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Binuclear and polymeric Zn(II) and Cd(II) coordination compounds with chromophore N-((pyridin-4-yl)methylene)benzene-1,4-diamine obtained *in situ*: preparation, structural and spectroscopic study

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Abstract. Four coordination compounds, that include the discrete binuclear complex $[Zn(H_2O)_4(bda4Py)]_2(SO_4)_2(1)$, isomorphous one-dimensional coordination polymers, $\{[Zn(NO_3)_2(bda4Py)_2] \cdot 2H_2O\}_n$ (2) two and $\{ [Cd(NO_3)_2(bda4Py)_2] \cdot 2H_2O \}_n$ (3), and one two-dimensional coordination polymer $\{ [Cd(bda4Py)_2(dpa)_2] \cdot 2H_2O \}_n$ (4) [where $bda4Py = N-((pyridin-4-yl)methylene)benzene-1,4-diamine, H_2dpa = diphenic acid, as a potential anionic$ competitor ligand having two carboxylic groups] were obtained as the products of partial hydrolysis of the ligand N¹,N⁴-bis(pyridin-4-ylmethylene)-benzene-1,4-diamine, (bda4bPy) in the reaction conditions. Single crystal X-ray data reveal that N-((pyridin-4-yl)methylene)benzene-1,4-diamine acts as a bidentate linker between two metal centers through nitrogen atoms of pyridino- and amino-groups. The additional stabilization of the crystalline solids 1-4 is provided via hydrogen bonds. N-((pyridin-4-yl)methylene)benzene-1,4-diamine (bda4Py) was also obtained by direct synthesis, and two ligands (bda4bPy and bda4Py) were characterized in the solid state and in solution by spectroscopic (FTIR, UV-vis, NMR) methods. Luminescence studies for the reported compounds are also documented.

Key words: Zn; Cd; coordination polymer; Schiff base ligand; crystal structure; spectroscopic studies

Introduction

Nowadays Schiff bases and their numerous azo derivatives are extensively studied owing to their potential applicability as selective receptors in optical sensors [1-4]. Due to their high metal affinity, these compounds demonstrate rich coordination chemistry acting as chelating and bridging

ligands that allows performing the targeted synthesis of chelate and molecular, mono-, bi- and polynuclear, homo- and heterometallic structures [5]. The optical response of azo groups towards Ni(II), Co(II), Cu(II), Pb(II), Hg(II), Zn(II) and Cd(II) metal ions was registered in DMSO solution by UV–vis spectroscopy [6]. The Zn(II) complexes with azomethine ligands in different solvents demonstrated excitation-dependent emission, which allowed tuning the emission color in a wide range using the variation in the excitation light and in the solvents [7]. The photoluminescent properties for these ligands and their metal complexes are successfully combined with their antioxidant and cytotoxic activity, that explains another aspect of the relentless interest to this class of organic compounds [6,8].

Being interested in the solid crystalline materials with the ligand-based emission properties [9,10] alongside with the others [11-13] we have recently reported the crystal structures and emissive properties for Zn(II) and Cd(II) one-dimensional (1D) coordination polymers (CPs) with two azines of the N,N' type, 1,2-bis(pyridin-3-ylmethylene)-hydrazine, and 1,2-bis(pyridin-4-ylmethylene)hydrazine as bridging ligands [14]. These long aromatic molecules with the conjugated system of alternating C=N and N–N bonds can coordinate transition metal ions by the nitrogen atoms of both terminal pyridine and azine fragments [15] and participate in hydrogen bonds in the presence of strong proton–donor agents [16].

So far our interest is further focused on a longer rigid π -conjugated linker, N¹,N⁴-bis(pyridin-4-ylmethylene)-benzene-1,4-diamine (bda4bPy), whose luminescence properties in the pure form and in the complexes have been reported [1,17]. The examination of the Cambridge Structural Database (CSD version 5.40, November 2018) has revealed very few examples containing bda4bPy ligand coordinated to the metal cations that include Pb(II) [17], Zn(II) [18-20], and Co(II) [20]. The reported sources indicated that the CPs generated from bda4bPy may display intense photoluminescence properties because of its structural rigidity that effectively decreases internal conversion and radiationless deactivation [1, 17]. On the other hand, Masoomi *et al.* have reported the unique to the best of our knowledge 3D network [Zn(oba)(bda4bPy)_{0.5}]_n(DMF)_z (TMU-6) (where oba = 4,4'-oxy-dibenzoate) with large pores and improved catalytic activity achieved through functionalization of MOF pore walls with azine groups enabled greater interaction between the walls and substrate molecules [19].

The scare information about CPs with the ligand bda4bPy, has motivated our research and synthetic attempts have been undertaken to obtain new Zn(II) and Cd(II) CPs with this ligand. However, instead, four coordination compounds $[Zn(H_2O)_4(bda4Py)]_2(SO_4)_2$ (1), $\{[Zn(NO_3)_2(bda4Py)_2]\cdot 2H_2O\}_n$ (2), $\{ [Cd(NO_3)_2(bda4Py)_2] \cdot 2H_2O \}_n$ (3), and $[Cd(bda4Py)_2(dpa)_2] \cdot 2H_2O \quad (4)$ [where bda4Py=N-((pyridin-4-yl)methylene)benzene-1,4diamine, dpa = anion of diphenic acid] containing the ligand bda4Py were obtained as the products of partial hydrolysis of the ligand bda4bPy in the reaction medium, that is in line with

the reported examples for this class of organic molecules [21-34]. A similar situation when the reaction was accompanied by the partial hydrolysis of the ligand was documented for the positional isomer of bda4Py, *N*-(2-pyridylmethylene)benzene-1,4-diamine [21].

Herein we report the synthesis, crystal structures and spectroscopic investigation of four coordination compounds containing the chromophore bda4Py, obtained as the product of hydrolization of chromophore bda4bPy *in situ* in the reaction medium. Our choice of dicarboxylic diphenic acid as a competitive ligand to small inorganic anions was justified by its excellent complexing ability towards the d¹⁰ metals in general and, in particular, by the reported series of five mixed-ligand coordination polymers with the structural anlogues of bda4bPy, bis(4-pyridylmethyl)piperazine and its positional isomer, bis(3-pyridylmethyl)piperazine [35]. Herein the direct synthesis of the ligand bda4Py is also reported together with the optical properties of the solutions of both ligands. The coordination compounds **1-4** were characterized by FTIR spectroscopy and single crystal X-ray diffraction, the limits of thermal stabilities for bda4bPy, bda4Py and **1** were determined by TGA method.

Experimental

Materials and Methods. Starting inorganic salts, 1,4-phenylenediamine dihydrochloride, 4pyridinecarboxaldehyde and solvents were obtained from commercial sources (Sigma-Aldrich) and were used without further purification. The IR spectra were obtained in ATR on a FTIR Spectrum-100 Perkin Elmer spectrometer in the range of 650-4000 cm⁻¹. Elemental analysis was performed on a vario EL III Element Analyzer. The thermal analysis of the ligands bda4bPy, bda4Py and complex 1 was performed on a PerkinElmer Analyzer derivatograf in the temperature range of 20-1000 °C under a flow of air with a heating rate of 10 °C min⁻¹. NMRspectra were recorded on a Bruker spectrometer at 400.13 MHz for ¹H and 100.61 MHz for ¹³C in DMSO-d₆ using TMS as an internal reference. Chemical shifts (δ) are reported in parts per million (ppm) and are referenced to the residual non-deuterated solvent peak (2.49 for ¹H and 39.70 for ¹³C). UV-Vis measurements were carried out at T60 UV/Vis spectrophotometer. Solid state emission spectra were recorded using a pulse nitrogen laser ($\lambda exc = 337.1$ nm) at 300 K. The excitation pulse duration was 15 ns, the repetition frequency was 50 Hz, and the pulse energy was 0.2 mJ. The emission was detected with a FEU-79 instrument (multialkaline photocathode Sb(Na₂K) with the adsorbed cesium layer on the surface, characteristic of the S20 type). The intrinsic time of the detecting system was 20 ns. The afterglow duration (at 300 K) for all studied compounds was shorter than the time resolution of the detecting system.

Crystallographic Studies. Diffraction measurements for **1-4** were carried out on an Xcalibur E diffractometer equipped with CCD area detector and a graphite monochromator utilizing MoK α radiation at room temperature. Final unit cell dimensions were obtained and refined on an entire data

set. All calculations to solve the structures and to refine the models proposed were carried out with the programs SHELXS97 and SHELXL2014 [36,37]. Hydrogen atoms attached to carbon atoms were positioned geometrically and treated as riding atoms using SHELXL default parameters with U_{iso}(H)=1.2U_{eq}(C), the O- and N-bounded H-atoms were found from differential Fourier maps at the intermediate stages of the refinement and their positions were constrained using the DFIX instructions in SHELXL $[d(O,N)-H=0.86 \text{ Å}, d(H\cdots H)=1.46 \text{ Å})$ for hydroxyl and amino-groups. Compounds 2 and **3** were refined as non-merohedral two-component twins with the twinning matrix [-1.0027 0.0019 -0.8746 -0.0014 -1.0001 -0.0019 0.0017 -0.0021 1.0005] and the component ratio 0.6383 : 0.3617 for 2; and the twinning matrix [1.0064 0.0015 0.8745 -0.0003 -1.0035 0.0001 -0.0012 -0.0002 -1.0042] and the component ratio 0.89997 : 0.10003 for 3. Compound 4 that crystallizes in the noncentrosymmetric *Iba2* space group was refined as a racemic twin with the component ratio 0.537 : 0.463. The pyridine ring in the bda4Py molecule is disordered over two positions which were refined with the 0.64(2) and 0.36(2) probabilities. Three localised outer sphere water molecules are disordered around a 2-fold rotation axis, two of them have site occupancy factor 0.5 and one of them was refined with occupancy factor 0.250, for all three molecules the hydrogen atoms were not found. The X-ray data and the details of the refinement for 1-4 are summarized in cif files. The Figures were produced using Mercury [38]. The solvent accessible voids (SAVs) were calculated using PLATON [39]. Crystallographic data (cif files) for 1-4 have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 1893503-1893506.

Synthesis

Synthesis of N¹,N⁴-bis(pyridin-4-ylmethylene)-benzene-1,4-diamine. Bda4bPy was first synthesized by Grasso et (1981) [40]. 1,4-Phenylenediamine dihydrochloride (3.84 g, 21 mmol) was dissolved in a beaker in 200 mL of water. Then 4-pyridinecarboxaldehyde (5 mL, 53 mmol) was added under stirring. To this mixture was added Na₂CO₃ (\approx 2.3 g), until the pH reached 7-8. The solution was further stirred for 3 hours at a temperature 70 °C. Then the sediment was filtered off through a glass Buchner funnel, then stirred again in water and filtered for purification. Reaction yield: 87 %. The reported analytical data correspond to the literature data [1]. Anal. Calc. for C₁₈H₁₄N₄: C, 75.50; H, 4.93; N, 19.57. Found: C, C, 75.49; H, 4.90; N, 19.54 %. IR-ATR (cm⁻¹): 3054 m, 3031 m, 2889 m, 1631 m, 1619 m, 1599 s, 1551 s, 1487 s, 1411 s, 1324 s, 1192 s, 1100 m, 890 s, 834 vs, 814 vs, 796 s; ¹H NMR: 8.76, 8.75, 7.87, 7.45; ¹³C NMR: 159.46, 150.94, 149.6, 142.9, 122.9, 122.69.

Synthesis of N-((pyridin-4-yl)methylene)benzene-1,4-diamine. Bda4Py was obtained under the same conditions as bda4bPy ligand, except that the molar ratio of aldehyde to diamine was 1:1. As a result, an orange precipitate was obtained. Reaction yield: 85 %. The compound is

soluble in MeOH, EtOH, DMF, DMSO, insoluble in water. The crystalline product was also obtained. To obtain it, 1,4-phenylenediamine dihydrochloride (0.5 g, 2.76 mmol) was dissolved in 40 mL of EtOH, to which NaOH (0.22 g, 5.52 mmol) then was added. The solution was stirred for 20 minutes, filtered off, then 4-pyridinecarboxaldehyde (0.2 mL, 2.1 mmol) was added without stirring. Over ~ 5 min in solution, orange crystals were formed. Anal. Calc. for $C_{12}H_{11}N_3$: C, 73.07; H, 5.62; N, 21.30. Found: C, 73.02; H, 5.79; N, 21.28 %. IR-ATR (cm⁻¹): 3434 m, 3315 m, 3179 m, 3080 m, 3030 m, 2879 m, 1635 s, 1618 s, 1574 vs, 1540 vs, 1507 vs, 1411 s, 1308 s, 1288 s, 1158 s, 1132 m, 941 m, 832 vs, 793 m; ¹H NMR: 8.68, 8.65, 7.7, 7.23, 6.63, 5.44; ¹³C NMR: 152.02, 150.07, 149.57, 143.95, 139.7, 123.7, 122.06, 114.46.

The synthetic pathways to the bda4bPy and bda4Py ligands are shown in Scheme 1.



bda4Py (down).

Synthesis of $[Zn(H_2O)_4(bda4Py)]_2(SO_4)_2$ (1). A solution of $ZnSO_4 \cdot 7H_2O$ (28 mg, 0.1 mmol) dissolved in 5 mL of water was added to a test tube. Then carefully 2 mL of H₂O/EtOH (1:1) solution were added following the ethanolic solution of bda4bPy ligand (28.6 mg, 0.1 mmol) that was added carefully. After about a week, crystals in the form of orange-red plates were precipitated from solution. Yield: 62 %. Anal. Calc. for $ZnC_{24}H_{30}N_6O_{12}S_2$: C, 39.81; H, 4.18; N, 11.61; O, 26.52; S, 8.86. Found: C, 39.80; H, 4.16; N, 11.60; O, 26.49; S, 8.84. %. IR-ATR (cm⁻¹): 3236 vs, 3183 vs, 1667 m, 1623 m, 1615 s, 1588 s, 1549 m, 1507 m, 1423 m, 1264 m, 1107 vs, 1035 vs, 983 vs, 956 s, 839 s, 828 m, 787 w.

Synthesis of $\{[Zn(NO_3)_2(bda4Py)_2]^2H_2O\}n$ (2). In 6 mL of CH_2Cl_2 was dissolved bda4bPy (28.6 mg, 0.1 mmol), then this solution was added to a test tube. Then carefully $CH_2Cl_2/EtOH$ (1:1, 2 mL) solution was

added. Then 5 mL of ethanolic solution of $Zn(NO_3)_2 \cdot 6H_2O$ (30 mg, 0.1 mmol) was carefully added. After about a week, crystals in the form of pale red plates were formed in solution. Yield: 38 %. Anal. Calc. for $ZnC_{24}H_{26}N_8O_8$: C, 46.50; H, 4.23; N, 18.08; O, 20.65. Found: C, 46.48; H, 4.20; N, 18.07; O, 20.63 %. IR-ATR (cm⁻¹): 3280 m, 3246 m, 3211 m, 3151 m, 2954 m, 2922 m, 2902 m, 1647 w, 1617 s, 1590 s, 1551 w, 1510 w, 1420 vs, 1312 vs, 1292 vs, 1254 vs, 1038 vs, 841 m, 814 s, 780 m.

Synthesis of {[Cd(NO₃)₂(bda4Py)₂]²H₂O}n (3). The compound was also obtained by diffusion method, but a barrier was used to separate the solution of the ligand from the salt solution. A porous membrane glass filter was used for this. In a small chamber of the filter was added the solution of $Cd(NO_3)_2 \cdot 4H_2O$ (18 mg, 0.6 mmol) in 8 mL of water then the hole was closed with a stopper. In the large chamber was added the bda4bPy ligand solution (17 mg, 0.6 mmol) in 30 mL of EtOH after which it was covered with parafilm. The filter was left in the horizontal position. After about two weeks, on the porous membrane pale red crystals were formed. Yield: 52 %. Anal. Calc. for $ZnC_{24}H_{26}N_8O_8$: C, 43.22; H, 3.93; N, 16.80; O, 19.19. Found: C, 43.19; H, 3.90; N, 16.77; O, 19.16 %. IR-ATR (cm⁻¹): 3454 w, 3305 m, 3249 m, 3157 m, 2953 m, 2924 m, 2854 m, 1651 w, 1623 m, 1614 m, 1593 s, 1550 w, 1510 m, 1428 vs, 1413 vs, 1316 vs, 1291 vs, 1258 vs, 1215 s, 1161 m, 1050 m, 1016 s, 987 s, 967 s, 839 s, 812 s, 782 s.

Synthesis of {[**Cd(bda4Py)₂(dpa)₂]·2H₂O**}_n (4). 6 mL of Cd(NO₃)₂·4H₂O solution (30 mg, 0.1 mmol) and diphenic acid (dpa, 22 mg) neutralized with NaOH were added to a test tube, then proceeded as in (1) synthesis. After about one week, pale orange-red crystals were formed in solution. Yield: 32 %. Anal. Calc. for CdC₃₈H₃₄N₆O₆: C, 58.28; H, 4.38; N, 10.73; O, 12.26. Found: C, 58.25; H, 4.37; N, 10.71; O, 12.23 %. IR-ATR (cm⁻¹): 3373 m, 3304 m, 3168 m, 2953 m, 2923 m, 2854 m, 1610 m, 1587 s, 1530 vs, , 1507 vs, 1455 s, 1439 s, 1405 vs, 1251 m, 1048 m, 859 s, 834 m, 748 vs, 683 s.

Results and discussion

Characterization of chromophores bda4bPy and bda4Py

The chemical purity of the chromophores bda4bPy and bda4Py was confirmed by IR and NMR spectra (Figures S1-S5). NMR values (Figure 1) have been established on the basis of literature data [41] taking into account the electronic effects of substitutes [41a, 41b]. In the ¹H NMR spectrum of the bda4Py molecule there are 6 signals. Four signals are doublets and belong to the protons in the pyridine and phenyl moieties. Two signals are singlets and belong to the protons of the amino group $\delta_{\rm H}(\rm NH_2)$ and the azomethine group $\delta_{\rm H}(\rm CH=N)$ which is close to the signal of the protons neighboring to the pyridine nitrogen atom. The ¹³C NMR spectrum shows 8 signals. The lower value of the chemical shift for the carbon nucleus of the azomethine group $\delta_{\rm C}(\rm C=N)$ is due to the fact that this linkage is conjugated to the pyridine moiety, which is also confirmed by the IR spectrum.



Fig. 1. Structural formula for compounds bda4bPy (left) and bda4Py (right) with indication of ¹H NMR (up) and ¹³C NMR (down) numerical values of the signals in the molecules.

The reactions between the synthesized ligand bda4bPy and zinc sulfate, and zinc and cadmium nitrate salts were aimed to obtain the corresponding CPs with the bda4bPy in a function of the potential bidentate mediator. However, in all cases the final crystalline products 1-4 whose crystal structures were unambigously identified by single crystal X-ray diffraction method, contain the chromophore, 4-((pyridin-4ylmethylene)amino)aniline (bda4Py) as a product of hydrolysis of bda4bPy in the reaction conditions. The hydrolysis of Schiff bases is an important reaction of biochemical and biological interest. The effect of hydroxonium, hydroxide and metal ions on the hydrolysis of Schiff bases has been studied [24]. It has been established that metal ion can play a determining role in stabilizing or destabilizing of the coordinated Schiff base [26,27]. Nickel(II) and copper(II) were documented to catalyse the hydrolysis of the C=N bond of the Schiff bases with the concomitant formation of the metal complex with the amine [23, 25]. This is explained by the effect of chelation and formation of stable or less stable cycles involving the metal ion and the nitrogen atom of the C=N group [23, 25,26]. The bda4bPy ligand can not form chelating cycles, otherwise, this molecule can coordinate to the metal in bidentate-bridging or monodentate modes. It is worth noting that stability of the azomethinic C=N bond represents an important factor in the synthesis of CPs with Schiff base bridge ligands. For example, bridge ligands of the azide class of the bis N,N-donor type [31-33] have been extensively used in the synthesis of CPs due to stability of the azine moiety (-HC=N-N=CH-). Upon complexation to the metal, when the nitrogen of the Schiff base becomes coordinated, the electronic cloud is reorientated in the direction of the metal ion and away from the C=N double bond. The azomethine bond becomes polarized ($>C^+-N^-$), so the reaction with a variety of nucleophilic reagents occurs easier [28, 29]. One class of such reactions is a hydrolysis of Schiff bases, those involving water as a nucleophilic agent [29, 30].

Single crystal structures and thermal stability.

Compound $[{Zn(H_2O)_4(bda4Py)}_2][SO_4]_2$ **1** crystallizes in the centrosymmetric orthorhombic space group *Pbca* (Table 1). The asymmetric unit comprises Zn(II) cation, sulfate anion, bda4Py and water ligands in the 1:1:1:4 molar ratio. The ionic crystal structure **1** is built of the centrosymmetric binuclear aqua cations, $[{Zn(H_2O)_4(bda4Py)}_2]^{4+}$ and outersphere sulfate-anions. In the centrosymmetric cation the metal centers

are linked by the two bda4Py ligands coordinated to the metal in the head-to-tail mode, Zn(II) cation has a distorted octahedral coordination surrounding with the N₂O₄ donors coming from two bda4Py ligands and four water molecules, the range of Zn-O distances being 2.077(3)-2.148(3) Å, Zn-N distances are 2.148(3) and 2.241(3) Å (Fig. 2a, Table 2). The bidentate-bridging bda4Py ligand adjusts the concave shape with the bending angle between the pyridine and phenyl rings of 12.77 °. The metal-metal separation in the binuclear cation across the ligand is 13.272(1) Å. The sulfate anions display in the metal's second coordination sphere being linked with the binuclear cation through OH(H₂O)···O(SO₄)²⁻ and NH(NH₂) ···O(SO₄)²⁻ hydrogen bonds with participation of the coordinated water molecules and amino-group of bda4Py ligand (Table 3). Each Zn(II) cation is surrounded by five SO₄²⁻ anions, and each anion is imprisoned in the aqua hydrophylic cages from 5 neighboring cations (Fig. 2b); all four coordinated water molecules and amino group act as double H-donors, while oxygen atoms of the SO₄²⁻ anion act as the double (O2, O3) and triple (O1, O4) H-acceptors and participate in the extended 3D H-bonded network in the crystal (Fig. 2c).



Fig. 2. Fragments of structure **1**. (a) View for the formula unit in **1**, thermal ellipsoids are shown with the 50 % probabilities; (b) environment of the sulfate anion in the crystal; (c) fragment of crystal packing with indication of hydrogen bonds.

Compounds $\{[Zn(NO_3)_2(bda4Py)_2] \cdot 2H_2O\}n$ (2) and $\{[Cd(NO_3)_2(bda4Py)_2] \cdot 2H_2O\}n$ (3) are isomorphs (Table 1) that crystallize in the same centrosymmetric monoclinic P2/c space group in the form of 1D polymeric chains. Due to the similarities in the crystal structures, only 2 will be further discussed in details. The Zn(II) coordination environment in 2 is shown in Fig. 3a. The metal atom resides on the two-fold axis, and has an N₄O₂ octahedral coordination surrounding that originates from four bda4Py ligands and two nitrate anions. Zn-O bond distance is equal to 2.185(2) Å, Zn-N distances are equal to 2.137(2) and 2.240(2) Å. For compound **3** Cd-O bond distance is equal to 2.369(5) Å, Cd-N distances are equal to 2.328(5) and 2.405(5) Å (Table 2). Nitrate anion coordinates as a terminal monodentate ligand; bda4Py ligand coordinates

in a bidentate-bridging mode, *via* both pyridine and amino-group N-binding sites, thus providing the joining of successive metal atoms in the coordination polymeric chain (Fig. 3b). Although the twisting of bda4Py molecule in **2-3** is a bit larger than in **1** as indicates the dihedral angle between the phenyl and pyridine rings of 20.3 °, the metal…metal separation remains virtually the same in **2** being 13.378 Å, and a bit longer as 13.610 Å in **3**. The coordination chain is running along the [201] direction in the crystal. The hydrogenbonding system includes two NH(NH₂)…O(NO₃) and two identical OH(H₂O)…N(bda4Py-azine) hydrogen bonds (Table 3). The coordinated nitro-group participates in the NH₂…O hydrogen bonds between the coordination chains packed along the crystalolographic *c* axis (Fig. 3b). The coordination chains are additionally interlinked *via* bridging water molecules that reside on a two-fold axis (Fig. 3c, Table 3).

Compound	1	2	3	4
Empirical formula	$C_{24}H_{38}N_6O_{16}S_2Z$	$C_{24}H_{24}N_8O_7Z$	$C_{24}H_{24}CdN_8O$	$C_{26}H_{23.50}CdN_3O_{6.25}$
	n_2	n	7	
Formula weight	861.46	601.88	648.91	590.38
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic
Space group	Pbca	P2/c	P2/c	Iba2
Unit cell dimensions				
a,Å	9.6998(6)	13.7846(17)	14.0355(10)	9.1187(9)
b,Å	9.7516(6)	8.2108(8)	8.1396(4)	23.567(3)
c,Å	36.092(2)	11.7428(15)	12.0004(9)	26.202(4)
β , $^{\circ}$	90	111.784(13)	112.033(8)	90
Volume , $Å^3$	3413.9(3)	1234.2(3)	1270.84(16)	5631.0(13)
Ζ	4	2	2	8
Density (cald) Mg/m ³	1.676	1.620	1.696	1.393
Absorption coefficient mm ⁻¹	1.608	1.059	0.921	0.818
F(000)	1776	620	656	2388
Reflections collected	7026	3108	2651	5792
Independent reflections	2992 [R(int) =	3108 [R(int)	2651 [R(int)	3407 [R(int) =
	0.0325]	= 0.0579]	= 0.0513]	0.0537]
Reflections with $[I>2\sigma(I)]$	2354	2456	1914	1857
Data / restraints / parameters	2992 / 15 / 256	3108 / 4 / 192	2651 / 3 / 193	3407 / 326 / 360
Goodness-of-fit on F^2	1.065	0.937	1.042	1.010
Final <i>R</i> indices $[I > 2\sigma(I)], R_1$,	0.0441, 0.0847	0.0310,	0.0460,	0.0683, 0.1507
wR_2		0.0663	0.1290	
<i>R</i> indices (all data) R_1 , wR_2	0.0615, 0.0917	0.0420,	0.0678,	0.1290, 0.1832
· · · · -	·	0.0682	0.1353	·
Largest diff. peak and hole	0.416 / -0.934	0.251 / -0.356	0.910 / -0.97	1.043 / -0.462
e.Å ⁻³				

	\bigcirc	
Table 1. Crystal data and structure refinement parameters	for 1 -	-4

Table 2.	Bond lengths [Å] and angles [°] for 1-4
	1

Zn(1)-O(5)	2.077(3)	Zn(1)-O(7)	2.148(3)
Zn(1)-O(6)	2.091(3)	Zn(1)-N(3)	2.148(3)
Zn(1)-O(8)	2.100(3)	$Zn(1)-N(1)^{i}$	2.241(3)
O(5)-Zn(1)-O(6)	87.89(12)	O(8)-Zn(1)-N(3)	175.21(12)
O(5)-Zn(1)-O(8)	85.83(12)	O(7)-Zn(1)-N(3)	90.51(11)
O(6)-Zn(1)-O(8)	91.80(12)	$O(5)-Zn(1)-N(1)^{i}$	92.61(12)
O(5)-Zn(1)-O(7)	173.84(13)	$O(6)-Zn(1)-N(1)^{i}$	174.48(11)
O(6)-Zn(1)-O(7)	90.17(11)	O(8)-Zn(1)-N(1) ⁱ	82.75(12)
O(8)-Zn(1)-O(7)	88.39(12)	O(7)-Zn(1)-N(1) ⁱ	88.77(11)
O(5)-Zn(1)-N(3)	95.42(12)	N(3)-Zn(1)-N(1) ⁱ	92.56(11)
O(6)-Zn(1)-N(3)	92.87(11)		
		2	
Zn(1)-N(1)	2.137(2)	Zn(1)-N(3)	2.240(2)
Zn(1)-O(1)	2.185(2)	$N(3)^{ii}$ -Zn(1)-N(3)	83.00(11)
$N(1)^{ii}$ -Zn(1)-N(1)	92.64(11)	$N(1)^{ii}$ -Zn(1)-N(3) ⁱⁱ	92.66(7)
$N(1)^{ii}$ -Zn(1)-O(1) ⁱⁱ	86.15(8)	$N(1)-Zn(1)-N(3)^{ii}$	171.10(8)
$N(1)$ - $Zn(1)$ - $O(1)^{ii}$	88.81(8)	$O(1)^{ii}$ -Zn(1)-N(3) ⁱⁱ	84.43(8)
N(1)- $Zn(1)$ - $O(1)$	86.15(8)	O(1)-Zn(1)-N(3) ^{<i>ii</i>}	101.10(8)
$O(1)^{ii}$ -Zn(1)-O(1)	172.7(1)	N(1)-Zn(1)-N(3)	92.66(7)
		3	
Cd(1)-N(1)	2.328(5)	Cd(1)-N(3)	2.405(5)
Cd(1)-O(1)	2.369(5)	$N(1)-Cd(1)-N(3)^{ii}$	171.16(17)
$N(1)-Cd(1)-N(1)^{ii}$	92.2(2)	$O(1)^{ii}$ -Cd(1)-N(3) ⁱⁱ	82.8(2)
$N(1)-Cd(1)-O(1)^{ii}$	90.62(19)	$O(1)-Cd(1)-N(3)^{ii}$	105.06(19)
N(1)-Cd(1)-O(1)	82.17(18)	N(1)-Cd(1)-N(3)	92.78(17)
$N(1)^{ii}$ -Cd(1)-O(1)	90.62(19)	O(1)-Cd(1)-N(3)	82.8(2)
$O(1)^{ii}$ -Cd(1)-O(1)	169.6(3)	$N(3)^{ii}$ -Cd(1)-N(3)	83.2(2)
		4	
Cd(1)-O(5)	2.268(10)	Cd(1)-O(1)	2.400(13)
Cd(1)-O(4)	2.404(15)	Cd(1)-N(1)	2.409(18)
Cd(1)-O(3)	2.402(17)	Cd(1)-O(2)	2.429(17)
Cd(1)-N(2)	2.43(2)	N(1)-Cd(1)-N(2)	160.1(14)
O(3)-Cd(1)-O(1)	177.7(6)	O(2)-Cd(1)-N(1)	100.5(6)
O(4)-Cd(1)-O(1)	126.4(5)	O(3)-Cd(1)-N(1)	104.7(7)
O(5)-Cd(1)-O(1)	89.0(6)	O(4)-Cd(1)-N(1)	83.0(7)
O(3)-Cd(1)-O(2)	128.1(5)	O(5)-Cd(1)-N(1)	84.9(10)
O(4)-Cd(1)-O(2)	85.1(4)	O(3)-Cd(1)-N(2)	87.7(13)
O(5)-Cd(1)-O(2)	138.1(7)	O(4)-Cd(1)-N(2)	117.1(13)
O(5)-Cd(1)-O(3)	89.1(6)	O(5)-Cd(1)-N(2)	79.4(14)
O(5)-Cd(1)-O(4)	136.7(8)	O(1)-Cd(1)-N(2)	93.3(13)
O(1)-Cd(1)-N(1)	73.7(5)	O(2)-Cd(1)-N(2)	83.3(13)

Symmetry transformations: *i* : -x, -y, -z; *ii* : 1-x, y, 1/2-z



Fig. 3. Fragments of structure 2. (a) fragment of coordination double chain showing the octahedral environment of Zn(II) atom; (b) packing of the coordination tapes; view along the b axis; (c) packing of the coordination tapes; view along the c axis.

Table 3. Geometry of hydrogen bonds in 1-4					
D-HA, Å	d(HA),	d(DA), Å	∠(DHA), °	Symmetry transformations	
	Å			used to generate	
				equivalent atoms	
		1			
N(1)-H(1N)O(3)	2.04(2)	2.889(4)	173(4)	1- <i>x</i> , - <i>y</i> , - <i>z</i>	
N(1)-H(2N)O(2)	2.12(2)	2.982(4)	172(4)	x-1/2, -y-1/2,-z	
O(5)-H(5A)O(3)	1.83(2)	2.684(4)	172(5)	1/2-x, y-1/2, z	
O(5)-H(5B)O(1)	1.96(2)	2.806(4)	164(4)	x-1, y, z	
O(6)-H(6B)O(1)	1.93(2)	2.760(4)	163(3)	x-1/2, y, 1/2-z	
O(6)-H(6A)O(4)	1.86(2)	2.699(4)	173(4)	х, у, г	
O(7)-H(7A)O(4)	2.19(2)	2.940(4)	149(4)	х, у, г	
O(7)-H(7B)O(2)	1.92(2)	2.772(4)	166(4)	1/2-x, y+1/2, z	
O(8)-H(8A)O(1)	1.88(2)	2.723(4)	167(5)	1/2-x, y+1/2, z	
O(8)-H(8B)O(4)	1.89(2)	2.718(4)	164(4)	x-1/2, y, 1/2-z	
		2			
N(3)-H(3A)O(3)	2.13(2)	2.928(3)	156(3)	x, 1-y, z-1/2	
N(3)-H(3B)O(2)	2.29(2)	3.138(3)	167(3)	1- <i>x</i> , 1- <i>y</i> , 1- <i>z</i>	
O(4)-H(4A)N(2)	2.29(3)	3.195(4)	160(4)	<i>x</i> +1, <i>y</i> +1, <i>z</i>	
		3			

N(3)-H(3A)O(3)	2.09(3)	2.925(7)	157(6)	x, 1-y, z-1/2
N(3)-H(3B)O(2)	2.41(3)	3.243(8)	161(6)	1-x, 1-y, 1-z
O(4)-H(4A)N(2)	2.3(1)	3.179(9)	157(9)	<i>x</i> +1, <i>y</i> +1, <i>z</i>
		4		
O(5)-H(5A)O(1)	2.21	2.69(2)	110.9	x-1/2, 3/2-y, z
 O(5)-H(5B)O(3)	2.13	2.64(2)	113.5	x+1/2, 3/2-y,z



Fig. 4. Fragments of structure **4**. (a) View for the Cd(II) coordination environment with thermal ellipsoids of 50% probabilities; (b) view of the coordination layer along the crystallographic b axis; (c) schematic representation of two interwoven coordination layers, top and side views; (d) packing of the layers with the voids shown by yellow color

Compound $[Cd(bda4Py)_2(dpa)_2] \cdot 2H_2O(4)$ crystallizes in the noncentrosymmetric orthorhombic space group *Iba*2 (Table 1). The Cd(II) atom is 7-coordinated (distorted pentagonal bipyramid), and the coordination surrounding comprises an N₂O₅ set of donor atoms going from two chelate carboxylate groups of dpa ligand and one water molecule in the equatorial plane, and two bda4Py ligands in two apical positions (Fig. 4a).

Cd-O distances are in the range 2.268(9)-2.431(17) Å, Cd-N distances adjust the values 2.43(2) and 2.448(18) Å (Table 3). Both ligands are in the twisted conformations with the dihedral angles between the cyclic fragments of 14.58 ° in bda4Py and 46.23 ° in dpa. Each ligand acts as a bridge. Similar to 1-3, in 4 bda4Py ligand coordinates in a bidentate-bridging mode, via N-binding sites of pyridine cycle and aminogroup, thus providing the joining of successive metal atoms along the crystallographic c axis, $Cd \cdots Cd$ separation across bda4Py ligand being 14.363 Å; the dicarboxylate anion dpa also works as a mediator between the successive Cd(II) atoms along the crystallographic a axis, providing Cd···Cd separation of 9.119 Å; these mediators provide the linking of the components in the layer of 4,4 topology parallel to the ac crystallographic plane (Fig. 4b). Herein, the incorporation of the bulky dicarboxylic ligand dpa reduces the number of bda4Py ligands coordinated to the same metal from 4 in 2-3 to 2 in 4. The layers stack along the crystallographic b axis with each two layers, that are related by the glide plane a, and interconnected via $OH(H_2O)\cdots O(COO)$ hydrogen bonds, being interwoven with formation of double sheet (Fig. 4c). These double-layered aggregates meet by their hydrophobic surfaces that form the phenyl rings of dpa. The interlayer space in the crystal occupy the disordered water molecules, since the loosely packed double sheets provide the channels running along the crystallographic c axis in the crystal that constitute 10.4% or 586 Å³ of the unit cell volume (Fig. 4d).

The attempts for the counter synthesis of **1-4** starting directly from bda4Py were succeeded only for compound **1** for now. For the other reaction mixtures, the oxidation of the ligand was observed indicated by the cloudy, dark in color solutions. The impossibility to directly reproduce compounds with the similar ligand, N-(2-pyridylmethylene)benzene-1,4-diamine, is reported [21, 42, 43].

To explore the stability of the ligand bda4Py and compound **1**, the thermogravimetric analysis was performed (Fig. 5, Fig.S7).



Fig. 5. Thermal behavior of 1

Ligand bda4Py melts at 208 °C, then decomposes oxidatively in two steps. The complex **1** is stable up to 53 °C, then decomposes in 6 steps (Fig. 5). The first stage between 53-142 °C is endothermic, where ~16% (calcd = 16.7%) of the mass assigned to the coordinating water is lost. The following oxidative decomposition steps are carried out between 330-530 °C involving ligand decomposition and ~43% loss of mass (calcd = 45.7%). The remaining 41% of the mass can be attributed to zinc sulfate (calcd = 37.5%) that decomposes in the range of 538-635 °C with the formation of SO₃, and the residue ZnO, 15.66% (calcd = 18.9%) (Fig. S8, Fig. S9).

Optical properties

IR characterization of the ligand bda4Py and coordination compounds 1-4

The IR spectroscopic investigation of **1-4** also confirmed the presence of the ligand with terminal aminogroup. The comparative IR specroscopic investigation has been undertaken for ligands and compounds **1-4** (Fig. S5). In the ligand bda4Py itself, the availability of amino (-NH₂) group is confirmed by the v_{as} (NH) 3434 cm⁻¹ and v_s (NH) 3315 cm⁻¹ characteristic bands. The band at 3179 cm⁻¹ represents a shoulder originated from the overtone of the N–H bending band. These bands are also present in compounds **1-4** shifted to the lower values. These shifts to smaller wavelengths are explained by coordination of amino group to the metal with the formation of NH···O hydrogen bond [44]. Ligand bda4Py has two δ (CH) bands at 832 and 793 cm⁻¹ which can be attributed to *p*-disubstituted aromatic structure. In compounds **1-4** these δ (CH) bands are also present in the range 841-780 cm⁻¹. For compound **4** there are also two strong bands, δ (CH) 770, 748 cm⁻¹ that can be attributed to the *o*-disubstituted diphenic acid.

In compound **1**, the SO₄²⁻ anion that is not bonded to the metal, reveals a very strong $v_3(SO)$ band at 1035 cm⁻¹. Due to the formation of hydrogen bonds between the sulfate ion and the water molecules, the symmetry of the sulfate ion decreases [44-46], so in the spectrum some specific bands of lower intensity appear for this group. For this compound, there is a broad and intense v(OH) characteristic band in the 3500-3100 cm⁻¹ region that indicates the formation of OH····O hydrogen bonds. An additional band of medium intensity for coordinated water molecules $\delta(H_2O)$ is present at 1667 cm⁻¹ [45, 46]. In **2** and **3** the NO₃⁻ anion is monodentate coordinated to the metal (C_{2v} symmetry). To this group is assigned a strong $v_3(A'_1)$ band at 987 cm⁻¹ for **3** and 1038 cm⁻¹ for **2**. The $v_3(E')$ band is split in the two bands $v_{as}(NO)$ 1413 cm⁻¹ for **3**, 1420 cm⁻¹ for **2**, and $v_s(NO)$ 1316 cm⁻¹ respectively 1312 cm⁻¹ [46]. For compound **4**, the bands characteristic for the carboxylate anion $v_{as}(CO)$ 1530 cm⁻¹ and $v_s(CO)$ 1405 cm⁻¹ are present.

Absorption and emission properties

To monitor the limits of stability of the ligands bda4bPy and bda4Py in the acidic medium, the absorption curves for EtOH solutions of both ligands in the UV-Vis range of spectrum were recorded. All experiments were carried out at room temperature (292 K). The solutions were prepared in EtOH solvent with a ligand concentration of 3.3 x 10⁻⁵ M. Ligand bda4bPy has four absorption peaks, λ_{max} , centered at 202, 234, 279 and 365 nm, while bda4Py revealed three absorption peaks centered at 203, 242 and 386 nm. Ligands

bda4bPy and bda4Py have characteristic absorption band C=N that corresponds to transitions $n \rightarrow \pi^*$. For bda4bPy $\lambda_{max} = 365$ nm, A = 0.64 and bda4Py at $\lambda_{max} = 386$ nm, A = 0.48. (Fig. 7).



Fig. 7. UV-Vis absorption spectra of bda4bPy and bda4Py in the EtOH solution upon gradual increase of acidity.

To the bda4bPy chromophore solution, 0.1 M HCl solution was added, gradually increasing the molar ratio of acid to chromophore. The UV-Vis spectra for all solutions were measured 5 minutes after acid addition. Starting from the ligand to acid molar ratio of 1: 0.25, the color of solution changed from yellow to orange, and the recorded curve becomes identical with the curve for bda4Py chromophore but lower intensity, A = 0.38. This demonstrates that hydrolysis of bda4bPy has taken place with bda4Py ligand formation. According to these measurements it was found that compound bda4bPy has a hydrolytic propensity in the acidic medium, so that at the molar ratio of 1: 3 the virtually total amount of compound bda4bPy is hydrolysed.

The stability of chromophores bda4bPy and bda4Py was also elucidated in the presence of Cd(II) cation. To study this, the cadmium nitrate Cd(NO₃)₂·4H₂O salt was used in admixture with the bda4bPy ligand in various molar ratios. All measurements were recorded in DMF solvent. To record the absorption curves the solutions were used with the concentration of ligand of 3.3×10^{-5} M, varying only the molar ratio of cadmium nitrate. First, the curves for the bda4bPy ligands $\lambda_{max} = 366$, A = 0.60 and bda4Py $\lambda_{max} = 392$, A = 0.54 were recorded. Then the curve for the solution of the mixture of cadmium nitrate and bda4bPy in the molar ratio of 1: 1, $\lambda_{max} = 368$, A = 0.55. It can be seen that these values do not differ much from bda4bPy. When this solution was heated to the boiling temperature of DMF for 10 min, the color of solution was changed to intense orange, and after the cooling the spectrum was recorded $\lambda_{max} = 390$, A = 0.53 (Fig. 8). The obtained values are characteristic for the bda4Py ligand which proves that the hydrolysis of the bda4bPy ligand has taken place. The following solutions were measured with the gradual increase of the ion concentration of Cd(II). Thus, it has been found that increasing the concentration of the metal ions (e.g., the last measured curve, the molar ratio of salt to ligand, 15:1) does not cause hydrolysis of the second azomethine group, C=N. The solution color remains constant, orange.



Fig. 8. UV-Vis absorption spectra of bda4bPy and bda4Py gradual increase of concentration of Cd(NO₃)₂



Fig. 9. Solid state emission spectra of free bda4Py ligand, 1 and 4 at room temperature.

The luminescent properties of free bda4Py chromophore and coordination compounds 1 and 4 were investigated in the solid state at room temperature. As shown in Fig. 9, upon excitation at $\lambda exc = 337.1$ nm, the free Schiff-base bda4Py displays an emission band at 545 nm, which can probably be attributed to the intraligand $\pi^* \cdots \pi$ transitions [47]. For the complex 1, the solid-state luminescent spectrum shows the bathochromic shift of an intense and broad emission maximum centered in the interval 620-650 nm; no pronounced signal was registered for 4, the emission quenching is most probably explained by the significant structure disorder and availability of big voids in this solid.

Conclusions

In summary, four coordination compounds $[Zn(H_2O)_4(bda4Py)]_2(SO_4)_2$ (1), $\{[Zn(NO_3)_2(bda4Py)_2] \cdot 2H_2O\}_n$ (2), $\{[Cd(NO_3)_2(bda4Py)_2] \cdot 2H_2O\}_n$ (3), and $\{[Cd(bda4Py)_2(dpa)_2] \cdot 2H_2O\}_n$ (4) with the generated *in situ* Schiff-base ligand bda4Py=N-((pyridin-4-yl)methylene)benzene-1,4-diamine have been isolated and structurally characterized. Everywhere this chromophore acts as a bidentate linker between two metal centers

through nitrogen atoms of pyridino- and amino-groups. The additional stabilization of the crystalline solids can be achieved *via* hydrogen bonds with participation of the ligand's amino-group. The tuning structures and emissive properties is possible by the metal and second ligand variations.

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GRAPHICAL ABSTRACT



Synopsis:

The chromophore, N-((pyridin-4-yl)methylene)benzene-1,4-diamine, obtained as the product of partial hydrolysis of the known ligand, N1,N4-bis(pyridin-4-ylmethylene)-benzene-1,4-diamine demonstrates promising potential for crystal engineering of emissive coordination polymers.

Highlights

- Chromophore N-((pyridin-4-yl)methylene)benzene-1,4-diamine obtained in situ •
- Hydrolytic transformation of N¹,N⁴-bis(pyridin-4-ylmethylene)-benzene-1,4-diamine •
- Spectroscopic study of organic chromophores and coordination compounds .
- Crystal structures of Zn and Cd new coordination compounds.