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Structure and property of unsymmetrical binuclear $[(3,5\text{-dimethylpyrazole})_2Pd_2(\mu\text{-}3,5\text{-dimethylpyrazolate})_2\text{-}(2,6\text{-dipicolinate})]$ and mononuclear $[Na_2(H_2O)_4Pd\text{-}(2,6\text{-dipicolinate})_2]$ complexes

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Abstract

This work describes the synthesis and characterization of two Pd(II) complexes $[(3,5\text{-Hdmpz})_2Pd_2(\mu\text{-}3,5\text{-dmpz})_2(2,6\text{-dipic})]$ (**1**) and $[Na_2(H_2O)_4Pd(2,6\text{-dipic})_2]$ (**2**) (3,5-Hdmpz = 3,5-dimethylpyrazole and 2,6-dipic = 2,6-pyridinedicarboxylate). The X-ray molecular structure determination shows that **1** is a binuclear complex bridged by two 3,5-dmpz units and is completely unsymmetric since one palladium atom contains two protonated 3,5-Hdmpz ligands and the other one contains the 2,6-dipic^{2-} unit that coordinates in a bidentate fashion. The central six-member Pd_2N_4 core shows a boat-like conformation where the palladium atoms are positioned at the vertices of the boat. The molecules are assembled in an extended zigzag one-dimensional network formed through 3,5-Hdmpz-carboxylate (2,6-dipic^{2-}) hydrogen bonds. The packing of complex **2** is constructed of cationic Na^+–H_2O and anionic Pd-2,6-dipic^{2-} units joined together to form an extended two dimensional network. Alternate short and long Na–Na distances are observed in the cationic layer. A detailed quantum-chemical calculation on the Na-chains in **2** has been made. Complex **1** shows a luminescence property and antimicrobial activity against *Bacillus subtilis*, *Escherichia coli* and *Aspergillus niger* where the MIC has been found to be 100 μg/mL for all three species.

Keywords: Mono- and binuclear palladium(II) complexes; Crystal structures; 1D and 2D hydrogen bonded and coordination network; Computational study; Luminescence property; Antimicrobial activity

1. Introduction

Pyrazole-type heterocycles are well known as versatile ligands that can interact with metal ions in several fashions: neutral monodentate (pyrazole-N), anionic monodentate (pyrazolato-N) or *exo*/*endo*-bidentate (pyrazolato-N,N′) [1–5]. Such ligands are extensively used for designing functional models for bimetallic biosites whereby the metal atoms are held in close proximity, allowing a wide range of intermetallic separations [6]. A number of potential properties e.g., catalytic activity and bioactivity of such compounds have been identified [7,8]. In this context, the binuclear platinum-group complexes stabilized through a pyrazolate bridge(s) are of much significance owing to their interesting structural features and reactivity toward Lewis acid metal complexes [9]. The use of palladium pyrazolyl complexes as precursors for the synthesis of new palladium containing rings, and further use of such rings as molecular subunits of supramolecular assemblies are well documented in the recent literature. A recent study reports the use of mono- and binuclear complexes having terminal 3,5-dmpz (hydrogen bond acceptor) and 3,5-Hdmpz (hydrogen

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bond donor) ligands bound to palladium centres [10]. These compounds have been used as starting materials to achieve organic-organometallic hydrogen bonded networks by reaction with carboxylic acids. A study on a Pd_2N_4 core incorporating a diazo ligand is also known [11]. We report herein a new complex [(3,5-Hdmpz)$_2$Pd$_2$(μ-3,5-dmpz)$_2$(2,6-dipic)] (**1**) that affords an unsymmetrical 1D chain, and the binuclear units assemble in a zigzag way propagated through 3,5-Hdmpz-carboxylate (2,6-dipic^{2-}) hydrogen bonds. The asymmetric unit of this compound shows a central Pd_2N_4 six-member heterocycle that adopts a distorted boat-like conformation.

We considered it of further interest to use another substituted pyrazole, 3-methyl-1-phenylpyrazole (3-me-1-phpz). An earlier report has been made that 3-me-1-phpz displaces acetonitrile from [$PdCl_2(CH_3CN)_2$] to form *trans*-[Pd(N$_3$)$_2$(3-me-1-phpz)$_2$] via [PdCl$_2$(3-me-1-phpz)$_2$] [12]. In addition, the unsymmetrical N-substituted pyrazoles offer the possibility of formation of cyclometallated products [13]. With the aim to generate a pyrazole based product, we carried out the reaction of $PdCl_2(CH_3CN)_2$, 3-me-1-phpz and NaH2,6-dipic. The compound [Na$_2$(H$_2$O)$_4$Pd(2,6-dipic)$_2$] (**2**) is formed without incorporation of the 3-me-1-phpz ligand. A couple of precedents of Pd-2,6-dipic^{2-} complexes are known in the literature [14,15]. The single crystal X-ray analysis shows that **2** is stabilized through cationic Na^+–H_2O and anionic Pd-2,6-dipic^{2-} units to form an extended two-dimensional coordination polymer. A detailed study of the molecular and electronic structures coupled with experimental results obtained from IR, UV–Vis, ^1H NMR and mass spectral studies have been made. Data on the luminescence property and antimicrobial activity of **1** are also presented.

2. Experimental

2.1. Materials

Palladium chloride ($PdCl_2$) used in the complex was obtained from Arora-Matthey Limited (India). $PdCl_2(CH_3CN)_2$ was prepared according to the literature procedure [16]. 3,5-Dimethylpyrazole was purchased from Fluka. Pyridine-2,6-dicarboxylic acid and 3-methyl-1-phenylpyrazole were obtained from Lancaster. Sodium hydroxide was a Merck product. All solvents were dried and kept over molecular sieves prior to use. Double distilled water was used throughout.

2.2. Physical measurements

Elemental analysis was carried out in a 2400 Series-II CHN analyzer, Perkin–Elmer, USA. IR spectra were recorded on a Nicolate Magna IR 750 Series-II IR spectrophotometer. The ^1H NMR spectra were recorded on a 300 MHz Bruker Avance DPX 300 machine, Switzerland in $(CD_3)_2SO$ and D_2O solvent with TMS as the internal standard at room temperature. The mass spectra were recorded on a Qtof Micro YA263 mass spectrometer. Absorption and luminescence spectra were studied on a Shimadzu UV2100 UV–VIS recording spectrophotometer and a Perkin–Elmer LS 55 Luminescence spectrometer, respectively.

2.3. Computational details

A detailed quantum-chemical calculation on the Na-chain as retrieved from the crystal geometry of **2** was made at the DFT-level of B3LYP/6-31G$^+$(d,p) [17]. These sets of calculations have been performed using the GAUSSIAN 03 program suite [18].

2.4. Synthesis of the complexes

2.4.1. Synthesis of [(3,5-Hdmpz)$_2$Pd$_2$(μ-3,5-dmpz)$_2$(2,6-dipic)] (1)

0.026 g (0.1 mmol) of $PdCl_2(CH_3CN)_2$ was dissolved in 10 cm^3 of methanol. To this deep orange solution was added a 10 cm^3 methanolic solution of 3,5-Hdmpz (0.020 g, 0.2 mmol). The resulting mixture was stirred for 10 min at room temperature and filtered off to remove any suspended material. To the filtrate, 15 cm^3 aqueous solution of NaH2,6-dipic (0.040 g, 0.2 mmol) was added and the solution was warmed at 50 °C for 30 min. The light yellow solution was cooled to room temperature. Deep yellow crystals suitable for X-ray diffraction were obtained after 7 days in a 71% yield based on Pd. *Anal.* Calc. for **1**: C, 42.60; H, 4.34; N, 16.57. Found: C, 42.26; H, 4.23; N, 16.43%. IR spectrum (KBr disk, ν/cm^{-1}): 3123 (w), 3090 (w), 1683 (s), 1673 (s), 1621 (s), 1573 (m), 1414 (m), 1375 (s). ^1H NMR spectrum (300 MHz, d_6-DMSO) δ: 2.43 (CH_3, s), 1.66 (CH_3, s), 6.08 (H, s), 2.43 (CH_3, s), 1.86 (CH_3, s), 5.93 (H, s); 2.11 (CH_3, s), 2.30 (CH_3, s), 5.44 (H, s), 12.96 (N–H,s), 2.20 (CH_3, s), 2.23 (CH_3, s), 5.61 (H, s), 17.21 (N–H, s); 7.90, 7,92 (H, d), 8.21, 8.24, 8.27 (H, t), 7.77, 7.79 (H, d). Mass spectrum (CH_3CN/H_2O): 762.28.

2.4.2. Synthesis of [Na$_2$(H$_2$O)$_4$Pd(2,6-dipic)$_2$] (2)

$PdCl_2(CH_3CN)_2$ (0.052 g, 0.2 mmol) was dissolved in 5 cm^3 of DMF. To the deep orange solution was added a solution of 3-me-1-phpz (0.063 g, 0.4 mmol) in 5 cm^3 of DMF under stirring. After 10 min, an aqueous solution of NaH2,6-dipic (0.080 g, 0.4 mmol) was added to the mixture and the solution stirred for 1 h. The resulting yellow solution was filtered off to remove any suspended material. Yellow crystals suitable for X-ray diffraction were obtained after 5 days in a 40% yield based on Pd. *Anal.* Calc. for **2**: C, 30.73; H, 1.10; N, 5.12. Found: C, 30.81; H 1.16; N, 5.14%. IR spectrum (KBr disk, ν/cm^{-1}): 3528 (s), 3426 (w), 1683 (s), 1633 (s), 1411 (m), 1376 (s). ^1H NMR spectrum (300 MHz, d_6-DMSO) δ: 7.90, 7.92 (H, d), 8.18, 8.20, 8.23 (H, t), 7.75, 7.72 (H, d). Mass spectrum (H_2O): 546.28.

Table 1
Crystal data and details for structure refinement for **1** and **2**

Formula	$C_{27}H_{33}N_9O_4Pd_2$	$C_{14}H_6N_2Na_2O_{12}Pd$
Formula weight	760.42	546.59
Crystal system	monoclinic	triclinic
Space group	$C2/c$ (no. 15)	$P\bar{1}$ (no. 2)
a (Å)	29.848(6)	6.4521(13)
b (Å)	11.649(2)	6.5686(13)
c (Å)	17.713(4)	11.661(2)
α (°)	90.00	106.19(3)
β (°)	94.18(3)	93.57(3)
γ (°)	90.00	107.21(3)
V (Å^3)	6143(2)	447.68(19)
Z	8	1
D_{calc} (g/cm^3)	1.645	2.027
μ (mm^{-1})	1.219	1.158
$F(000)$	3056	268
Temperature (K)	293	294
λ (Å) (Mo Kα)	0.71073	0.71073
$\theta_{\text{min–max}}$ (°)	2.2–25.0	3.3–25.0
Reflections collected	5511	1631
Independent reflections [R_{int}]	5403 [0.055]	1541 [0.061]
Observed data [$I > 2\sigma(I)$]	3429	1522
Data/restraints/parameters	5403/0/372	1541/0/142
Goodness-of-fit on F^2	0.973	1.114
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0602$ $wR_2 = 0.1289$	$R_1 = 0.0437$ $wR_2 = 0.1197$
R indices (all data)	$R_1 = 0.1108$ $wR_2 = 0.1451$	$R_1 = 0.0442$ $wR_2 = 0.1205$

*2.5. Crystal structure determination and structural refinement of complexes **1** and **2***

Crystals of dimensions $0.19 \times 0.21 \times 0.49$ mm (**1**) and $0.19 \times 0.26 \times 0.55$ mm (**2**) were mounted on a Siemens P4 4-circle-diffractometer which was equipped with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Unit cell dimensions and intensity data were measured at 293 K for both **1** and **2**. All calculations for data reduction, structure solution and refinement were done by standard procedures (SHELXS-97) [19], (SHELXL-97) [20]. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques on F^2. All the hydrogen atoms of **1** and **2** were included at calculated positions and refined isotropically. Information concerning crystallographic data collection and refinement of the structures are summarized in Table 1.

3. Results and discussion

3.1. Synthesis and spectroscopic characterization of the complexes

The complexes reported here are formed by the process of slow crystallization. Sometimes it takes a long time to isolate the desired product. Moreover, the reported complexes are sparingly soluble in common organic solvents. We have tried to crystallize the products from an optimum dilution so that we could strike a balance between improved crystal quality and time of crystallization. Compound **1** [(3,5-Hdmpz)$_2$Pd$_2$(μ-3,5-dmpz)$_2$(2,6-dipic)] has been obtained as a deep-yellow crystalline solid by addition of 3,5-Hdmpz and NaH2,6-dipic to $PdCl_2(CH_3CN)_2$ in methanol at 50 °C without addition of the hydroxide ion or other bases. Compound **2** was obtained also as a well-formed deep-yellow crystalline solid by the addition of 3-me-1-phpz and an aqueous solution of NaH2,6-dipic to a DMF solution of $PdCl_2(CH_3CN)_2$. The formation of compound **2** instead of a substituted pyrazolate one is the result of a failed experiment. It clearly points out the relevance of the strength of the bidentate chelate (Hdipic$^-$) in determining the course of the reaction. In the absence of 3-me-1-phpz, no product is obtained. However, a similar compound, *trans*-$Na_2[Pd(2,6\text{-dipic})_2 \cdot 2H_2O$, was obtained earlier by the addition of K_2PdCl_4 to a warm aqueous solution of pyridine-2,6-dicarboxylic acid and maintaining the pH to 6 with 1 N NaOH solution. The yellow crystalline product was characterized by elemental analysis, ^{1}H NMR, IR and UV–Vis spectroscopy [14]. There is no report of the single crystal X-ray structural study of this compound. The IR spectrum of complex **1** displays all the characteristic bands of the coordinated 3,5-Hdmpz and 2,6-dipic^{2-} ions. These include a pair of strong bands at ca. 1683 and 1621 cm^{-1} corresponding to $\nu_{\text{asym}}(COO^-)$ vibrations of the bonded and free carboxylates, respectively, and another pair for $\nu_{\text{sym}}(COO^-)$ at 1414 and 1375 cm^{-1}, respectively for the bonded and free carboxylate groups. The ring-breathing mode for 3,5-Hdmpz is observed at 1573 cm^{-1}. The relatively low value of the ν(N–H) frequency at 3123 cm^{-1} indicates that the N–H $\cdots$ O hydrogen bonds observed in the X-ray structure of the compound must be quite strong. The IR spectrum of complex **2** is quite simple. The bands at 1683 and 1411 cm^{-1} correspond to the $\nu_{\text{asym}}(COO^-)$ and $\nu_{\text{sym}}(COO^-)$ vibrations, respectively, of the bonded carboxylates whilst that for the free carboxylates are observed at 1633 and 1376 cm^{-1}. A strong band at 3528 cm^{-1} is observed for the ν(O–H) frequency, which reveals the presence of the solvent water molecules. The ESIMS of compounds **1** and **2** corroborate well with their simulated spectra. The ^{1}H NMR spectrum of **1** at room temperature shows three sets of signals, one for the bridging 3,5-dmpz ($\delta = 2.43$ (CH$_3$, s), 1.66 (CH$_3$, s), 6.08 (H, s), 2.43 (CH$_3$, s), 1.86 (CH$_3$, s) 5.93 (H, s) ppm) and another one for the terminal 3,5-Hdmpz groups ($\delta = 2.11$ (CH$_3$, s), 2.30 (CH$_3$, s), 5.44 (H, s), 12.96 (N–H, s) 2.20 (CH$_3$, s), 2.23 (CH$_3$, s) 5.61 (H, s), 17.21 (N–H, s) ppm). The third set is for the 2,6-dipic^{2-} moiety ($\delta = 7.90$, 7.92 (H, d), 8.21, 8.24, 8.27 (H, t) and 7.77, 7.79 (H, d) ppm). The ^{1}H NMR spectrum of **2** at room temperature shows signals only for the 2,6-dipic^{2-} unit comparable to the signals observed in complex **1**.

3.2. Description of the crystal structures

As can be seen from the asymmetric unit (Fig. 1), **1** is a binuclear Pd(II) complex that contains two 3,5-Hdmpz,

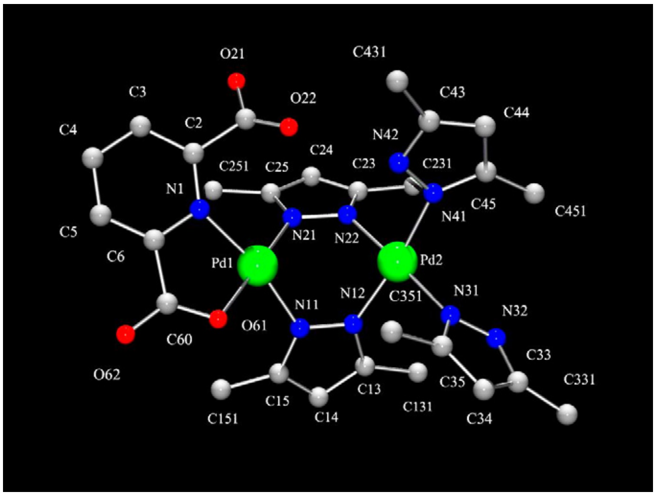

Fig. 1. Molecular structure of complex $[(3,5\text{-Hdmpz})_2Pd_2(\mu\text{-}3,5\text{-dmpz})_2(2,6\text{-dipic})]$ (**1**). All hydrogen atoms have been omitted for clarity.

two 3,5-dmpz and a 2,6-dipic unit. Pd2 contains two Hdmpz units as coordinating ligands whereas Pd1 contains only one 2,6-pyridinedicarboxylate unit. The two 3,5-dmpz units bridge the metal centres in a bidentate fashion. Table 2 lists selected bond distances and angles. Despite the presence of bridging 3,5-dmpz groups between the metal atoms, the intermetallic separation (3.397 Å) indicates no metal–metal bond. The intermetallic distance is comparable to $[\{Pd_2(\mu\text{-}3,5\text{-dmpz})(3,5\text{-dmpz})(3,5\text{-Hdmpz})\}_2]$ [9] (3.4020 Å) and $[Pd(\mu\text{-}3,5\text{-dmPz})(\eta^3\text{-}C_3H_4)]_2$ [21] (3.343 Å) but is longer than the corresponding distances in $[Pd_2Cl_2(\mu\text{-}3,5\text{-dmpz})_2(PMe_2Ph)_2]$ [22] (3.115(1) Å) and $[\{Pd_2(CH_2C_6H_4P(o\text{-tolyl})_2\text{-}\kappa C,P)_2(\mu_3\text{-}3,5\text{-dmpz-}N,N',C^4)_2Ag(\mu\text{-}ClO_4)\}_2]$ [4] (3.2297(7) Å). Each palladium atom is in an almost square-planar coordination environment. The central six-member $[Pd(\mu\text{-}3,5\text{-dmpz})_2Pd]$ core is non-planar with Pd–$N_{3,5\text{-dmpz}}$ distances between 1.981(7) and 2.007(7) Å. These fall in the range found in other Pd and Pt complexes with this type of ligand [4,22–28]. The N–Pd–N angles are 87.8(3)° and 86.2(3)° between the 3,5-dimethylpyrazolate groups. The Pd_2N_4 six-member ring reveals a boat-like conformation; the dihedral angle formed by the best least-squares coordination planes of the metals being 89.7°. The metal atoms are positioned at the vertices of the boat and the angle between the planes containing the Pd–N–N–Pd fragments is 73.8° [29]. The boat folding of the Pd_2N_4 core has also been observed earlier for other pyrazolato bridged palladium complexes [9,30,31]. The mean deviation of the plane constructed by the four nitrogen atoms N11, N12, N21 and N22 is 0.0589 Å. The displacement of Pd1 towards N22 is 0.9391 Å while that for Pd2 towards N22 is 1.1145 Å. All of the 3,5-Hdmpz, 3,5-dmpz and 2,6-dipic^{2-} ligands are planar, within experimental error. Comparable bond lengths within the 3,5-dimethylpyrazolate rings suggest substantial delocalization upon deprotonation. The bow angles between the planes N11–N12–N21–N22 and N12–Pd2–N22, N11–Pd1–N21 are 40.73°, 50.12°, respectively. This difference reflects the unsymmetrical environment around the metal centres. The dihedral angles between the monodentate 3,5-Hdmpz ligands N31–N32–C33–C34–C35 and N41–N42–C43–C44–C45, and bridging 3,5-dmpz ligands N11–N12–C13–C14–C15 and N21–N22–C23–C24–C25 are 91.1° and 90.3°, respectively. The ligand 2,6-dipic^{2-} coordinates to Pd1 in a bidentate fashion through its pyridine nitrogen and one carboxylate oxygen atom while the other carboxylate remains free. To achieve internal charge balance, the non-coordinated oxygen atom O21 of the free carboxylate group must be deprotonated. The complex exhibits a zigzag chain configuration of the 1D network through intermolecular 3,5-Hdmpz-carboxylate hydrogen bonds. This arrangement results from the *trans* orientation of one protonated pyrazole and a free carboxylate group of 2,6-dipic^{2-} moieties. This network is clearly affected by the intermolecular and intramolecular hydrogen bonding occurring between the atoms N32–H32 ⋯ O21 and N42–H42 ⋯ O22, respectively, which is responsible for the conformation and stability.

Table 2
Selected bond lengths (Å) and angles (°) in complex **1** with esds in parentheses

Bond lengths (Å)			
Pd1–O61	2.018(6)	Pd2–N41	2.053(6)
Pd1–N1	2.059(7)	N11–N12	1.368(10)
Pd1–N11	2.007(7)	N21–N22	1.375(10)
Pd1–N21	1.996(7)	N31–N32	1.364(10)
Pd2–N12	2.002(6)	N41–N42	1.360(10)
Pd2–N22	1.981(7)	N32–H32	0.8604
Pd2–N31	2.029(7)	N42–H42	0.8597
Bond angles (°)			
O61–Pd1–N1	81.1(2)	Pd1–O61–C60	111.9(6)
O61–Pd1–N11	91.1(3)	Pd1–N1–C2	132.2(6)
O61–Pd1–N21	177.1(2)	Pd1–N1–C6	107.7(5)
N1–Pd1–N11	169.1(3)	Pd1–N11–N12	123.0(5)
N1–Pd1–N21	99.5(3)	Pd1–N11–C15	127.4(6)
N11–Pd1–N21	87.8(3)	Pd2–N12–N11	116.6(5)
N12–Pd2–N22	86.2(3)	Pd2–N12–C13	134.4(6)
N12–Pd2–N31	91.0(3)	Pd1–N21–N22	120.6(5)
N12–Pd2–N41	170.5(3)	Pd1–N21–C25	131.5(5)
N22–Pd2–N31	176.9(3)	Pd2–N22–N21	120.4(5)
N22–Pd2–N41	91.2(3)	Pd2–N22–C23	127.7(6)
N31–Pd2–N41	91.7(3)		
Hydrogen bonds (Å, °)			
D–H–A	D–A	H–A	∠D–H–A
N32–H32–O21	2.740(10)	1.8800	173.00
N42–H42–O22	2.720(10)	2.0200	138.00

The X-ray structure and numbering scheme for complex **2** are shown in Fig. 2. Selected bond lengths and angles are listed in Table 3. The crystal is built up by centrosymmetric Pd-2, 6-$(dipic)_2{}^{2-}$ anions and Na^+ cations hexacoordinated by four water molecules and two carboxylate oxygens belonging to the dipic^{2-} moiety. The 2,6-dipicolinate ion chelates in a bidentate fashion to the palladium atom and the resulting coordination around the palladium is square planar with Pd–N1 and Pd1–O1 bond distances of 2.028 and 2.004 Å, respectively. The arrangement of the oxygen atoms around the Na^+ ion is approximately octahedral

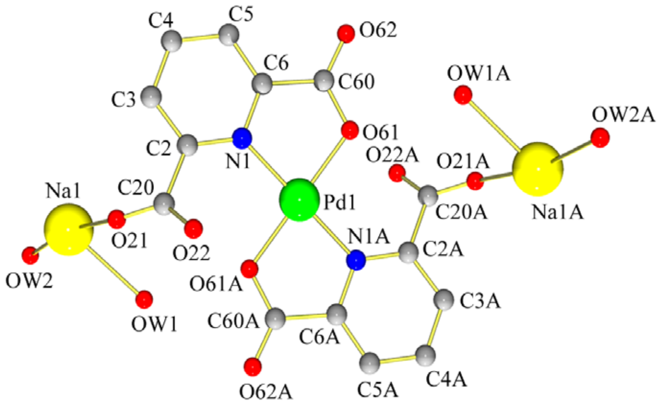

Fig. 2. Molecular structure of complex $[Na_2(H_2O)_4Pd(2,6\text{-dipic})_2]$ (**2**). All hydrogen atoms have been omitted for clarity.

Table 3
Selected bond lengths (Å) and angles (°) in complex **2** with esds in parentheses[a]

Bond lengths (Å)			
Pd1–O61	2.004(3)	Na1–O21	2.384(5)
Pd1–N1	2.028(4)	Na1–O2_a	2.410(4)
Na1–OW1	2.478(5)	Na1–OW1_b	2.541(5)
Na1–OW2	2.411(4)	Na1–OW2_d	2.509(5)
Bond angles (°)			
O61–Pd1–N1	81.43(16)	O61_c–Pd1–N1	98.57(16)
O61–Pd1–O61_c	180.00	N1–Pd1–N1_c	180.00
OW1–Na1–OW2	106.28(17)	OW1–Na1–O21	99.90(18)
OW1–Na1–O2_a	77.99(16)	OW1–Na1–OW1_b	89.99(16)
OW1–Na1–OW2_d	169.71(17)	OW2–Na1–O21	85.61(16)
O2_a–Na1–OW2	171.5(2)	OW1_b–Na1–OW2	90.51(16)
OW2–Na1–OW2_d	84.01(15)	O2_a–Na1–O21	101.00(16)
OW1_b–Na1–O21	170.04(18)	OW2_d–Na1–O21	80.63(17)
OW1_b–Na1–O2_a	82.11(16)	O2_a–Na1–OW2_d	91.80(15)
OW1_b–Na1–OW2_d	89.85(16)	Na1–OW1–Na1_b	90.01(17)
Na1–OW2–Na1_d	95.99(15)		

[a] Symmetry transformations used to generate equivalent atoms: $a = -x, 1 - y, 1 - z$; $b = -x, 2 - y, 2 - z$; $c = 1 - x, 1 - y, 1 - z$; $d = 1 - x, 2 - y, 2 - z$.

as shown in Fig. 2. The cation coordination can be rationalized in terms of bond valence [32,33], which assumes that the total charge of the cations has to be saturated by the summation of the separated bond valence s_i of each coordinated atom or ion. The quantity s can be calculated by the expression $s = \exp[(r_0 - r)/B]$, where r is the actual Na–O distance, and r_0, B are parameters empirically determined ($r_0 = 1.803$ and $B = 0.37$) [34]. In the present structure, the value of 1.04 for $\sum s_i$ obtained for the sodium cation is in good agreement with the expected charge value of 1.00. The packing arrangement of **2** consists of cationic Na^+-water and anionic Pd-2,6-dipic^{2-} units to form a two-dimensional coordination-polymeric network as shown in Fig. 3. In the cationic part, solvent water molecules OW1 and OW2 link the Na atoms to form a –Na1–H_2O–Na– zigzag chain where there are two types of Na–Na distances, 3.656 and 3.550 Å. The chains line up in the *ab*-plane and are parallel to the Pd-2,6-dipic^{2-} sheet. Finally, every Pd-2,6-dipic^{2-} layer links two adjacent parallel Na-layers through the oxygen atoms (O2 and O21) to form the two dimensional network. No short contacts between Pd(II) atoms exist, the minimum Pd–Pd distance being 6.569 Å.

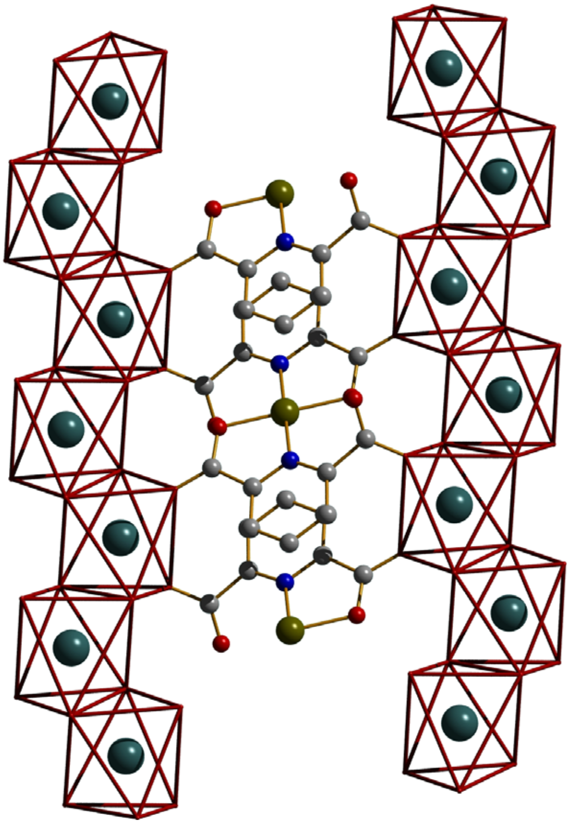

Fig. 3. The perspective view of the packing of $[Na_2(H_2O)_4Pd(2,6\text{-dipic})_2]$ (**2**) comprising of cationic Na^+–H_2O and anionic Pd-2,6-dipic^{2-} units.

A detailed analysis of the crystal geometries reveals an interesting phenomenon in compound **2**. The 1D Na-chain in the crystal shows a significant distortion with short and long alternating Na–Na distances [Na–Na (type 1) = 3.550 Å; Na–Na (type 2) = 3.655 Å]. Examples of Na–H_2O chains are known in the literature whereby alternating Na–Na distances in a particular system do not show any difference. The Na–Na distance in polyhedral $[Na_3(O)_4(H_2O)_{10}]^{3+}$ is 3.477(8) Å [35] and that in the cationic Na–H_2O-malonate chain is 3.786 Å [36]. A marginal difference in Na–Na distances (3.566(3) and 3.534(4) Å) has been reported in $[(L^3VO_2Na)_2(H_2O)_7]_\infty$ (L^3 = a schiff base ligand) [37]. Our observation is very similar to that known in the famous case of Peierls-distortion in *trans*-polyacetylene that leads formation of a gap near the Fermi-energy and leads to insulating behavior of polyacetylene [38,39]; for *trans*-polyacetylene, C=C (type 1) = 1.355 Å; C–C (type 2) = 1.54 Å. Thus, our system with a 1D Na-chain also exhibits a Peierls-distortion. To quantify the hypothesis, we performed a detailed quantum-chemical calculation on the Na-chain as retrieved from the crystal geometry at the DFT-level of B3LYP/6-31G$^+$(d,p). The calculations are performed on a finite sized

Fig. 4. Highest molecular orbital plot for the Na-chain: clearly seen electron localization over alternate Na–Na distances leading to alternate short and long distances supporting the Peierls-distortion in **2**.

(10 atoms) Na-atom chain. The Na atom, having one unpaired electron in the $3s^1$ orbital, shares a similarity to the polyacetylene chain which has one unpaired electron in the p_π orbital. The highest occupied molecular orbital (HOMO) indeed shows a localization of electrons on each alternating short bond and thereby supports the existence of alternating short and long Na–Na bonds with a Na–Na–Na angle of 127.11° (Fig. 4). It is true that the Na-chains do not have conventional bonding in terms of organic molecules. The Na–Na distance in the BCC Na-crystal is 3.72 Å. Of course, Na-crystal is bound through bonding interactions albeit weak in the solid state. One cannot argue that Na-atoms are packed with just hard-sphere packing with no Na–Na interactions. Anyway, in our system the Na–Na bonds are smaller than that in Na-crystal, rendering the possibility of weak interactions between the Na-atoms in the 1D-chains. Otherwise, one could see such localization on each atom and not on the bonds.

3.3. Absorption spectra and luminescence properties

Luminescent Pd(II) complexes are exceedingly rare if compared to the analogous Pt(II) luminophores [40]. With few notable exceptions [41,42], most systems emit only at low temperature and with low efficiency [43–46]. It has been also recognized that when incorporated in polynuclear complexes, Pd(II) centers may lead to partial quenching of luminescence. Nevertheless despite these unfavorable premises, several photoactive palladium(II) complexes recently have been the subject of accurate photophysical studies. The absorption spectrum of complex **1** in DMF solution is dominated by an intense band with the maxima at 267 nm in the ultraviolet region ($\varepsilon = 1.56 \times 10^4\ M^{-1}\ cm^{-1}$) which is assigned to a spin-allowed π–π^* transition. At longer wavelength in the range 320–400 nm, a shoulder is obtained which may be attributed to a metal-to-ligand charge transfer (MLCT) transition. Complex **2** also exhibits a strong band centered at 274 nm with a molar absorption coefficient of $7.19 \times 10^3\ M^{-1}\ cm^{-1}$. In addition, the lower energy band in the range 320–450 nm is assigned to the spin allowed MLCT transition. In the fluorescence emission spectrum of a solution of **1** in DMF (5.0×10^{-6} M) at room temperature, on excitation at 270 nm, the emission peaks are observed at 410 and 430 nm in the visible region and these are independent of the concentration of the solution. A value for quantum efficiency $\Phi_F = 0.04$ has been calculated using *p*-cresol in cyclohexane as a standard. The aqueous solution of compound **2** is very weakly emissive with a Φ_F value of 6.0×10^{-3} (measured against *p*-cresol in cyclohexane).

3.4. Antimicrobial activity

The antimicrobial activity of compound **1** was determined against *Bacillus subtilis*, *Escherichia coli* and *Aspergillus niger* in a medium of nutrient and Czapek-dox broth, respectively for bacteria and mold. 0.1 mL of cell suspension (5.0×10^5 cfu/mL) from 18 h cell culture of bacteria grown on nutrient agar at 37 °C was added per 5 ml of the medium. For *A. niger*, spore suspension was added instead of cell suspension. The compound was dissolved in a mixture of 1:1 DMF and absolute ethanol. The tubes were incubated at 37 °C for 24 h for the growth of the bacteria and at 30 °C for 48 h for mold. The lowest concentration of the compound that resulted in complete inhibition of the visible growth after incubation was recorded as the minimum inhibitory concentration (MIC). The MIC of the compound against *B. subtilis*, *E. coli* and *A. niger* has been found to be 100 μg/mL.

4. Conclusion

In conclusion, we have here shown two palladium derivatives, $[(3,5\text{-Hdmpz})_2Pd_2(\mu\text{-}3,5\text{-dmpz})_2(2,6\text{-dipic})]$ and $[Na_2(H_2O)_4Pd(2,6\text{-dipic})_2]$ which form hydrogen bonded 1D and 2D coordination networks, respectively. Compound **1** has been obtained as a homobimetallic complex bridged by two 3,5-dmpz units without addition of any external base. The central Pd_2N_4 core adopts a boat-like conformation. Compound **2** on the other hand, forms a 2D coordination polymeric network constructed of cationic Na^+–water and anionic Pd-2,6-dipic^{2-} units. Quantum-chemical calculation shows that alternate short and long Na–Na distances observed are due to Peierls-distortion in the Na-chains.

The binuclear compound **1** has been investigated as an inhibitory agent against microbial organisms and shows luminescence property with a Φ_F value of 0.04.

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Appendix A. Supplementary material

Full details of the crystal structure analyses of **1** and **2** have been deposited with the Cambridge Crystallographic Data Center, (CCDC Nos. 299284 and 299285). Copies may be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk or on the www.ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2006.05.030.

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