Journal of Advanced Scientific Research

Available online through http://www.sciensage.info

ISSN
0976-9595
Research Article

SUPRAMOLECULAR INTERACTIONS THROUGH ANION-π, π-π, CH-π, C_{ARENE}-H---ANION IN COMPOUNDS OF Zn (II), Cd (II) AND IN H_2L^{2+} INVOLVING MULTIRING NITROGEN-HETEROCYCLIC LIGAND: A STRUCTURAL STUDY

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ABSTRACT

The extended structure of the protonated form $[H_2(L)](CF_3SO_3)_2$ (**1**) of a new redox-active bis-bidentate nitrogenous heterocyclic ligand, viz., 3,3′-dipyridin-2-yl[1,1′]bi[imidazo[1,5-a]pyridinyl] (**L**), and its zinc(II) and cadmium(II) complexes (**2** and **3**) have been characterized by single-crystal X-ray diffraction analysis. The structures of **1-3** also involve anion−π, π-π, CH−π-type noncovalent interactions as well as C_{arene}-H---anion type non-classical H-bonding interactions that play dominant roles in shaping the extended structures of these molecules in the solid state.

Keywords: Zinc (II), Cd (II) compounds, Multiring nitrogen heterocyclic ligand, Non-covalent interactions.

1. INTRODUCTION

A recently developed branch of supramolecular chemistry has unveiled novel types of non-covalent forces between electron deficient aromatic ring and anion (anion-π interaction) as well as between electron deficient aromatic systems and lone-pair of electrons. Anions are essential species in biological systems in which they often play crucial structural and functional roles [1]. Several electron deficient aromatic moieties are found to be present in biomolecules. In biological system anion recognition is of prime importance since more than 70% of enzyme substrates and cofactors are anions [2]. Such interactions have received much attention in recent years as important strategy in developing receptors [3a-c,3e,4] and transporters [5] which are of prime importance for environmental [3a,6], biological and medicinal applications [3a,3d,4a-b,7] as well as in catalysis [8].

We have recently synthesized [9,10] a π-electron-deficient N-heterocyclic compound, viz., 3,3′-dipyridin 2-yl[1,1′]bi[imidazo[1,5-a] pyridinyl] (**L**) containing a pair of biologically relevant [11] imidazo[1,5-a]pyridine moieties. The ligand L is capable of acting as a bis-bidentate ligand, and its copper (II) compound (**1**) offers a unique example of valence tautomerism in solution [9]. Herein, we report the non-covalent interactions in the protonated form of this ligand (**1**) as well as its zinc(II) (**2**) and cadmium(II) (**3**) helicate complexes. This unique heteroaromatic ligand with its flexible backbone as well as electron deficient aromatic rings is capable of influencing the supramolecular structures of these helicates (**1-3**) through a variety of non-covalent interactions of viz. π-π, anion-π and CH-π types.

2. SYNTHESES

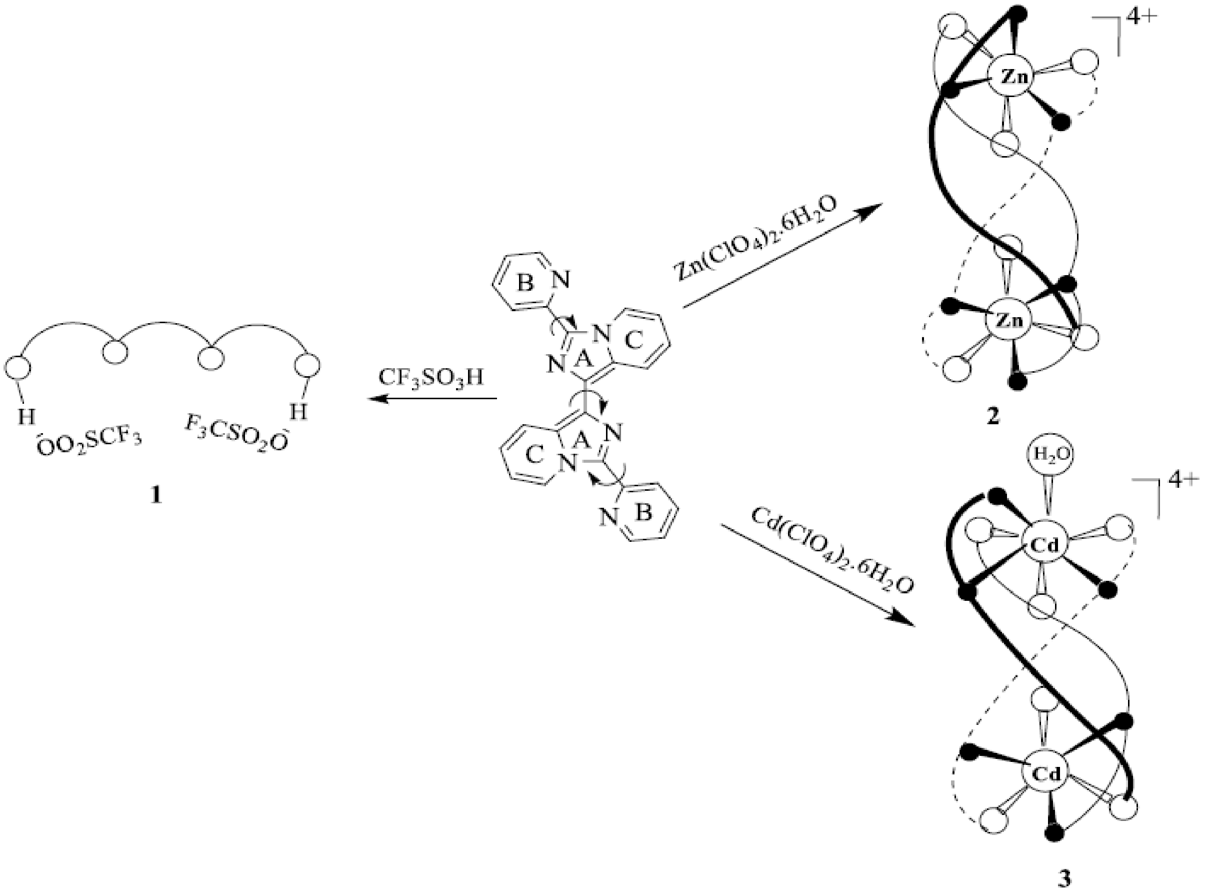
Compounds **1-3** were prepared as described elsewhere [9].

$[H_2(L)](CF_3SO_3)_2$ (**1**), $[Zn_2(L)_3](ClO_4)_4\cdot 2.25H_2O$ (**2**), $[Cd_2(L)_3(H_2O)](ClO_4)_4\cdot 0.5H_2O$ (**3**)

3. RESULTS AND DISCUSSION

3.1. Syntheses

The protocol followed for the synthesis of **1-3** is summarized in scheme 1. Being electron deficient, the aromatic rings of the ligand is capable of interacting with anions and solvent of crystallizations of the complexes (anion-π and solvent-π types) to generate different supramolecular structures. The ligand L has identical halves, each containing three different heterocyclic rings, viz., imidazole (A), isolated pyridine (B), and fused pyridine (C) rings, which will be designated as im, py, and azopy rings, respectively, in the following part of this discussion.



Scheme 1: Protocol followed for the synthesis of compounds 1-3

3.2. Description of crystal structures

The crystal structure of the $[H_2(3,3'\text{-dipip})](CF_3SO_3)_2$ (**1**) reveals its pronounced ability to show significant non-covalent interactions between the triflate anion and the π-electron deficient aromatic rings (Figure 1). The oxygen atom O(3) of triflate anion shows moderate [3f] interaction with one of the im rings (N(4)-C(6)-N(5)-C(8)-C(7)) of ligand **L**. The close contacts of O(3) with N(5) (O(3)---N(5) distance 3.155(4) Å) and C(6) (O(3)---C(6) distance 3.258(4) Å) result in short O(3)---im$_{\text{centroid}}$ distance of 3.341(3) Å. This anion (O(3)) interacting im ring further aligns itself parallel to and within the π-stacking distance of the proximal azopy (N(5)-C(8)-C(9)-C(10)-C(11)-C(12)) and im (N(4)-C(6)-N(5)-C(8)-C(7) rings (Table 1) to establish anion-π-π interactions (Fig. 1). The fluorine atom F(2) of the same triflate resides above one of the pyridine rings (Fig. 1) with F(2)---Py$_{\text{centroid}}$ distance of 3.703(3) Å, indicative of weak interaction[3f]. The cation $[H_2(L)]^{2+}$ also exhibits extensive π-π-stacking interactions along the b axis (Fig. 1) between overlapping im-azopy and im-im rings on the adjacent ligand strands. The π centroid-centroid distances are 3.475(2) and 3.518(2) Å, respectively. The anion-π interactions present in the molecule are associated with strong to moderate[12] non classical hydrogen bonding interactions [12]. The C-H---O/F$_{\text{triflet}}$ separation ranges from 2.36-3.52 Å.

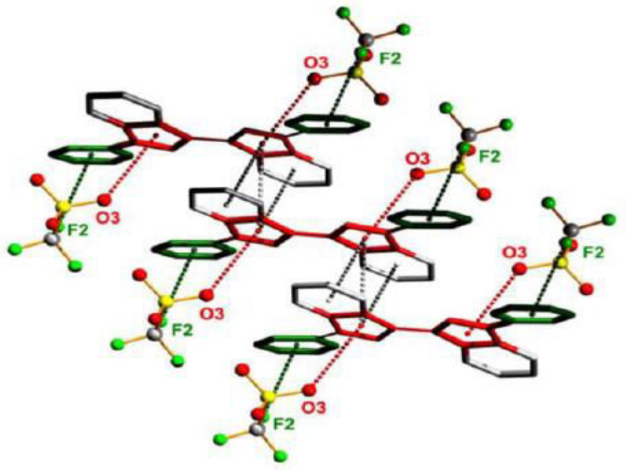


Fig. 1: Illustration of the triflate-π and π-π interactions in compound 1

The most striking feature in the solid state structure of **2** is the presence of several anion-π-π-anion, anion-π-π and anion-π type interactions. The oxygen atom O(11) of perchlorate $ClO_4^-(1)$ counter anion interacts with two electron deficient aromatic rings (im and azopy) which in turn are involved in strong intramolecular π-π-stacking intractions with im and azopy rings of another ligand strand (vide supra). The O(11)---im and azopy ring distances are 3.221(7) and 3.532(7) Å, respecttively, indicative of strong and moderate interactions, respectively [3f]. In addition, the perchlorate atom O(22) from a second perchlorate anion ($ClO_4^-(2)$) is located on top of the other faces of the intramolecular π-π-stacked aromatic rings, with a longer centroid---O(22) distances of 3.710(11) and 3.767(11) Å, thus generating anion-π-π-anion interactions (Fig. 2, Table 1).

Table 1: Distances Characterizing the Anion-π and π-π Interactions in Compounds 1-3

Compound	Atom involved	Rings per atom	O..C(N) contact distance range (Å)	C-H…O hydrogen bonding distance (Å)	Shortest O…centroid distance (Å)	π-π distance (Å)
1	O(3)	1	2.598-3.581	2.36-3.52	3.341(3) (im$_1^a$)	3.518(2) (im$_1$-im$_1$)
						3.475(2) (azopy$_1^b$-im$_1$)
	F(2)	1	3.267-3.591	2.67-3.39	3.703(3)(py$_1^c$)	-
2	O(11)	2	3.200-3.587	2.53-3.49	3.221(7) (im$_2^d$)	3.372(4) (im$_2$-im$_3^e$)
					3.532(7) (azopy$_2^f$)	3.650(4) (azopy2-azopy$_3^g$)
	O(22)	2	3.411-3.584	2.55-2.75	3.767(11) (im$_3$)	3.372(4) (im$_2$-im$_3$)
					3.710(11) (azopy$_2$)	3.650(4) (azopy$_2$-azopy$_3$)
	O(24)	2	3.095-3.499	3.21-3.51	3.419(10) (im$_3$)	3.372(4) (im$_2$-im$_3$)
					3.730(9) (py$_2^h$)	-
	O(24′)	2	2.937-3.516	2.75	2.991(19) (im$_3$)	3.372(4) (im$_2$-im$_3$)
					3.339(17) (py$_2$)	-
	O(21′)	1	3.06-3.38	2.28-3.34	3.770(2) (azopy$_3$)	3.650(4) (azopy$_2$-azopy$_3$)
3	O(13)	1	3.039-3.524	2.33-3.35	3.419(10) (py$_2$)	-
	O(32)	1	3.198-3.575	2.46-3.59	3.665(17) (azopy$_3$)	3.543(6) (azopy$_2$-azopy$_3$) contd.
					-	3.875(7) (azopy$_3$-azopy$_3$)
	O(33)	3	3.29-3.48	2.60-3.45	3.526(16) (im$_3$)	3.348(6) (im$_2$-im$_3$)
					3.534(15) (azopy3)	3.543(6) (azopy$_2$-azopy$_3$)
						3.875(7) (azopy$_3$-azopy$_3$)
					3.585(16) (py$_3^i$)	3.596(6) (py$_3$-im$_4^j$)
						3.862(6) (py$_3$-azopy$_4^k$)
						3.623(6) (azopy$_4$-azopy$_4$)
	O(33′)	2	3.12-3.55	2.71-3.59	3.430(2) (im$_3$)	3.348(6) (im$_2$-im$_3$)
					3.040(2)(azopy$_3$)	3.543(6) (azopy$_2$-azopy$_3$)
						3.875(7) (azopy$_3$-azopy$_3$)
	O(41′)	1	3.555	2.74-3.31	3.681(16) (py$_4^l$)	3.870(7) (py$_4$-azopy$_5^m$)

^{a}im$_1$ = N(4)-C(6)-N(5)-C(8)-C(7), ^{b}azopy$_1$ = N(5)-C(8)-C(9)-C(10)-C(11)-C(12), ^{c}py$_1$ = N(1)-C(1)-C(2)-C(3)-C(4)-C(5), ^{d}im$_2$ = N(4)-C(13)-C(14)-N(5)-C(19), ^{e}im$_3$ = N(8)-C(30)-N(9)-C(35)-C(36), ^{f}azopy$_2$ = N(5)-C(14)-C(15)-C(16)-C(17)-C(18), ^{g}azopy$_3$ = N(9)-C(31)-C(32)-C(33)-C(34)C-(35), ^{h}py$_2$ = N(6)-C(20)-C(21)-C(22)-C(23)-C(24), ^{i}py$_3$ = N(12)-C(44)-C(45)-C(46)-C(47)-C(48), ^{j}im$_4$ = N(14)-C(54)-N(15)-C(59)-C(60), ^{k}azopy$_4$ = N(15)-C(55)-C(56)-C(57)-C(58)-C(59), ^{l}py$_4$ = N(13)-C(49)-C(50)-C(51)-C(52)-C(53), ^{m}azopy$_5$ = N(10)-C(38)-C(39) -C(40)-C(41)-C(42).

Similarly, the disordered perchlorate atom O(24) (O(24′)) and O(21′) of the same perchlorate ($ClO_4^-(2)$) interact significantly with the same electron deficient π-π-stacked im and azopy aromatic rings, respectively from other sides to establish several anion-π-π-anion interactions. O(24) (O(24′)) also exhibits short contact with a py ring. The O(24)---im, O(24)---Py and O(21′)---azopy ring plane distances are 3.419(10), 3.730(9) and 3.770(2) Å, respectively. For O(24′), the O(24′)---$im_{centroid}$ and O(24′)---$Py_{centroid}$ distances are much shorter, 2.991(19) and 3.339(17) Å, respectively. The later distances denote strong interactions because according to Crystal Structure Database (CSD), the mean distances between perchlorate oxygen atom and pyridine ring and between perchlorate oxygen atom and much more electron deficient triazine ring are 3.267 and 3.141 Å, respectively [3f].

In addition, the anion-π interactions are associated with non-classical hydrogen bonding C_{arene}-H---O interactions (Fig. 3) [12]. The $C_{aromatic}$-H---$O_{perchlorate}$ distances lie in the range from 2.13 - 3.51 Å, indicative of very strong to moderate hydrogen bonds [12b]. Simultaneous occurrence of both anion-π and C_{arene}-H---anion interactions reinforce the non-covalent interactions and anion binding properties of the system. A combination of such non-covalent interactions are of prime importance for the design of anion receptors with important biological and medicinal applications [3a, 3d, 13a-b].

Finally, the individual dinuclear helical units are involved in intermolecular edge to face (EF) CH---π interactions with the aromatic rings of the neighbouring ligand strands. The EFs operate in a concerted manner (d_{CH}---centroid = 2.93 Å) which give rise to a 2D network as displayed in Fig. 4. Cavities generated by EF interactions are occupied by perchlorate molecules.

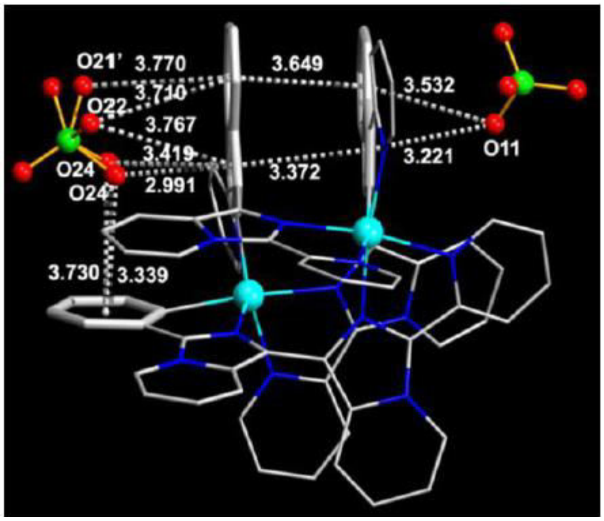


Fig. 2: Drawing of the cation of 2 and two anions showing the anion-π and anion-π-π interactions

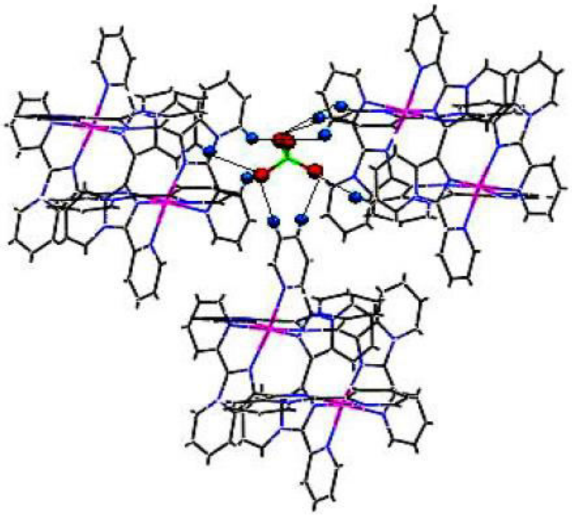


Fig. 3: Representation of the C_{arene}-H---$O_{perchlorate}$ H-bonding interactions in 2 which strengthen the ClO_4^----L supramolecular pairing.

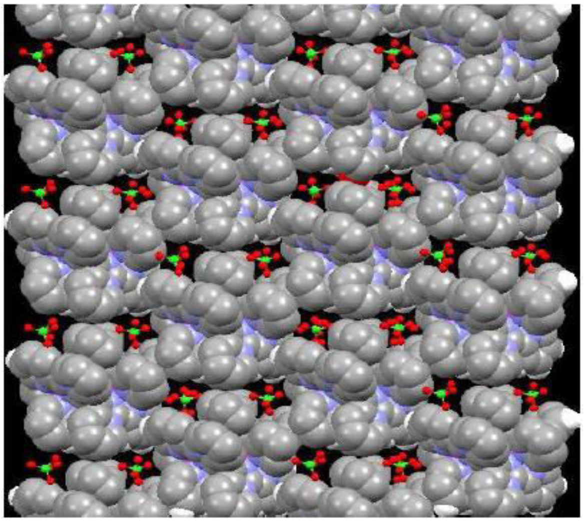


Fig. 4: 2D supramolecular network generated by the concerted CH---π (EF) interactions in 2. Perchlorates are located in the voids.

In compound **3** the disordered perchlorates $ClO_4^-(2)$ and $ClO_4^-(3)$ are located on top of an im and a pyridine ring, respectively with O(33)(O(33′)) and O(41′) atoms pointing to the center of the aromatic rings. O(33), O(33′) and O(41′)---ring plane distances are in the range 3.430(2)-3.681(16) Å. In turn, these anion interacting im and py rings are in close contacts as well with the im rings of the same dication to establish multiple anion-π-π interactions (Fig.5). These intramolecular $\pi_{centroid}$-$\pi_{centroid}$ distances are in the range 3.348(6) - 3.596(6) Å (Table 1). The oxygen atom

O(13) of perchlorate ClO_4^-(1) resides above one of the pyridine rings (Figure 4) with short contact distances with atoms C(20) and N(6) (distances are 3.039(14) and 3.377(12) Å, respectively), where the distance between the centroid of this pyridine ring and the O(13) is 3.419(10) Å, indicative of moderate interaction [3f].

In addition to the multiple anion-π interactions, **3** also shows a plenitude of strong C_{arene}-H---$O_{perchlorate}$ interactions with the surrounding anions.[12] The C_{arene}-H---$O_{perchlorate}$ separation distances lie in the from 2.33 - 3.59 Å. Co-operativity between the anion-π and C_{arene}-H---O_{anion} interactions enhances the anion binding ability of the system.

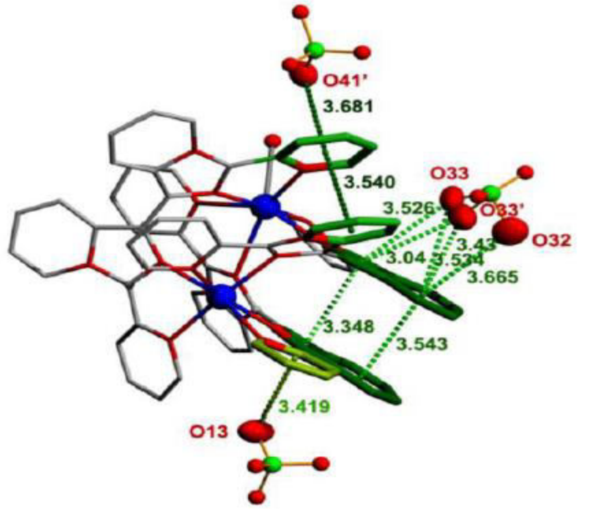


Fig. 5: Illustrations of the anion-π-π and anion-π interactions in 3.

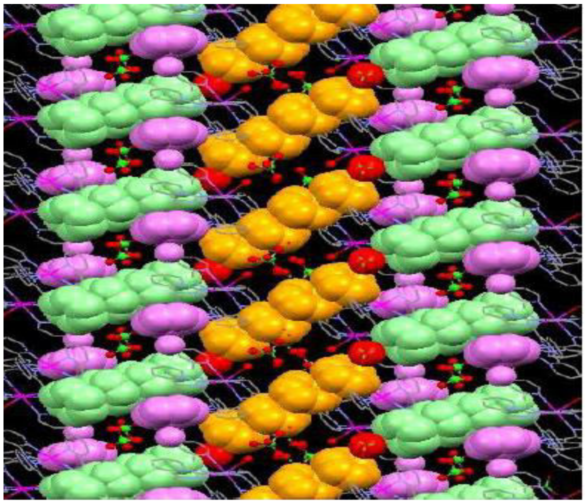


Fig. 6: **Perspective view of the channels in the packing of 3, generated by CH---π and -anion-π-π-π-π-anion- chain interactions. Perchlorate molecules are inside the channels**

Finally, the edge-to-face CH---π-stacking (EF) interactions involving one of the pyridine rings and H(27A) connect adjacent molecules to form compact and ordered chains. The individual chains are connected together via two types of π/π/π/π-stacking interactions, generating two types of cavities. Both types of cavities are occupied by perchlorate molecules (Fig. 5). The perchlorates present in the central cavities participate in hydrogen bonding interactions with coordinated water molecules.

4. CONCLUSION

Compounds 1-3 display multiple anion---π, lone-pair---π, CH- π and π-π interactions involving the ligand aromatic rings. Interplay between such interactions has been demonstrated by several theoretical investigations [14]. Results reported in this paper exhibit crystallographic evidence for such multiple supra-molecular interactions.

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