of the two 2,4,6-trimethylbenzoate moieties at 295 °C leading to the formation of nickel oxide. The saturation temperature above which there is no obvious weight loss occurs at ~370 °C.

Complex **3** (Fig. 8) loses 8.4% (calculated 7.5%) of its mass in the temperature range of 78–114 °C, corresponding to the loss of two coordinated methanol molecules. The second stage involves the loss of 38.4% (calculated 38.6%) of its mass in the temperature range of 221–268 °C corresponding to the loss of two tmb components. The third stage occurs with the gradual decomposition of the remaining two 2,4,6-trimethylbenzoate species, leading to the formation of copper oxide. No obvious weight loss occurs above 375 °C.

3.4. Magnetic properties

Temperature-dependent magnetic susceptibility measurements for complexes **1** and **1a** were performed on polycrystalline sam-

ples. The effective magnetic moments of 1 and 1a are 4.7 and 2.8
$\mu_{\rm B}$, being close to the expected values (4.3–5.2 and 2.9–3.9 $\mu_{\rm B}$)
for the isolated high-spin Co(II) and Ni(II) (S = 5/2). A χ_M versus T
plot for 1 over the temperature range of 8.3-296.5 K (Fig. 9), in
which χ_M is the corrected magnetic susceptibility per Co(II) unit,
could be fitted according to the Curie–Weiss law $\chi_{\rm M} = C/(T-\theta)$,



Infrared	spectral	data	for	1-3.
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Frequency range (cm ⁻¹)				Mode of vibration	
1	1a	2	2a	3	
_	-	36213410 and 3200	36283404 and 3216	3397	O–H _{str} (water)
3133	3133				N-H _{str}
3061	3061	3027			Aromatic C–H _{str}
2925 and 2857	2929 and 2863	2924 and 2857	2923 and 2857	2924 and 2856	Aliphatic C–H _{str}
1613 and 1539	1609 and 1531	1684 (free acid) 1526 and 1448	1533 and 1446	1600 and 1440	COO ⁻ asymmetric and COO ⁻ symmetric stretching
1455-1039	1450-1038	1404–1114	1401-1113	1440-1028	aromatic C=C and/or C-N stretching vibrations
758	754	-	-	-	N–H out of plane bending
948 and 650	1000 and 650	851 and 820	853 and 822	754 and 846	C-H out of plane bending
Below 600	Below 600	Below 600	Below 600	Below 600	M-N and M-O stretching vibrations



Fig. 9. χ_{M} and χ_{MT} versus *T* plots for complex **1**. The solid lines represent the best fit of the experimental data.



Fig. 10. χ_M and χ_{MT} versus *T* plots for complex **1a**. The solid lines represent the best fit of the experimental data.



Fig. 11. UV-vis absorption spectra of 1-3.

giving a Curie constant $C = 3.20 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, and a Weiss constant θ = -8.13 K. The negative value of θ indicates weak antiferromagnetic interactions between Co(II), since the adjacent Co(II) ions are separated with a distance of 8.936 Å as revealed by the X-ray crystal structure. The χ_M value of 9.41×10^{-3} cm³ mol⁻¹ at room temperature increases as the temperature decreases, attaining 37.4×10^{-3} cm³ mol⁻¹ at 8.3 K. A χ_{M} versus T plot for **1a** over the temperature range of 9.5–294.6 K (Fig. 10), in which χ_{M} is the corrected magnetic susceptibility per Ni(II) unit, could be fitted according to the Curie–Weiss law $\chi_M = C/(T-\theta)$ giving a Curie constant C = 0.7956 cm³ mol⁻¹ K and a Weiss constant θ = -51 K. Similarly, the negative value of θ indicates antiferromagnetic interactions between Ni(II), since the adjacent Ni(II) ions are separated by imidazole ligands with a distance of 8.913 Å. The $\gamma_{\rm M}$ value $2.8\times 10^{-3}\,\text{cm}^3\,\text{mol}^{-1}$ at room temperature increases as the temperature decreases, attaining 56.39×10^{-3} cm³ mol⁻¹ at 9.5 K.

3.5. Antibacterial activity

The *in vitro* biological screening effects of **1–3** were tested against the bacteria: *Escherichia coli, Staphylococcus aureus, Pseudomonas aeruginosa*, and *Bacillus subtilis* by the well-diffusion method [63] using agar nutrient as the medium. The antifungal activities of the compounds were evaluated by the well-diffusion method against the fungi *viz., Aspergillus niger, Aspergillus flavus* and *Rhizoctonia bataicola* cultured on potato dextrose agar as medium. The compounds were tested at a concentration of 50 µg/0.01 mL in aqueous solution. In a typical procedure [64], a well was made on the agar medium inoculated with microorganisms. The well was filled with the test solution using a micropipette and the plate was incubated 24 h for bacteria and 72 h for fungi at 35 °C. During this period, the test solution diffused and the growth of the inoculated microorganisms was affected. The concentration was noted

Table 5Antibacterial activity of the complexes 1, 1a, 2, 2a and 3.

Complex	Bacterial species					
	a	b	с	d	e	
[Co(imi) ₂ (tmb) ₂]	+ +	+ ++	++ +	+ + +	+ +	
[Ni(imi) ₂ (tmb) ₂]	+ +	+ ++	+ ++	+ + +	+ +	
$\{[Ni(tmb)_2(H_2O)_3] \cdot 2H_2O\}_n$	+ + +	+ +	++	++	++	
$\{[Co(tmb)_2(H_2O)_3] \cdot 2H_2O\}_n$	+ + +	+ +	++	++	++	
[Cu ₂ (µ-tmb) ₄ (CH ₃ OH) ₂]	+ + +	+ +	++	+++	++	

a. Escherichia coli, b. Staphylococcus aureus, c. Pseudomonas aeruginosa d. Bacillus subtilis e. Klebsiella pneumoniae Inhibition zone diameter mm (% inhibition): +, 6–10 (27–45%); + +, 10–14 (45–64%); + +, 14–18 (64–82%); + + +, 18–22 (82–100%). Percent inhibition values were relative to inhibition zone (22 mm) of standard antibacterials (sulfadiazine, sulfathiazole), considered as 100% inhibition, tested under the same conditions as the new compounds reported here.

Table 6	
A	 - 6 +1-

Antifungal activity of the complexes 1, 1a, 2, 2a and 3.

Complex	Fungal species			
	a	b	с	
[Co(imi) ₂ (tmb) ₂]	+ + +	+ +	+ +	
$[Ni(imi)_2(tmb)_2]$	+ + +	+ +	+ +	
$\{[Ni(tmb)_2(H_2O)_3] \cdot 2H_2O\}_n$	+ +	+ +	+ +	
$\{[Co(tmb)_2(H_2O)_3] \cdot 2H_2O\}_n$	+ +	+ +	+ +	
[Cu ₂ (µ-tmb) ₄ (CH ₃ OH) ₂]	+ + +	+ +	+ +	

a. Aspergillus niger, b. Aspergillus flavus, c. Rhizoctonia bataicola Inhibition zone diameter mm (% inhibition): +, 6–10 (27–45%); + +, 10–14 (45–64%); + +, 14–18 (64–82%); + + + +, 18–20 (82–100%), (–), no inhibition zone. Percent inhibition values were relative to inhibition zone (20 mm) of standard antifungal (Bavistin), considered as 100% inhibition, tested under the same conditions as the new compounds reported here.

at the inhibition zone developed. The percentage inhibition was calculated as 100(C-T)/C, where C is the average diameter of bacteria or fungal growth on the control plate (water) and T is the average diameter of bacteria or fungal growth on the test plate. The susceptibility zones were measured in diameter (mm) and the results are shown in Tables 5 and 6. The susceptibility zones measured were the clear zones around the discs killing the bacteria. The complexes individually exhibit varying degrees of inhibitory effect on the growth of the tested bacterial species. On complexation, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with the donor groups. Further, it increases the delocalization of π -electrons over the whole ligand and enhances the penetration of complexes into lipid membranes leading to the blocking of the metal binding sites in the enzymes of microorganisms. The complexes may also disturb the respiration process of the cell and thus block the synthesis of proteins, which restricts further growth of the organism [65].

4. Conclusion

In summary, three new complexes, $[Co(imi)_2(tmb)_2]$ (1), $\{[Ni(tmb)_2(H_2O)_3] \cdot 2H_2O\}_n$ (2) and $[Cu_2(\mu-tmb)_4(CH_3OH)_2]$ (3), were synthesized by hydrothermal reactions. Their structures were characterized by X-ray crystallography, UV/VIS, IR spectra, elemental analysis, TGA and magnetic susceptibility measurements. Small negative value of Weiss constant (θ) shows a weak intermolecular antiferromagnetic interaction in 1 and 1a. The synthesized complexes show considerable antimicrobial activity.

5. Supplementary material

CCDC 689650, 689651, 689652, 689653 and 695666 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.

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