

Synthesis, Crystal Structure and Characterization of Cu(II) and Cd(II) Coordination Compounds Based on Ligand 2-(3-(Pyridin-2-yl)-1H-pyrazol-1-yl)acetic Acid

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Two novel coordination compounds $[\text{Cu}_2(\text{pypya})_3(\text{H}_2\text{O})_2]\cdot\text{Cl}\cdot(\text{H}_2\text{O})_5$ (**1**) and $\{[\text{Cd}(\text{pypya})(\text{ta})_{1/2}]\cdot\text{H}_2\text{O}\}_n$ (**2**) (Hpypya=2-(3-(pyridin-2-yl)-1H-pyrazol-1-yl)acetic acid, H₂ta=terephthalic acid) were synthesized and characterized by single X-ray diffraction. Structure determination reveals that complex **1** and complex **2** crystallize in the triclinic system, with the *P*-1 space group. The asymmetric unit of **1** contains two Cu(II) ions, and their coordination modes are different. These units of complex **1** are linked together *via* hydrogen bonds and π - π interactions, and the 3D structure of complex **1** was formed. Complex **2**, a mononuclear Cd(II) coordination compound, has a 2D structure which was constructed *via* coordination bonds. TGA and fluorescence spectra analysis of complex **1** and complex **2** have also been studied. In addition, the geometry parameters of complex **1** have been optimized with the B3LYP method of density functional theory (DFT) to explain its coordination behavior. The electronic properties of the complex **1** and ligand Hpypya have been investigated based on the nature bond orbital (NBO) analysis at the B3LYP level of theory. The result verifies that the synergistic effect have occurred in the compound.

Key Words : Coordination compound, TGA, Fluorescence spectra, DFT calculations

Introduction

In recent years, much attention has been paid to the design and construction of metal-organic coordination complexes.¹⁻⁶ One reason is that the structure of these complexes is novel. The other reason is that these complexes have many potential applications in, for example, magnetism, gas separation, optoelectronics and biomimetic materials.⁷⁻¹¹ Studies in this field have been focused on the design and preparations of coordination complexes, as well as structure-property relationships. Among the reported organic ligands, carboxylate compounds and *N*-donor compounds are the most efficient families and play dominant roles in fabrication of coordination complexes. Hpypya and H₂ta (Scheme 1) are examples of these organic ligands. Moreover, in ligand Hpypya, the -CH₂- spacer between the pyrazole ring and carboxylate group offers flexible orientations of the carboxylate arm, favoring the formation of varied framework structures. In conclusion, Hpypya and H₂ta are excellent and versatile building blocks. Several studies of coordination frameworks coordinated by Hpypya or H₂ta have been reported.¹²⁻¹⁴

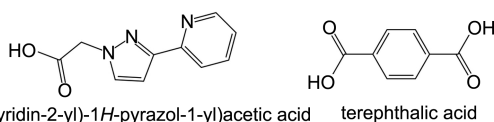
In this study, coordination sites come from N atoms and O atoms which are provided by ligand pypya anions, ta anions and water molecules. Weak interactions, such as hydrogen bonds¹⁵ and π - π interactions,¹⁶ play important

roles in the formation of complexes; they can link discrete subunits or low-dimensional entities into high-dimensional supramolecular networks.^{17,18} Herein, we report the synthesis, X-ray single crystal structure of coordination complexes $[\text{Cu}_2(\text{pypya})_3(\text{H}_2\text{O})_2]\cdot\text{Cl}\cdot(\text{H}_2\text{O})_5$ and $\{[\text{Cd}(\text{pypya})(\text{ta})_{1/2}]\cdot\text{H}_2\text{O}\}_n$, together with DFT studies to explain coordination behavior of complex **1**.

Experimental

Materials and Physical Measurements. All reagents and solvents employed were commercially available and used as it was received without further purification. Elemental analyses were determined with a Perkin-Elmer model 240C instrument. Thermo gravimetric analyses (TGA) were performed under a NETZSCHSTA 449C thermal analysis instrument from room temperature to 800 °C under a N₂ atmosphere (flow rate 10 mL·min⁻¹) at a heating rate of 10 °C·min⁻¹. Fluorescence spectra were determined on a Varian CARY Eclipse spectrophotometer.

Synthesis of $[\text{Cu}_2(\text{pypya})_3(\text{H}_2\text{O})_2]\cdot\text{Cl}\cdot(\text{H}_2\text{O})_5$ (1**).** Hpypya (30.5 mg, 0.15 mmol), NaOH (6.0 mg, 0.15 mmol) and NaCl (3.0 mg, 0.05 mmol) were dissolved in water (10 mL). Cu(NO₃)₂·3H₂O (24 mg, 0.1 mmol) was dissolved in ethanol (10 mL). The two solutions above were mixed and stirred for 30 min. The resulting mixture was kept at room temperature and X-ray-quality blue rectangular crystals of complex **1** were obtained after about three weeks. (Yield: 41.6% based on Hpypya). Elemental analysis (%) for C₃₀H₃₈ClCu₂N₉O₁₃, Found (calcd): C, 40.39 (40.25); H, 4.51 (4.25); N, 14.58 (14.09).



Scheme 1. Chemical structure of ligands Hpypya and H₂ta.

Synthesis of $\{[Cd(pypya)(ta)_{1/2}] \cdot H_2O\}_n$ (2**).** A mixture of $Cd(CH_3COO)_2 \cdot 2H_2O$ (26.7 mg, 0.1 mmol), Hpyppya (20.3 mg, 0.1 mmol), H_2ta (7.3 mg, 0.05 mmol), NaOH (8.0 mg, 0.2 mmol) and H_2O (10 mL) was placed in a 15 ml Teflon-lined stainless steel vessel and was heated to 130 °C for 72 h. Upon cooling to room temperature at a rate of 5 °C/h, X-ray-quality colorless crystals of complex **2** were obtained. (Yield 34% based on Hpyppya). Elemental analysis (%) for $C_{14}H_{12}CdN_3O_5$, Found (calcd): C, 40.93 (40.52); H, 2.94 (2.89); N, 10.25 (10.13).

Crystal Structure Determination. Single-crystal X-ray diffractions of complex **1** and complex **2** were performed on a BRUKER SMART 1000 CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection. Crystallographic data was collected with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293(2) K. The structure was solved by direct method and refined with the full-matrix least-squares technique using the SHELXS-97¹⁹ and SHELXL-97²⁰ programs. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached to C atoms were located at geometrically calculated positions to their carrier atoms and refined with isotropic thermal parameters included in the final stage of the refinement. A summary of the detailed crystallographic data and structure refinement is given in Table 1, and selected bond lengths and angles of complex **1** and complex **2** are listed in Table 2 and Table 3 respectively.

Computation Details. The calculations were carried out using Gaussian03 program suite,²¹ including optimized geometries and calculation of vibrational frequencies were

carried out at the B3LYP^{22,23} level of theory. Mulliken population analysis was also performed under this method. We employed 6-31G(d) basis set for H, C, N and O, and the LANL2DZ effective core potential (EPC) set of Hay and Wadt²⁴ for Cu. Geometry optimization was performed for complex **1**, and the attainment of energy minimum was verified by calculating the vibrational frequencies that result

Table 2. Selected bond lengths (Å) and bond angles (°) of **1**

	Experimental	Optimized
Cu(1)-O(3)	1.951(6)	1.981(3)
Cu(1)-O(7)	1.968(6)	2.006(0)
Cu(1)-N(2)	2.020(7)	2.029(9)
Cu(1)-N(1)	2.026(7)	2.034(5)
Cu(2)-O(2)	1.971(6)	1.985(7)
Cu(2)-N(5)	1.995(7)	2.023(1)
Cu(2)-N(18)	2.002(7)	2.031(4)
Cu(2)-N(4)	2.048(8)	2.163(0)
Cu(2)-N(7)	2.236(7)	2.237(3)
O(3)-Cu(1)-O(7)	91.1(2)	89.5(2)
O(3)-Cu(1)-N(2)	96.2(3)	96.8(6)
O(7)-Cu(1)-N(1)	91.3(3)	93.5(2)
N(2)-Cu(1)-N(1)	80.3(3)	80.3(3)
O(2)-Cu(2)-N(18)	89.2(3)	91.2(9)
N(5)-Cu(2)-N(18)	173.2(3)	172.0(3)
N(5)-Cu(2)-N(4)	79.6(3)	78.3(3)
N(18)-Cu(2)-N(4)	93.5(3)	94.9(5)
N(18)-Cu(2)-N(7)	78.7(3)	78.4(5)

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

	1	2
Empirical formula	$C_{30}H_{38}ClCu_2N_9O_{13}$	$C_{14}H_{12}CdN_3O_5$
Formula weight	895.22	414.67
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic
Space group	$P-1$	$P-1$
a (Å), α (°)	11.1068(8), 78.953(6)	4.7823(8), 78.319(2)
b (Å), β (°)	11.9974(9), 84.648(6)	10.8136(2), 82.939(2)
c (Å), γ (°)	15.9469(1), 73.592(6)	14.3253(0), 89.346(1)
Volume (Å ³)	1998.9(3)	719.9(2)
Z, Calculated density (Mg/m ³)	2, 1.487	2, 1.913
μ (mm ⁻¹)	1.201	1.547
Crystal size (mm ³)	0.04 × 0.03 × 0.02	0.03 × 0.02 × 0.02
F (000)	920	410
θ range for data collection	2.60 to 25.02°	2.64 to 25.02
Reflections collected	13256	4389
Independent reflections	7038 [$R_{int} = 0.0650$]	2536 [$R_{int} = 0.0738$]
Data/restraints/parameters	7038 / 0 / 496	2536 / 498 / 208
Goodness-of-fit on F^2	1.066	1.038
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0841$, $wR_2 = 0.2276$	$R_1 = 0.0660$, $wR_2 = 0.1283$
R indices (all data)	$R_1 = 0.1409$, $wR_2 = 0.2843$	$R_1 = 0.1012$, $wR_2 = 0.1602$
Largest diff. peak and hole	1.694 and -0.896 e. Å ⁻³	1.297 and -1.403 e. Å ⁻³

^a $R_1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$. ^b $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2) / \Sigma(wF_o^2)]^{1/2}$

Table 3. Selected bond lengths (Å) and bond angles (°) of **2**

Cd(1)-O(1)#1	2.228(6)	O(4)-Cd(1)-N(1)	84.0(3)
Cd(1)-O(2)#2	2.261(6)	O(1)#1-Cd(1)-N(2)	99.6(2)
Cd(1)-O(4)	2.298(7)	O(4)-Cd(1)-N(2)	129.8(3)
Cd(1)-N(1)	2.319(8)	N(1)-Cd(1)-N(2)	69.4(2)
Cd(1)-N(2)	2.437(7)	O(1)#1-Cd(1)-O(3)	77.7(2)
Cd(1)-O(3)	2.568(7)	O(2)#2-Cd(1)-O(3)	90.5(2)
O(1)#1-Cd(1)-O(2)#2	90.4(2)	O(4)-Cd(1)-O(3)	53.0(3)
O(1)#1-Cd(1)-O(4)	130.6(2)	N(1)-Cd(1)-O(3)	114.6(3)
O(2)#2-Cd(1)-O(4)	91.6(2)	N(2)-Cd(1)-O(3)	175.9(3)
O(1)#1-Cd(1)-N(1)	120.0(2)	O(2)#2-Cd(1)-N(2)	86.4(2)
O(2)#2-Cd(1)-N(1)	143.1(2)		

Symmetry codes: (#1) $-x+1, -y+1, -z$; (#2) $-x+2, -y+1, -z$.

in absence of imaginary eigenvalues.

Results and Discussion

Structure of $[\text{Cu}_2(\text{pypya})_3(\text{H}_2\text{O})_2]\cdot\text{Cl}\cdot(\text{H}_2\text{O})_5$ (1**).** Single-crystal X-ray diffraction analysis reveals that complex **1** crystallizes in the triclinic space group $P-1$. The asymmetric unit of **1** is composed of two Cu(II) ions, three pypya anions, one chloride ion and seven water molecules. The two Cu(II) ions are all five coordinated, and the coordination geometry around Cu(II) in complex **1** is a distorted tetragonal pyramid.

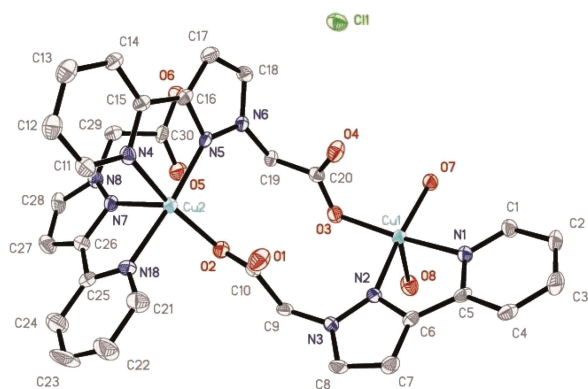


Figure 1. Coordination environment of Cu(II) atoms in complex **1** with thermal ellipsoids at 30% probability level.

The Cu1 center is coordinated by two nitrogen atoms from pypya anion, one carboxylic oxygen atom from pypya anion and two oxygen atoms from water molecules. The Cu2 center is coordinated by four nitrogen atoms from two pypya anions and one carboxylic oxygen atom from pypya anion (Figure 1). The Cu-N distances fall in the range 1.996–2.237 Å, while the Cu-O distances range from 1.952 to 1.972 Å. The Cu-N and Cu-O distances are quite similar to literature date.^{25–27} It reveals that the coordination ability of O atoms is stronger than N atoms in complex **1**.

Hydrogen bonds and π - π interactions are important in forming extended solid state structure. Chloride ion and carboxyl group which is not coordinated to metal ion are bonded to water molecules through hydrogen bonds. The information of hydrogen bonds is shown in Table 4. As shown in Figure 2, the asymmetric units are interlinked *via* the hydrogen bonding interactions and offset π - π interactions (between ring N1-C1-C2-C3-C4-C5 and ring N2-N3-C6-C7-C8, centroid-to-centroid 3.7708 Å). Thus, infinite one-dimensional (1D) 20-membered ring-shaped chains are formed. As is shown in Figure 3, these chains are further stacked together into 2D structure *via* interchain π - π stacking interactions (between ring N4-C11-C12-C13-C14-C15 and ring N5-N6-C16-C17-C18, centroid-to-centroid 3.9234 Å).

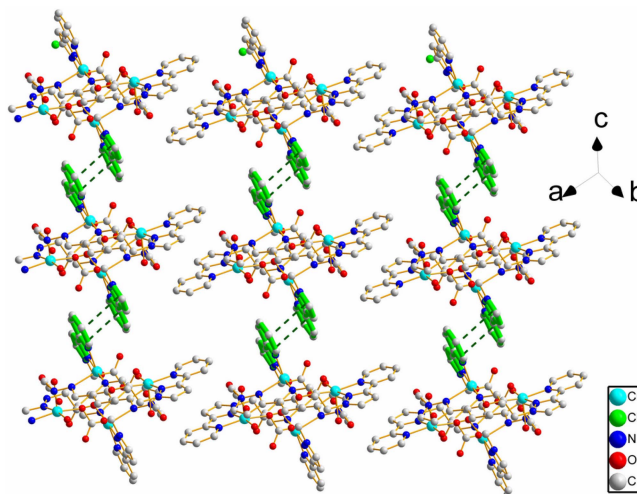


Figure 3. Interchain π - π stacking interactions of complex **1**.

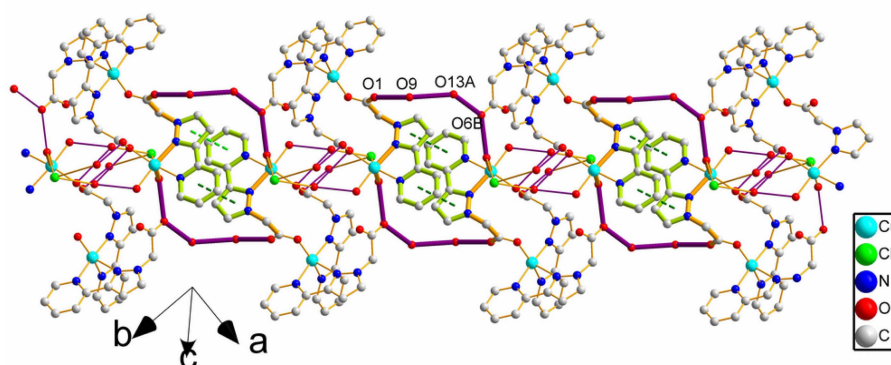


Figure 2. The 1D supramolecular architecture of **1** constructed by hydrogen bonds and π - π interactions.

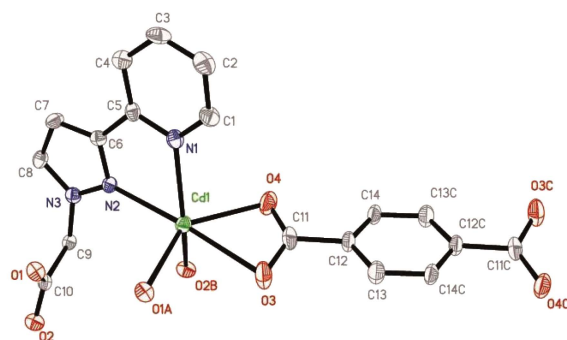
Table 4. Hydrogen bond lengths (Å) and bond angles (°) of **1**

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠DHA
O(7)-H(7C)...O(5)#1	0.85	1.95	2.6221	135
O(7)-H(7D)...O(11)	0.85	2.02	2.6769	134
O(8)-H(8B)...Cl(1) #1	0.85	2.60	3.2008	129
O(8)-H(8C)...O(6) #1	0.85	1.85	2.68	167
O(9)-H(9F)...O(1)	0.85	1.96	2.7712	159
O(10)-H(10C)...O(12) #1	0.85	2.23	2.793	123
O(11)-H(11B)...Cl(1)	0.85	2.75	3.0978	106
O(11)-H(11C)...O(3) #1	0.85	1.96	2.8031	173
O(12)-H(12A)...Cl(1)	0.85	2.36	3.1811	163
O(12)-H(12C)...O(4)	0.85	2.16	3.0041	170
O(13)-H(13C)...O(6) #1	0.85	1.95	2.7811	165
O(13)-H(13D)...O(9) #2	0.85	1.95	2.7802	165

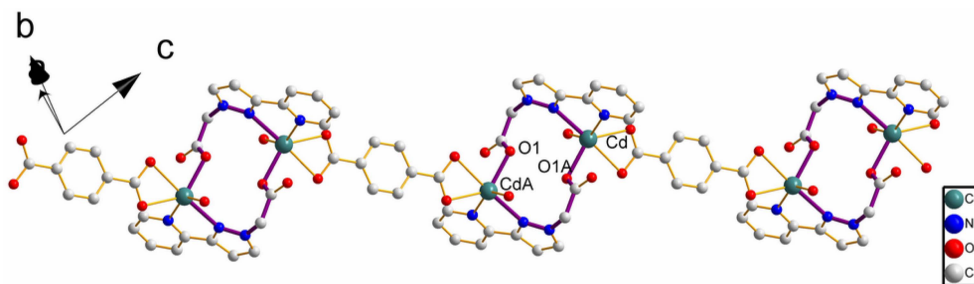
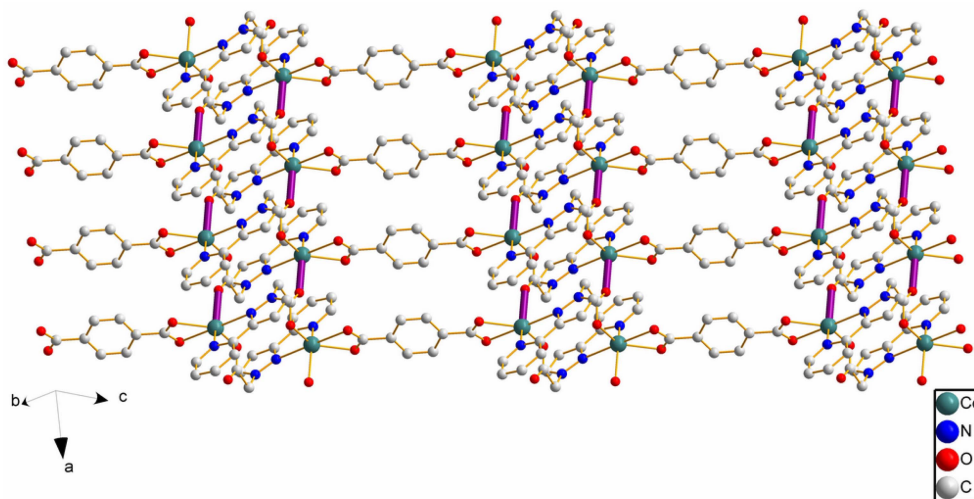
Symmetry codes: (#1) 1-x, 1-y, 1-z; (#2) -x, 2-y, 1-z.

At last, these 2D planes are stacked together into 3D structure *via* interplane π - π stacking interactions (between ring N1-C1-C2-C3-C4-C5 and ring N7-N8-C26-C27-C28, centroid-to-centroid 3.6350 Å).

Structure of $\{[Cd(\text{pypya})(\text{ta})_{1/2}] \cdot \text{H}_2\text{O}\}_n$ (1**).** Single-crystal X-ray diffraction analysis reveals that complex **2** crystallizes in the triclinic system, with space group *P*-1. The asymmetric unit of complex **2** is composed of one Cd(II) ion, one

**Figure 4.** Coordination environment of Cd(II) atom in complex **2** with thermal ellipsoids at 30% probability level.

pypya anion, half of ta anion and one water molecule. The Cd(II) center is coordinated by two nitrogen atoms from pypya anion, two carboxylic oxygen atoms from two pypya anions and two carboxylic oxygen atoms from ta anion to form a six-coordinated distorted octahedral geometry (Figure 4). The Cd-N distances fall in the range 2.320-2.438 Å, while the Cd-O distances range from 2.230 to 2.569 Å. The Cd-N and Cd-O distances agree well with reported values.²⁸ The water molecule of the asymmetric unit does not take part in coordination. It is linked to O3 *via* hydrogen bond, and the length of the hydrogen bond is 2.853 Å.

**Figure 5.** The 1D supramolecular architecture of complex **2**.**Figure 6.** The 2D network structure of complex **2**.

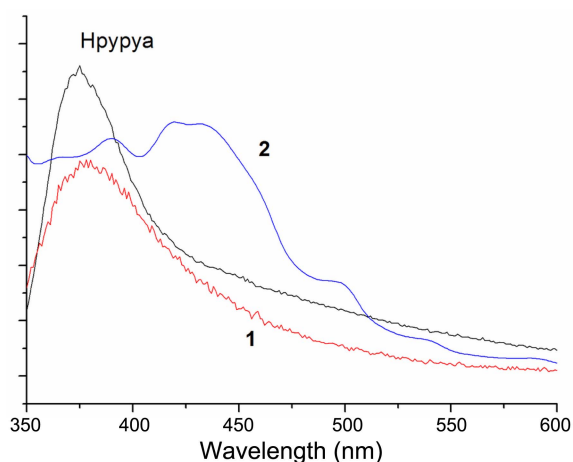


Figure 7. Solid emission spectra of complex **1**, complex **2** and ligand Hpyppa at room temperature.

As shown in Figure 5, adjacent pypya anions are bridged by Cd ions to form 12-membered rings. These Cd ions from above rings are further coordinated by carboxylic oxygen atoms from ta anions. As a result, those rings are linked by ta anions. Thus, infinite one-dimensional (1D) chains are formed. As shown in picture, adjacent chains are linked by Cd-O bonds. Thus, a two-dimensional (2D) network structure is formed (Figure 6).

Thermal Stability. Thermogravimetric analysis (TGA) was carried out in the interest of studying the thermal stability of complex **1** and complex **2**. The TGA curve of complex **1** shows two main weight loss stages (Figure S1). The initial weight loss of 13.1% in the 50-160 °C temperature range is corresponding to water molecules (14.1% calculated). When the temperature is above 350 °C, the product begins to decompose and oxidize. The residual weight percentage at the end of the decomposition of complex **1** is consistent with the formation of CuO, and the observed residue percentage is 18.7% (17.8% calculated).

The thermal decomposition process of complex **2** can be divided into two stages (Figure S2). The initial stage starts from 100 °C to 150 °C with the weight loss of 4.9%, which corresponds to the loss of water molecules (4.3% calculated). The second weight loss occurs in the range of 320 to 460 °C, where the product begins to decompose and oxidize. The residual weight percentage at the end of the decomposition of complex **2** is consistent with the formation of CdO, and the observed residue percentage is 27.8% (30.8% calculated).

Fluorescence Spectra. The fluorescence spectra of complex **1**, complex **2** and ligand Hpyppa in the solid state was measured at room temperature, with the results shown in Figure 7. The excitation wavelengths of complex **1**, complex **2** and ligand are at 320, 335 and 283 nm, respectively. The emission peaks of complex **1** and ligand Hpyppa are all at 375 nm. Considering the structures of the ligand Hpyppa and complex **1**, the emissions probably originated from the ligand-centered π - π^* transition. Coordination does not change the position of emission peak, the fluorescent quenching of Cu(II) only influences the emission strength of complex **1**.

Table 5. Mulliken atomic charges (e) for **1** and ligand pypya

Atom	1	pypya
Cu1	0.682	
Cu2	0.711	
N1	-0.652	-0.104
N4	-0.582	-0.104
N18	-0.644	-0.104
N2	-0.277	-0.457
N5	-0.368	-0.457
N7	-0.303	-0.457
O2	-0.599	-0.608
O3	-0.605	-0.608

It's known from literature²⁹ that ligand ta is non-fluorescent. Complex **2** has two emission peaks at 385 and 430 nm, respectively, probably due to two kinds of ligands pypya and ta, owning different emission peak. Coordination with Cd ions red-shifted the emission peaks of pypya and ta ligands. The result suggests that complex **2** is potential luminescent material.

Computation Results. To get an insight on the electronic structures and bonding properties of the complex **1**, calculations *via* DFT methods were carried out. The optimized bond lengths and angles are presented in Table 2. In general, the calculated bond lengths and angles are in agreement with experimental crystal data and the largest differences (~ 0.0038 nm, $\sim 1.6^\circ$) may be noticed for deviations around Cu1 and O7 atoms.

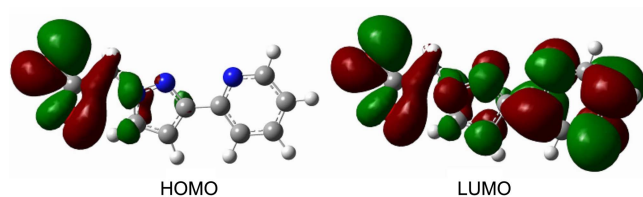
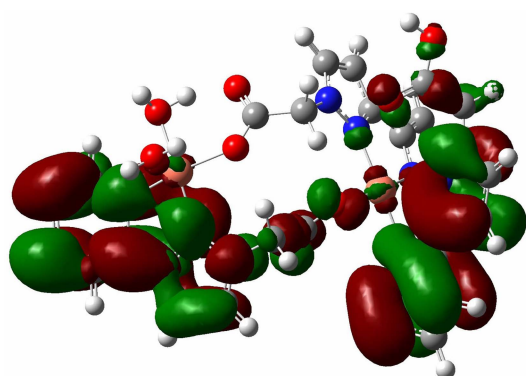
Mulliken charge of the center metal Cu changed from +2 to 0.682 and 0.711 (Table 5), it is obvious Cu has been coordinated by the ligand and its charge transferred to the ligand. Compared to the free pypya ligand, the Mulliken charges of N1, N4 and N18 are reduced while N2, N5 and N7 increased. All these show strong complexation between Cu and its coordinated atoms. It is worth to note that the net atomic charges of N1, N4 and N18 (which are chemically identical in ligand pypya) are different. So are N2, N5 and N7. These differences confirm that, in the asymmetric unit of complex **1**, the coordination modes of three pypya groups are not identical.

Based on the natural charges and electron configurations on the atoms of complex **1** and free pypya ligand which have been calculated by natural bond orbital (NBO) analysis (Table 6), one will find that, in complex **1**, the electrons distribution in the outer orbital of coordinated nitrogen atoms have been increased, the natural charges of coordinated nitrogen atoms have been decreased, compared to ligand pypya. It can be considered that coordination bond effects increase the electron density of those coordinated nitrogen atoms. As Cu(II) ions are electron-withdrawing, more electrons of ligand pypya are concentrated to coordinated nitrogen atoms.

An interesting feature, the schematic representation of HOMO and LUMO orbitals of the free pypya ligands in Figure 8, demonstrate higher MO distributions around oxy-

Table 6. Natural configurations and natural charges for the atoms of complex **1** and pypya which calculated by B3LYP method

Atom	Complex 1		Ligand Hpypya	
	Configuration	Natural charge	Configuration	Natural charge
Cu1	[core]4S(0.33)3d(9.34)4p(0.31)5p(0.01)	1.017		
Cu2	[core]4S(0.30)3d(9.31)4p(0.42)5p(0.01)	0.971		
N1	[core]2S(1.32)2p(4.18)3p(0.01)	-0.513	[core]2S(1.36)2p(4.05)3p(0.02)	-0.434
N4	[core]2S(1.33)2p(4.15)3p(0.01)	-0.487	[core]2S(1.36)2p(4.06)3p(0.01)	-0.434
N18	[core]2S(1.32)2p(4.17)3p(0.01)	-0.499	[core]2S(1.36)2p(4.06) 3p(0.01)	-0.434
N2	[core]2S(1.35)2p(3.98)3p(0.01)	-0.340	[core]2S(1.42)2p(3.82) 3p(0.02)	-0.266
N5	[core]2S(1.34)2p(3.96)3p(0.02)	-0.324	[core]2S(1.42)2p(3.82) 3p(0.02)	-0.266
N7	[core]2S(1.37)2p(3.92)3p(0.01)	-0.307	[core]2S(1.42)2p(3.82) 3p(0.02)	-0.266
O2	[core]2S(1.69)2p(5.00) 3p(0.01)	-0.701	[core]2S(1.73)2p(5.034) 3p(0.01)	-0.711
O3	[core]2S(1.72)2p(5.01) 3p(0.01)	-0.753	[core]2S(1.73)2p(5.02) 3p(0.02)	-0.711

**Figure 8.** The 3D representation of HOMO and LUMO frontal orbitals of free (pypya)⁻ ligand.**Figure 9.** HOMO orbitals of complex **1**.

gen atoms in HOMO and nitrogen atoms in LUMO frontal orbitals. As would be expected and the HOMO orbitals of complex **1** show in Figure 9, the overlapping of the electron clouds have been done between ligands with atomic orbitals of Cu metal.

Conclusion

In this work, we synthesized two novel supramolecular compounds [Cu₂(pypya)₃(H₂O)₂]-Cl·(H₂O)₅ (**1**) and {[Cd(pypya)-(ta)_{1/2}]-H₂O}_n (**2**) by solvent evaporation method and hydrothermal method respectively. In complex **1**, Cu(II) ions adopt five-coordinated geometry (CuN₂O₃ or CuN₂O₃), while hydrogen bonds and π-π interactions play crucial roles in the construction of the three-dimensional (3D) network architecture. Different from complex **1**, complex **2** is a coordination polymer. In complex **2**, Cd(II) ions, pypya

anions and ta anions are bonded together *via* coordination bonds, and two-dimensional (2D) structure are formed. The DFT calculations of the complex **1** and Ligand pypya at the B3LYP level of theory verifies that the special coordination behavior have been occurred in the complex **1**. Our results provide an effective route for the preparation of supramolecular architectures.

Supplementary Material. Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre. CCDC 963155 and 978923 contain the supplementary crystallographic data for complex **1** and complex **2**, respectively. The data can be obtained free of charge *via* <http://www.ccdc.cam.ac.uk/cperl/catreq.cgi> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Tel: (+44) 1223-336-408; Fax: (+44) 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk)

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References

- James, S. L. *Chem. Soc. Rev.* **2003**, 32, 276.
- Zhao, B.; Cheng, P.; Chen, X.; Cheng, C.; Shi, W.; Liao, D. *Angew. Chem. Int. Ed.* **2003**, 42, 934.
- Wang, R.; Hong, M.; Luo, J.; Cao, R.; Weng, J. *Chem. Commun.* **2003**, 1018.
- Zhu, K.; Xu, H. M.; Liu, G. X. *Chinese J. Inorg. Chem.* **2009**, 25, 1677.
- Cerdeira, A. C.; Simão, D.; Santos, I. C.; Machado, A.; Pereira, L. C. J.; Waerenborgh, J. C.; Almeida, M. *Inorg. Chim. Acta* **2008**, 361, 3836.
- Estrader, M.; Diaz, C.; Ribas, J.; Solans, X. *Inorg. Chim. Acta* **2008**, 361, 3963.
- Zhai, Q. G.; Li, S. N.; Gao, X.; Ji, W. J.; Jiang, Y. C.; Hu, M. C. *Inorg. Chem. Commun.* **2010**, 13, 211.
- Henninger, S. K.; Habib, H. A.; Janiak, C. *J. Am. Chem. Soc.* **2009**, 131, 2776.
- Habib, H. A.; Hoffmann, A.; Höpfe, H. A.; Steinfeld, G.; Janiak, C. *Dalton Trans.* **2009**, 10, 1742.
- Li, D. S.; Fu, F.; Zhao, J.; Wu, Y. P.; Du, M.; Zou, K.; Wang, Y. Y. *Dalton Trans.* **2010**, 39, 11522.
- Zeng, M. H.; Wang, Q. X.; Tan, Y. X.; Hu, S.; Zhao, H. X.; Long,

- L. S.; Kurmoo, M. *J. Am. Chem. Soc.* **2010**, *132*, 2561.
12. Yang, J.; Shen, L.; Yang, G. W.; Li, Q. Y.; Zhu, L. L.; Shen, W. *Inorg. Chim. Acta* **2012**, *392*, 25.
13. Li, Q. Y.; He, M. H.; Shen, Z. D.; Yang, G. W.; Yuan, Z. L. *Inorg. Chem. Commun.* **2012**, *20*, 214.
14. Figueiredo, S.; Gomes, A. C.; Neves, P.; Amarante, T. R.; Almeida Paz, F. A.; Soares, R. *Inorg. Chem.* **2012**, *51*, 8629.
15. Mareque Rivas, J. C.; Brammer, L. *Coord. Chem. Rev.* **1999**, *183*, 43.
16. Lee, C. K.; Chen, J. C.; Lee, K. M.; Liu, C. W.; Lin, I. J. *Chem. Mater.* **1999**, *11*, 1237.
17. Zeng, X. Y.; He, Y. H.; Feng, Y. L. *Chinese J. Inorg. Chem.* **2008**, *24*, 1400.
18. Liu, S. W.; Wu, X. M.; Liu, Q. X. *Chinese J. Inorg. Chem.* **2008**, *24*, 1444.
19. Bruker. *SADABS*, *SAINT*, and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA, 2002.
20. Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112.
21. Frisch, M. J. *et al.* *Gaussian 03*, revision C.02. wallingford, CT: Gaussian, Inc.; 2004.
22. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
23. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *37*, 785.
24. Vrkic, A. K.; Taverner, T.; James, P. F.; Richard, A. J. *Dalton Trans.* **2004**, *2*, 197.
25. Chawla, S. K.; Arora, M.; Nättinen, K.; Rissanen, K.; Yakhmi, J. V. *Polyhedron* **2004**, *23*, 3007.
26. Qiu, G. M.; Wang, C. J.; Zhang, Y. J.; Huang, S.; Liu, X. L.; Zhang, B. J.; Zhou, X. L. *Bull. Korean Chem. Soc.* **2012**, *33*, 2603.
27. Yang, J.; Ma, J. F.; Liu, Y. Y.; Ma, J. C.; Batten, S. R. *Cryst. Growth Des.* **2008**, *8*, 4383.
28. Liu, G. X.; Xu, Y. Y.; Ren, X. M. *Chinese J. Inorg. Chem.* **2010**, *10*, 029.
29. Barreto, J. C.; Smith, G. S.; Strobel, N. H.; McQuillin, P. A.; Miller, T. A. *Life Sciences* **1994**, *56*, 89.
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