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Synthesis, structures and magnetic properties of nicotinato-copper(II) complexes with polybenzimidazole and polyamine ligands

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ABSTRACT

Four novel nicotinato-copper(II) complexes containing polybenzimidazole and polyamine ligands were synthesized with formula $[Cu_2(bbma)_2(nic)_2](CIO_4)_2$ ·CH₃OH-0.5H₂O (1), $[Cu_2(dien)_2(nic)_2](CIO_4)_2$ ·2CH₃OH (2), $[Cu(ntb)(nic)]CIO_4$ ·H₂O (3) and $[Cu(tren)(nic)]BPh_4$ ·CH₃OH·H₂O (4), in which bbma is bis(benzimidazol-2-yl-methyl)amine, dien is diethylenetriamine, ntb is tris(2-benzimidazolylmethyl)amine, tren is tris(2-aminoethyl)amine and nic is nicotinate anion. All of the complexes were characterized by elemental analysis, IR and X-ray diffraction analysis. Complexes 1 and 2 contain centrosymmetric dinuclear entity with the two Cu(II) atoms bridged by two nicotinate anions in an anti-parallel mode. The Cu-Cu separation is 7.109 Å for 1 and 6.979 Å for 2. Complexes 3 and 4 are mononuclear with nicotinate coordinated to Cu(II) ion by the carboxylate O atom in 3 and the pyridine N atom in 4. All of the complexes exhibit abundant hydrogen bonds to form 1D chain for 1, 3, 4 and 2D network for 2. Magnetic susceptibility measurements over the 2–300 K range reveal very weak ferromagnetic interaction between the two Cu(II) ions in 1 and antiferromagnetic interaction in 2 mediated by nicotinate ligand, with *J* value to be 0.15 and -0.19 cm^{-1} , respectively.

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1. Introduction

Nicotinic acid plays an important role in the metabolism of the living cells and possesses very interesting pharmaceutical properties [1,2]. It can also be used to transmit magnetic interactions. Therefore, much interest has been directed towards their metal complexes [3–8]. Nicotinic acid, namely 3-pyridinecarboxylic acid, is one of the three isomers of pyridine monocarboxylic acid. It has potential coordination sites involving the nitrogen atom of the pyridine and the carboxylate oxygen atoms. It can coordinate with copper(II) atom via one or two O atoms of carboxylate group or the pyridine N atom or both of them. At the same time, the pyridine N atom and carboxylate group of nicotinate can also serve as hydrogen bond accepter. This makes it a good candidate to construct novel multidimensional structures through its versatile coordination modes, hydrogen bonds and π – π interactions.

A number of copper(II) complexes of nicotinate with discrete mononuclear unit [9–12], dinuclear unit [13] and extended polymeric 1D, 2D and 3D [5,8,12–22] structures have been reported and characterized. Some of these complexes contain dien (diethylenetriamine) [9–11,13], bipy (2,2'-bipyridine) [8,16], phen (1,10-phenanthroline) [15], trans-oxap, trans-oxen (H₂oxen = N,N'-bis(2-aminoethyl)oxamide, H₂oxap = N,N'-bis(2-aminopro-

pyl)oxamide) [14], azide [5] and isonicotinic acid [21] as coligands. But nicotinato-copper(II) complexes by using polybenzimidazole and polyamine as terminal ligands have rarely been reported [13], and the investigation of magnetic interaction mediated by nicotinate anion is relatively less [5,8,11,14,17,20].

Polybenzimidazole and polyamine terminal ligands have long been used in coordination chemistry [23–25]. These ligands can differ both in the lengths of the arms and the nature of N-donor atoms on each arm. Tris(2-benzimidazolylmethyl)amine (ntb) and bis(benzimidazol-2-yl-methyl)amine (bbma) contain aromatic N-donor atoms on their arms, while tris(2-aminoethyl)amine (tren) and diethylenetriamine (dien) contain aliphatic N-donor atoms. They are widely used to prepare a variety of metal complexes to model the active site structures of some relevant metalloenzymes. Compared to Cu(II) complexes of polyamine tren and dien, the crystallograpically characterized Cu(II) complexes of ntb and bbma are relatively less. Except two isophthalato-bridged dinuclear copper(II) complexes of ntb and bbma, only mononuclear copper(II) complexes have been obtained and structurally characterized [26].

We are interested in the preparation of copper(II) nicotinate complexes with polybenzimidazole and polyamine terminal ligands for the following reasons. First we would like to see how the structural change of the terminal ligands with aromatic benzimidazole side arms (ntb, bbma) or aliphatic side arms (tren, dien) influence the coordination behavior of nicotinate as coligand. Second, the nicotinato-copper(II) complexes of these ligands may afford versatile



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Scheme 1. Bonding modes of nicotinate anion in the four copper(II) complexes.

intermolecular interactions such as hydrogen bonds and π - π interactions to form interesting supramolecular coordination assembly. Third, we would like to investigate the magnetic interaction mediated by nicotinate anion. In this paper, two novel dinuclear nicotinato-copper(II) complexes [Cu₂(bbma)₂(nic)₂](ClO₄)₂·CH₃OH·0.5H₂O (1), $[Cu_2(dien)_2(nic)_2](ClO_4)_2 \cdot 2CH_3OH$ (2) and two mononuclear complexes $[Cu(ntb)(nic)]ClO_4 H_2O$ (3) and $[Cu(tren)(nic)]BPh_4 ·$ CH₃OH·H₂O (**4**) were synthesized and characterized. In the above four complexes, nicotinate coordinates to Cu(II) in three bonding modes which could be described as μ_2 -N, O chelating mode in **1** and **2** (see Scheme 1a), one carboxylate O atom in **3** (see Scheme 1b) and the pyridine N atom in 4 (see Scheme 1c). The magnetic susceptibility measurements at variable temperature over the 2–300 K range for 1 and 2 suggested very weak ferromagnetic coupling interaction of the two Cu(II) ions for 1 but weak antiferromagnetic coupling interaction in 2.

2. Experimental

2.1. Materials

All chemicals including diethylenetriamine, tris(2-aminoethyl)amine were purchased from commercial sources and used as received without further purification. Sodium nicotinate was prepared by reacting nicotinic acid with a stoichiometric amount of NaOH in water. The blue solid $Cu(nic)_2 \cdot 2H_2O$ was prepared by the reaction of $CuSO_4 \cdot 5H_2O$ and sodium nicotinate at the ratio of 1:2 in water.

Caution! Salts of perchlorate and their metal complexes are potentially explosive and should be handled with great care and in small quantities.

2.2. Physical measurements

Elemental analyses for C, H and N were performed using Elemental Vario MICRO CUBE (Germany) elemental analytical instrument, IR spectra were recorded as KBr pellets on Bruker TENSOR 27 FT-IR spectrometer in the range of 4000–400 cm⁻¹. The magnetic measurement was carried out with a Quantum Design MPMS-7 SQUID magnetometer in the temperature range of 2–300 K and in a field of 1000 Oe. Diamagnetic correction for the constituent atoms was made by using Pascal's constants.

2.3. Preparation of ligands

The ligand tris(2-benzimidazolylmethyl)amine (ntb) was synthesized following the literature method and bis(benzimidazol-2yl-methyl)amine (bbma) was prepared according to published procedures [27,28].

2.4. Preparation of complexes

2.4.1. Preparation of [Cu₂(bbma)₂(nic)₂](ClO₄)₂·CH₃OH·0.5H₂O (1)

A methanol solution (50 ml) of bbma (0.277 g, 1 mmol) was added to a stirred solution (100 ml) of $Cu(nic)_2 \cdot 2H_2O$ (0.345 g, 1 mmol) in methanol with the formation of a blue solution. After

half an hour, a methanol (50 ml) solution of NaClO₄·H₂O (0.140 g, 1 mmol) was added dropwise to this solution. The mixture was refluxed for 3 h and then filtered and left for slow evaporation. Blue block crystals were formed after a week. Yield: 350 mg (60%). *Anal.* Calc. for Cu₂C₄₅H₄₃N₁₂O_{13.5}Cl₂ (1165.89 g/mol): C, 46.35; H, 3.72; N, 14.42. Found: C, 46.36; H, 4.05; N, 13.98%. IR (KBr pellet): 3431 (br, s) (for H-bonded water molecules), 3263(sh, s), 2923(s), 1600(s), 1588(s), 1491(w), 1474(m), 1456(m), 1377(s), 1279(m), 1111(s), 1094(s), 742(s) (for out-of-plane bending vibrations of the o-disubstituted phenyl rings of the bbma ligand).

2.4.2. Preparation of [Cu₂(dien)₂(nic)₂](ClO₄)₂·2CH₃OH (**2**)

To a methanol solution (10 ml) of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.185 g, 0.5 mmol) was added a methanol solution (10 ml) of sodium nicotinate (0.073 g, 0.5 mmol). Sky-blue precipitate formed. Then a methanol solution (10 ml) of diethylenetriamine (0.052 g, 0.5 mmol) was added under stirring to give dark blue solution. Violet crystals suitable for X-ray structure determination were obtained after one week by slow evaporation of the filtrate. Yield: 165 mg (81%). Elemental analysis shows that two lattice methanol molecules were replaced by two water molecules during storage in air. *Anal.* Calc. for Cu₂C₂₀H₃₈N₈O₁₄Cl₂ (812.56 g/mol): C, 29.56; H, 4.71; N, 13.79. Found: C, 29.90; H, 4.74; N, 13.92%. IR (KBr pellet): 3423(br, s), 3341(br, s), 3273(br, s), 2960(s), 1619(s), 1569(m), 1462(m), 1385(s), 1260(m), 1096(s), 762(m), 623(s).

2.4.3. Preparation of $[Cu(ntb)(nic)]ClO_4 H_2O(3)$

A methanol solution (15 ml) of $Cu(ClO_4)_2$ · $6H_2O$ (0.185 g, 0.5 mmol) was added to a methanol solution (15 ml) of ntb (0.204 g, 0.5 mmol) and sodium nicotinate (0.073 g, 0.5 mmol). The mixture was refluxed for 6 h. The resulting solution was allowed to stand in air at room temperature. After 10 h, green crystals were formed. The products were filtered and washed with cold methanol and dried *in vacuo* over P₄O₁₀. Yield: 284 mg (80%). *Anal.* Calc. for C₃₀H₂₇ClCuN₈O₇ (710.59 g/mol): C, 50.71; H, 3.83; N, 15.77. Found: C, 50.74; H, 3.82; N, 15.25%. IR (KBr pellet): 3423(br, s), 3193(s), 2923(s), 1625(s), 1595(m), 1544(m), 1491(w), 1474(m), 1453(s), 1370(s), 1277(m), 1120(s), 743(s) (for out-of-plane bending vibrations of the o-disubstituted phenyl rings of the ntb ligand).

2.4.4. Preparation of [Cu(tren)(nic)]BPh₄·CH₃OH·H₂O (4)

A methanol solution (20 ml) of tren (0.36 g, 0.25 mmol) and $Cu(nic)_2 \cdot 2H_2O$ (0.086 g, 0.25 mmol) in methanol solution (30 ml) were mixed to give a blue solution and stirred for half an hour. NaBPh₄ (0.085 g, 0.25 mmol) in methanol solution (10 ml) was added. The mixture was stirred overnight and then filtered. Slow evaporation of the filtrate yielded blue chunk crystals after one week. Yield: 105 mg (64%). Elemental analysis shows that half a lattice water molecule and one lattice methanol molecule were lost during storage in air. *Anal.* Calc. for $CuC_{36}H_{43}N_5O_{2.5}B$ (660.11 g/mol): C, 65.50; H, 6.56; N, 10.61. Found: C, 65.70; H, 6.41; N, 10.61%. IR (KBr pellet): 3431(br, s), 3330(s), 3282(s), 2886(s), 1628(s), 1479(m), 1451(w), 1427(m), 1369(s), 737(s).

2.5. X-ray structural analysis

Crystals of **1** and **4** were mounted on Bruker Smart 1000 area detector and the Rigaku Saturn724+ diffractometer at 273(2) and 93(2) K, respectively. Single-crystal X-ray diffraction data for **2** and **3** were collected on a Rigaku RAXIS-RAPID single-crystal diffractometer at 293(2) K. All of the diffractometers are equipped with graphite-monochromated Mo K α radiation (λ = 0.71073 Å). Empirical absorption correction was made for the collected reflections [29]. All of the structures were solved with direct method by using SHELXS-97 [30] and refined on F^2 by full-matrix least-squares

Table 1	
Crystallographic data and stru	cture refinement for 1-4.

	1	2	3	4
Empirical formula	$C_{35}H_{38}C_{12}N_{12}Cu_2O_2$	$C_{22}H_{42}Cl_2Cu_2N_8O_{14}$	C ₃₀ H ₂₇ ClCuN ₈ O ₇	C37H48BCuN5O4
Formula weight	988.13	840.62	710.59	701.15
Crystal size (mm)	$0.30 \times 0.25 \times 0.20$	$0.40 \times 0.46 \times 0.12$	$0.48\times0.30\times0.20$	$0.47 \times 0.27 \times 0.27$
Crystal system	triclinic	monoclinic	triclinic	triclinic
Space group	<i>P</i> 1̄ (no. 2)	$P2_1/n$ (no. 14)	<i>P</i> 1̄ (no. 2)	<i>P</i> 1̄ (no. 2)
a (Å)	11.097(4)	14.9542(5)	9.8515(8)	9.7084(13)
b (Å)	11.154(4)	7.3680(3)	12.3343(10)	11.0230(15)
<i>c</i> (Å)	11.288(4)	15.7904(5)	13.3912(12)	17.112(2)
α (°)	75.588(6)	90	83.116(5)	75.391(4)
β(°)	81.124(6)	102.483(1)	80.226(3)	79.695(5)
γ (°)	66.315(6)	90	77.856(3)	79.227(5)
$V(Å^3)$	1236.9(7)	1698.7(1)	1561.7(2)	1724.0(4)
$ ho_{ m calc}~(m g~ m cm^{-3})$	1.618	1.643	1.511	1.351
Ζ	1	2	2	2
F(0 0 0)	618	868	730	742
μ (mm ⁻¹)	1.051	1.484	0.846	0.681
$T_{\rm max}/T_{\rm min}$	0.8174/0.7434	1.2904/0.7751	1.0958/0.8962	0.8391/0.7416
hkl range				
	-13 to 7	-19 to 19	-11 to 12	-9 to 12
	-13 to 7	-9 to 9	-15 to 15	-14 to 14
	-12 to 13	-20 to 20	-17 to 17	-20 to 22
θ Range (°)	2.66-24.02	2.12-27.48	2.19-27.44	3.06-27.49
Measured reflections	5155	7254	10788	14229
Unique reflections (R _{int})	4353 (0.0264)	3899 (0.0182)	6916 (0.0237)	7594 (0.0209)
Observed reflections $I > 2\sigma(I)$	2978	3104	5690	6685
Data/restraints/parameters	4353/0/354	3899/0/238	6916/0/425	7594/3/443
Goodness-of-fit	1.044	1.039	1.036	0.997
$R_1/wR_2 \ (I > 2\sigma(I))$	0.0602/0.1281	0.0339/0.0889	0.0462/0.1224	0.0380/0.0846
R_1/wR_2 (all data)	0.1011/0.1447	0.0456/0.0931	0.0568/0.1285	0.0434/0.0878
Resid. el. dens. (e Å ⁻³)	0.601/-0.349	0.629/-0.396	0.814/-0.613	0.617/-0.343

Table 2

The IR spectral bands (cm⁻¹) for complexes **1–4**.

_	Complex	v(N–H), v(O–H)	$v_{as}(COO^{-})$	$v_{\rm s}({\rm COO^-})$	$\Delta v(COO^{-})$	v(Cl-O)
	1	3431	1600	1377	223	1111
		3263	1588			
	2	3423	1619	1385	234	1096
		3341	1569			
	3	3423	1625	1370	255	1120
		3193	1595			
	4	3431	1628	1369	259	_
		3330	1479			

"-" Means complex 4 contain no perchlorate anions.

techniques using the SHELXL-97 program [31]. The non-hydrogen atoms were subjected to anisotropic refinement and the hydrogen atoms were located geometrically. In complex 1, O(8) atom of the water molecule was assigned with occupancy to be 0.5 and the hydrogen atoms on it were not located. In complex 2, the disordered C(4) atom of dien including H atoms on it were located at two sites with a total occupancy of 1. The detailed crystallographic data and structure refinement parameters for 1–4 are summarized in Table 1.

3. Results and discussion

3.1. Synthesis and characterization

3.1.1. Synthesis and the solubility of the complexes

The synthetic procedures used to prepare the four complexes can be divided into two categories: the first pathway is based on the reaction of $Cu(ClO_4)_2 \cdot 6H_2O$, dien or ntb ligand and sodium nicotinate in the ratio of 1:1:1, while the second one involves the reaction of $Cu(nic)_2 \cdot 2H_2O$ with bbma or tren and $NaClO_4 \cdot H_2O$ or



Fig. 1. Cation structure of complex 1 (30% probability thermal ellipsoids).

NaBPh₄ used as the source of counter anions. All of the four complexes are soluble in DMF and DMSO. Complexes **1** and **3** containing bbma and ntb can slightly dissolve in methanol but are *insoluble* in water. Complexes **2** and **4** containing dien and tren as main ligands can dissolve in methanol and water in some extent.

Table 3							
Selected bond lengths	(Å)) and	angles	(°)	for	complex	< 1 .

Cu(1)-N(2)	2.008(4)	Cu(1)-N(1)	2.021(5)
Cu(1)-N(4)	1.997(4)	Cu(1)-N(6)#1	2.013(4)
Cu(1)–O(1)	2.362(4)		
N(4)-Cu(1)-N(2)	160.12(16)	N(4)-Cu(1)-N(6)#1	100.60(16)
N(2)-Cu(1)-N(6)#1	97.53(15)	N(4)-Cu(1)-N(1)	80.82(19)
N(2)-Cu(1)-N(1)	80.98(18)	N(6)#1-Cu(1)-N(1)	178.46(19)
N(4)-Cu(1)-O(1)	94.19(16)	N(2)-Cu(1)-O(1)	93.26(16)
N(6)#1-Cu(1)-O(1)	91.98(14)	N(1)-Cu(1)-O(1)	88.5(3)
	. ,		. ,

Symmetry transformations used to generate equivalent atoms: #1 -x + 1, -y + 2, -z + 1.

3.1.2. Spectroscopy

The most relevant absorption bands in the IR spectra of 1-4 are listed in Table 2. There are two absorption bands in the range of $3200-3500 \text{ cm}^{-1}$ for all of the four complexes, these bands correspond to N-H and O-H stretching vibrations and indicate the presence of the NH groups of ntb, the lattice water or methanol molecules in the complexes. The bands around 1111–1120 cm⁻¹ in **1**, **3** and 1096 cm^{-1} in **2** are due to the ionic perchlorate groups [32,33]. Each of the four complexes exhibits the typical carboxylate stretching frequencies $v_{as}(COO^{-})$ which split into two bands and $v_{\rm s}({\rm COO^-})$ of nicotinate (Table 2). The two bands at about 1600 cm⁻¹ are assigned to the antisymmetric stretching frequencies $v_{as}(COO^{-})$ and the band around 1370 cm⁻¹ contributed to symmetric stretching frequencies $v_s(COO^-)$. The difference between the antisymmetric stretching and symmetric stretching gives information on the carboxylate bonding mode for the complexes. The $\Delta v(COO^{-})$ values for **1–4** are from 223 to 259 cm⁻¹, which are typical for unidentate bonded carboxylate group of nicotinate [34]. These findings are also consistent with the X-ray analysis results.

3.2. Description of the structures

3.2.1. [Cu₂(bbma)₂(nic)₂](ClO₄)₂·CH₃OH·0.5H₂O (**1**)

Complex 1 contains one dinuclear $[Cu_2(bbma)_2(nic)]_2^{2+}$ cation, two perchlorate anions, one lattice methanol and half a disordered water molecules. The cation structure of 1 is shown in Fig. 1; selected bond lengths and angles are given in Table 3.

In the centrosymmetric dinuclear cation, the two Cu(II) are bridged by two anions of nicotinic acids through the pyridyl nitrogen atom and one of the carboxylate oxygen atoms in an antiparallel bridging way [13] and the Cu…Cu separation is 7.109 Å.

Each Cu(II) atom is coordinated with three N atoms of bbma and one N atom of the first nicotinate defining the base and one O atom from the carboxylate group of the second nicotinate occupying the apex of the pyramid in a distorted square pyramidal geometry. The Addison τ value of **1** is 0.30, where τ = 1 for perfect trigonal bipyramidal geometry and $\tau = 0$ for perfect square pyramidal geometry [35]. The equatorial bond angels are in the range of 80.82(19)- $100.60(16)^{\circ}$ and the bond angles for the apex O(1) with the four N atoms in equatorial plane are in the range of 88.5(3)-94.19(16)°, which are all deviated from the ideal value of 90°. The four basal Cu(II)-N bond distances are in the range of 1.997(4) - 2.021(5) Å. The axial Cu(1)-O(1) is 2.362(4) Å, which is longer than the normal Cu(II)-carboxylate oxygen bond length. This feature is frequently found in Cu(II) crystal chemistry and characterized with square-pyramidal configuration [26]. It is noted that the O(4) atom of perchlorate makes very weak interaction with Cu(1)–O(4) bond distance of 2.695 Å, which is close to the reported nicotinate-copper(II) complexes with the same coordination feature [13].

As shown in Fig. 2, 1D chain structure is formed by intermolecular H-bond interactions between the NH group of benzimidazole from bbma and the uncoordinated carboxylate oxygen atom of nicotinate $(N(3)\cdots O(2) = 2.743(6) \text{ Å}, \angle N(3)-H(3)-O(2) = 152^\circ)$. The 1D



Fig. 2. The 1D chain connected through hydrogen bonding interactions in 1.



Fig. 3. Cation structure of complex 2 (30% probability thermal ellipsoids).

Table 4Selected bond lengths (Å) and angles (°) for complex 2.

Cu(1)-N(2)	2.0103(18)	Cu(1)-N(1)	2.022(2)
Cu(1)-N(3)	2.0233(19)	Cu(1)-N(4)	2.0234(17)
Cu(1)-O(1)	2.2398(16)		
N(2)-Cu(1)-N(4)	178.44(8)	N(2)-Cu(1)-N(3)	84.83(8)
N(2)-Cu(1)-O(1)	88.22(7)	N(4)-Cu(1)-N(3)	96.39(8)
N(4)-Cu(1)-O(1)	90.36(7)	O(1)-Cu(1)-N(3)	115.62(8)
N(2)-Cu(1)-N(1)	84.78(8)	N(1)-Cu(1)-N(3)	144.57(9)
N(4)-Cu(1)-N(1)	94.75(8)	O(1)-Cu(1)-N(1)	97.79(9)

chain is further expanded to a two-dimensional (2D) structure (see Fig. S1) by the π - π stacking interactions between the benzene ring and the imidazole ring of the neighboring bbma, forming a 2D network structure (with the centroid-to-centroid distance to be 3.759 Å, Cg1 = C11-C12-C13-C14-C15-C16, Cg2 = C10-N4-C11-C16-N5).

3.2.2. [Cu₂(dien)₂(nic)₂](ClO₄)₂·2CH₃OH (**2**)

As can be seen for **1**, complex **2** has the same type of coordination structure with complex **1** but different terminal ligand. Complex **2** comprised of a centrosymmetric $[Cu_2(dien)_2(nic)_2]^{2+}$ cation, two perchlorate anions and two lattice methanol molecules. The cation structure of **2** is shown in Fig. 3, selected bond distances and angles are summarized in Table 4.

In the cation structure of **2**, two nicotinate anions bridge the adjacent Cu(II) through both the pyridine N and the carboxylate O atoms to form a dinuclear copper complex in an anti-parallel bridging way. The Cu…Cu distance is 6.979 Å, which is shorter than that of complex **1** (7.109 Å) and nearly the same as that found in $[Cu_2(dien)_2(nic)_2](BF_4)_2$ ·2MeOH [13]. Each Cu(II) is coordinated by three N atoms of dien, one pyridine N atom of the first nicotinate and one carboxylate O atom from another nicotinate in a distorted trigonal bipyramidal geometry with τ value to be 0.56. The trigonal plane is defined by two terminal nitrogen atoms



Fig. 4. The 2D structure interacted through Hydrogen bonding interactions in 2.



Fig. 5. Cation structure of complex 3 (30% probability thermal ellipsoids).

Table 5

Selected bond lengths (Å) and angles (°) for complex 3

Cu(1)-N(21)	2.014(2)	Cu(1)-N(1)	2.157(2)			
Cu(1)-N(41)	2.122(2)	Cu(1)-N(31)	2.038(2)			
Cu(1)-O(1)	1.9392(18)					
O(1)-Cu(1)-N(21)	96.64(8)	O(1)-Cu(1)-N(31)	105.86(8)			
N(21)-Cu(1)-N(31)	135.05(9)	O(1)-Cu(1)-N(41)	96.95(8)			
N(21)-Cu(1)-N(41)	112.65(9)	N(31)-Cu(1)-N(41)	102.77(9)			
O(1)-Cu(1)-N(1)	172.43(8)	N(21)-Cu(1)-N(1)	79.65(8)			
N(31)-Cu(1)-N(1)	81.23(8)	N(41)-Cu(1)-N(1)	78.62(8)			

N(1), N(3) and the O(1) with bond lengths Cu(1)–N(1) = 2.022(2), Cu(1)–N(3) = 2.0233(19) Å, and Cu(1)–O(1) = 2.2398(16) Å. The axial sites were occupied by N(2) and N(4) atoms with bond distances of Cu(1)–N(2) and Cu(1)–N(4) to be 2.0103(18) and 2.0234(17) Å, similar Cu(1)–N(2) bond length is also found in other copper(II) complexes of dien [36–38] and more approximate to that of [Cu₂(dien)₂(nic)₂](BF₄)₂·2MeOH [13]. Bond angles in the trigonal plane are in the range of 97.79(9)–144.57(9)°, which deviate significantly from 120° of the ideal trigonal bipyramid. The axial bond angle is 178.44(8)° for N(2)–Cu(1)–N(4).

The lattice methanol molecule is H-bonded to the NH₂ group of dien $[N(3)\cdots O(3) = 2.989(3) \text{ Å}, \angle N(3)-H(3)-O(3) = 173^{\circ}]$ and the uncoordinated carboxlylate O atom $[O(3)\cdots O(2) = 2.782(3) \text{ Å},$

 $\angle O(3)-H(3)-O(2) = 168(5)^{\circ}$ to connect the adjacent dinulcear cation units forming a 2D network structure as shown in Fig. 4.

3.2.3. [Cu(ntb)(nic)]ClO₄·H₂O (3)

Complex **1** consists of a [Cu(ntb)(nic)]⁺ cation, one perchlorate and one disordered water molecule. The cation structure of **3** is depicted in Fig. 5. Relevant bond distances and angles are presented in Table 5.

The central Cu(II) is coordinated by four nitrogen atoms of ntb and one carboxylate O atom of nicotinate. The geometry around Cu(II) can be described as distorted trigonal bipyramidal as revealed by the magnitude of the trigonality index τ of 0.62. The three benzimidazole N(21), N(31) and N(41) atoms of ntb make up the trigonal plane. The amine N(1) atom of ntb and the O(1)atom of nicotinate are in the axial positions with the axial angle of O(1)-Cu(1)-N(1) is 172.43(8)°. The Cu(II) deviates from the trigonal plan towards O(1) by 0.385 Å. The distortion of the coordination environment of Cu(II) can be illustrated by the deviation of the equatorial angles from 120°. The bond angles of the equatorial plane N(21)-Cu(1)-N(31), N(31)-Cu(1)-N(41), N(41)-Cu(1)-N(21) are 135.05(9)°, 102.77(9)° and 112.65(9)°, respectively. The bond angles of tertiary amine N(1) with the three benzimidazole N atoms [N(21)-Cu(1)-N(1), N(31)-Cu(1)-N(1) and N(41)-Cu(1)-N(1)] are in the range of 78.62(8)–81.23(8)°, which is in part due to the straining nature of ntb.

The bond distances of Cu(II) and the benzimidazole N atoms are 2.014(2) Å for Cu(1)–N(21), 2.038(2) Å for Cu(1)–N(31) and 2.122(2) Å for Cu(1)–N(41). They are shorter than the Cu(1)–amine N(1) bond distance 2.157(2) Å, which is also observed in other copper(II) complexes of ntb [32,39–41]. This is in part due to the greater π -bonding ability of benzimidazole pendants compared to alkylamines, which is exclusively σ -donors, and in part to the straining nature of the tripodal ligand [23]. Except the coordination of four nitrogen atoms of ntb to Cu(II), the fifth coordination is from nicotinate. Nicotinate coordinated to Cu(II) via the carboxylate O atom with Cu(1)–O(1) bond length of 1.9392(18) Å.

Intermolecular H-bond of type N–H···O [N(22)···O(2) = 2.736(3) Å, \angle N(22)–H(22A)···O(2) = 142°] between the NH group of ntb and the uncoordinated carboxylate oxygen atom of nicotinate connected the two adjacent molecules to form a double molecular unit, which is also stabilized by π – π stacking interaction from the imidazole ring and the imidazole ring of adjacent benzimidazole with the centroid-to-centroid distance to be 3.601 Å (Cg1 = Cg2 = C22–N21–C28–C23–N22). The double molecular units are further connected via H-bond of type N–H···N [N(42)···N(11) = 2.785(3) Å, \angle N(42)–H(42A)···N(11) = 166°] between the NH group of ntb and the nitrogen atom of nicotinate to form 1D chain structure as shown in Fig. 6.



Fig. 6. The 1D chain connected through hydrogen bonding interactions in 3.



Fig. 7. Cation structure of complex 4 (30% probability thermal ellipsoids).

Table 6			
Selected bond le	engths (Å) and	angles (°) for	complex 4.

Cu(1)-N(5) Cu(1)-N(2) Cu(1)-N(4)	2.0087(16) 2.0655(16) 2.1144(15)	Cu(1)-N(1) Cu(1)-N(3)	2.0437(16) 2.0907(16)
N(5)-Cu(1)-N(1)	177.34(6)	N(5)-Cu(1)-N(2)	94.21(6)
N(1)-Cu(1)-N(2)	84.89(6)	N(5)-Cu(1)-N(3)	94.45(6)
N(1)-Cu(1)-N(3)	84.12(6)	N(2)-Cu(1)-N(3)	126.91(6)
N(5)-Cu(1)-N(4)	98.97(6)	N(1)-Cu(1)-N(4)	83.59(6)
N(2)-Cu(1)-N(4)	124.09(6)	N(3)-Cu(1)-N(4)	105.96(6)

The 1D chain is further expanded to a two-dimensional (2D) structure through H-bond interactions involving the NH groups of ntb, the water molecules and perchlorate anions as shown in Fig. S2. Similar hydrogen bond interaction was also found in complex $[Mn(ntb)(nic)]CIO_4$ ·H₂O [42].

3.2.4. [Cu(tren)(nic)]BPh₄·CH₃OH·H₂O (**4**)

Complex **4** is composed of one $[Cu(tren)(nic)]^+$ cation, one BPh₄⁻, one methanol and one lattice water molecules. The cation

Table 7					
Selected	hydrogen	bond	parameters	for	1-4.

structure of **4** is shown in Fig. 7, main bond distances and angles are listed in Table 6.

The Cu(II) is coordinated by four N atoms of tren and the pyridine N atom of nicotinate in distorted trigonal bipyramidal geometry with τ value of 0.84, which is comparable to the reported Cu(II) complexes of tren [33,43-46]. The equatorial plane is defined by three primary amine nitrogen atoms N(2), N(3) and N(4)of tren and the axial positions are occupied by the tertiary amine N(1) and pyridine N(5) atoms. The Cu(II) lies 0.209 Å below the equatorial plane toward N(5). The equatorial Cu-N bond distances are 2.0655(16) Å for Cu(1)-N(2), 2.0907(16) Å for Cu(1)-N(3), and 2.1144(15) Å for Cu(1)–N(4). The axial bond distances are 2.0437(16) Å for Cu(1)-N(1) and 2.0087(16) Å for Cu(1)-N(5)(pyridine). The equatorial bond angles are 105.96(6)° for N(3)-Cu(1)-N(4), 124.09(6)° for N(4)–Cu(1)–N(2) and 126.91(6)° for N(2)– Cu(1)-N(3). The bond angles of tertiary amine N(1) with the three primary amine N atoms are in the range of 83.59(6)-84.89(6)°. The striking feature of complex 4 is that nicotinate coordinates to Cu(II) via the pyridine N atom not the carboxylate O atom as that found in complex 3 Fig. 7.

Intermolecular H-bond of type N–H···O [N(4)···O(1) = 2.946(2) Å, \angle N(4)–H(4)···O(1) = 146°] between the NH₂ group of tren and one of the uncoordinated carboxylate oxygen atoms of nicotinate connected the two neighboring molecules to form a double molecular unit (Table 7). The adjacent double molecular units are further bridged by intermolecular H-bond of type O–H···O [O(4)···O(2) = 2.815(2) Å, \angle O(4)–H(7)···O(2) = 167(2)° and O(4)···O(1) = 2.827(2) Å, \angle O(4)–H(4)···O(1) = 174.8(19)°] through two water molecules to form 1D chain structure as shown in Fig. 8.

3.3. Magnetic measurements

The molar magnetic susceptibility χ_M and effective magnetic moment of 1 and 2 were measured in the temperature range of 2–300 K in the field of 1000 Oe. The plots of $\chi_{\rm M}$ and $\mu_{\rm eff}$ versus T for 1 and 2 are shown in Fig. 9 and Fig. 10. As shown in Fig. 9, the value of $\mu_{\rm eff}$ for **1** is 2.67 B.M. at room temperature. Upon cooling, it increases slowly and reaches to a maximum value of 2.71 B.M. at 2 K. This result supports the presence of weak ferromagnetic coupling interaction between the adjacent Cu(II) ions in **1**. The value of μ_{eff} is 2.75 B.M. for **2** at room temperature. It decreases slowly between 40 and 300 K as the temperature decreases, the value of μ_{eff} then decreases much faster and reaches to 2.62 B.M. at 2 K. These features are characteristic of the occurrence of weak antiferromagnetic interaction between the Cu(II) ions in 2. The experimental magnetic data for the two complexes have been fitted by using the Bleany-Bowers expression derived through the Hamiltonian $\hat{H}=-2J\hat{S}_{Cu1}\hat{S}_{Cu2}$ [Eq. (1)], where J is the exchange coupling parameter, the parameters N, β and K in Eq. (1)

D–H…A	d(D-H)	d(H…A)	d(D…A)	∠(DHA)	Symmetry codes
Complex 1 N(3)-H(3)…O(2)	0.86	1.95	2.743(6)	152	-x + 1, $-y + 2$, $-z + 2$
Complex 2 N(3)-H(3D)O(3) O(3)-H(3E)O(2)	0.90 0.77(5)	2.09 2.03	2.989(3) 2.782(3)	173 168(5)	1/2 + x, $3/2 - y$, $1/2 + z$
Complex 3 N(22)–H(22A)…O(2) N(42)–H(42A)…N(11)	0.86 0.86	2.00 1.94	2.736(3) 2.785(3)	142 166	1 - x, 1 - y, -z x, -1 + y, z
Complex 4 N(4)-H(04B)O(1) O(4)-H(40A)O(2) O(4)-H(40B)O(1)	0.92 0.84(2) 0.842(16)	2.14 1.99(2) 1.987(16)	2.946(2) 2.815(2) 2.827(2)	146 167(2) 174.8(19)	1 - x, -y, 1 - z 2 - x, -y, 1 - z



Fig. 8. The 1D chain connected through hydrogen bonding interactions in 4.



Fig. 9. Plots of $\chi_M(0)$ and $\mu_{\text{eff}}(\Delta)$ vs. *T* for complex **1**. The solid line corresponds to the theoretical best fit.



Fig. 10. Plots of $\chi_M(0)$ and $\mu_{eff}(\Delta)$ vs. *T* for complex **2**. The solid line corresponds to the theoretical best fit.

have their usual meanings. Least-squares fitting of all experimental data leads to the following parameters $J = 0.15 \text{ cm}^{-1}$, g = 2.16, $R = 9.43 \times 10^{-5}$ for complex **1** and $J = -0.19 \text{ cm}^{-1}$, g = 2.12, $R = 8.90 \times 10^{-5}$ for complex **2** (R: agreement factor, defined as $\sum (\chi_{obsd} - \chi_{calcd})^2 / \sum \chi_{obsd}^2$). Small positive J value reveal the very weak ferromagnetic coupling interaction between the adjacent Cu(II) ions mediated through the bridging nictinate anions in complex **1**. Rather small negative J value reveals the very weak antifer-

romagnetic coupling interaction between the adjacent Cu(II) ions mediated by the bridging nicotinate anions in complex **2**. Such weak magnetic coupling interaction may be resulted from the long Cu…Cu separation in **1** and **2** [8].

$$\chi_{M} = \frac{2Ng^{2}\beta^{2}}{KT} \left[\frac{1}{3 + \exp(-2J/KT)} \right] + N_{\alpha} \tag{1}$$

4. Conclusion

In this work, two dinuclear nicotinato-copper(II) complexes $[Cu_2(bbma)_2(nic)_2](ClO_4)_2 \cdot CH_3OH \cdot 0.5H_2O$ (1), $[Cu_2(dien)_2(nic)_2]-(ClO_4)_2 \cdot 2CH_3OH$ (2) and two mononuclear complexes $[Cu(ntb)-(nic)]ClO_4 \cdot H_2O$ (3) and $[Cu(tren)(nic)]BPh_4 \cdot CH_3OH \cdot H_2O$ (4) were synthesized and characterized, in which nicotinate ligand exhibits three types of bonding modes, namely, μ_2 -N, O chelating mode in 1 and 2, by one carboxylate O atom in 3 and the pyridine N atom in 4. Magnetic susceptibility measurements for 1 and 2 show very weak ferromagnetic interaction of the two Cu(II) ions for 1 but weak antiferromagnetic interaction in 2.

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Appendix A. Supplementary material

CCDC 777725, 777726, 777727 and 777728 contain the supplementary crystallographic data for complexes **1**, **2**, **3** and **4**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010. 09.038.

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