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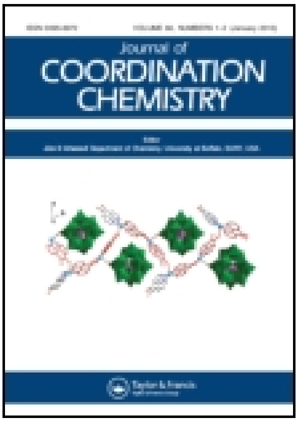

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Coordination complexes based on 4-aminobenzonitrile with different dimensionalities

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Coordination complexes based on 4-aminobenzonitrile with different dimensionalities

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Reaction of 4-aminobenzonitrile with different transition metal ions in the presence of chloride provides metal complexes of different dimensionalities. Whereas platinum forms a 0-D mononuclear complex $\{[PtCl_2(4\text{-}ABN)_2\}$ **1**, three new coordination polymers $\{[Zn(4\text{-}ABN)_2(H_2O)_2](ClO_4)_2\}_n$ **2**, $\{[Cu(4\text{-}ABN)_2(MeOH)_2](ClO_4)_2\}_n$ **3**, and $\{Cd(4\text{-}ABN)Cl_2\}_n$ **4** have been synthesized and characterized.Complexes **2** and **3** crystallize in 1-D polymeric chains, whereas **4** forms a 3-D coordination network, based on fused 12-membered rings of cadmium and chloride. A topological analysis of **4** reveals a uninodal five-connected network with the point (Schlafli) symbol of $(4^4 \times 6^6)$ and the *nov* (5/4/08) topology. All the isolated complexes were characterized by IR, elemental, and X-ray single crystal structural analyses. Complexes **1**, **2,** and **4** were additionally characterized by NMR spectroscopy.

Keywords: Self-assembly; Supramolecular chemistry; Coordination polymer; 4-Aminobenzonitrile

1. Introduction

In coordination polymers, the use of polypyridine-, amine-, and carboxylate ligands is advantageous [1–9] because of the extra stability associated with metal-pyridine and metal-carboxylate bonds and the greater flexibility shown by these types of ligands. Curiously, nitriles are not much explored for the construction of coordination polymers. The common nitriles used for the synthesis of polymers are tetracyanoethylene (TCNE) [10–14], tetracyanoquinodimethane [15–18], dicyanamide (DCM) [19–21], and tricyanomethanide [20–23]. The use of other nitriles having more than one type of donor is scarce [24–35]. However, 4-aminobenzonitrile (4-ABN) has been used as a linker to generate a few polymeric metal complexes [36–41]. Here, we report platinum(II), copper(II), zinc(II), and cadmium(II) complexes with extended structural networks involving 4-ABN. Though **1** has been synthesized in its monomeric form, two other coordination polymers, **2** and **3**, self-assemble as a 1-D chain, while **4** has a 3-D structure with a network of 12-membered

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*Corresponding author. Email: suman@iiti.ac.in fused rings of cadmium and chloride. The bridging 4-ABN has the capability to form complexes of different dimensionalities with different metal ions.

2. Experimental

2.1. *Materials and instrumentation*

Solvents and reagents were obtained from commercial sources (Aldrich) and were used as received. Infrared spectra (4000–500 cm^{-1}) were recorded with a Bio-Rad FTS 3000MX instrument in KBr pellets. Elemental analyses were carried out with a ThermoFlash 2000 elemental analyzer. ^{1}H and ^{13}C NMR spectra (in CD_3OD and in DMSO-d_6) were measured on a Bruker 400 MHz spectrometer at an ambient temperature.

2.2. *X-ray crystallography*

Single crystal X-ray structural studies of **1**, **2**, **3,** and **4** were performed on a CCD Agilent Technologies (Oxford Diffraction) SUPER NOVA diffractometer. Data were collected at 293(2) K using graphite-monochromated MoKα radiation ($\lambda_\alpha = 0.71073$ Å). The strategy for data collection was evaluated using the CrysAlisPro CCD software. The data were collected by the standard phi-omega scan techniques, and were scaled and reduced using CrysAlis Pro RED software. The structures were solved by direct methods using SHELXS-97 and refined by full matrix least-squares with SHELXL-97, refining on F^2 [42].

The positions of all atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The hydrogens were placed in geometrically constrained positions and refined with isotropic temperature factors, generally $1.2U_{eq}$ of their parent. The crystal and refinement data are summarized in table 1, and selected bond distances and angles are shown in table 2.

2.3. *Synthesis*

2.3.1. Synthesis of $[Pt(4\text{-}ABN)_2Cl_2]\cdot 4DMF$ (1). To an aqueous solution of $K_2[PtCl_4]$ (0.08 g, 0.2 mmol in 5 mL), a methanolic solution of 4-ABN (0.05 g, 0.4 mmol in 10 mL) was added slowly and the resulting light pink solution was stirred for 1 h. A light yellow precipitate formed which was filtered off and washed with water, followed by methanol and diethylether. The resultant yellow compound was recrystallized from DMF by slow diffusion of diethyl ether. Yield: 0.08 g 60%; IR: $\nu = 3227$ and 3194 (–NH), 2232 (–C≡N) cm^{-1} $C_{26}H_{40}Cl_2N_8O_4Pt$ (%): Calcd C, 39.30; H, 5.07; N, 14.10. Found (%): C, 39.56; H, 5.15; N, 14.01. ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 7.38$ (d, 2H, –CH = C–C≡N, $J = 8.8$), 6.60 (d, 2H, –CH = C–NH2, $J = 8.8$), 4.1 (s, 2H, $–NH_2$). Due to poor solubility of the compound no reliable data for ^{13}C NMR could be obtained.

2.3.2. Synthesis of $\{[Zn(4\text{-}ABN)_2(H_2O)_2](ClO_4)_2\}_n$ (2). Method A: A methanolic solution of 4-ABN (0.098 g, 0.83 mmol, 10 mL) was added to a solution of $ZnCl_2$ dissolved in methanol (0.056 g, 0.41 mmol, 10 mL). The resultant solution was stirred for 1 h and then colorless methanolic solution of sodium perchlorate monohydrate (0.115 g, 0.83 mmol,

Table 1. Crystal data of **1–4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{26}H_{40}Cl_2N_8O_4Pt$	$C_{14}H_{16}Cl_2N_4O_{10}Zn$	$C_{16}H_{20}Cl_2CuN_4O_{10}$	$C_{14}H_{12}Cd_2C_{l4}N_4$
Mr [g mol^{-1}]	794.65	536.58	562.80	602.88
Crystal system	Triclinic	Triclinic	Triclinic	Orthorhombic
Space group	$P\,\bar{1}$	$P\,\bar{1}$	$P\,\bar{1}$	$P\ b\ c\ a$
a [Å]	9.1614(3)	7.7545(4)	8.0499(15)	11.7892(8)
b [Å]	9.4409(2)	8.5242(4)	9.2028(15)	7.1869(4)
c [Å]	9.8628(3)	9.4489(5)	9.2204(17)	21.0629(19)
α [°]	90.814	100.348(4)	109.562(16)	90
β [°]	102.281	110.055(5)	107.257(16)	90
γ [°]	96.280	109.740(4)	105.077(15)	90
V [Å^3]	827.91(4)	520.49(5)	563.49(17)	1784.6(2)
Z	1	2	2	4
Dcalcd [mgm^{-3}]	1.594	1.712	1.658	2.244
F(000)	396	272	287	1152
GOF	1.1.08	1.124	1.122	1.323
Reflections collected/unique	5749/2911 [$R_{int} = 0.0194$]	3583/1819 [$R_{int} = 0.0170$]	3874/1981 [$R_{int} = 0.0202$]	11,426/1573 [$R_{int} = 0.0393$]
Final R indices	$R_1 = 0.0164$, $wR_2 = 0.0431$	$R_1 = 0.0228$, $wR_2 = 0.0636$	$R_1 = 0.0541$, $wR_2 = 0.1560$	$R_1 = 0.0179$, $wR_2 = 0.0440$
R indices (all data)	$R_1 = 0.0164$, $wR_2 = 0.0431$	$R_1 = 0.0238$, $wR_2 = 0.0640$	$R_1 = 0.0573$, $wR_2 = 0.1587$	$R_1 = 0.0185$, $wR_2 = 0.0442$

15 mL) was added and stirred for 10 min more. The solvent evaporated under vacuum and upon the addition of diethyl ether gives a colorless solid which was washed with water. The resultant compound was recrystallized from acetone. However, the yield of the resultant product was poor (0.06 g) and an alternative reaction methodology provides much better yield, which was adopted later on.

Method B: A methanolic solution of 4-ABN (0.098 g, 0.83 mmol, 10 mL) was added to a solution of $Zn(ClO_4)_2 \cdot 6H_2O$ dissolved in methanol (0.15 g, 0.41 mmol, 20 mL). The resultant colorless solution was stirred for 1 h. After that the solvent was evaporated under vacuum and upon the addition of diethyl ether gives a colorless solid. The resultant solid was recrystallized from acetone. Slow evaporation of the acetone solution furnished single crystals suitable for X-ray crystallographic measurements. Yield: 0.10 g 92% (method B); IR: $\nu = 3261$ and 3209 (–NH), 2231 (–C≡N) cm^{-1} $C_{14}H_{16}N_4Cl_2O_{10}Zn$ (%): Calcd C, 31.34; H, 3.01; N, 10.44. Found (%): C, 31.68; H, 3.23; N, 10.91. ^{1}H NMR (400 MHz, CD_3OD): $\delta = 7.38$ (d, 2H, –CH=C–C≡N, $J = 8.8$), 6.60 (d, 2H, –CH=C–NH_2, $J = 8.8$), 4.1 (s, 2H, $-NH_2$), $^{13}C\{^1H\}$ NMR (CD_3OD), 96.0, 120.2, 133.2, 153.0 ($C_{aromatic}$) and 113.7 (–C≡N).

2.3.3. Synthesis of $\{[Cu(4\text{-}ABN)_2(MeOH)_2](ClO_4)_2\}_n$ (3). Method A: A methanolic solution of 4-ABN (0.098 g, 0.83 mmol, 10 mL) and a solution of $CuCl_2 \cdot 2H_2O$ also dissolved in methanol (0.069 g, 0.41 mmol, 10 mL) were mixed together to obtain a brown solution. The resultant solution was stirred for 1 h and then a methanolic solution of sodium perchlorate monohydrate (0.115 g, 0.83 mmol, 15 mL) was added and stirred for 10 min more. After that the solvent was evaporated under vacuum and upon the addition of diethyl ether gave a brown solid which was washed with water. The resultant compound was recrystallized from a mixture of methanol and dichloromethane and washed with water. In this case also the yield of the resultant product was poor (0.05 g) and an improved method (method B) has been adopted.

Table 2. Bond lengths and angles of selected bonds of **1**, **2**, **3**, and **4**.

1			
Pt(1)-N(1)	2.050(2)	N(1)–Pt(1)–Cl(1)	91.22(7)
Pt(1)-Cl(1)	2.3028(7)	N(1)–Pt(1)–N#(1)	180.0(18)
		Cl(1)–Pt(1)–Cl#(1)	180.0(5)

Symmetry transformations used to generate equivalent atoms: #1 $-x,-y,-z$.

2					
Zn(1)–O(1)	2.0921(15)	N(1)–Zn(1)–N(1)#1	180.0	N(2)–Zn(1)–N(2)#1	180.000(1)
Zn(1)–N(2)	2.1245(16)	N(1)–Zn(1)–O(1)	86.89(6)	N(2)–Zn(1)–O(1)#1	90.21(7)
Zn(1)–N(1)	2.1977(16)	N(1)–Zn(1)–N(2)#1	94.54(6)	N(2)–Zn(1)–O(1)	89.79(7)
		N(1)–Zn(1)–N(2)	85.46(6)	O(1)–Zn(1)–O(1)#1	180.00(10)
		N(1)–Zn(1)–O(1)#1	93.11(6)		

Symmetry transformations used to generate equivalent atoms: #1 $-x+1$, $-y+1$, $-z+1$.

3					
Cu(1)–N(1)	1.983(3)	N(1)#1–Cu(1)–N(1)	180.00(16)	N(1)–Cu(1)–O(111)#1	91.37(16)
Cu(1)–N(2)	2.089(3)	N(1)–Cu(1)–N(2)	94.27(12)	N(2)–Cu(1)–N(2)#1	180.0(2)
Cu(1)–O(111)	2.330(4)	N(1)–Cu(1)–N(2)#1	85.73(12)	N(2)–Cu(1)–O(111)	88.69(15)
		N(1)–Cu(1)–O(111)	88.62(16)	N(2)#1–Cu(1)–O(111)	91.31(15)
		N(1)#1–Cu(1)–N(2)	85.73(12)	N(2)–Cu(1)–O(111)#1	91.31(15)
		N(1)#1–Cu(1)–O(111)	91.38(16)	O(111)–Cu(1)–O(111)#1	180.0(3)
		N(1)#1–Cu(1)–O(111)#1	88.63(16)		

Symmetry transformations used to generate equivalent atoms: #1 $-x+1$, $-y$, $-z$.

4					
Cd(1)–N(1)	2.407(2)	N(1)–Cd(1)–N(2)	82.87(9)	Cl(1)–Cd(1)–Cl(1)#2	87.02(2)
Cd(1)–N(2)	2.426(2)	N(1)–Cd(1)–Cl(2)	87.10(6)	Cl(1)–Cd(1)–Cl(2)#1	169.86(2)
Cd(1)–Cl(2)	2.5453(6)	N(1)–Cd(1)–Cl(1)	98.18(6)	Cl(2)–Cd(1)–Cl(1)	97.07(2)
Cd(1)–Cl(1)	2.5595(6)	N(1)–Cd(1)–Cl(2)#1	88.14(6)	Cl(2)–Cd(1)–Cl(2)#1	91.133(12)
Cd(1)–Cl(2)#1	2.6430(6)	N(1)–Cd(1)–Cl(1)#2	172.94(6)	Cl(2)–Cd(1)–Cl(1)#2	97.05(2)
Cd(1)–Cl(1)#2	2.6525(6)	N(2)–Cd(1)–Cl(2)	166.52(7)	Cl(2)#1–Cd(1)–Cl(1)#2	86.060(19)
Cl(1)–Cd(1)#2	2.6525(6)	N(2)–Cd(1)–Cl(1)	93.25(6)	Cd(1)–Cl(1)–Cd(1)#2	92.98(2)
Cl(2)–Cd(1)#3	2.6430(6)	N(2)–Cd(1)–Cl(2)#1	79.61(6)	Cd(1)–Cl(2)–Cd(1)#3	133.61(3)
		N(2)–Cd(1)–Cl(1)#2	92.11(7)		

Symmetry transformations used to generate equivalent atoms: #1 $-x+3/2$, $y-1/2$, z; #2 $-x+1,-y+1,-z+1$; #3 $-x+3/2$, $y+1/2$, z.

Method B: A solution of 4-ABN (0.094 g, 0.4 mmol) in methanol (10 mL) was added to a methanolic solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.075 g, 0.2 mmol, 20 mL). The resultant light brown solution was stirred for 2 h. The solvent was then evaporated under vacuum and the brown solid obtained was washed thoroughly with diethyl ether, followed by dichloromethane. The solid was recrystallized from a mixture of methanol and dichloromethane. On slow diffusion of DCM into methanol, needle-shaped brown crystals suitable for X-ray analysis were obtained.

Yield: 0.095 g 82%; IR: $\nu = 3291$(s), 3227(s) and 2233(s) cm^{-1}. $C_{16}H_{20}N_4O_{10}Cl_2Cu$ (%): C, 34.11; H, 3.55; N, 9.95. Found (%): C, 34.65; H, 3.49; N, 9.78.

2.3.4. Synthesis of $\{Cd(4\text{-}ABN)Cl_2\}_n$ (4). A solution of 4-ABN (0.06 g, 0.6 mmol) in methanol (10 mL) is added to an aqueous solution of $CdCl_2{\cdot}H_2O$ (0.06 g, 0.3 mmol, 20 mL); the resultant colorless solution was stirred for 2 h. Then the solvent was evaporated under vacuum and a white solid was obtained and washed thoroughly with diethyl ether, followed by DCM. The solid was recrystallized from acetone. Slow evaporation of acetone at room temperature yields colorless crystals suitable for X-ray analysis. Yield: 0.077 g 74%; IR: $\nu = 3238$(s), 3164(s) and 2280(s) cm^{-1}. $C_7H_6N_2Cl_2Cd$ (%): C, 27.86; H, 1.99; N, 9.29. Found (%): C, 27.36; H, 2.05; N, 9.43. ^{1}H NMR (400 MHz, DMSO-d$_6$): $\delta = 7.38$ (d, 2H, –CH=C–C≡N, $J = 8.8$), 6.60 (d, 2H, -CH=C–NH$_2$, $J = 8.8$), 4.1 (s, 2H, –NH_2), ^{13}C{^{1}H} NMR (DMSO-d$_6$), 96.0, 121.1, 133.9, 153.4 (C$_{\text{aromatic}}$) and 113.9 (–C≡N).

3. Results and discussion

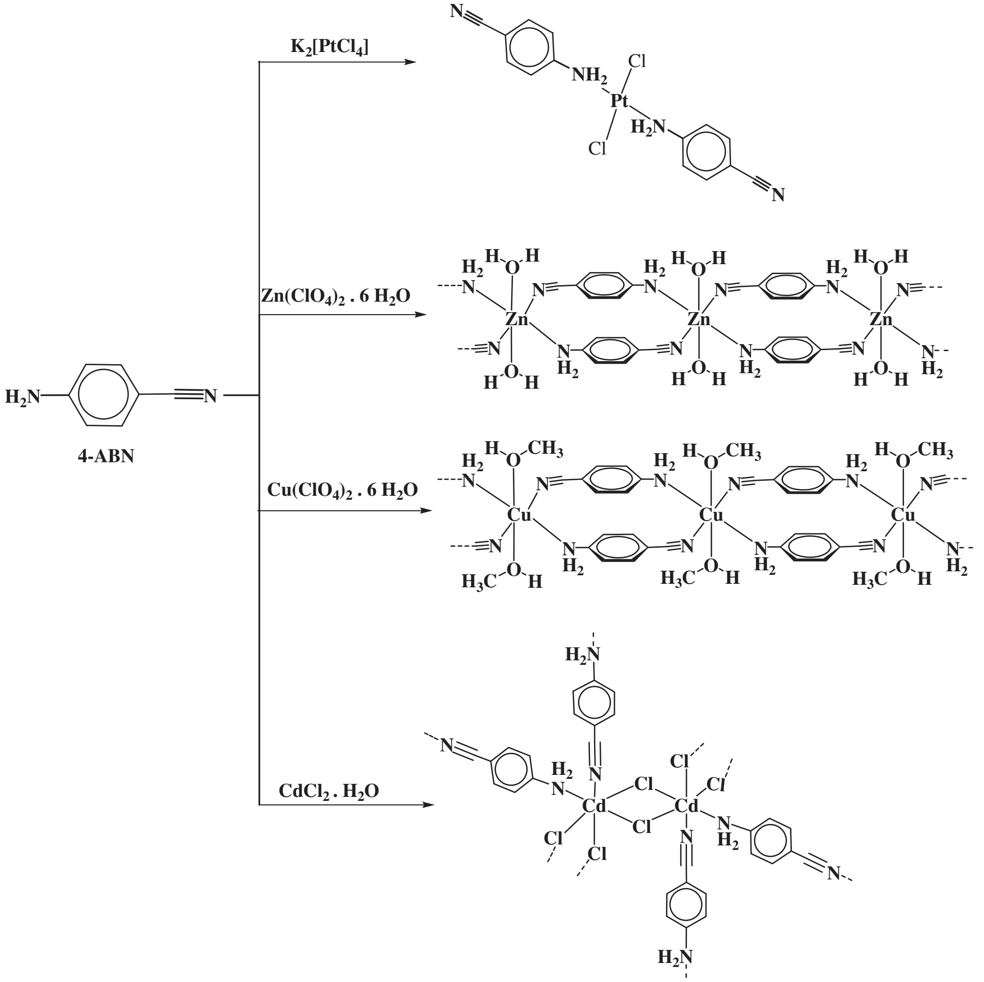
3.1. *Syntheses of 4-ABN coordination complexes*

[Pt(4-ABN)$_2$Cl$_2$]·4DMF (**1**) was prepared by stirring an aqueous solution of K_2PtCl_4 with a methanolic solution of 4-ABN (scheme 1). The resultant compound was recrystallized from DMF/diethyl ether solution. $\{[Zn(4\text{-}ABN)_2(H_2O)_2](ClO_4)_2\}_n$ (**2**) was prepared by two different methods. In the first method, zinc chloride was treated with 4-ABN and subsequent treatment with sodium perchlorate yielded the complex. However, as the yield was moderate (50%) with no incorporation of chloride in the final product, we used the direct approach (method B) by stirring a methanolic solution of zinc perchlorate in the presence of two equivalents of 4-ABN (schemes 1 and 5). The compound obtained was recrystallized from acetone which gives diffraction-quality crystals. $\{[Cu(4\text{-}ABN)_2(MeOH)_2](ClO_4)_2\}_n$ (**3**) was prepared in two different methods. However, it has been recrystallized by diffusing dichloromethane to a methanolic solution of the compound. $\{Cd(4\text{-}ABN)Cl_2\}_n$ (**4**) was prepared by stirring a solution of cadmium chloride with an equivalent amount of 4-ABN in an aqueous methanolic solution. Diffraction-quality crystals of **4** were prepared by slow evaporation of the acetone solution of the compound.

3.2. *Crystal structures*

3.2.1. Crystal structure of {[PtCl$_2$(4-ABN)$_2$}·4DMF (1). The molecular structure of **1** shows that platinum(II) is coordinated by two nitrogens of amino of 4-ABN and two chlorides (figure 1). The 4-ABN ligands coordinates in *trans* fassion. Values of the bond length distances between platinum and donating atoms are well within the range reported previously for similar complexes [43, 44]. The mononuclear unit crystallizes with four DMF.

In the packing, each monomeric unit of **1** is connected to two other units through hydrogen bonding from phenyl hydrogen to metal-coordinated chloride (C6–H6···Cl1) which results in a 1-D chain along the *c*-axis (figure 1(b)). DMF molecules of crystallization play a crucial role holding the chains together by interacting through carbonyl oxygen to hydrogen amine of one chain (N1–H1N···O1) and phenyl proton of the adjacent chain (C3–H3···O1) in the *a*-direction. As a result, a 2-D hydrogen-bonded network is generated in the *ac*-plane (figure 1(c)). The planes are further interconnected by hydrogen-bonding interactions of methyl protons of solvent molecules with nitrile nitrogen of neighboring planes (C8–H8C···N2, C9–H9C2···N2), resulting in a 3-D hydrogen-bonded network with 1-D channels in the direction of the *c*-axis and are occupied by a second set of DMF molecules, stabilized through hydrogen-bonded interactions (C10–H10···O2, N1–H2N···O2) (figure 1(d)).



Scheme 1. Schematic diagram of **1**–**4**.

3.2.2. Crystal structure of $\{[Zn(4\text{-}ABN)_2(H_2O)_2](ClO_4)_2\}_n$ (2). The crystal view around Zn^{II} is shown in figure 2a. X-ray analysis reveals that Zn^{II} is bridged by 4-ABN ligands. Zn^{II} is surrounded by 4-ABN ligands to form the equatorial plane with amine and nitrile coordinated in alternate fashion. Zn^{II} is also coordinated by two waters in apical sites. The 4-ABN bridge between zinc centers to form a 1-D chain polymer which runs along the *c*-axis. Zinc is located on the center of symmetry, coordinated octahedrally by four nitrogens of four different 4-ABN ligands and two water molecules. All metal-ligand bond distances are within expected values (2.092(1)–2.198(2) Å) [36, 45]. The angles between 4-ABN ligands also lie within the anticipated range [36].

The charge of Zn^{II} is balanced by two perchlorates. The packing of **2** is shown in figure 2 (b) with 1-D chain polymers stacked along the *b*-axis through O–H$\cdots$O hydrogen bonds between coordinated waters and entrapped perchlorates (O–O 2.804–2.775 Å). A perchlorate interconnects three strands which are parallel along the *c*-axis. One of the strands is

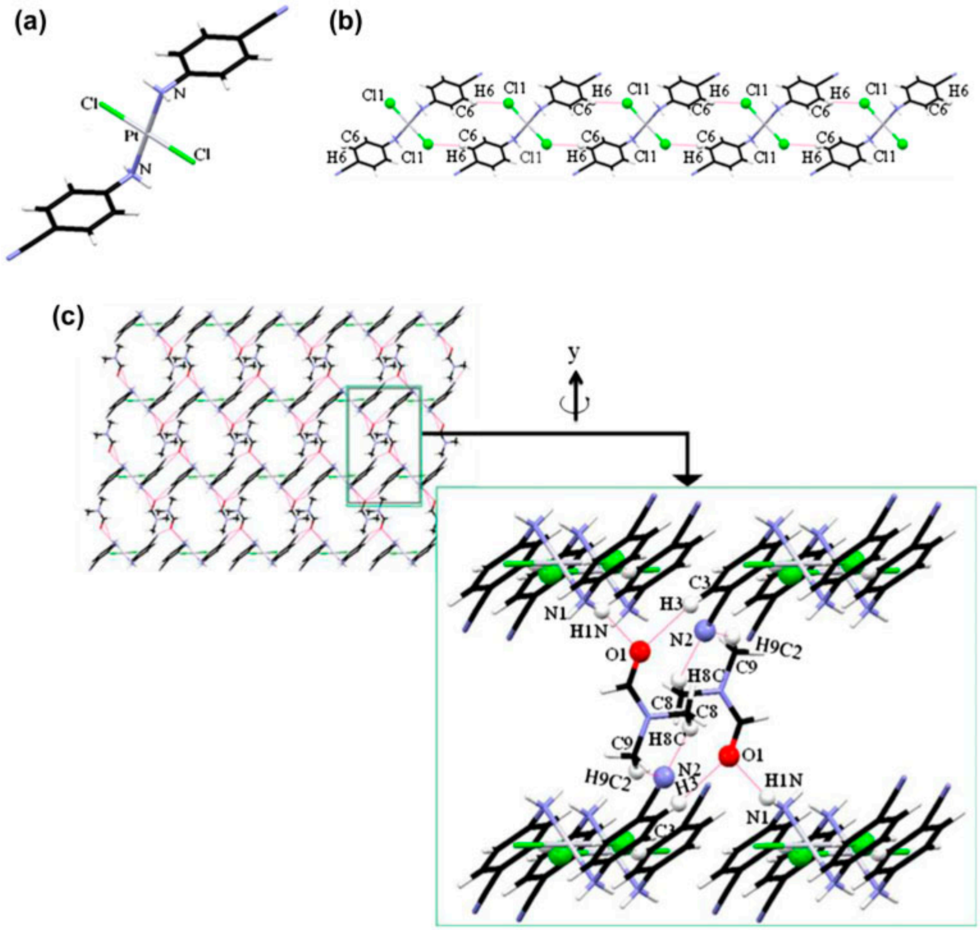


Figure 1. (a) Structure around platinum of {[PtCl$_2$(4-ABN)$_2$]} **1**, (b) mutual interaction of monomeric units to give 1-D chain, (c) and (d) interactions resulting in 2-D and 3-D supramolecular structures, respectively. Pt ions are shown in light yellow, C in black, N in blue, Cl in green, O in red and H in white. Hydrogen bonds are shown in pink (see http://dx.doi.org/10.1080/00206814.2013.783698 for color version).

connected to perchlorate via amine hydrogen (N1–H1N···O111). The second strand is connected via amine hydrogen and coordinated water (N1–H2N···O333, O1–H102···O222) and the third strand via water and phenyl hydrogen (O1–H101···O444 and C3–H3···O444) (figure 2(c)). The interactions (represented in table 3) result in a 3-D hydrogen-bonded network (figure 2(d)). The distance between two adjacent Zn^{II} in a single strand is 9.449 Å; the inter-chain distance of Zn^{II}–Zn^{II} is 7.755 Å.

3.2.3. Crystal structure of {[Cu(4-ABN)$_2$(MeOH)$_2$](ClO$_4$)$_2$}$_n$ (3).

Compound **3** has been crystallized in centrosymmetric space group $P\bar{1}$. The structure is similar to a coordination polymer involving copper and 4-ABN [36]. The structure surrounding the metal center is shown in figure 3(a). The metal–nitrogen bond distance involving the cyanide of the ligand is 1.983(4) Å, which is less than that of metal–nitrogen (amine) bond distance 2.088 (4) Å. Each copper in a polymeric chain is in a distorted octahedral coordination

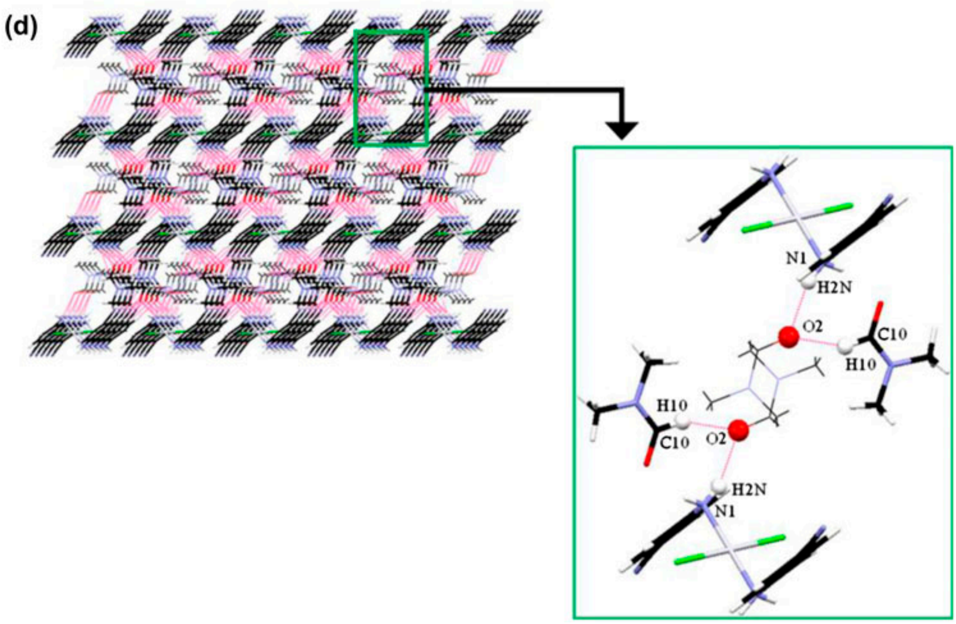


Figure 1. *(Continued)*

environment due to the Jahn Teller effect. Two axially coordinated methanols are 2.330(4) Å away from copper. The angles within CuN_4O_2 are from 85.7° to 94.3°. Perchlorates are disordered; however, they play an important role interconnecting the molecular strands which are parallel along the *b*-axis. The first strand is connected through amine and alcoholic hydrogen (N2–H2N···O22, O111–H101···O33, O111–H101···O44). The second strand is connected via phenylic hydrogen (C6–H6···O44) and the third chain via amine hydrogen (N2–H3N···O11) (figure 3b). Similar to **2**, hydrogen-bonding interactions form a 3-D network as shown in figure 3c.

3.2.4. Crystal structure of $\{Cd(4\text{-}ABN)Cl_2\}_n$ (4). The crystal view of Cd^{II} is depicted in figure 4a. Each Cd^{II} of **4** is surrounded by two μ-Cl and two bridging Cl, whereas the other two positions are occupied by two 4-ABN ligands. One 4-ABN coordinates through the nitrile nitrogen and the other through the amine nitrogen. This leads to the formation of distorted octahedral geometry around Cd^{II} center.

The bridging chloride along with cadmium forms 12-membered crown like metal-halide rings which are fused together in a *zig–zag* fashion along the *a*-axis (figure 3(b)). Metal-halide rings are further extended towards the *c*-axis via two different 4-ABN forming another metallacyclic ring, leading to a 3-D network. Because of the presence of two sets of doubly bridged metal centers, there are two four-membered (Cd_2Cl_2) rings that are inscribed within the bigger 12-membered ring itself. Each 12-membered ring shares edges with six other similar rings which are present in the same plane (figure 4(b)). The mean

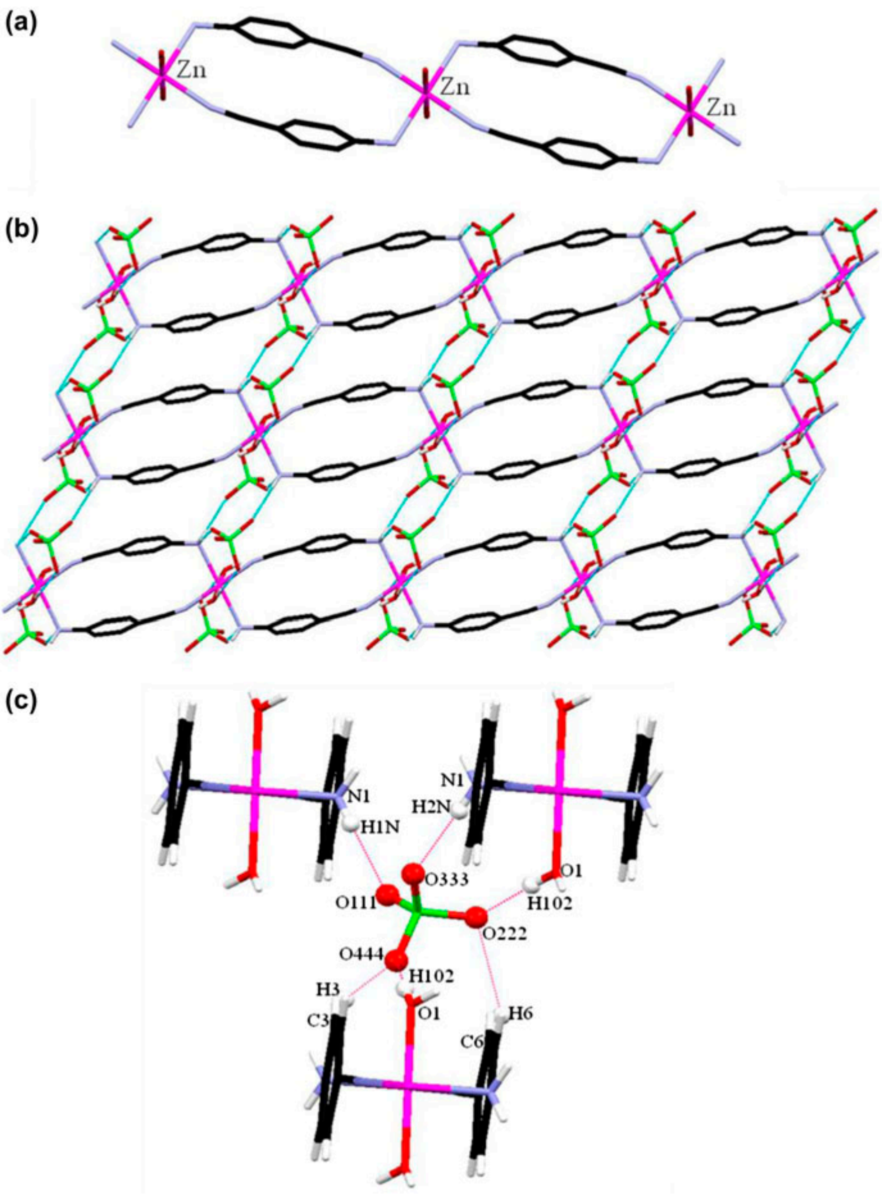


Figure 2. Structure of $\{[Zn(4\text{-}ABN)_2(H_2O)_2](ClO_4)_2\}_n$ **2.** (a) Crystal structure around zinc, (b) packing view along the *b*-axis, (c) connectivity of perchlorate to 1-D chains through the *c*-axis, (d) 3-D packing diagram of **2**. Zn ions are shown in purple, C in black, N in sky blue, Cl in green and O in red. Hydrogen bonds are shown in sky blue/pink (see http://dx.doi.org/10.1080/00206814.2013.783698 for color version).

distance between planes of the two adjacent cadmium chloride rings is 9.36 Å. The size of the metal-halide ring is 9.393×9.939 Å^2.

The cadmium chloride bond distance is 2.5465(6)–2.6431(6) Å, which is similar to those reported earlier [46, 47]. The cadmium nitrogen bond distances are also in the predictable range of 2.407(2)–2.426(2) Å [40]. However, the distorted geometry surrounding the

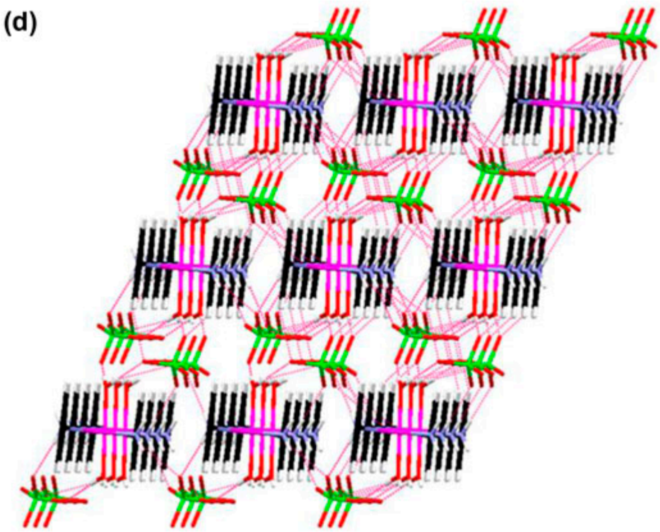


Figure 2. *(Continued)*

Table 3. Geometric features of internal hydrogen bonding interactions.

D–H···A	d(D–H)/Å	d(H···A)/Å	d(D···A)/Å	∠D–H···A/Å
1				
C(6)–H(6)···Cl(1)	0.950	2.868	3.782	161.73
N(1)–H(1)N···O(1)	0.810	2.048	2.826	160.94
C(3)–H(3)···O(1)	0.950	2.417	3.359	171.35
C(8)–H(8)C···N(2)	0.980	2.637	3.522	150.24
C(9)–H(9)C(2)···N(2)	0.979	2.629	3.515	150.51
C(10)–H(10)···O(2)	0.981	2.580	3.437	145.92
N(1)–H(2)N···O(2)	0.836	2.045	2.841	158.76
2				
N(1)–H(1)N···O(111)	0.814	2.184	2.998	177.53
N(1)–H(2)N···O(333)	0.814	2.189	3.027	174.42
O(1)–H(102)···O(222)	0.813	1.964	2.775	175.63
O(1)–H(101)···O(444)	0.782	2.035	2.804	167.93
C(3)–H(3)···O(444)	0.949	2.627	3.416	140.82
3				
N(2)–H(2)N···O(22)	0.921	2.109	3.011	166.05
O(111)–H(101)···O(33)	0.670	2.393	2.956	143.14
O(111)–H(101)···O(44)	0.670	2.680	3.182	133.96
C(6)–H(6)···O(44)	0.930	2.634	3.347	133.96
N(2)–H(3)N···O(11)	0.884	2.168	3.048	173.69

cadmium center is quite evidenced by the large deviation in N1–Cd–N2 and Cl1–Cd–Cl2 bond angles of 82.86(8)° and 97.08(2)°, respectively.

Reducing the 4-ABN ligands to centroids, the resulting 3-D network in **4** can be considered as an underlying net composed of the five-connected Cd nodes and two-connected Cl1, Cl2, and 4-ABN linkers. The topological analysis of this net assisted by TOPOS software [48] reveals a uninodal five-connected network with the point (Schlafli) symbol

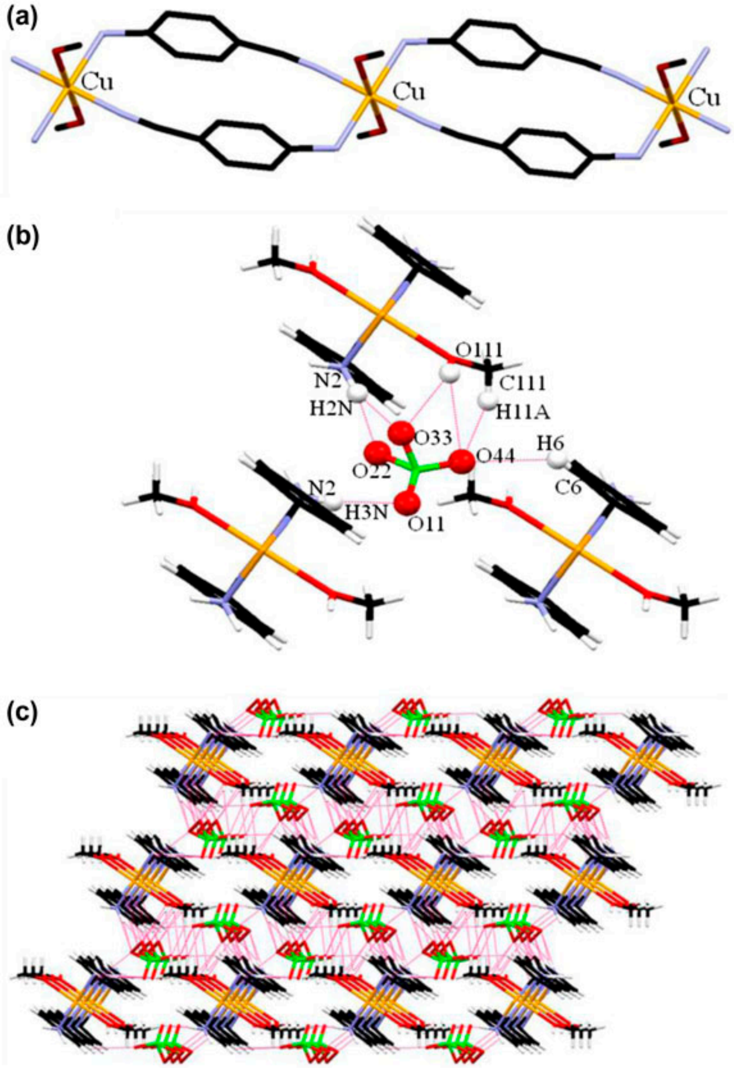


Figure 3. Crystal structure of $\{[Cu(4\text{-}ABN)_2(MeOH)_2](ClO_4)_2\}_n$ **3.** (a) Crystal structure around copper, (b) packing view along the *b*-axis, (c) packing diagram of **3**. Hydrogens are omitted for clarity. Cu ions are shown in orange, C in black, N in sky blue, Cl in green and O in red. Hydrogen bonds are shown in pink (see http://dx.doi.org/10.1080/00206814.2013.783698 for color version).

of $(4^4 \times 6^6)$ and the *nov* (5/4/08) topology according to the RCSR classification [49]. A few compounds with the *nov* topology have been recently reported [50].

3.3. *Characterization of the 4-ABN based coordination polymers*

Bulk samples of **1**–**4** are stable in air. IR spectra show the peaks for nitrile (2231–2280 cm^{-1}) which is higher than the value for free 4-ABN (2214 cm^{-1}). The trend is in agreement with

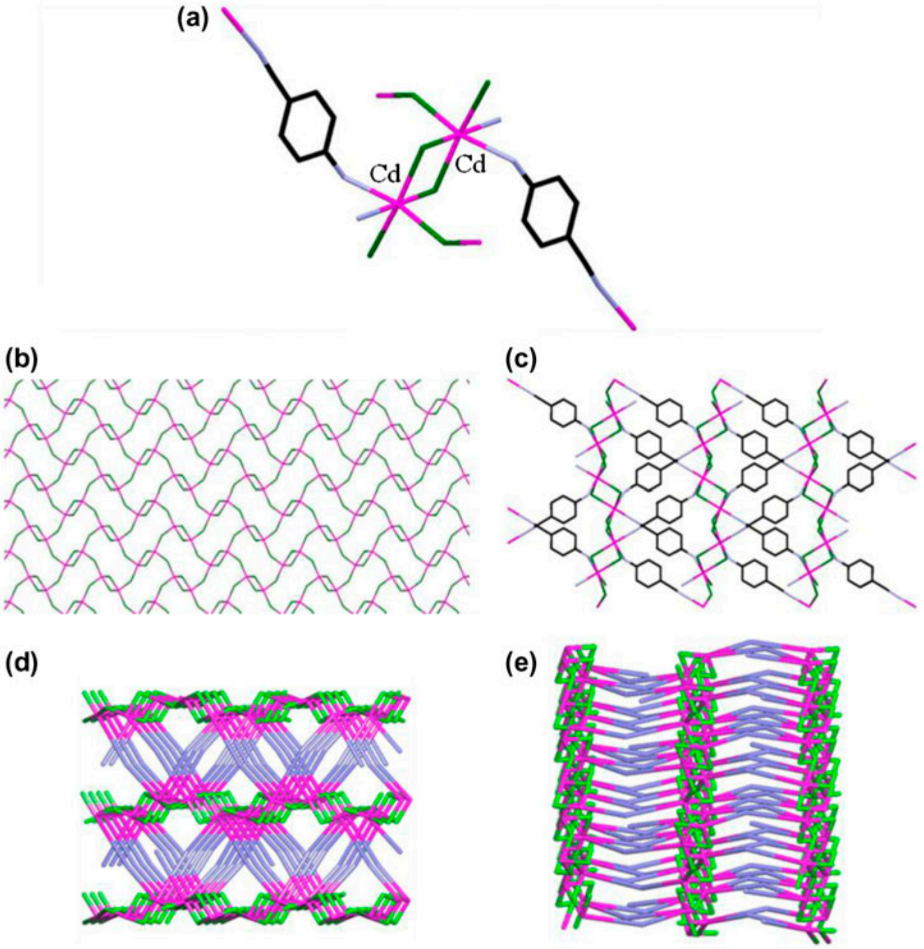


Figure 4. Crystal structure of $\{Cd(4\text{-}ABN)Cl_2\}_n$ **4.** (a) Crystal structure around cadmium, (b) plane of 12-membered rings composed of cadmium and chlorides, (c) packing view along the *b*-axis. Hydrogens are omitted for clarity. Topological representations of the underlying uninodal five-connected net in **4** with the *nov* topology and the point symbol of $(4^4 \times 6^6)$. Views along the *b* (left) and *a* (right) axes. Color codes: five-connected Cd nodes (pink), 2-connected Cl linkers (green), centroids of 2-connected 4-ABN linkers (see http://dx.doi.org/10.1080/00206814.2013.783698 for color version).

previous examples reported for nitrile ligands [51]. The increase in nitrile stretching frequency has been attributed to the increased bond polarity as the electronegativity of the nitrogen of the nitrile group increases on nitrogen-metal bond formation [52]. Moreover, the complexes are also characterized by CHN analyses and ^1H and ^{13}C NMR spectra (**1**, **2** and **4**). The spectra are within the expected range showing the purity of the samples. From the NMR data, it is not possible to infer structures of different dimensionalities since the components are in solution state.

3.4. *Thermogravimetric analyses*

From thermogravimetric analysis of **2**, there was weight loss of 7.09% (Calcd 6.70) from 43° to 146° attributed to two coordinated water molecules. There was no weight loss from

146° to 262°, where the compound started to decompose (Supplementary Material). We were unable to collect TGA data for **3,** as it tends to explode at higher temperatures.

4. Conclusions

A bridging 4-ABN has been used to synthesize metal complexes with different dimensionalities. Complex **1** is mononuclear with a square-planar geometry, while **2** and **3** form 1-D chain compounds where the metal ions are coordinated octahedrally by four 4-ABN ligands and two solvent molecules. However, **4** with chlorides forms a 3-D coordination polymer, produced by the formation of a cadmium-chloride network in the *ab*-plane along with the interconnection of these networks via 4-ABN. A topological analysis of **4** reveals a uninodal five-connected network with the point (Schlafli) symbol of $(4^4 \times 6^6)$ and the *nov* (5/4/08) topology.

Supplementary material

CCDC-908144 (for **1**), −873137 (for **2**), −873136 (for **3**) and −873135 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via http://www.ccdc.cam.ac.uk/data_request/cif.

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