Syntheses, characterization and crystal structures of potassium and barium complexes of a Schiff base ligand with different anions

BHAVESH PARMAR^a, KAMAL KUMAR BISHT^{a,b}, PRATYUSH MAITI^c, PARIMAL PAUL^{a,b}, and ERINGATHODI SURESH^{a,b,*}

^aAnalytical Discipline and Centralized Instrument Facility, ^bAcademy of Scientific and Innovative Research (AcSIR), ^cScale-up and Process Engineering Unit, CSIR–Central Salt and Marine Chemicals Research Institute, Council of Scientific and Industrial Research, G B Marg, Bhavnagar 364 002, Gujarat, India
e-mail: esuresh@csmcir.org; suresh123@rediffmail.com

MS received 5 April 2014; accepted 1 September 2014

Abstract. New pseudopolymorph of a O,N,N'-donor hydrazone ligand, 2-pyridylcarboxaldehyde isonicotinoylhydrazone (**L**) and its discrete complexes with K⁺ and Ba²⁺ have been reported. **L** forms isostructural dinuclear complexes with K⁺ when bromide and iodide were employed as counter anions. However, a monomeric complex in the case of Ba²⁺ with existence of coordinated as well as lattice perchlorate counter anions was observed. All compounds were characterized by single crystal X-ray analysis and other physicochemical techniques. Structural analysis and spectral features of all compounds are described in detail.

Keywords. Potassium; Barium; Schiff base; dinuclear complex; 2-pyridylcarboxaldehyde isonicotinoylhydrazone; single crystal x-ray analysis.

1. Introduction

Crystal engineering utilizes intermolecular interactions and offers the synthesis of molecular solids from neutral or ionic building blocks.¹ Supramolecular assemblies involving O,N,N'-donor organic molecules and coordination compounds thereof have been of much research interest owing to their potent biological activity as well as variety of structural diversity.² Significant structural differences observed in various complexes involving O,N,N'-donor molecules have shown to impart diverse features such as catalytic property and second harmonic generation.³

O,N,N'-donor hydrazone ligands which are often synthesized by Schiff base condensation have been excellent supramolecular precursors for their ability to exist in keto- and enol- tautomeric forms (scheme 1). Interestingly, hydrazone ligands can coordinate with metal centres either as neutral molecule or deprotonated anionic form, which enhances the coordination diversity in the resulting architectures (scheme 1). A large number of mono- and dinuclear metal complexes are available in literature involving hydrazone ligands and transition metal ions. In fact, the Schiff base, 2-pyridylcarboxaldehyde isonicotinoylhydrazone (**L**), has been exploited to realize a range of organic

co-crystals/salts and coordination compounds with different transition metal ions.^{4,5} An oxidized derivative of **L** (N-(isonicotinoyl)-N'-(picolinoyl)hydrazine), which has been obtained in presence Fe(III) ions has also been reported.⁵ Moreover, Bernhardt *et al.* have explored the notable iron chelator efficacy of numerous transition metal complexes of **L** and derivative ligands.⁶

Recently, **L** has been utilized to fabricate extended materials such as coordination polymers or metal organic frameworks.⁷ Dehnen *et al.* reported mixed ligand In(III) helical coordination polymers in its neutral as well as anionic forms involving aryl thiolates and **L**. Interestingly, the coordination polymer possessing anionic form showed a centrosymmetric structure, whereas, the one comprising neutral hydrazone revealed non-centrosymmetric structure exhibiting second harmonic generation (SHG) effect.⁸

On the contrary, variation in the solid state forms of biologically active substances remains of significant interest.⁹ Different solid state forms of any molecule of interest; typically, an active pharmaceutical ingredient may exhibit different stability, dissolution or solubility behaviour. Thus, the studies on the polymorphic and pseudopolymorphic forms of potent organic molecules remain the subject of interest among crystal engineers.⁹ We have been involved in the studies on crystal engineering aspects and supramolecular interactions of self assembled systems including hybrid

*For correspondence

Scheme 1. Neutral keto-enol tautomers and anionic enolate form of O,N,N'-donor, **L**.

organic materials, discrete metal complexes and coordination polymers.¹⁰ Despite the rich literature reports on the coordination compounds of **L** with transition metals, coordination behaviour of **L** towards the alkali and alkaline earth metal ions are scantily investigated. The present study is outlined to understand the crystal engineering aspects of Schiff base ligand **L** and its coordination behaviour towards the alkali and alkaline metal ions K^+ and Ba^{+2} . Thus, a new polymorphic form of ligand **L** has been crystallized and complexes **1**, **2** and **3** have been synthesised by treatment of the metal precursors with **L** in appropriate stoichiometry. **L** and all three complexes have been characterized by single crystal X-ray diffraction analysis and other physicochemical techniques.

2. Experimental

2.1 Materials and methods

All reagents and solvents were purchased from commercial sources and were used without further purification. Distilled water was used for synthetic manipulations. CHNS analyses were done using a Perkin-Elmer 2400 CHNS/O analyzer. 1H and ^{13}C NMR spectra for the ligands and complexes were recorded on Bruker AX 500 spectrometer (500 MHz at temperature $25^\circ C$ and was calibrated with respect to internal reference TMS). IR spectra were recorded using KBr pellets on a Perkin-Elmer GX FTIR spectrometer. For each IR spectra 10 scans were recorded at 4 cm^{-1} resolution. TGA was carried out using Mettler Toledo Star SW 8.10. Absorption spectra were recorded using Shimadzu UV-3101PC spectrometer. X-ray powder diffraction data were collected using a Philips X-Pert MPD system with $CuK\alpha$ radiation. Single crystal structures were determined using BRUKER SMART APEX (CCD) diffractometer.

2.2 Synthesis of 2-pyridylcarboxaldehyde isonicotinoylhydrazone (**L**)

2-pyridylcarboxaldehyde isonicotinoylhydrazone or (E)-N'-(pyridin-2-ylmethylene) isonicotinohydrazide

(**L**) was synthesized by adopting a reported procedure with slight modifications.¹¹ Pyridine-2-carboxaldehyde (1.0 mL, 10 mmol) and isonicotinohydrazide (1.37 gm, 10 mmol) were dissolved in 25 mL of ethanol and few drops of acetic acid were added. Resulted solution was refluxed with continuous stirring for 8 h and then the solvent was reduced by rotator evaporation to 10 mL which on cooling to room temperature yielded white precipitate. The precipitate thus obtained was washed with cold methanol and recrystallized in ethanol. Yield = 85%. 1H NMR ($DMSO-d_6$): δ 7.46 (m,1H), 7.93 (m,4H), 8.50 (d,1H), 8.65 (d,1H), 8.81(d, 2H), 12.26(s,1H). Elemental analysis (%) calc.: C, 63.71; H, 4.46; N, 24.76; found: C, 63.32; H, 4.72; N, 24.14; IR cm^{-1} (KBr): 3446 (br), 3174 (w), 2998 (m), 2365 (w), 1665 (s), 1549 (s), 1472 (m), 1407 (w), 1346 (w), 1286 (s), 1148 (m), 1073 (m), 997 (w), 956 (w), 849 (w), 787 (w), 749 (w), 688 (m), 628 (w), 512(w).

2.3 Crystallization of 2-pyridylcarboxaldehyde isonicotinoylhydrazone dihydrate (**L.2H₂O**)

L (23 mg, 0.10 mmol) and KNO_3 (11 mg, 0.10 mmol) were dispersed in 7 mL of water-methanol solvent mixture (water : methanol = 1 : 2.5) and heated for 6 h at $75-80^\circ C$ then cooled down to ambient temperature and allowed to evaporate slowly. X-ray quality fibrous needle shaped crystals were harvested in *ca* 2 months time. Yield = 70.5%. Elemental analysis (%) calc.: C, 54.96; H, 5.38; N, 21.36; found: C, 54.77; H, 5.78; N, 20.87; IR cm^{-1} (KBr): 3450 (s), 3069 (m), 2928 (w), 2850 (w), 2362 (m), 1665 (s), 1567 (s), 1471 (w), 1437 (m), 1415 (m), 1363 (m), 1291 (s), 1146 (w), 1067 (m), 1001 (w), 949 (w), 855 (w), 784 (w), 748 (w), 689 (s), 522 (w), 460 (w).

2.4 Synthesis of $[K_2L_4(H_2O)_2]Br_2 \cdot 6H_2O$ (**I**)

L (23 mg, 0.10 mmol) and KBr (12 mg, 0.10 mmol) were dispersed in a mixture of 2 mL H_2O and 5 mL methanol and then refluxed for 6 h. The reaction mixture was cooled to room temperature, filtered and

allowed to evaporate slowly when fibrous needle shape crystals suitable for single crystal analysis were obtained after 40–45 days. Yield = 74.2%. Elemental analysis (%) calc.: C, 44.79; H, 4.39; N, 17.41; found: C, 43.96; H, 5.01; N, 16.82; IR cm^{-1} (KBr): 3456 (br), 3163 (w), 3056 (w), 3008 (m), 2925 (w), 2849 (w), 2360 (w), 2208 (w), 1664 (s), 1560 (s), 1480 (w), 1437 (w), 1409 (w), 1361 (m), 1300 (s), 1154 (m), 1065 (m), 948 (w), 850 (w), 775 (w), 686 (m), 520 (w).

2.5 Synthesis of $[K_2L_4(H_2O)_2]I_2 \cdot 6H_2O$ (**2**)

Method was same as adopted for **1** except KI (17 mg, 0.10 mmol) was used instead of KBr. Yield = 78.4%. Elemental analysis (%) calc.: C, 41.74; H, 4.09; N, 16.23; found: C, 40.92; H, 4.24; N, 15.62; IR cm^{-1} (KBr): 3476 (br), 3173 (s), 3035 (m), 2866 (w), 2367 (w), 2215 (w), 1678 (s), 1547 (s), 1471 (w), 1430 (w), 1409 (w), 1361 (w), 1292 (s), 1147 (m), 1065 (m), 999 (w), 847 (w), 776 (w), 692 (m), 480 (w).

2.6 $\{[Ba(L)_2(H_2O)_2(ClO_4)] \cdot (ClO_4)\}$ (**3**)

$Ba(ClO_4)_2$ (168 mg, 0.5 mmol) was dissolved in 5 mL H_2O then 5 mL methanol was layered carefully over which **L** (112 mg, 0.5 mmol) dissolved in ethanol were layered. The container was covered and kept for slow diffusion of reactants at room temperature which afforded white crystals within 45–50 days. Yield = 71.2%. Elemental analysis (%) calc.: C, 34.95; H, 2.93; N, 13.59; found: C, 35.11; H, 2.878; N, 14.17; IR cm^{-1} (KBr): 3546 (m), 3265 (s), 2932 (w), 2857 (w), 2364 (w), 1665 (s), 1552 (s), 1477 (w), 1438 (w), 1369 (w), 1293 (s), 1089 (s), 928 (w), 849 (w), 781 (w), 750 (w), 694 (w), 627 (m), 514 (w).

2.7 X-ray crystallography

Summary of crystallographic data and details of data collection for **L** and **1–3** is given in table 1. Single crystals with suitable dimensions were chosen under an optical microscope after immersing in paratone oil and mounted on a glass fibre for data collection. Intensity data for all the crystals were collected using MoK_{α} ($\lambda = 0.71073 \text{ \AA}$) radiation on a Bruker SMART APEX diffractometer equipped with CCD area detector at 150 K except for complex **3** for which data was collected at room temperature (296 K). The data integration and reduction were processed with SAINT software.¹² An empirical absorption correction was applied to the collected reflections with SADABS.¹³ Structures were solved by direct methods using SHELXTL and were

refined on F^2 by the full-matrix least-squares technique using the program SHELXL-97.^{14,15} Hydrogen atoms attached to the organic ligand is either located from the difference Fourier map or fixed stereochemically in all the compounds. Hydrogen atoms of the coordinated/lattice water molecules are located from the difference Fourier map and kept fixed using DFIX card. In the case of Ba complex **3** some oxygen atoms of both perchlorate anions showed extensive disorder. The site and occupancy factor for the disordered oxygen atoms were determined using PART and FVAR cards of SHELXL-97 package. All non-hydrogen atoms were refined anisotropically till convergence is reached.

3. Results and Discussion

Conformational flexibility of ligand **L** makes it interesting and suitable for the crystal engineering studies. In fact, the O,N,N'-donor sites can presume *syn* and *anti* conformation as depicted in scheme 2. Structure of **L** reported by Richardson *et al.* revealed *anti* conformation by the pyridyl nitrogen with respect to the imine nitrogen.⁴ Interestingly, *syn* conformation is espoused by the ligand moiety in pseudopolymorph **L.2H₂O** with water of crystallization which is reported in present work. This is attributable to the supramolecular interactions of **L** with lattice water molecules in the pseudopolymorph. It is worthy to mention that Cambridge Structure Database (CSD version 5.35) search involving **L** and transition metal ions showed 6 complexes involving keto tautomer and 12 complexes involving enol or enolate tautomers of **L**.^{7,8} However, no structural report on the K^+ and Ba^{+2} complexes of **L** is available in CSD and literature. Evidently, the current study presents first report on the complexation between **L** and alkali and alkaline earth metal ions. Complexes **1**, **2** and **3** reveal the *syn* conformation of ligand moiety in keto tautomeric form which is attributable to the wrapping of ligand around the cations to facilitate effective tridentate chelation. Keto tautomeric form of **L** in all complexes as well as in its free states was established by 1H and ^{13}C NMR spectra (figure S4). Structural features of ligand as well as all complexes are discussed in following sections.

3.1 Crystal and molecular structure of **L.2H₂O**

Ligand **L** was appropriately prepared by Schiff base condensation between pyridine-2-carboxaldehyde and isonicotinohydrazide. Crystal structure of the unhydrated form of ligand **L** was previously reported by Richardson *et al.* in *Fdd2* space group of orthorhombic

Table 1. Crystal data and refinement parameters for **L** and **1–3**^[a].

Identification code	L.2H₂O	1	2	3
Chemical formula	C ₁₂ H ₁₄ N ₄ O ₃	K ₂ C ₄₈ H ₅₆ Br ₂ N ₁₆ O ₁₂	K ₂ C ₄₈ H ₅₆ I ₂ N ₁₆ O ₁₂	BaC ₂₄ H ₂₄ Cl ₂ N ₈ O ₁₂
Formula weight	262.27	1287.11	1381.09	824.75
Crystal Colour	Colourless	Pale-White	Yellow	White
Crystal Size (mm)	0.25 × 0.05 × 0.04	0.11 × 0.08 × 0.05	0.26 × 0.08 × 0.07	0.60 × 0.40 × 0.30
Temperature (K)	150(2)	150(2)	150(2)	296(2)
Crystal System	Monoclinic	Triclinic	Triclinic	Triclinic
Space Group	P2 ₁ /n	P-1	P-1	P-1
a(Å)	7.077(4)	10.1656(13)	10.2966(9)	9.8642(17)
b(Å)	14.237(8)	12.7671(16)	12.7918(11)	10.8398(19)
c(Å)	12.632(7)	13.0956(17)	13.2334(11)	15.784(3)
α(°)	90	111.469(2)	110.6820(10)	84.846(3)
β(°)	98.248(12)	102.801(2)	102.7650(10)	74.006(2)
γ(°)	90	106.544(2)	106.8600(10)	87.718(3)
Z	4	1	1	2
V(Å ³)	1259.5(13)	1411.5(3)	1455.2(2)	1615.6(5)
Density (Mg/m ³)	1.383	1.514	1.576	1.695
μ (mm ⁻¹)	0.102	1.657	1.295	1.466
F(000)	552	660	696	820
Reflections Collected	6176	11807	12117	13325
Independent Reflections	2204	6031	6210	6916
R _{int}	0.0852	0.0376	0.0196	0.0177
Number of parameters	226	401	402	496
GOF on F ²	1.122	1.111	1.156	1.035
Final R ₁ /wR ₂ (I ≥ 2σ(I))	0.0792/0.1536	0.0597/0.1163	0.0349/0.0805	0.0286/0.0787
Weighted R ₁ /wR ₂ (all data)	0.1183/0.1700	0.0780/0.1227	0.0382/0.0821	0.0301/0.0800
CCDC number	992911	992912	992913	992914

^[a]R = $\sum ||F_o| - |F_c|| / \sum |F_o|$; wR = $[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$

Scheme 2. *Syn*- and *anti*-conformations of O,N,N'-donor **L**.

system.⁴ However, colourless shiny single crystals of new pseudopolymorph **L.2H₂O** suitable for X-ray crystallography were harvested from slow evaporation of methanol/water mixture in presence of potassium nitrate. Pseudopolymorph **L** crystallized along with two water molecules as solvent of crystallization in monoclinic system with P2₁/n Space group (figure 1a). Crystal structure revealed that **L** moiety is almost planar with the *syn* conformation adopted by the pyridyl nitrogen N1 with respect to the imine nitrogen N2 which is the favourable conformation to make tridentate

chelation in wrapping around the metal upon coordination. In an attempt to understand the supramolecular interactions we have analyzed the packing and hydrogen bonding interactions in detail. Packing diagram with hydrogen bonding interactions viewed down *a*-axis is depicted in figure 1c. Pairs of π stacked **L** moieties in opposite orientations are engaged along *b*-axis with the centroid...centroid stacking distance between the pyridyl rings are 3.45 Å and 3.56 Å respectively. Lattice water molecules are positioned between the π stacked **L** layers and involved in extensive hydrogen bonding interactions generating a two dimensional network.

Close up view of the various hydrogen bonding contacts are depicted in figure 1b. Thus, O2 and O3 are involved as a donor and making O-H...O and O-H...N interactions with water oxygen O3, pyridyl nitrogen N4 and amide oxygen O1 and pyridyl nitrogen N1 respectively. Lattice water molecules O2, is involved as acceptor in C-H...O interaction with imine hydrogen H6, pyridyl hydrogen H9 and N-H...O contact with amide hydrogen H1C. Nevertheless, O3 is

Figure 1. (a) ORTEP digram of $L \cdot 2H_2O$ with atom numbering scheme; (b) close-up view of various Hydrogen bonding interactions between the organic moiety and the lattice water molecules (turquoise dotted lines); (c) packing diagram viewed down a-axis showing the various supramolecular interactions in the two dimensional H-bonded network.

involved as acceptor in making $C-H \cdots O$ interaction with the pyridyl hydrogen H2 and $O-H \cdots O$ interaction with water hydrogen H4D respectively in making the two dimensional sheet like hydrogen bonded nets. Details of these H-bonding interactions with symmetry code are summarised in table 2.

3.2 Crystal and molecular structures of $[K_2L_4(H_2O)_2]Br_2 \cdot 6H_2O$ (1) and $[K_2L_4(H_2O)_2]I_2 \cdot 6H_2O$ (2)

Compound 1 and 2 are isostructural dimers crystallized in triclinic system with P-1 space group and the structural description is limited to 1. Cationic part of the

Table 2. Details of hydrogen bonding interactions observed in L.2H₂O and 1-3.

L.2H ₂ O			
D-H...A	d(H...A) (Å)	d(D...A) (Å)	∠D-H...A (°)
N(3)-H(1C)...O(2) ¹	1.94(4)	2.848(5)	172(4)
O(3)-H(3C)...N(1) ²	2.07(5)	2.945(4)	161(5)
O(3)-H(3D)...O(1) ²	2.10(6)	2.939(4)	164(5)
O(2)-H(4C)...N(4) ³	2.05(4)	2.871(4)	171(4)
O(2)-H(4D)...O(3) ⁴	1.75(4)	2.785(4)	165(4)
C(2)-H(2)...O(3) ⁵	2.57(3)	3.416(5)	155(3)
C(6)-H(6)...O(2) ¹	2.58(3)	3.345(5)	138(2)
C(9)-H(9)...O(2) ¹	2.37(3)	3.255(4)	158(3)
Symmetry code: 1. 1/2-x,-1/2+y,1/2-z; 2. 1/2+x,3/2-y,1/2+z; 3. x,1+y,z; 4. -1+x,y,z; 5. 1-x,2-y,-z			
Complex 1			
D-H...A	d(H...A) (Å)	d(D...A) (Å)	∠D-H...A (°)
O(3)-H(3A)...N(4) ¹	2.13(5)	2.892(5)	168(5)
O(3)-H(3B)...N(5) ²	2.16(6)	2.862(5)	168(7)
N(3)-H(3N)...Br(1) ³	2.65(4)	3.414(3)	168(4)
O(4)-H(4A)...O(3) ²	2.04(5)	2.784(6)	174(5)
O(4)-H(4B)...O(6) ²	2.02(5)	2.748(5)	156(5)
O(5)-H(5A)...N(8) ⁴	2.14(5)	2.859(6)	160(6)
O(5)-H(5B)...Br(1) ⁵	2.58(5)	3.363(4)	165(5)
O(6)-H(6A)...O(5) ³	1.93(7)	2.707(6)	163(5)
O(6)-H(6B)...Br(1) ⁶	2.61(5)	3.372(4)	174(5)
N(7)-H(7N)...O(4) ⁴	2.06(4)	2.835(5)	171(4)
C(1)-H(1)...O(2) ²	2.4824	3.154(5)	129.33
C(14)-H(14)...Br(1) ⁵	2.8987	3.721(4)	148.15
C(18)-H(18)...O(6) ⁴	2.5405	3.414(5)	156.44
C(21)-H(21)...O(4) ⁴	2.4894	3.203(5)	133.63
Symmetry code: 1. 1-x,-y,1-z; 2. x, y, z; 3. 1-x,1-y,1-z; 4. -x,1-y,1-z; 5. x,-1+y,z; 6. x,y,1+z			
Complex 2			
D-H...A	d(H...A) (Å)	d(D...A) (Å)	∠D-H...A (°)
O(3)-H(3A)...N(8) ¹	2.14(5)	2.912(4)	170(5)
O(3)-H(3B)...N(1) ²	2.2762	2.861(3)	128.64
N(3)-H(3C)...O(4) ²	2.07(4)	2.842(4)	168(4)
O(4)-H(4A)...O(3) ²	2.08(5)	2.792(4)	174(4)
O(4)-H(4B)...O(6) ²	1.93(6)	2.731(4)	162(7)
O(5)-H(5A)...N(4) ²	2.05(7)	2.800(5)	164(7)
O(5)-H(5B)...I(1) ²	2.89(4)	3.576(4)	166(4)
O(6)-H(6A)...O(5) ³	1.92(5)	2.690(5)	167(6)
O(6)-H(6B)...I(1) ⁴	2.81(5)	3.571(3)	180(5)
N(7)-H(7C)...I(1) ³	2.88(3)	3.643(3)	166(4)
C(2)-H(2)...I(1) ²	3.0188	3.843(4)	148.53
C(3)-H(3)...O(5) ⁴	2.56(4)	3.411(5)	152(3)
C(6)-H(6)...O(6) ²	2.555	3.421(4)	154.93
C(12)-H(12)...O(4) ²	2.4725	3.167(3)	131.51
C(13)-H(13)...O(1) ⁵	2.5203	3.196(4)	129.85
Symmetry code: 1. 1+x,y,z; 2. x, y, z; 3. -1+x,y,z; 4. 1-x,1-y,-z; 5. 1-x,1-y,1-z			
Complex 3			
D-H...A	d(H...A) (Å)	d(D...A) (Å)	∠D-H...A (°)
N(2)-H(3C)...O(5) ¹	2.1646	2.996(3)	162.27
O(3)-H(3D)...O(9) ²	2.33(2)	3.231(6)	164(2)
O(3)-H(3E)...N(5) ³	1.93(2)	2.855(4)	168.4(19)
O(4)-H(4D)...O(9) ²	2.26(2)	3.032(5)	146(3)
O(4)-H(4E)...N(1) ⁴	1.93(2)	2.809(4)	166(2)
N(6)-H(6C)...O(10) ⁵	2.1759	2.916(6)	144.04
C(4)-H(4)...O(5) ¹	2.3913	3.264(4)	156.46
Symmetry code: 1. -x,1-y,1-z; 2. -1+x,1+y,z; 3. 1-x,2-y,-z; 4. -1-x,1-y,1-z; 5. x, y, z			

dimeric compound **1** with atom numbering scheme is depicted in figure 2a. Asymmetric unit of **1** is composed of one K^+ centre, one Br^- anion, two molecules of **L**, one coordinated water molecule and three water molecules as solvent of crystallization.

Each symmetrically disposed K^+ in the dimeric unit is wrapped around by two **L** moieties. One of the **L** act as a tridentate ligand via N_2O coordination with K^+ through its imine and pyridyl nitrogens (N6, N5) and the amide oxygen (O2), while from the second **L** moiety the amide oxygen (O1) is making a μ_2 -type coordination with the symmetrically disposed K^+ generating the centrosymmetric dimeric compound. Each K^+ is involved in an octa coordination provided by the imine/pyridyl nitrogen and amide oxygen atoms from two different **L** moieties in which amide oxygen O1 from one of the **L** is making μ_2 -type coordination

to bridge the adjacent K^+ along with one coordinated water molecule. K-O distances in ranges from 2.787(3) to 2.945(2) / 2.815(3) to 3.026(2) Å and K-N distance is in the range 2.843(3) to 3.275(3)/2.856(2) to 3.302(2) Å respectively for **1** and **2** (Table S1).

Diverse supramolecular interactions are anticipated due to the presence of amide group in the ligand moiety and lattice/coordinated water molecules in **1** & **2**. Packing diagram viewed down *a*-axis with hydrogen bonding interactions are depicted in figures 2b and S1. Symmetrically disposed water molecule O4 positioned between the dimers are involved in bridging the adjacent dimeric unit to form a hydrogen bonded layers along *b*-axis. Thus, symmetrically placed water (O4) acts as a donor through O-H...O contact with the coordinated water O3 and an acceptor via N-H...O contacts with the amide hydrogen H7N in the formation

Figure 2. (a) ORTEP diagram of **1** depicting 50% probability for thermal ellipsoids with atom numbering scheme (Some of the hydrogen atoms, bromide anions and lattice water molecules have been omitted for clarity); (b) packing diagram presenting the hydrogen bonded 2D sheets spreading along *bc*-plane; (c) centrosymmetric hexameric $[(H_2O)_4(Br^-)]_2$ cluster observed in **1**.

of the hydrogen bonded layers along *b*-axis. Extensive hydrogen bonding interactions do exist in **1** & **2** between the lattice water molecules O5 and O6 with the bromide/iodide anions in generating a hybrid water-bromide puckered ring with chair conformation as depicted in figure 2c. Lattice Water molecules O5 and O6 are mutually involved in O-H...O hydrogen bonding in which O6 acts as a donor and O5 as acceptor. Thus, H6A attached to O6 render as the donor and involved in O-H...O interactions with O5 and H6B and H5B from O6 and O5 respectively are drawn into O-H...Br⁻ contacts generating a cyclic centrosymmetric hexameric [(H₂O)₄(Br⁻)₂] cluster (figure 2c). The O...O distances, O-H...O and angles within this basic centrosymmetric [(H₂O)₄(Br⁻)₂] unit generating a eleven membered cyclic ring are O(5)...O(6) = 2.707(6) Å, with ∠O(6)-H(6A)...O(5) = 163(5)° and; the O...Br1 distances and O-H...Br⁻ angles are (Br1...O5 = 3.363(4) Å, Br1...O6 = 3.372(4) Å and ∠O5-H5B...Br1 = 165(5)°, ∠O6-H6B...Br1 = 174(5)°) respectively. Centrosymmetric six membered [(H₂O)₄(Br⁻)₂] rings are placed between the hydrogen bonded 1D layers and involved in O-H...O, N-H...O and N-H...Br contacts along *c*-axis generating a two dimensional hydrogen bonded network (figure 2b). In addition to the above mentioned hydrogen bonds inter and intra molecular C-H...O as well as C-H...Br⁻ contacts are also observed in supramolecular assembly resulting in the stabilisation of molecules in crystal lattice. Similar molecular interactions are persistent in the isostructural compound **2** with counter anion I⁻ (figure S1). Details of all the hydrogen bonding interactions present in **1** and **2** with symmetry codes are given in table 2.

3.3 Crystal and molecular structure of [Ba(L)₂(H₂O)₂(ClO₄)]ClO₄ (**3**)

Complex **3** crystallized in triclinic system with P-1 space group. ORTEP diagram for mono-cationic complex part of **3** is depicted in figure 3. Nona coordination adopted by Ba⁺² is provided by two **L** moieties in chelated tridentate fashion through its pyridyl, imine nitrogen atoms (N4, N8 and N3, N7), amide oxygen atoms (O1 and O2), two water molecules (O3 and O4) and one perchlorate oxygen (O5). Ba-O distances involving the amide oxygen and water molecules ranges from 2.714(2) to 2.956(3) Å and Ba-N distances involving the pyridyl/amide nitrogen is in the range of 2.893(2) to 2.965(2) Å respectively.

In an attempt to understand the supramolecular interaction in **3** we have analysed the packing and

Figure 3. ORTEP diagram depicting of the monocationic part of **3** with atom numbering scheme (50% probability for thermal ellipsoids; only amide hydrogen atoms and one of the disordered position for the coordinated perchlorate moiety is shown).

hydrogen bonding interaction in detail. Packing diagram with hydrogen bonding interaction viewed down *b*-axis is depicted in figure 4a and shows that the monomeric cations are oriented along *c*-axis. Detailed analysis of observed hydrogen bonding interaction (figure 4b) expose that the 2D supramolecular sheet is stabilized by several weak molecular contacts. N-H...O, O-H...O and C-H...O interactions involving the coordinated/lattice perchlorate anion with complex moiety play a crucial role for the association of the discrete complex entities generating a layered motif along *c*-axis. Thus, amide hydrogen atoms H6C and H3C from N6/N2, water hydrogen H3D and H4D from O3/O4 and pyridyl hydrogen H4C from C4 is involved in intermolecular contacts with perchlorate oxygen atoms as cited [N6-H6C...O10: H6C...O10 = (2.18 Å), N(2)-H3C...O(5): H3C...O(5) = (2.16 Å), O3-H3D...O9: H3D...O9 = (2.33(2) Å, O4-H4D...O9: H4D...O9 = (2.26(2) Å), C4-H4...O5: H4...O5 = (2.39 Å)]. Intermolecular O-H...N interactions involving coordinated water hydrogen (H4E and H3E) and terminal pyridine nitrogen of ligand **L** [(O4-H4E...N1: H4E...N1 = 1.93(2) Å and O3-H3E...N5: H3E...N5 = 1.93(2) Å] from neighbouring units of layered hydrogen bonded motif extending the supramolecular array along *a*-axis generating a two dimensional hydrogen bonded network in **3**. In addition to the above mentioned hydrogen bonding interactions the pyridyl rings (N(5)-C(13) to C(17)) of the ligand moieties are involved in intermolecular π ... π stacking interactions along *a*-axis with centroid...centroid distance between the pyridyl rings 3.68 Å [symmetry code 1-x,2-y,-z].

Figure 4. (a) Packing diagram viewed down *b*- and *a*- axes for **3**; (b) close-up view of the various H-bonding (Black dotted lines) present in **3**.

3.4 TGA and PXRD analyses

The lattice guests and composition of **L** and **1–3** were estimated and ascertained by thermal, elemental and single crystal analyses. Lattice water molecules in case of **L.2H₂O** (C₁₂H₁₀N₂O.(H₂O)₂) escape from the crystal lattice in the temperature range 40–128°C, evident from the thermogram showing *ca* 9% weight loss (calc. 13.73%) in the mentioned temperature range (figure 5). Dehydrated ligand **L** thus obtained exhibits thermal stability up to 200°C and further increment in temperature resulted in the decomposition of ligand. Complex **1**, ([K₂L₄(H₂O)₂]Br₂.6H₂O) lose lattice water molecules at ambient conditions; however, expulsion of coordinated water molecules (obs. *ca* 3%; calc. 2.8%) in temperature range 70–165°C was observed. Compound **1** decomposes at temperature higher than 200°C. Lattice (calc. 7.82%) and coordinated (calc. 2.60%) water molecules in case of complex **2**, ([K₂L₄(H₂O)₂]I₂.6H₂O) escape step-wise manner in the temperature range 30–165°C for which 9.2% weight loss was observed. Complex **3**, [BaL₂(H₂O)₂(ClO₄)].(ClO₄) exhibit 3.10% weight loss when heated up to 150°C which is attributable to the

two coordinated water molecules (calc. 4.36%). Complex **3**, exhibits thermal stability up to 285°C and further increase in temperature cause rapid decomposition of compound. Experimental PXRD data obtained for bulk samples of **L.2H₂O** as well as complexes corroborate well with those simulated from respective single crystal data (figures S2 and S3) confirming the phase purity of synthesized samples.

3.5 FTIR and absorption spectra

FTIR spectra for both pseudopolymorphs and all three complexes were recorded at room temperature by dispersing minute amount of solids in KBr pellets (figure 6). FTIR spectra of ligand pseudopolymorphs featured comparable bands for carbonyl and imine stretching modes at 1665 and 1549 cm⁻¹ for **L** and at 1665 and 1567 cm⁻¹ for **L.2H₂O**. Presence of water molecules in pseudopolymorph **L.2H₂O** was revealed by broad band for OH stretching mode observed in 3200–3550 cm⁻¹ range. Carbonyl and imine stretching bands in case of complexes **1–3** were observed at *ca* 1665 and 1550 cm⁻¹ whereas all three complexes

Figure 5. TGA traces for ligand pseudopolymorph $L.2H_2O$ and complexes **1-3**.

Figure 6. FTIR spectra recorded by KBr pellet method for $L.2H_2O$ and complexes **1-3**.

exhibit broad OH stretching bands for coordinated and/or lattice water molecules at $ca\ 3475\text{ cm}^{-1}$. Cl-O stretching band was distinctly observed at $ca\ 1100\text{ cm}^{-1}$ in case of complex **3**.

Absorption behaviour of both pseudopolymorphic forms (**L** and $L.2H_2O$) of ligand and synthesized complexes **1-3** was studied in solid state at room temperature (figure 7). **L** revealed two overlapping bands at $ca\ 326$ and 261 nm which can be ascribed as $\pi-\pi^*$ and $\pi-n$ transitions. However, these bands were much diffused in case of $L.2H_2O$ and appeared as a broad band spanning in $360-233\text{ nm}$ range. Complexes **1-3** showed similar absorption spectral feature as of

Figure 7. Solid state absorption spectra for pseudopolymorphs **L**, $L.2H_2O$ and complexes **1-3**.

constituting ligand, suggesting the persistent intraligand or metal perturbed intraligand electronic transitions.

4. Conclusions

We have reported a new pseudopolymorph of a O,N,N'-donor hydrazone ligand, 2-pyridylcarboxaldehyde isonicotinoylhydrazone (**L**) and its discrete complexes with K^+ and Ba^{2+} which present as first examples of complexes between **L** and alkali or alkaline earth metal ions. All compounds were characterized by single crystal X-ray structural analysis and other physicochemical techniques such as FTIR, TGA, PXRD and solid state absorption spectra. **L** formed isostructural dinuclear complexes with K^+ when bromide and iodide were employed as counteranion, whereas, a mononuclear complex with Ba^{2+} was formed which showed coordinated as well as uncoordinated perchlorate counter anion. Various structural aspects including hydrogen bonding interactions and spectral features of **L**·2H₂O and **1-3** have been studied in detail.

Supplementary Information

Crystallographic data of for the pseudopolymorphic form of **L**·2H₂O, complexes **1**, **2** and **3** has been deposited at the Cambridge Crystallographic Data Centre with CCDC nos. 992911 to 991914 respectively. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>). Characterization data for the ligand and complexes such experimental and simulated PXRD for **L**·2H₂O (figure S2), Experimental and simulated PXRD for **1-3** (figure S2), ¹H and ¹³C NMR Spectra of ligands and complexes (figure S4) and ORTEP diagram and crystal structure for complex **2** (figure S1) and selected bond lengths and angles (table S1) are available in the supporting information (www.ias.ac.in/chemsci).

Acknowledgement

Authors acknowledge the CSIR, India (K-TEN Project, Grant no. CSC 0105) for financial support, Mrs. Monika Gupta for TGA data, Ms. Riddhi Laiya for XRPD data, Mr. Satyaveer Gothwal for elemental data, Mr. Viral Vakani for IR data. BP and KKB acknowledge CSIR (India) for research fellowships. Publication Registration Number: CSIR-CSMCRI No. : 066/2014.

References

- (a) Desiraju G R 2007 *Angew. Chem. Int. Ed.* **46** 8342; (b) Vantomme G and Lehn J M 2013 *Angew. Chem. Int. Ed.* **52** 3940
- (a) Fahmi N, Shrivastava S, Meena R, Joshi S C and Singh R V 2013 *New J. Chem.* **37** 1445; (b) Armstrong C M, Bernhardt P V, Chin P and Richardson D R 2003 *Eur. J. Inorg. Chem.* 1145; (c) Singh N, Watts S, Joshi S C and Singh R V 2013 *Appl. Organometal. Chem.* **27** 269; (d) Ababei L V, Kriza A, Andronesu C and Musuc A M 2012 *J. Therm. Anal. Calorim.* **107** 573; (e) Shahverdizadeh G H, Tiekinck E R T and Mirtamizdoust B 2011 *Acta Crystallogr., Sect. E: Struct. Rep. Online* **67** m1727
- (a) Bernhardt P V, China P and Richardson D R 2004 *Dalton Trans.* 3342; (b) Sharma V K, Srivastava S and Srivastava A 2006 *J. Coord. Chem.* **59** 1321; (c) Sastry P S S J and Rao T R 1995 *Proc. Indian Acad. Sci. (Chem. Sci.)* **107** 25; (d) Bikas R, Hosseini-Monfared H, Zoppellaro G, Herchel R, Tucek J, Owczarzak A M, Kubicki M and Zboril R 2013 *Dalton Trans.* **42** 2803
- Richardson D R, Becker E and Bernhardt P V 1999 *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **55** 2102
- Bernhardt P V, Chin P and Richardson D R 2001 *J. Biol. Inorg. Chem.* **6** 801
- (a) Bernhardt P V, Caldwell L M, Chaston T B, Chin P and Richardson D R 2003 *J. Biol. Inorg. Chem.* **8** 866; (b) Bernhardt P V, Chin P, Sharpe P C and Richardson D R 2007 *Dalton Trans.* 3232; (c) Bernhardt P V, Mattsson J and Richardson D R 2006 *Inorg. Chem.* **45** 752; (d) Kalinowski D S, Sharpe P C, Bernhardt P V and Richardson D R 2008 *J. Med. Chem.* **51** 331
- (a) Shin H and Min B 2013 *J. Inorg. Organomet. Polym.* **23** 1305; (b) Li D Q, Liu X and Zhou J 2008 *Inorg. Chem. Commun.* **11** 367; (c) Xua C, Maoa H, Shena X, Zhanga H, Liua H, Wua Q, Houa H and Zhua Y 2007 *J. Coord. Chem.* **60** 193; (d) Shaabani B, Khandar A A, Kazemi S S, Shaghaghi Z, Boudalis A K, Psycharis V and Raptopoulou A 2013 *Polyhedron* **49** 61; (e) Hanifehpour Y, Saraei N, Asl S M and Joo S W 2012 *J. Inorg. Organomet. Polym.* **22** 1271; (f) Ni W X, Li M, Zhan S Z, Hou J Z and Li D 2009 *Inorg. Chem.* **48** 1433; (g) Yu Q, Zhu L G, Bian H G, Deng G H, Bao X G and Liang H 2007 *Inorg. Chem. Commun.* **10** 437; (h) He Z, He C, Gao E Q, Wang Z M, Yang X F, Liao C S and Yan C H 2003 *Inorg. Chem.* **42** 2206; (i) Li D Q, Liu X and Zhou J 2010 *Z. Naturforsch. B: Chem. Sci.* **65** 1084; (j) Li G, Yan W B, He C, Duan C Y, Meng Q J and Li Y Z 2008 *Chin. J. Inorg. Chem.* **24** 1767; (k) Li D Q, Liu X and Zhou J 2008 *Z. Naturforsch. B: Chem. Sci.* **63** 1343; (l) Cai T J, Long Y F, Deng Q and Peng Z S 2005 *Z. Kristallogr. New Cryst. Struct.* **220** 506; (m) Cai T J, Peng Z S, Deng Q, Long Y F, Deng T T and Yu K B 2004 *Chin. J. Inorg. Chem.* **20** 731; (n) Hanifehpour Y, Khanalilou S, Paknahad E, Joo S W, Sadr M H and Soltani B 2012 *J. Inorg. Organomet. Polym. Mater.* **22** 1248
- Heine J, Hołyńska M, Reuter M, Haas B, Chatterjee S, Koch M, Gries K I, Volz K and Dehnen S 2013 *Cryst. Growth Des.* **13** 1252
- (a) Rodríguez-Spong B, Price C P, Jayasankar A, Matzger A J and Rodríguez-Hornedo N. 2004 *Adv. Drug Deliv. Rev.* **56** 241; (b) Mukherjee A, Tothadi S,

- Chakraborty S, Ganguly S and Desiraju G R 2013 *CrystEngComm* **15** 4640; (c) Bhargavi G, Rajasekharan M V, Costes J P and Tuchagues J P 2013 *Dalton Trans.* **42** 8113; (d) Grobelny P, Mukherjee A and Desiraju G R 2012 *CrystEngComm* **14** 5785; (d) Aravinda S, Shamala N, Karle I L and Balaran P 2012 *Pept. Sci.* **98** 76; (e) Aitipamula S, Banerjee R, Bansal A K, Biradha K, Cheney M L, Choudhury A R, Desiraju G R, Dikundwar A G, Dubey R, Duggirala N, Ghogale P P, Ghosh S, Goswami P K, Goud N R, Jetty R K R, Karpinski P, Kaushik P, Kumar D, Kumar V, Moulton B, Mukherjee A, Mukherjee G, Myerson A S, Puri V, Ramanan A, Rajamannar T, Reddy C M, Rodriguez-Hornedo N, Rogers R D, Row T N G, Sanphui P, Shan N, Shete G, Singh A, Sun C C, Swift J A, Thaimattam R, Thakur T S, Thaper R K, Thomas S P, Tothadi S, Vangala V R, Vishweshwar P, Weyna D R and Zaworotko M J 2012 *Cryst. Growth Des.* **12** 4290; (f) Mukherjee A, Grobelny P, Thakur T S and Desiraju G R 2011 *Cryst. Growth Des.* **11** 2637; (g) Chieng N, Rades T and Aaltonen J 2011 *J. Pharm. Biomed. Anal.* **55** 618; (h) Thakur T S, Sathishkumar R, Dikundwar A G, Row T N G and Desiraju G R 2010 *Cryst. Growth Des.* **10** 4246; (i) Nangia A and Desiraju G R 1999 *Chem. Commun.* 605
10. (a) Patidar R, Paul P and Ganguly B 2013 *J. Mol. Graph. Model.* **46** 22; (b) Maiti P, Ghosh P K, Ghara K K, Solanki J, Brahmabhatt H R, Chunawala J R, Suresh E and Paul P 2013 *PCT Int. Appl.* WO 2013150363 A1 20131010; (c) Ramakrishna V, Patra S, Suresh E, Bhatt A K, Bhatt P A, Hussain A and Paul P 2012 *Inorg. Chem. Commun.* **22** 85; (d) Patra S, Suresh E and Paul P 2007 *Polyhedron* **26** 4971; (e) Bisht K K, Rachuri Y, Parmar B and Suresh E 2014 *J. Solid State Chem.* **213** 43; (f) Kathalikkattil A C, Damodaran S, Bisht K K and Suresh E 2011 *J. Mol. Struct.* **985** 361; (g) Kathalikkattil A C, Bisht K K, Subramanian P S and Suresh E 2010 *Polyhedron* **29** 1801; (h) Bisht K K, Patel P, Rachuri Y and Suresh E 2014 *Acta Crystallogr. Sect. B-Struct. Sci.* **70** 63; (i) Bisht K K, Rachuri, Y, Parmar B and Suresh E 2014 *RSC Adv.* **4** 7352
 11. (a) Aakeröy C B, Forbes S and Desper J 2012 *Cryst. Eng. Comm.* **14** 2435; (b) Johnson D K, Murphy T B and Rose N J 1982 *Inorg. Chim. Acta* **67** 159
 12. Sheldrick G M SAINT 5.1 ed., Siemens Industrial Automation Inc., Madison, WI, 1995
 13. SADABS, Empirical Absorption Correction Program, University of Göttingen, Göttingen, Germany, 1997
 14. Sheldrick G M SHELXTL Reference Manual: Version 5.1, Bruker AXS, Madison, WI, 1997
 15. Sheldrick G M SHELXL-97: Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997