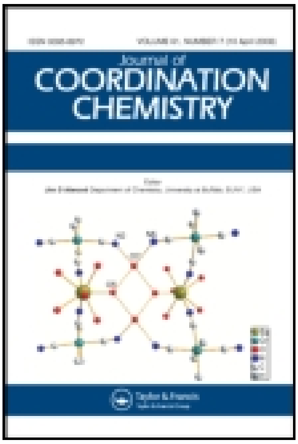

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A self assembled 3-D network propagated by coordination polymerization and H-bonding: synthesis and X-ray crystal structure of $[\{Co(L)_2(H_2O)_2\}(ClO_4)_2(CH_3COCH_3)_2(H_2O)_2]_n$, where L=N,N-diisopropylisonicotinamide

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A self assembled 3-D network propagated by coordination polymerization and H-bonding: synthesis and X-ray crystal structure of $[\{Co(L)_2(H_2O)_2\}(ClO_4)_2(CH_3COCH_3)_2(H_2O)_2]_n$, where L = N,N-diisopropylisonicotinamide

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Reaction of $Co(ClO_4)_2 \cdot 6H_2O$ with N,N-diisopropylisonicotinamide (**L**) has yielded a 1-D coordination polymer $[\{Co(L)_2(H_2O)_2\}(ClO_4)_2(CH_3COCH_3)_2(H_2O)_2]_n$ (**1**). Complex **1** has been characterized by infrared (IR) and UV-Vis spectroscopies, thermal analysis, and single crystal X-ray diffraction techniques. The structure has alternate arrangement of parallel 1-D cationic metal-ligand chains and H-bonded anionic chains containing perchlorate, acetone and water in the lattice. Further hydrogen bonding among both chains leads to formation of 2-D networks along almost perpendicular planes. Interpenetrations of such perpendicular 2-D sheets create a 3-D supramolecular structure.

Keywords: N,N-Diisopropylisonicotinamide; Coordination network; H-Bonding; Crystal structure; Thermal stability

1. Introduction

The search for multidimensional frameworks among coordination and organometallic complexes is a challenge in crystal engineering [1–30]. Metal-containing supramolecular networks are associated with many magnetic, electronic, zeolitic, catalytic, and optical properties. Furthermore, the metal ions display a wide range of coordination geometries that impart structural elements not usually present in organic compounds. Thus, the presence of metal ions provides greater flexibility in constructing ‘‘functional materials’’ with valuable properties having specific dimensions and topologies [1–9].

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Coordination polymerization is an effective route to assemble metal-ligand complexes into "infinite" networks of varying dimensionalities using covalent bonding with organic ligands as bridges between metal centers [1–15]. However, synthesis in coordination polymerization depends on polymerization events which sometimes lead to poor solubility and unpredictability in structure. Where coordination polymerization is not possible strong and directional intermolecular hydrogen bonding may be used as an "adhesive" to link discrete metal complexes to form extended networks [16–26]. Mingos and co-workers were the first to introduce hydrogen bonding as a tool for supramolecular assembly of coordination complexes [16]. Since then several groups have examined the efficacy of the hydrogen bond in crystal engineering of transition-metal systems [17–26].

Recent work on crystal engineering involves construction of frameworks using both coordination polymerization as well as hydrogen bonding [27–37]. The strength of the coordinate bond along with flexibility imparted by hydrogen bonding provides an ideal environment for multidimensional framework expansion. Pyridine based ligands such as nicotinamides and isonicotinamides are ideal as they have the structural adaptability for metal-ligand coordination as well as intermolecular hydrogen bonding [10–15, 17–26].

We have been involved in metal-containing frameworks based on N,N-dialkylisonicotinamides and have recently reported the reaction of anhydrous $CoCl_2$ with N,N-diisopropylisonicotinamide (**L**) which yielded a metal-organic framework (MOF) containing linear trinuclear $[Co_3L_4Cl_6]$ units with a rare, mixed $Co^{II}(T_d)$–$Co^{II}(O_h)$–$Co^{II}(T_d)$ assembly [10]. In this polymer the ligand is bidentate, bridging between metal centers using the pyridine nitrogen and carbonyl oxygen to form a 1-D coordination chain. Furthermore, these metal-ligand coordinated 1-D parallel chains are held together through intermolecular hydrogen-bonding interactions to give 2-D and 3-D networks. In continuation of our pursuit for such multidimensional networks, here we report the synthesis and crystal structure of a new 1-D coordination polymer $[\{Co(L)_2(H_2O)_2\}(ClO_4)_2(CH_3COCH_3)_2(H_2O)_2]_n$ (**1**), which further assemble into 2-D and 3-D networks through intermolecular hydrogen bonding. An X-ray structure analysis of **L** is also discussed.

2. Experimental

2.1. *Materials and methods*

All manipulations for synthesis of ligand were carried out under dry dinitrogen. Solvents and other reagents were dried using standard techniques [38]. The ligand N,N-diisopropylisonicotinamide (**L**) was prepared as described earlier [10]. $Co(ClO_4)_2 \cdot 6H_2O$ (Aldrich) was used as received.

2.1.1. Preparation of $[\{Co(L)_2(H_2O)_2\}(ClO_4)_2(CH_3COCH_3)_2(H_2O)_2]_n$ (1). This complex was prepared from a reaction mixture containing $Co(ClO_4)_2 \cdot 6H_2O$ (0.73 g, 2 mmol) and diisopropylisonicotinamide (0.82 g, 4 mmol) dissolved in about 25 mL of isopropyl alcohol. The contents were stirred for 3–4 h and kept for 2 days at room temperature yielding a pink solid which was filtered and dried *in vacuo*. The compound was recrystallized from 1 : 1 solution of isopropyl alcohol and acetone. Anal.: C, 41.80; H, 6.53; N, 6.40. Calcd for $C_{30}H_{56}Cl_2CoN_4O_{16}$: C, 41.93; H, 6.57; N, 6.52%. M.p.: 270°C(d). Molar conductance ($\Omega^{-1}\,cm^2\,mol^{-1}$): 183 ($CH_3OH$). Infrared (IR): ν_{OH}: 3420 m, br; 3160 w, sh; ν_{CO} 1590 s; ν^{-}_{ClO4} 1086 s, br and 627 m cm^{-1}.

2.2. *Physical measurements*

Elemental analyses (C, H, N) were performed on a Perkin-Elmer model 2400 CHN analyzer. IR spectra were recorded as KBr pellets on a Perkin-Elmer RX-1 FTIR spectrophotometer. Thermal analysis was carried out on a Shimadzu-DTG 60 analyzer. ^{1}H-NMR spectra of ligand were recorded on a 300 MHz JEOL FT NMR spectrometer with TMS as the reference. UV-Vis spectrum was recorded on a Shimadzu Pharmaspec UV-1700 UV–Vis spectrophotometer in CH_3OH. Molar conductance of millimolar solution of the complex was measured on a conductivity bridge-Digital Conductivity Meter CC 601 at 25°C.

2.3. *X-ray crystallography*

Crystallization of **L** by very slow evaporation from its saturated solution in acetonitrile at room temperature yielded suitable single crystals for X-ray analysis. Intensity data for **L** were collected with a Siemens P4 single crystal X-ray diffractometer using a graphite monochromated Mo-Kα ($\lambda = 0.71069$ Å). The lattice parameters and standard deviations were obtained by least squares fit to 40 reflections $20° < \theta < 25°$. The data were collected by the θ–2θ scan mode with a variable scan speed ranging from 2.0 to a maximum of 60° per minute. Three reflections were used to monitor the stability and orientation of the crystal and were measured after every 97 reflections. Their intensities showed only statistical fluctuations during exposure time.

Light pink crystals of **1** were obtained from a saturated solution in isopropyl alcohol and acetone (1 : 1 v/v). The crystals were not of very high quality and diffracted poorly at high $\sin\theta$. Repeated trials to grow crystals by changing conditions did not help improve the situation. Many crystals were tried before choosing the one which the final data set was measured at 120 K on a Nonius kappa CCD2000 with a graded mirror, using Cu-Kα radiation ($\lambda = 1.5418$ Å). Only data up to $\theta = 59°$ could be measured. The structures of both compounds were solved by direct methods using SIR97 [39] and refined by full-matrix least-squares on F^2 using SHELXL-97 [40] in the WINGX package [41] of programs. All non-hydrogen atoms were refined anisotropically. The perchlorates in **1** showed disorder which could be resolved by splitting each of these atoms into two parts with total site occupancy factor (SOF) of one. Their SOFs and U_{iso} values were refined as free variables. The Cl–O distances were restrained to be equal by using SADI. The acetone and lattice water also showed disorder. Attempts to resolve the disorder by the usual methods did not improve the model but only increased the number of parameters, therefore no disorder was applied to them. Only the abnormal C=O distance had to be restrained to 1.210(3) Å. The hydrogens of coordinated water were located from the difference Fourier map. These were refined in the initial cycles of refinement but not in the final ones. The hydrogens of the lattice water could not be located. All other hydrogens (in **L** and **1**) were attached geometrically riding on their respective carrier atoms with U_{iso} being 1.5, 1.2, and 1.2

Table 1. Crystal data and structure refinement for **L** and **1**.

	L	**1**
Empirical formula	$C_{12}H_{18}N_2O$	$C_{30}H_{52}Cl_2CoN_4O_{16}$
Formula weight	206.28	854.59
Wavelength (Å)	0.71069	1.54180
Space group	*Pbca*	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	10.800(5)	7.548(2)
b	7.690(4)	9.942(4)
c	29.757(5)	12.968(3)
α	90	106.01(2)
β	90	90.13(3)
γ	90	95.23(2)
Volume (Å^3), Z	2471(2), 8	931.1(5), 1
Calculated density ρ (Mg m^{-3})	1.109	1.524
Absorption coefficient (mm^{-1})	0.072	5.603
F(000)	896	449
θ range for data collection (°)	2.70–50.98	3.55–58.76
Reflections collected/unique	2303/2303 [R(int) = 0.0000]	4548/2366 [R(int) = 0.0305]
Max. and min. transmission	0.9872 and 0.9858	0.6042 and 0.4004
Data/restraints/parameters	2303/0/136	2366/29/258
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0737$, $wR_2 = 0.21660$	$R_1 = 0.0731$, $wR_2 = 0.2097$
R indices (all data)	$R_1 = 0.1787$, $wR_2 = 0.3192$	$R_1 = 0.0739$, $wR_2 = 0.2106$

times the U_{iso} of their carrier methyl, methylene, and aromatic carbons, respectively. A summary of crystal data, experimental, and refinement details for **L** and **1** are given in table 1 and selected bond lengths and angles are given in table 2. Because of the disorder in acetone, lattice water and perchlorate, missing hydrogens of water, and relatively low θ value of the measured reflections, the crystallographic information file shows a few "A" level errors which are justifiable, e.g., the short intermolecular contacts between water and carbons of acetone have been treated as C–H $\cdots$ O H-bonding interactions. The C $\cdots$ O distances between methyl/sp^2 C of acetone and water lie in the range 2.15–2.71 Å, within the range found in various complexes having acetone and water in their crystal structures. A CSD search for such complexes with no disorder gave 18 hits and 29 such distances were observed in the range 1.889–3.218 Å (av. 2.397 Å) and 1.886–3.196 Å (av. 2.351 Å) for methyl C $\cdots$ O and sp^2 C $\cdots$ O, respectively.

3. Results and discussion

3.1. *Molecular structure of ligand N,N-diisopropylisonicotinamide (L)*

N,N-diisopropylisonicotinamide (**L**) crystallizes in orthorhombic crystal system with *Pbca* space group having eight molecules per unit cell. Figure 1 shows the ORTEP diagram and atom numbering scheme used for structure analysis of **L**. The molecular structure consists of a pyridine with carboxamide side arm having a fully substituted

Table 2. Selected bond lengths (Å) and angles (°) for **L** and **1**.

Ligand **L**	
C3–N1	1.330(6)
C2–N1	1.329(6)
C6–N2	1.346(5)
C7–N2	1.483(5)
C10–N2	1.462(6)
N1–C3–C4	123.9(5)
N1–C3–H3	118.1
N1–C2–C1	124.5(5)
N1–C2–H2	117.8
N2–C6–C5	119.0(4)
N2–C7–C8	112.5(4)
N2–C7–C9	111.2(4)
Complex **1**	
O1–Co1	2.135(4)
Co1–O1W	2.093(4)
Co1–N1	2.170(4)
O1–Co1–O1	180.0
O1–Co1–N1	95.4(2)
O1–Co1–N1	84.5(2)
O1–Co1–N1	84.5(3)
O1–Co1–N1	95.4(2)
N1–Co1–N1	180.0

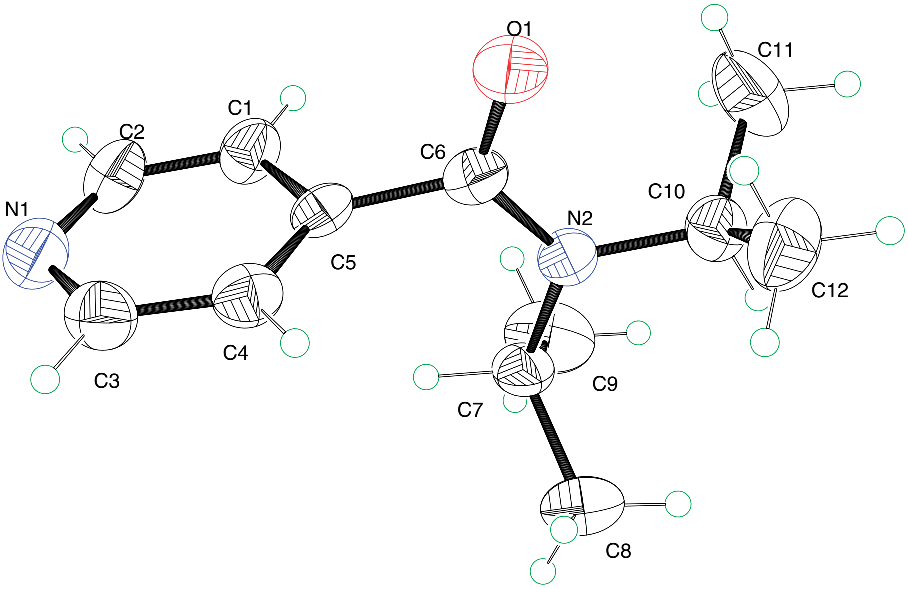

Figure 1. The ORTEP diagram and labeling scheme used for **L**.

nitrogen N2 containing two isopropyl groups. The amide moiety is attached *para* to the pyridyl nitrogen N1.

The torsion angles of 86.6° [C1–C5–C6–O1] and −86.9° [C4–C5–C6–O1] indicate that the amide plane is "twisted away" from the pyridine ring plane (figure S1(a), Supplementary material), attributed to the presence of two bulky isopropyl groups on N2, because in its unsubstituted analog pyridine-4-carboxamide (isonicotinamide), the amide plane is oriented more toward the pyridine ring plane [18]. Parameters such as bond lengths and bond angles are normal and are in accord with the corresponding values in pyridine-4-carboxamide (isonicotinamide) [18, 22]. Relatively high thermal parameters are reported for C11 and C12 terminal carbons. The crystal packing shows both intra- and inter-molecular H-bonding involving carbonyl oxygen O1 and pyridine nitrogen N1. The carbonyl oxygen O1 is an acceptor in hydrogen bonds C11–H11C $\cdots$ O1^{i} (2.444(4) Å) and C12–H12B $\cdots$ O1^{i} (2.412(3) Å), where $i = x,\ y,\ z$ (figure S1(b), Supplementary material). This H-bonding explains the bending of terminal carbons C11 and C12 toward carbonyl oxygen O1. Accordingly, the other two terminal carbons C(8) and C(9) bend away in the opposite direction so as to acquire a staggered conformation to minimize steric strain. The pyridine nitrogen N1 is a H-bond acceptor to phenylene carbon C1, resulting in formation of C1–H1 $\cdots$ N1^{ii} (where $ii = -x + 2,\ +y + 1/2, -z + 1/2 + 1$, 2.883(2) Å) hydrogen bonded chains running along the *a* axis (figure S2, Supplementary material).

3.2. *Molecular and crystal structure of 1*

$[\{Co(L)_2(H_2O)_2\}(ClO_4)_2(CH_3COCH_3)_2(H_2O)_2]_n$ (**1**) consists of a 1-D coordination double chain in which each Co^{II} rides on a crystallographic inversion center and has octahedral geometry (CoN_2O_4). Figure 2(a) shows the ORTEP representation of the asymmetric unit of the complex along with atom numbering scheme and figure 2(b) gives the pictorial depiction of the coordination environment around each Co^{II} in the polymeric chain. In this 1-D coordination polymer, two ligands are bidentate bridging using pyridine nitrogen and carbonyl oxygen between every two neighboring Co^{II} centers, thereby leading to formation of a 1-D cationic double chain/tape $[CoL_2(H_2O)_2]_n^{+2}$ running along the *a* axis (figure 3a). Each Co^{II} in the double chain is bonded to two pyridine nitrogens and two carbonyl oxygens with Co–N$_{\mathrm{pyd}}$ and Co–O$_{\mathrm{amide}}$ distances of 2.172(4) Å and 2.132(3) Å, respectively. The remaining two vacancies around each Co^{II} are water molecules with Co–O distance of 2.093(3) Å (figure 2b). The $\pi \cdots \pi$ interactions between pyridine rings which are oriented in an antiparallel fashion with respect to each other provide further stability to the coordination chain (figure 3). The Co $\cdots$ Co non-bonding distance in the polymeric chain is 7.548 Å.

Formation of networks in which ligands are bridges between metal centers has been observed in similar rod like bi-exodentate ligands based on pyridine such as isonicotinamides, pyrazine (pyz) and 4,4′-bipyridyl (bipy). For $[Cu(CCl_3CO_2)_2(\text{isonicotinamide})_2]_n$, isonicotinamide in a bidentate bridging mode between metal centers leads to a 2-D sheet structure [14]. The structure of $[Cu(CCl_3CO_2)_2(\text{isonicotinamide})_2]_n$ consists of (py)N–Cu–N(py) and (amide)O–Cu–O(amide) bonds across the metal ion, thus forming a 2-D network of coordinate bonds. $[Ag(\text{isonicotinamide})]_n[BF_4]_n$ is a 1-D coordination polymer with linear (pyd)N–Ag–O(amide) coordination [15]. In coordination polymers like $-[Cu_2(RCO_2)_4]-A-[Cu_2(RCO_2)_4]-$ (where A = nicotinamide) [13] and $-[Cu_2(ClCH_2CO_2)_4]-B-Cu_2(ClCH_2CO_2)_4]-$ (where B = diethylnicotinamide) [14], the ligands bridge in a similar fashion between dinuclear paddle-wheel units giving coordination polymers. $[Co(NCS)_2(pyz)_2]$

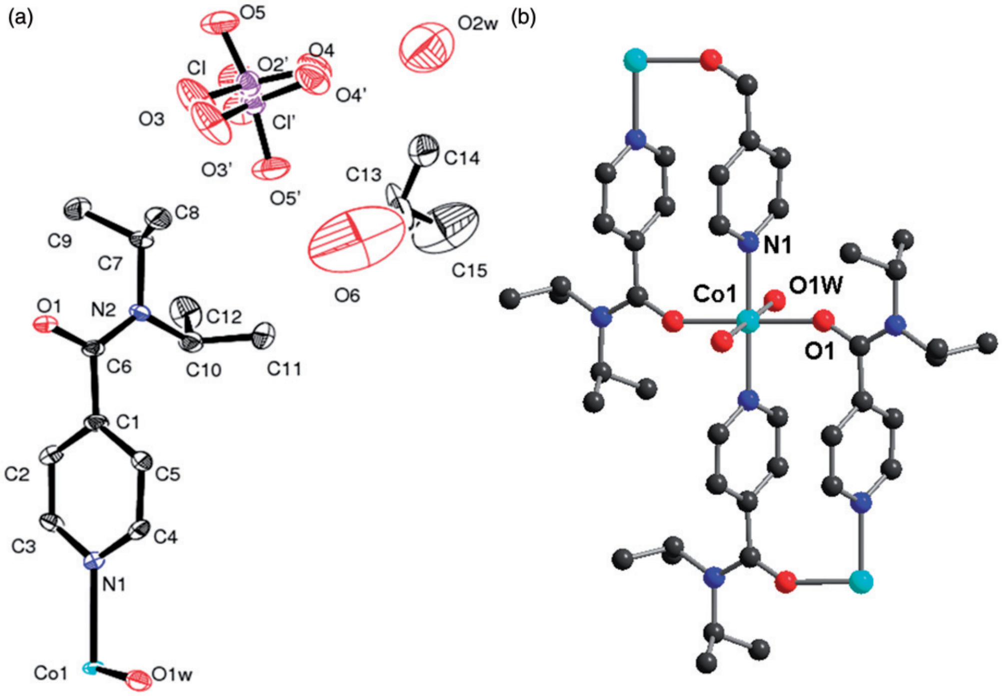

Figure 2. (a) The ORTEP diagram of the asymmetric unit with atom numbering used for **1** and (b) coordination environment around each Co^{II} in the 1-D polymeric chain. The hydrogens have been removed for clarity.

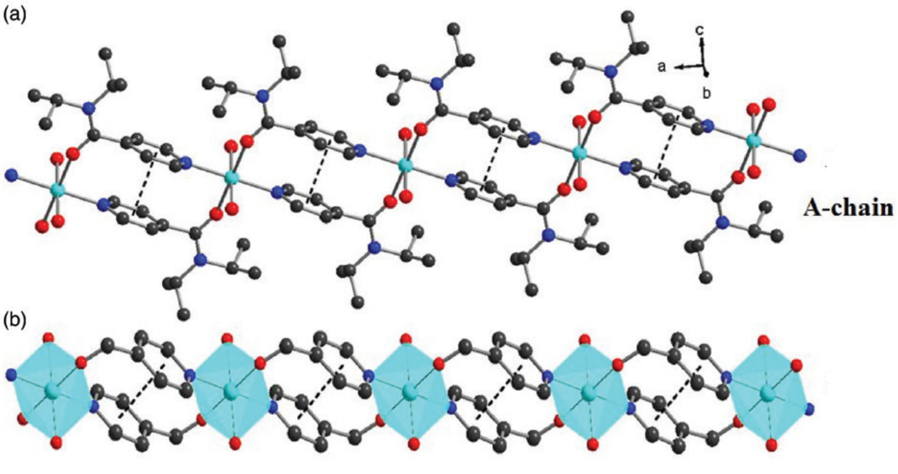

Figure 3. (a) A single 1-D double chain formed by metal-ligand coordination polymerization and (b) coordination polyhedra around each metal in the polymeric chain.

is a 2-D coordination network in which pyz molecules are bidentate bridging between Co^{II} centers [42]. In $[Co(NCS)_2(H_2O)_2(bipy)] \cdot bipy$, the bipy molecules play a similar role in constructing the 1-D linear chain. Changing the solvent from ethanol to ether in $[Co(NCS)_2(bipy)_2] \cdot 2(CH_3CH_2)_2O$ a 2-D network is formed. The formation of double

Table 3. Hydrogen bond geometries in **1**.

D–H···A	D···A [Å]	H···A [Å]	D–H···A [°]
*C14–H14A···O4^{i}	3.101(2)	2.126(2)	148
*C14–H14B···O2W^{i}	2.215(2)	1.641(2)	113
*C15–H15A···O5^{ii}	3.238(3)	2.597(3)	123
*C15–H15C···O4^{iii}	3.498(3)	2.635(3)	147
*C14–H14B···O2W^{iii}	2.648(2)	2.074(4)	116
*C15–H15C···O2W^{iv}	2.152(3)	1.397(2)	131
**C3–H3···O2W^{vi}	3.395(2)	2.454(3)	170
**O1W–H11W···O2W^{vii}	2.951(4)	2.175(4)	120
**C14–H14C···O1W^{vii}	2.892(3)	1.993(2)	128
**C5–H5···O4^{iv}	3.428(2)	2.479(2)	166
**O1W–H12W···O2^{v}	2.872(4)	1.955(3)	150
***C11–H11C···O3^{ii}	3.741(4)	2.820(4)	157

Symmetry transformations used to generate equivalent atoms: $i = x,y,z$; $ii = x-1,+y,+z$; $iii = -x+1,-y+1,-z+2$; $iv = -x+1,-y+1,-z+1$; $v = x-1,+y,+z+1$; $vi = x-1,+y-1,+z-1$; $vii = -x,-y+1,-z+1$.

*Hydrogen-bonding interactions among perchlorates, acetone, and water molecules to form 1-D chain.

Type-I H-bonding interactions between **A and **B** chains involving the coordinated water molecules of the complex.

***Type-II H-bonding interactions between **A** and **B** chains involving the propyl group hydrogen H11C.

chains/tapes has been reported for $[Co(cpoa)_2(H_2O)_2][Co(bipy)(H_2O)_4] \cdot 2H_2O$ (where H_2cpoa = 4-carboxyphenoxyacetic acid) in which two successive Co^{II} centers of a $[Co(cpoa)(H_2O)_2]$ double-chain are connected by a pair of antiparallel cpoa ligands [4].

Complex **1** displays extensive intermolecular hydrogen bonding in the crystal lattice due to the presence of perchlorate, acetone, coordinated, and uncoordinated water thereby forming 1-D, 2-D, and 3-D architectures with interesting topologies. Apart from having 1-D cationic linear double chains (**A**-chains; figure 3a) formed through metal-ligand coordination, the lattice also contains parallel 1-D anionic linear chains formed by hydrogen-bonding interactions* (table 3) among perchlorate, acetone, and lattice water (**B**-chains; figure 4). The arrangement of **A** and **B** chains around each other in the crystal lattice is such that a very interesting 3-D network is formed. The hydrogen-bonding interactions** (type-I, see table 3) involving the coordinated water between the two types of 1-D chains lead to formation of 2-D sheet structure running parallel to *ab* plane with ABABAB···. arrangement in the crystal lattice.

Almost perpendicular to this plane, the hydrogen-bonding interactions*** (type-II, see table 3) among both chains involving propyl hydrogen H11C of the complex leads to formation of another 2-D sheet with ABABAB···type of packing in the crystal lattice (figure 5). The orientation of coordinated water and propyl hydrogen H11C is such that two 2-D sheets propagate in almost perpendicular directions with respect to each other (figure 6a). Interpenetration of both these types of 2-D sheets opens up a 3-D network built upon coordination polymerization in 1-D and intermolecular hydrogen bonding in the other two dimensions as indicated in figure 6(b).

3.3. *IR, UV-Vis, and thermal analyses*

The IR spectrum of **1** shows strong ν_{CO} at 1590 cm^{-1}, markedly lower from ν_{CO} at 1660 cm^{-1} in **L** [10], indicating coordination to Co^{II} through carbonyl oxygen. The presence of a strong, broad band at 1086 and a medium intensity band at 627 cm^{-1}

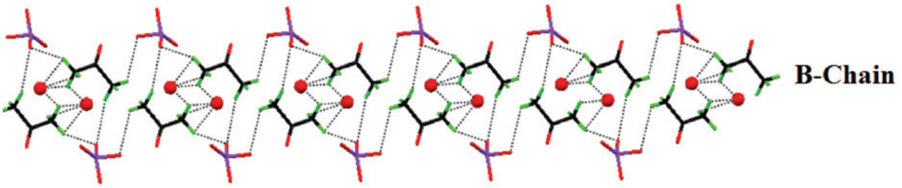

Figure 4. An anionic 1-D linear chain (**B**-chain) formed through H-bonding among perchlorates, acetone, and uncoordinated water.

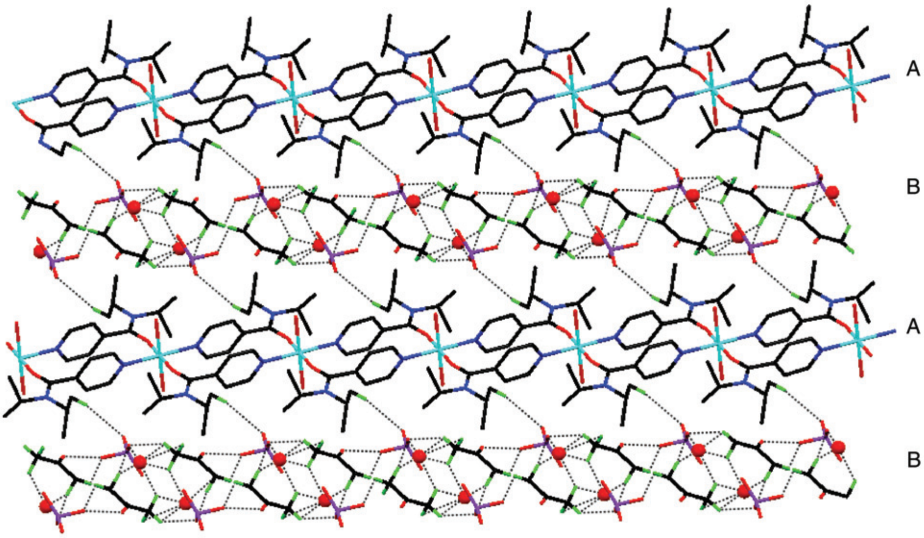

Figure 5. A 2-D sheet formed by intermolecular hydrogen bonding*** (type-II, involving isopropyl hydrogen) between parallel **A** and **B** chains. The hydrogens other than those involved in hydrogen-bonding interactions have been removed for clarity.

suggest ionic perchlorate [43, 44]. The ν_{OH} at 3420 and 3160 cm^{-1} are assigned to lattice and coordinated H_2O. A fairly high molar conductivity in methanol shows significant ionic dissociation of the complex in this solvent.

The six coordinated octahedral and pseudo-octahedral species exhibit three transitions: $^4T_{2g} \leftarrow {}^4T_{1g}(\nu_1)$, $^4A_{2g} \leftarrow {}^4T_{1g}(\nu_2)$, and $^4T_{1g}(P) \leftarrow {}^4T_{1g}(\nu_3)$ [45]. The ν_2 transition is very weak (formally two electrons) and is often not observed. Therefore, generally two principal regions of absorption are observed. One of the bands at 1000–1260 nm (10,000–8000 cm^{-1}) with intensities 1–10 L mol^{-1} cm^{-1} can be assigned to $^4T_{2g} \leftarrow {}^4T_{1g}(\nu_1)$, while the other band corresponding to $^4T_{1g}(P) \leftarrow {}^4T_{1g}(\nu_3)$ lies near 500 nm (20,000 cm^{-1}) with intensity 5–20 L mol^{-1} cm^{-1}. In the present case, pink solution of **1** in CH_3OH gave a band near 504 nm (19,840 cm^{-1}, $\varepsilon = 16$ mol^{-1} cm^{-1}) corresponding to $^4T_{1g}(P) \leftarrow {}^4T_{1g}(\nu_3)$, indicating distorted octahedral geometry. The other band may have been shifted to far IR region beyond 1100 nm.

Thermogravimetric analysis on **1** is shown in figure S3 (Supplementary material). The complex undergoes weight loss in two major steps, initial loss consisting of two

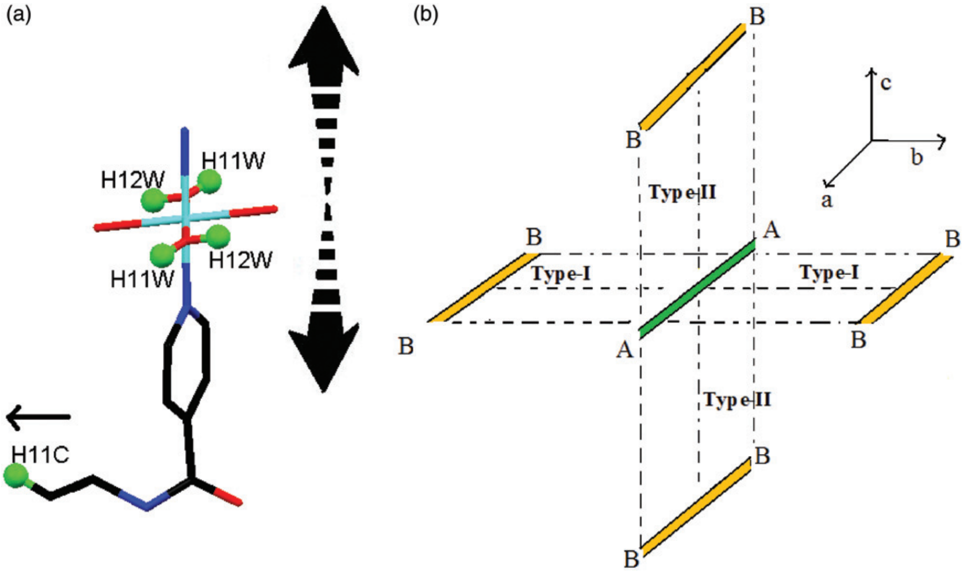

Figure 6. (a) Orientation of coordinated water with respect to isopropyl hydrogen H11C and (b) depiction of 3-D network formed by interpenetration of two types of 2-D layers through type-I and type-II hydrogen bonding (see table 3 for type-I and type-II). **A** (green) and **B** (yellow) chains are oriented perpendicular to the plane of this article.

overlapping steps between room temperature and 110°C, from loss of two acetones followed by four water molecules (obs. wt loss: 21.5; Calcd wt loss: 21.8%). The rate of mass loss is maximum above 80°C for acetone owing to the fact that these are involved in extensive intermolecular hydrogen-bonding interactions in the crystal lattice of the complex. Between 115°C and 310°C the dehydrated complex does not undergo any appreciable weight loss. On heating above this temperature it undergoes a rapid mass loss to 345°C losing the ligands and perchlorate, leaving behind black CoO around 400°C (obs. wt loss: 69.5; Calcd wt loss: 69.1).

4. Conclusions

In continuation of our work involving N,N-diisoalkylisonicotinamide ligands [10], in this article we present the synthesis and structure of a new Co^{II} 1-D coordination network containing N,N-diisopropylisonicotinamide as ligand. This study shows that the fully substituted amide of pyridine mono carboxylic acids (isonicotinic acid in the present case) provides the necessary rigidity and binding sites that enhance formation of coordination networks instead of isolated entities and therefore, provide a fertile route to MOFs.

Intermolecular interactions among 1-D coordinated and H-bonded chains form complex networks (2-D and 3-D). Each of these levels contains remarkable features that have been discussed making **1** unique from a structural point of view.

The creation of 1-D, 2-D, or 3-D metal embedded networks provides us with an opportunity of having a large number of metal centers in close proximity. Therefore, the chances and magnitude of magnetic exchanges between these moment carriers are usually more than that in case of mononuclear complexes, magnetism being a cooperative phenomenon; variable temperature magnetic studies of the present complex are underway. In moving from an isolated cluster to a 1-D, 2-D, or 3-D framework, we progress from an isolated magnetic cluster to bulk magnets.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC nos 795848 and 795849 for **1** and **2**, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2, 1EZ, UK [Fax: +44 1223 336033; Email: deposit@ccdc.cam.uk or www: http://www.ccdc.cam.ac.uk].

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