Synthesis, Crystallographic and Spectral Characterization of a Cadmium Chloride Complex Containing a Novel Imidazo[1,5-*a*]Pyridine Derivative

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The reaction between 2-(2-amino-ethylamino)ethanol and pyridine-2-carbaldehyde in a 1 : 3 molar ratio gave 3-(pyridin-2-yl)-1-(pyridin-2-ylmethyl)imidazo[1,5-*a*]pyridine (PPIP) which was characterized by elemental analysis and spectroscopic methods. The study of CSD-deposited structures revealed that PPIP is a new derivative of imidazo[1,5-*a*]pyridine. The cadmium chloride complex of this ligand [Cd(PPIP)Cl$_2$][Cd(PPIP)Cl$_2$]′·3H$_2$O (**1**) was prepared and identified by elemental analysis, FT-IR, Raman and ^{1}H NMR spectroscopy, and single-crystal X-ray diffraction. In the crystal structure of **1**, there are two cadmium complexes with slightly different coordination bond lengths and angles. Also water molecules are incorporated in the crystal network. The geometry around the cadmium atom which is coordinated by two pyridine and one imine nitrogen atoms and two chloride ions is distorted square pyramidal. All bond lengths compare well with CSD averages of similar structures. The hydrogen bonds including O–H···Cl and O–H···O present in the crystal structure of **1** are also comparable to those in analogs.

Key words: Imidazo-[1,5-*a*] pyridine Derivative, Cadmium Complex, Synthesis, X-Ray Crystal Structure

Introduction

The chemistry of fused nitrogen heterocyclic imidazo[1,5-*a*]pyridines has attracted increasing attention due to their unique photophysical and biological properties [1, 2]. Potential applications of these substances have been actively probed in the context of organic light-emitting diodes (OLEDs) [3 – 5] and organic thin layer field effect transistors (FETs) [6]. This class of ligands has emissions in the blue region of the visible range (450 – 470 nm), which is a desirable, but critical, feature in OLED technology. Imidazo[1,5-*a*]pyridines possess thromboxane A2 synthetase inhibiting property [7]. In addition, this family has potential applications in the treatment of a diverse range of ailments *e. g.* gastric disorder because of their ability to inhibit gastric H$^+$/K$^+$-ATPase [8], and action as analgesic drugs [9]. They also act as antagonist for the dopamine d3 receptor [10] and the PI 3-kinase inhibitor [11] which results in them being used for the treatment of psychosis as well as respiratory and cardiovascular diseases, respectively.

In this paper a novel potentially tridentate ligand, 3-(pyridin-2-yl)-1-(pyridin-2-ylmethyl)imidazo[1,5-*a*]pyridine (PPIP) was prepared which is a new derivative of imidazo[1,5-*a*]pyridine-based compounds (Scheme 1). Previously we reported the synthesis of 2-(2-(pyridin-2-yl)oxazolidin-3-yl)-*N*-(pyridin-2-ylmethylene)ethanamine (POPME) which was produced from the reaction between 2-(2-amino-ethylamino)ethanol and pyridine-2-carbaldehyde with a 1 : 2 molar ratio [12].

In the past few years, we have studied complexation of some d^{10} metal ions and presented a series of papers in this field [13 – 18]. In continuation of our previous studies, in this work the preparation of the PPIP and its cadmium chloride complex [Cd(PPIP)Cl$_2$][Cd(PPIP)Cl$_2$]′·3H$_2$O (**1**) are described.
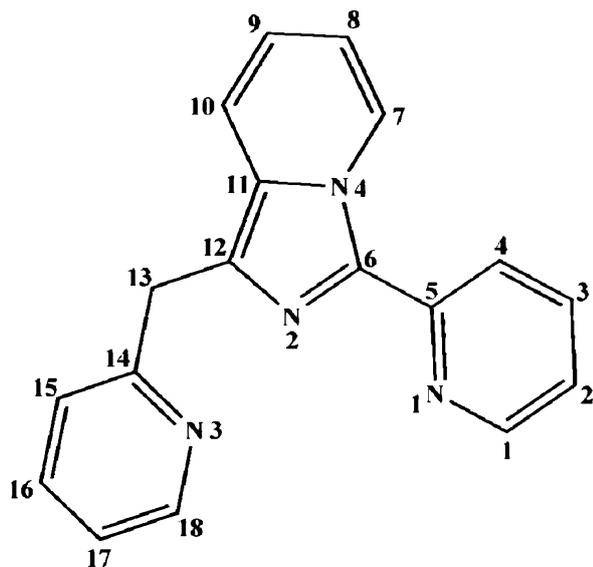
Scheme 1. The PPIP structure and the numbering scheme used for the ^{1}H NMR and ^{13}C NMR spectra of the free ligand and complex **1**.

Results and Discussion

Reaction between 2-(2-amino-ethylamino)ethanol and pyridine-2-carbaldehyde with a 1 : 3 molar ratio afforded PPIP. This ligand is a new derivative of imidazo [1,5-*a*]pyridine-based compounds. All compounds with the imidazo [1,5-*a*]pyridine base that have been deposited in CSD are presented in Scheme 2. Pyridine-2-carbaldehyde in the reaction with 2-(2-amino-ethylamino)ethanol produces the corresponding imine which in turn reacts with another molecule of pyridine-2-carbaldehyde. After proton removal and an addition-elimination process, PPIP is obtained.

PPIP is an interesting tridentate asymmetric ligand with an imidazole ring and two pyridine rings containing two different types of donor centers: two nitrogen atoms from pyridines and a nitrogen atom from an imidazole ring. Reaction of PPIP with an ethanolic solution of cadmium(II) chloride with a molar ratio of 1 : 1 gave complex **1**. The complex was air-stable and soluble in methanol, DMF and DMSO.

In the IR spectrum of **1**, the absorption at 3448 cm^{-1} confirmed the presence of H_2O in this complex. The ring wagging vibrations of the pyridine groups were observed at 663 and 779 cm^{-1} for PPIP and at 640 and 756 cm^{-1} for **1**. The ^{1}H NMR spectrum gave a singlet at 4.0 ppm for methylene protons and signals in

the region of 7.1 – 8.5 ppm for protons on the pyridine and imidazole rings. The ^{13}C NMR spectrum exhibited a signal at 60.5 ppm for methylene carbons and from 120.6 to 162.8 ppm for unsaturated ring carbons. The numbering scheme used for the assignment of the ^{1}H NMR and ^{13}C NMR spectra of the free ligand and complex **1** are given in Scheme 1.

Information about the low frequency of metal-halide and metal-ligand vibrations can be obtained by Raman spectroscopy. In the Raman spectrum of **1**, the strong band at 430 cm^{-1} was assigned to Cd–N stretching [19a]. The terminal Cd–Cl stretching vibration was assigned to the strong band at 320 cm^{-1} for the complex consistent with the values reported for $CdCl_2$ in the literature (200 – 400 cm^{-1}) [19b]. In the low-frequency region water lattice exhibits "librational modes" which are due to rotational oscillations of the molecules, restricted by interactions with neighboring atoms. They are classified into three types (wagging, twisting and rocking) depending on the direction of the principal axis of rotation [19c]. In the Raman spectrum of **1**, these "librational modes" are observed at 555 and 187 cm^{-1} for rocking and twisting, respectively. In the IR spectrum of **1**, the band at 524 cm^{-1} for the rocking librational mode confirms the assignment.

The crystal and molecular structure of [Cd(PPIP)Cl$_2$][Cd(PPIP)Cl$_2$]′·3H$_2$O was determined by X-ray single-crystal diffraction. Crystallographic data and details of the data collection and structure refinement are listed in Table 1. Bond lengths and angles are reported in Table 2, and the hydrogen bonding geometry in Table 3. The molecular graphics were drawn with ORTEP-III [20] and MERCURY (version 2.3) [21].

The ORTEP-III diagrams for the crystal structure of **1** are shown in Fig. 1. There are three different parts, two of them consisting of two similar complexes with slightly different coordinative bond lengths and angles while the last part consists of the three H$_2$O molecules that are not coordinated to cadmium atoms and are trapped in the crystal network by hydrogen bonds.

The cadmium atoms are coordinated by two pyridine and one imine nitrogen atoms and two chloride ions. This pentacoordinate geometry can adopt either a square-pyramidal or a trigonal-bipyramidal structure. To identify such structures, the formula of Addison *et al.* [22] was applied in which the angular structural parameter (τ) is represented as the index of trigonality. The parameter $\tau = (\beta - \alpha)/60$, where α and β

3-(2-Pyridyl)imidazo(1,5-a)pyridine
[34]

2-(2-Pyridyl)-*N*³-(4-chlorophenyl)imidazo(1,5-a)pyridinium
perchlorate [35]

Bis(3-(2-pyridyl)imidazo(1,5-a)pyrid-1-yl)sulfide [34]

1,1'-Bis(3-(pyridin-2-yl)*H*-imidazo(1,5-a)pyridine) [36]

2-(2-(1H-Imidazol-3-ium-5-yl)ethyl)-3-(pyridin-2-yl)imidazo[1,5-a]pyridin-2-ium diperchlorate [37]

1,1'-Selanylbis(3-(pyridin-2-yl)imidazo[1,5-a]pyridine) [38]

3-(2-Pyridinyl)-*N*-(2-pyridinylmethylene)imidazo[1,5-a]pyridin-1-amine [39]

1,1'-((4-Chlorophenyl)methylene)bis(3-(pyridin-2-yl)imidazo[1,5-a]pyridine)
[40]

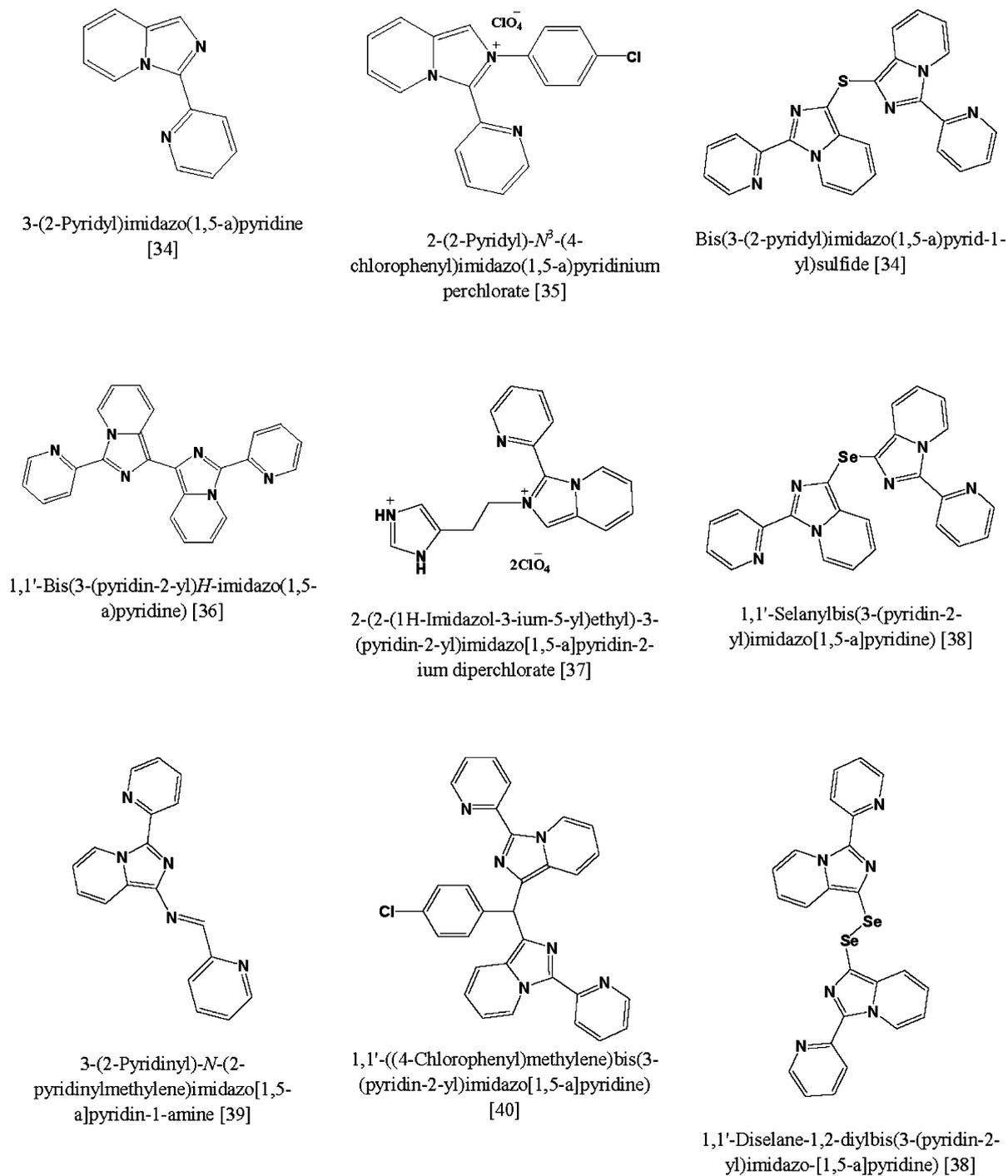1,1'-Diselane-1,2-diylbis(3-(pyridin-2-yl)imidazo-[1,5-a]pyridine) [38]

Scheme 2. Compounds with imidazo[1,5-*a*]pyridine base that have been deposited in the CSD.

Table 1. Crystal data and numbers pertinent to data collection and structure refinement for **1**.

	1
Empirical formula[a]	[Cd(PPIP)Cl₂][Cd(PPIP)Cl₂]′ ·3H₂O C₃₆H₃₄Cd₂Cl₄N₈O₃
Formula weight, g mol⁻¹	993.31
Crystal size, mm³	0.12 × 0.08 × 0.05
Temperature, K	150
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a, Å	13.7785(4)
b, Å	18.0868(5)
c, Å	15.5099(4)
β, deg	100.437(3)
Volume, Å³	3801.27(19)
Z	4
Calculated density, g cm⁻³	1.74
Absorption coefficient, mm⁻¹	1.4
$F(000)$, e	1976
2θ range for data collection, deg	6.28–58.6
h, k, l ranges	$-17 \leq h \leq 17$, $-23 \leq k \leq 17$, $-19 \leq l \leq 18$
Reflections collected/ independent/R_{int}	21 710/8769/0.0275
Data/ref. parameters	8769/487
Goodness-of-fit on F^2	1.043
$R1/wR2$ [$I > 2\sigma(I)$]	0.0324/0.0658
$R1/wR2$ (all data)	0.0493/0.0734
Largest diff. peak/hole, e Å⁻³	0.85/ − 0.49

[a] The empirical formula is given for two individual, crystallographically independent complex molecules and three water molecules.

Table 2. Selected bond length (Å) and angles (deg) for **1** with estimated standard deviations in parentheses.

Distances			
Cd1–N1	2.433(2)	Cd2–N5	2.488(3)
Cd1–N2	2.237(2)	Cd2–N6	2.231(2)
Cd1–N3	2.379(2)	Cd2–N7	2.395(3)
Cd1–Cl1	2.4613(8)	Cd2–Cl4	2.4998(8)
Cd1–Cl2	2.4488(8)	Cd2–Cl3	2.4138(8)
Angles			
N1–Cd1–N2	68.76(8)	N5–Cd2–N6	68.11(9)
N2–Cd1–N3	79.33(8)	N6–Cd2–N7	80.20(9)
N1–Cd1–N3	134.25(8)	N5–Cd2–N7	135.98(8)
N1–Cd1–Cl2	91.65(6)	N5–Cd2–Cl3	90.23(6)
N3–Cd1–Cl1	103.00(6)	N7–Cd2–Cl4	100.27(6)
Cl1–Cd1–Cl2	113.35(3)	Cl4–Cd2–Cl3	113.31(3)

be coordinated to a metal atom in facial or meridional forms. In the *mer* form there are two angles of 90° and one of 180°, and in the *fac* form there are three angles of 90°. In **1**, two angles are deviating from 90° due the chelating bite angle, while the third one is about 135°, exactly half way between *fac* and *mer*.

A search for similar structures by the CON-QUEST [24] software reveals that the complex **1** is the first example of imidazo[1,5-*a*]pyridine-based ligands coordinated to a cadmium atom. Each cadmium atom is coordinated by the tridentate ligand forming two five- and one six-membered chelate rings. The five-membered chelate rings are planar (rms deviations 0.025 Å for C5 and C24 at Cd1 and Cd2, respectively) while the six-membered chelate ring is not planar. The Cd–N$_{imine}$ distances are shorter than the other Cd–N distances (2.237(2) and 2.231(2) Å for Cd1–N$_{imine}$ and Cd2–N$_{imine}$, respectively). The CSD [25, 26] average for Cd–N$_{imine}$ bond lengths in similar structures that have a Cl₂Cd–N$_{imine}$ base is 2.324 Å. The average of the four Cd–N$_{pyridine}$ distances (2.424 Å) is larger than the CSD average (2.367 Å for all complexes with Cl₂Cd–N$_{pyridine}$ base). The two terminal Cd–Cl bond lengths are different and smaller than those in other complexes that have a N₃CdCl₂ base.

are the two largest angles at the cadmium atom with $\beta \geq \alpha$. An ideal square pyramid will have $\beta = 180°$ and $\alpha = 180°$, and therefore $\tau = 0\%$, but an ideal trigonal-bipyramidal structure will have $\beta = 180°$ and $\alpha = 120°$ and therefore $\tau = 100\%$ [23]. The τ value is calculated to be 21.5 and 15.42 % for Cd1 and Cd2, respectively, indicating a distorted square-pyramidal geometry around each cadmium atom. In addition to the distorted geometry at the two Cd atoms, also the ligand coordination geometry (facial *vs.* meridional) is worth to be discussed. Each tridentate ligand can

Table 3. Hydrogen bonds and short contact dimensions (Å and deg) in **1**. The CSD average is calculated by means of the program VISTA [33] for each interaction.

D–H⋯A	d(D–H)	d(H⋯A)	<(DHA)	d(D⋯A)	Symmetry code	CSD average for d(H⋯A)
O2–H2A⋯Cl2	0.850	2.3922	167.5	3.227(3)	$1 - x, 0.5 + y, 1.5 - z$	2.434
O1–H1B⋯O2	0.850	2.030	151.6	2.807(6)	x, y, z	2.111
O3–H3B⋯O1	0.851	2.010	164.1	2.838(6)	$x, 1.5 - y, -0.5 + z$	2.111
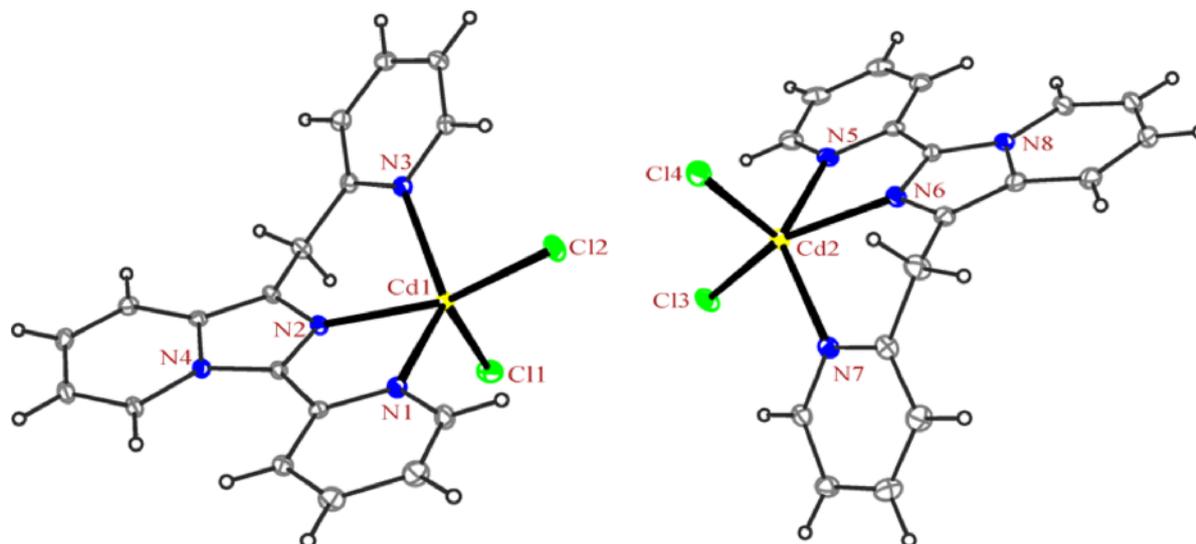
Fig. 1 (color online). ORTEP-III drawing of [Cd(PPIP)Cl$_2$][Cd(PPIP)Cl$_2$]′·3H$_2$O (**1**). The ellipsoids are drawn at the 30% probability level. The water molecules have been omitted for clarity.

In the crystal structure of **1**, strong hydrogen bonds (strong hydrogen bonds range in the literature from 1.5 to 2.2 Å [27]) appear and connect the three H$_2$O molecules sequentially, and one of them to the complex. In this way the Cl2 atom acts as proton acceptor whereas the O3 atom of a H$_2$O molecule participates in hydrogen bonding as a proton donor. Two water O atoms that connect Cl2 and O3 atoms by hydrogen bonding act as proton donor and acceptor at the same time. The structure with partial hydrogen bonding grows to a 3D network by participation of uncounted short contacts such as C(sp^2)–H···π [28] between the imidazo[1,5-*a*]pyridine portion and the pyridine ring, C(sp^2)–H···Cl and O–H···Cl.

In addition to these short contacts there are π···π stacking interactions [29] between parallel aromatic rings belonging to adjacent complexes. These interactions appear between two imidazo[1,5-*a*]pyridine units, an imidazo[1,5-*a*]pyridine moiety and a pyridine ring and also between two pyridine rings. A study of the crystal structure by MERCURY shows that there are 24 π···π stacking interactions with an average distance of 3.33 Å and a range of 3.20 – 3.40 Å. These bond lengths are comparable with the CSD average (3.21 Å). Parallel arrays of the planes of the aromatic rings indicate that these interactions are of the π stacking type, rather than edge-to-face or vertex-to-face types [30].

Conclusion

In this paper, the preparation of a new tridentate ligand, PPIP, and its cadmium complex [Cd(PPIP)Cl$_2$][Cd(PPIP)Cl$_2$]′·3H$_2$O are presented and their spectral (IR, Raman, ^{1}H and ^{13}C NMR), and structural properties are described. The crystal structure determination of **1** revealed that this crystal is assembled from two cadmium complexes with slightly different coordinative bond lengths and angles. Also water molecules are present in the crystal structure trapped by hydrogen bonds. The geometries around the cadmium atoms are distorted square pyramidal with two pyridine- and one imine-nitrogen atoms and two chloride ions as donors. In the crystal of **1**, hydrogen bonds and weak interactions such as C(sp^2)–H···π, C(sp^2)–H···Cl and O–H···Cl give rise to a supramolecular network. The synthesis of new complexes of the PPIP ligand is continued by our research group.

Experimental Section

Materials and instrumentation

All starting chemicals and solvents were reagent or analytical grade and used as received. The microwave-assisted reaction was carried out using a Microwave Laboratory Systems MicroSYNTH. The infrared spectra of a KBr pellet

in the range $4000 - 400 \, \text{cm}^{-1}$ were recorded with a FT-IR 8400-Shimadzu spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Aspect 3000 instrument operating at 250 MHz; chemical shifts δ are given in parts per million, with values relative to TMS as internal standard. The carbon, hydrogen and nitrogen contents were determined in a Thermo Finnigan Flash Elemental Analyzer 1112 EA. The Raman spectrum was performed using a Nicolet Model 910 Fourier transform spectrometer. The melting point was determined with a Barnsted Electrothermal 9200 electrically heated apparatus.

3-(Pyridin-2-yl)-1-(pyridin-2-ylmethyl)imidazo[1,5-a]pyridine, PPIP

A mixture of 3.75 g (35 mmol) of pyridine-2-carbaldehyde and 1.04 g (10 mmol) of 2-(2-aminoethylamino)ethanol was irradiated inside a microwave oven for 20 min with a power up to 1 kW. After microwave irradiation, an oily liquid was obtained and the redundant precursors removed at the rotary evaporator. The mixture was dissolved in chloroform (20 mL) and washed three times with water (20 mL). The isolated chloroform layer was evaporated to dryness. A thick brown oil was obtained. Several attempts to crystallize the compound were unsuccessful. Yield: 1.32 g, 46 %. – $C_{18}H_{14}N_4$ (286.33): calcd. C 75.50, H 4.93, N 19.64; found C 74.83, H 4.93, N 19.55. – IR (KBr disk): $\nu = 3055$ (CH)$_{\text{ar}}$, 2939 (CH$_2$), 1589 (C=N), 1466 (C=C)$_{\text{ar}}$, 1149 (C–N), $\delta_{\text{as}} = 1435$ (CH$_2$), $\delta_{\text{s}} = 1366$ (CH$_2$), $\gamma = 779$ and 663 (py) cm^{-1}. – ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 4.0$ (s, 2 H, CH$_2$); 7.1–8.5 (m, 12 H, CH$_{\text{py}}$). – ^{13}C NMR (250 MHz, CDCl$_3$): $\delta = 60.5$, 120.6, 121.1, 121.7, 122.7, 123.4, 124.7, 127.8, 136.3, 136.5, 136.6, 148.8, 149.2, 149.3, 150.1, 154.2, 159.3, 162.8.

[Cd(PPIP)Cl₂][Cd(PPIP)Cl₂]'·3H₂O, (1)

A solution of 0.28 g (1 mmol) of PPIP, dissolved in EtOH (15 mL), was added with stirring to a solution of 0.22 g (1 mmol) of CdCl$_2$·2.5 H$_2$O in EtOH (25 mL). The reaction mixture was stirred at 60 °C for 3 h. Brown crystals suitable for X-ray diffraction were obtained from the solution after standing for 5 d. Yield: 0.31 g, 65 %. M. p.: 208 °C. – (C$_{36}$H$_{28}$Cd$_2$Cl$_4$N$_8$)·3H$_2$O (993.31): calcd. C 43.53, H 3.45, N 11.28; found C 43.49, H 3.45, N 11.20. – IR (KBr disk): $\nu_{\text{as}} = 3449$ (H$_2$O), $\nu_{\text{s}} = 3251$ (H$_2$O), $\nu = 3070$ (CH)$_{\text{ar}}$, 2931 (CH$_2$), 1596 (C=N), 1481 (C=C)$_{\text{ar}}$, $\delta = 1633$ (H$_2$O), $\delta_{\text{as}} = 1435$ (CH$_2$), 1373 (CH$_2$), $\nu = 1157$ (C–N), $\gamma = 756$ and 640 (py), $\rho_{\text{r}} = 524$ (H$_2$O), $\nu = 417$ (Cd–N) cm^{-1}. – Raman: $\nu = 3025$ (CH)$_{\text{ar}}$, 2950 (CH$_2$), $\delta = 1634$ (H$_2$O), $\nu = 1461$ (C=C)$_{\text{ar}}$, 1150 (C–N), $\gamma = 744$ and 647 (py), $\rho_{\text{r}} = 555$ (H$_2$O), $\nu = 430$ (Cd–N), 320 (Cd–Cl), $\rho_{\text{t}} = 187$ (H$_2$O) cm^{-1}. – ^{1}H NMR (250 MHz, [D$_6$]DMSO): $\delta = 4.5$ (s, 2 H, CH$_2$), 7.2–9 (m, 12 H, CH$_{\text{py}}$).

X-Ray structure determination

A suitable crystal of **1** was selected and investigated on an Oxford Diffraction Gemini Ultra diffractometer. The crystal was kept at 150 K during data collection. Using OLEX-II [31], the structure was solved with the SHELXS [32] structure solution program using Direct Methods and refined with the SHELXL [32] refinement package using least-squares minimization.

CCDC 865364 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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