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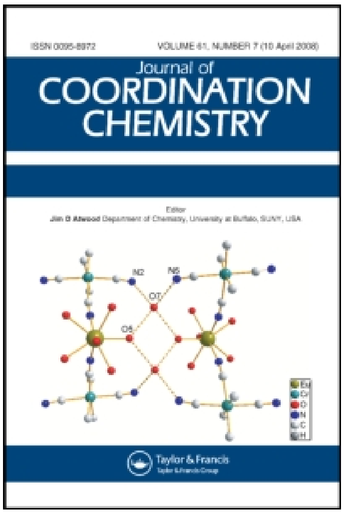

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Mixed-ligand Co^{II} and Cd^{II} complexes with 4-aminoantipyrine

Qian Wang[a]; Ming-Jie Wu[a]; En-Cui Yang[a]; Xiu-Guang Wang[a]; Xiao-Jun Zhao[a]
[a] Tianjin Normal University, Tianjin, P. R. China

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Mixed-ligand Co^{II} and Cd^{II} complexes with 4-aminoantipyrine

QIAN WANG, MING-JIE WU, EN-CUI YANG,
XIU-GUANG WANG and XIAO-JUN ZHAO*

Key Laboratory of Molecular Structure and Materials Performance, College of Chemistry
and Life Science, Tianjin Normal University, Tianjin 300074, P. R. China

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Self-assembly of 4-aminoantipyrine (AAP) and 5-nitroisophthalic acid (H_2NIP) with $Co(CH_3COO)_2$ or $Cd(NO_3)_2$ in $CH_3OH–H_2O$ at room temperature generated $\{[Co_2(AAP)(NIP)(H_2O)_8][Co(AAP)(NIP)_2(H_2O)_2](H_2O)_{4.5}\}$ (**1**) and $\{[Cd(AAP)(NIP)(H_2O)](H_2O)\}_n$ (**2**), which were further characterized by X-ray diffraction, IR spectra, elemental analysis and solid-state fluorescence spectra. The structure analysis indicates that **1** contains two individual fragments, one NIP-bridged six-coordinate binuclear Co^{II} cation and a mononuclear Co^{II} dianion. The binuclear units are connected into 1-D chains via $O–H \cdots O$ hydrogen bond interactions, which were further assembled into a 2-D supramolecular layer bridged by the mononuclear Co^{II} unit. Complex **2** is a linear NIP bridged seven-coordinate Cd^{II} polymeric chain with the terminal AAP ligands as decorations, and are further extended into 2-D network by classic hydrogen bonds and $\pi \cdots \pi$ stacking interactions. Both solid complexes exhibit emission spectra from intraligand electron transfer at room temperature.

Keywords: Crystal structures; 4-Aminoantipyrine; Self-assembly; Metal-organic coordination polymers

1. Introduction

Considerable efforts have been devoted to the design and preparation of metal-organic coordination polymers and supramolecular complexes with intriguing network topologies and diverse applications [1–4]. Of these, 4-aminoantipyrine (AAP) and its versatile Schiff base derivatives have been extensively investigated and effectively applied in biological, analytical, clinical and pharmacological areas [5–10]. Utilization of AAP and its derivatives to construct metal-antipyrine networks in crystal engineering has also become widespread [11–16]. Abdullin *et al.* [17] have investigated systematically the coordination behaviour of AAP with rare earth ions, finding that it binds poorly with metal centers, although AAP contains electron rich oxygen and nitrogen donors. Fortunately, the mixed-ligand strategy, as an effective method for constructing metal-organic frameworks, allows tuning the coordination ability of ligands to corporately bind with metal centers. To further explore AAP-based coordination

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*Corresponding author. Tel./Fax: 86-22-23540315. Email: xiaojun_zhao15@yahoo.com.cn

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behaviour, in the present article, 5-nitroisophthalic acid (H_2NIP) with diverse acidity-dependent coordination modes [18–21] was selected as co-ligand of AAP to construct Co^{II} or Cd^{II} complexes. Nitro-group with strong electron-withdrawing ability from H_2NIP is expected to contribute to the structure of the polymeric networks [22–23] by participating in the formation of hydrogen bonds. Herein we describe the preparation, structural characterization and fluorescence properties of the two complexes.

2. Experimental

2.1. *Materials and instrumentations*

All chemicals were of reagent grade, obtained from commercial sources and used without further purification. Doubly deionized water was used for the synthesis. Elemental analyses of carbon, hydrogen and nitrogen were carried out with a CE-440 (Leeman-Labs) analyzer. Fourier transform (FT) IR spectra (KBr pellets) were taken on an AVATAR-370 (Nicolet) spectrometer in the 4000–400 cm^{-1} range. Fluorescence spectra of polycrystalline powder samples were performed on a Cary Eclipse fluorescence spectrophotometer (Varian) equipped with a xenon lamp and quartz carrier at room temperature.

2.2. *Preparation of* $\{[Co_2(AAP)(NIP)(H_2O)_8][Co(AAP)(NIP)_2(H_2O)_2](H_2O)_{4.5}\}$ *(1)*

To a solution of H_2NIP (42 mg, 0.2 mmol) in methanol (5 mL) was slowly added a solution of AAP (20.3 mg, 0.1 mmol) in methanol (10 mL) with stirring for 10 min. Then an aqueous (5 mL) solution of $Co(CH_3COO)_2 \cdot 4H_2O$ (49.8 mg, 0.2 mmol) was added dropwise. The pH value of the reaction mixture was carefully adjusted to about 9.0 by slow addition of 0.1 M NaOH solution. The mixture was filtered to remove the precipitate after further stirring for about an hour. Upon slow evaporation of the filtrate at room temperature, the pink strip-shaped crystals were obtained within a week in 48% yield (based on AAP). IR (KBr, cm^{-1}): 3405w, 3273s, 1620vs, 1568w, 1534w, 1497w, 1455m, 1351vs, 1077m, 1015w, 918w, 761w, 731s. Anal. Calcd for $C_{46}H_{67}Co_3N_9O_{34.50}$: C, 37.54; H, 4.38; N, 8.56%. Found: C, 37.40; H, 4.60; N, 8.85%.

2.3. *Preparation of* $\{[Cd(AAP)(NIP)(H_2O)](H_2O)\}_n$ *(2)*

Complex **2** was synthesized by similar procedure to **1** only using $Cd(NO_3)_2 \cdot 4H_2O$ (61.7 mg, 0.2 mmol) instead of $Co(CH_3COO)_2 \cdot 4H_2O$. After the mixture was slowly evaporated at room temperature, orange strip crystals were obtained within five days in 56% yield (based on AAP). IR (KBr, cm^{-1}): 3452w, 3310w, 3248w, 1618vs, 1551m, 1456m, 1372vs, 1085m, 988w, 928w, 766m, 734s. Anal. Calcd for $C_{19}H_{20}CdN_4O_9$: C, 40.69; H, 3.59; N, 9.99%. Found: C, 40.50; H, 3.40; N, 10.22%.

2.4. *X-ray structure determination*

Single-crystal X-ray diffraction data for **1** and **2** were collected on a Bruker Apex II CCD diffractometer at 293(2) K with Mo-Kα radiation ($\lambda = 0.71073$ Å). Semi-empirical absorption corrections were applied using SADABS. The programmme SAINT was used for integration of the diffraction profiles [24]. The structures were solved by direct methods using the SHELXS programme of the SHELXTL package and refined with SHELXL [25]. All non-H atoms were modeled with anisotropic displacement parameters and refined by full-matrix least-squares methods on F^2. Generally, C-bound H atoms of the ligand were placed geometrically and refined as riding atoms. The starting positions of H attached to oxygen were located in difference Fourier syntheses and then fixed geometrically as riding atoms. Isotropic displacement parameters of the H atoms were derived from the parent atoms. The oxygen atoms of the waters of crystallization are disordered: one, O(35) in **1**, varies between two symmetry-related positions, each with a 50% occupation factor; while O(9) in **2** varies between three positions with occupancies that refined to 0.50(1) for O(9), 0.25(1) for O(9′) and 0.25(1) for O(9″). A summary of the crystallographic data and refinement conditions are listed in table 1.

3. Results and discussion

3.1. *Synthesis and IR spectra*

Considering that the drug-related AAP is very soluble in common organic solvents and aqueous solution, the judicious choice of suitable solvent for controlling the crystalline

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

	1	**2**
Empirical formula	$C_{46}H_{64}Co_3N_9O_{34.50}$	$C_{19}H_{20}CdN_4O_9$
Molecular weight	1471.85	560.79
Crystal system	Triclinic	Orthorhombic
Crystal size (mm^3)	0.35 × 0.18 × 0.08	0.45 × 0.34 × 0.30
Space group	$P\bar{1}$	*Pbca*
a (Å, °)	10.9210(15)	18.568(2)
b (Å, °)	12.5545(17)	10.3675(13)
c (Å, °)	22.309(3)	23.104(3)
α (Å, °)	94.044(2)	90.00
β (Å, °)	93.628(2)	90.00
γ (Å, °)	97.403(2)	90.00
V (Å^3)	3017.6(7)	4447.5(10)
Z	2	8
D_c (g cm^{-3})	1.620	1.675
μ (mm^{-1})	0.921	1.040
$F(000)$	1520	2256
Measured reflections	16499	22699
Independent reflections	10496	3921
R_{int}	0.0371	0.0243
Goodness of fit on F^2	1.031	1.039
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0500$, $wR_2 = 0.1205$	$R_1 = 0.0285$, $wR_2 = 0.0757$
R indices (all data)	$R_1 = 0.0927$, $wR_2 = 0.1386$	$R_1 = 0.0356$, $wR_2 = 0.0794$
Largest diff. peak and hole (e Å^{-3})	0.563 and −0.591	0.523 and −0.371

rate thus became an important factor for successful preparation of **1** and **2**. Complexes **1** and **2** are successfully achieved in a CH_3OH–H_2O mixed media with a 1 : 2 : 2 AAP/acid/metal ratio. In fact, some other molar ratios such as 1 : 2 : 1 and 1 : 1 : 2 were also tried to synthesize the title complexes with higher yields. However, the results showed that the yield at 1 : 2 : 2 molar ratio is the highest and the crystal quality is also the best. Two complexes are air stable and retain their crystalline integrity at ambient conditions for a considerable length of time. The IR spectra of the compounds have been interpreted by comparing the spectra with those of free ligands. The NH_2 bands of AAP at 3431 and 3326 cm^{-1} are slightly shifted to 3405 cm^{-1} for **1** and 3452 cm^{-1}, 3310 cm^{-1} for **2** upon complexation. The absorptions ascribed to the benzene ring of both complexes were shifted to 1568–1400 cm^{-1} compared with the free ligand peaks at 1588–1400 cm^{-1}. The absence of the characteristics peaks at ca 1700 cm^{-1} for the protonated carboxylate groups indicates complete deprotonation of the H_2NIP. The asymmetric and symmetric C=O stretching vibration bands of carboxylate groups at 1620, 1455 cm^{-1} for **1** and 1618, 1456 cm^{-1} for **2**, suggest diverse coordination modes of the NIP dianion as monodentate and chelating bidentate, respectively [26]. Sharp bands at 1588, 1351 cm^{-1} for **1** and 1567, 1372 cm^{-1} for **2** are due to the N=O vibration of the nitro-group in NIP.

3.2. *Crystal structure of* $\{[Co_2(AAP)(NIP)(H_2O)_8][Co(AAP)(NIP)_2(H_2O)_2](H_2O)_{4.5}\}$ *(1)*

Single-crystal X-ray diffraction analysis reveals that **1** contains discrete mononuclear $[Co(AAP)(NIP)_2(H_2O)_2]$ dianion, binuclear $[Co_2(AAP)(NIP)(H_2O)_8]$ cation and independent lattice water molecules. As shown in figure 1, the three Co^{II} centers

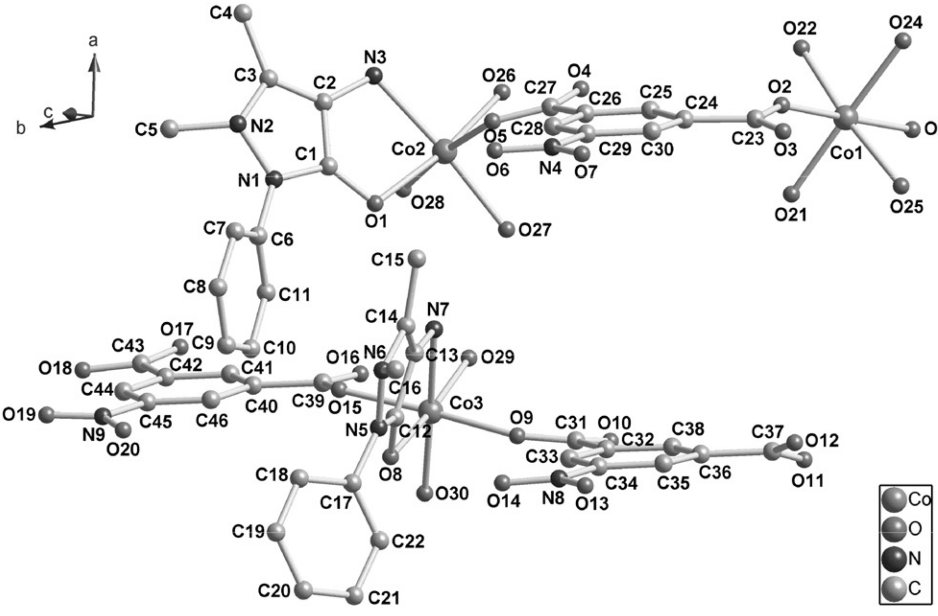

Figure 1. Coordination environment of cobalt atoms in **1** (lattice H_2O molecules are omitted for clarity).

in the asymmetric unit are all six-coordinate to AAP, NIP and/or water molecules. The crystallographically independent Co1 in the binuclear unit is coordinated to six oxygen atoms from five-coordinated water molecules and one bi-monodentate NIP dianion. The Co–O bond lengths around the central Co1 range from 2.031(3) to 2.190(3) Å and the bond angles vary from 84.81(13) to 179.21(14)° (see table 2), indicating that the geometry of Co1 is a distorted octahedron. Much different from Co1, the six-coordinate Co2 is constructed by three H_2O molecules, one bridged NIP dianion and one bidentate chelating AAP ligand. The average Co–O bond distance (2.112 Å) is shorter than that of Co–N (2.195(4) Å). Besides being coordinated by two H_2O molecules and one AAP, Co3 ion is bound to two separate NIP dianions in monodentate binding mode. Both AAPs in the fundamental unit of **1**, bind through nitrogen of the amino-group and exocyclic ketonic oxygen in bidentate chelating fashion. The separations of Co2–O1 and Co3–O8 are generally shorter than those of Co2–N3 and Co3–N7, suggesting that the binding of AAP is asymmetric. The phenyl rings C1–C6 of the antipyrine moiety are tilted by 43.1° and 41.5° with respect to the central five-member rings. The fully-deprotonated NIPs exhibit monodentate binding to the Co3 center and act as bridges in bi-monodentate fashion to connect Co1 and Co2 together with Co $\cdots$ Co separation of 8.661(7) Å.

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

Co1–O2	2.031(3)	Co1–O22	2.078(3)
Co1–O23	2.084(3)	Co1–O21	2.125(3)
Co1–O25	2.137(3)	Co1–O24	2.190(3)
Co2–O28	2.033(3)	Co2–O5	2.047(3)
Co2–O27	2.110(3)	Co2–O26	2.184(3)
Co2–O1	2.186(3)	Co2–N3	2.195(4)
Co3–O9	2.084(3)	Co3–O30	2.100(3)
Co3–O29	2.115(3)	Co3–O15	2.124(3)
Co3–O8	2.155(3)	Co3–N7	2.178(4)
O2–Co1–O22	90.19(13)	O2–Co1–O23	179.21(14)
O22–Co1–O23	89.68(13)	O2–Co1–O21	90.37(14)
O22–Co1–O21	95.57(14)	O23–Co1–O21	90.42(13)
O2–Co1–O25	95.27(13)	O22–Co1–O25	173.39(12)
O23–Co1–O25	84.81(13)	O21–Co1–O25	88.13(14)
O2–Co1–O24	89.78(13)	O22–Co1–O24	85.65(12)
O23–Co1–O24	89.43(12)	O21–Co1–O24	178.77(13)
O25–Co1–O24	90.64(12)	O28–Co2–O5	174.12(13)
O28–Co2–O27	84.65(13)	O5–Co2–O27	89.47(12)
O28–Co2–O26	88.44(12)	O(5)–Co(2)–O26	91.89(12)
O27–Co2–O26	93.41(12)	O28–Co2–O1	87.68(12)
O5–Co2–O1	92.73(12)	O27–Co2–O1	93.68(12)
O26–Co2–O1	171.57(11)	O28–Co2–N3	93.14(13)
O5–Co2–N3	92.73(13)	O27–Co2–N3	175.54(12)
O26–Co2–N3	90.39(12)	O1–Co2–N3	82.35(12)
O9–Co3–O30	94.35(12)	O9–Co3–O29	95.75(12)
O30–Co3–O29	92.03(12)	O9–Co3–O15	176.17(12)
O30–Co3–O15	85.76(11)	O29–Co3–O15	88.07(11)
O9–Co3–O8	84.76(12)	O30–Co3–O8	93.66(11)
O29–Co3–O8	174.23(12)	O15–Co3–O8	91.41(11)
O9–Co3–N7	85.45(13)	O30–Co3–N7	176.67(12)
O29–Co3–N7	91.29(12)	O15–Co3–N7	94.21(13)
O8–Co3–N7	83.02(12)		

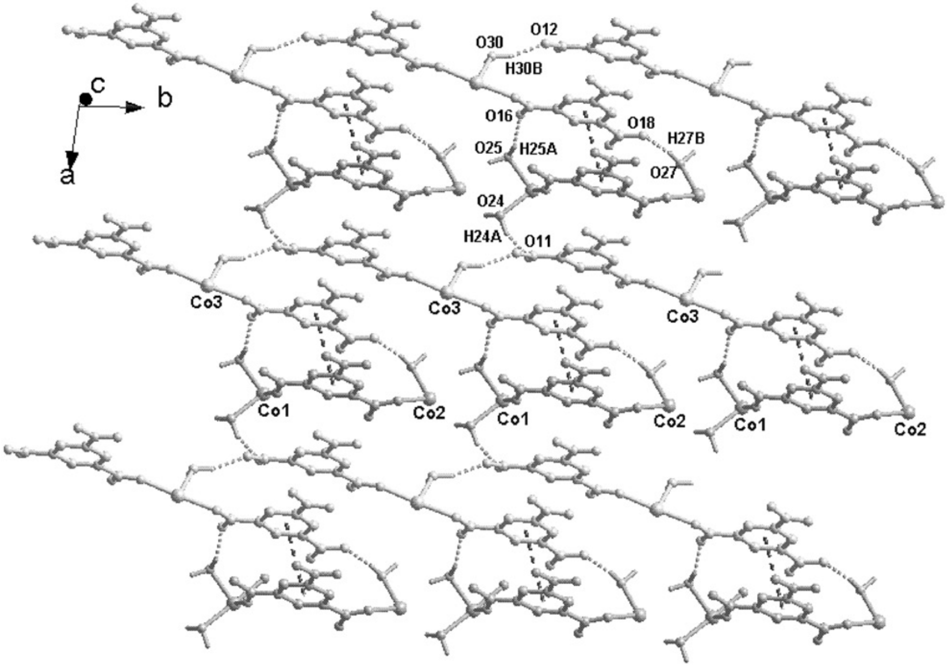

Figure 2. 2-D network of **1** formed by hydrogen bonds and π–π stacking interactions (AAP and coordinated H_2O molecules not involved in hydrogen bonds are omitted for clarity).

Additionally, adjacent mononuclear fragments are linked together through hydrogen bond interactions to yield a 1-D chain (see figure 2), in which coordinated H_2O molecules of Co3 are hydrogen bonds donors forming the O–H $\cdots$ O bond with carboxylate O atom of the monodentate coordinated NIP (see table 4). Furthermore, two parallel chains are connected via individual binuclear fragments as a bridge to generate a 2-D hydrogen bond network (see figure 2), in which the carboxylate group of NIP and the coordinated water molecules of Co1 and Co2 form O24–H24A $\cdots$ O11, O25–H25A $\cdots$ O16 and O27–H27B $\cdots$ O18. Offset $\pi \cdots \pi$ stacking interaction is also observed between the benzene rings of adjacent mononuclear and binuclear subunits. The center-to-face and center-to-center distance are 3.420 and 3.805 Å, respectively, and the angle between center-to-face and center-to-center is 21.433°. Therefore the O–H $\cdots$ O hydrogen bonds and $\pi \cdots \pi$ stacking interactions play important roles for the formation of the structure of **1**.

3.3. *Crystal structure of* $\{[Cd(AAP)(NIP)(H_2O)](H_2O)\}_n$ *(2)*

Complex **2** consists of a 1-D polymeric coordination chain, $\{[Cd(AAP)(NIP)(H_2O)](H_2O)\}_n$. The asymmetric unit of **2** (see figure 3) is made up of a central Cd^{II} ion, a neutral AAP ligand, a NIP dianion and one coordinated water molecule. The Cd^{II} is seven-coordinate to one nitrogen atom from the amino-group of AAP and four oxygen atoms from two different NIP dianions, one coordinated H_2O, and one exocyclic ketonic oxygen of AAP. The geometry around each Cd^{II} can be

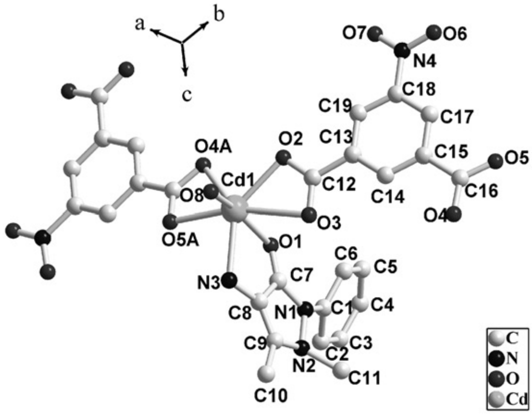

Figure 3. Coordination environment of Cd(II) centers in **2**. (Symmetry codes (A): $x+1/2$, $-y+1/2$, $-z+1$).

Table 3. Selected bond lengths (Å) and angles (°) for **2**.[a]

Cd1–O2	2.257(2)	Cd1–O8	2.331(3)
Cd1–O5A	2.333(2)	Cd1–N3	2.347(2)
Cd1–O1	2.388(2)	Cd1–O4A	2.453(2)
Cd1–O3	2.624(3)		
O2–Cd1–O8	88.07(9)	O2–Cd1–O5A	140.39(8)
O8–Cd1–O5A	98.70(9)	O2–Cd1–N3	136.47(9)
O8–Cd1–N3	87.93(9)	O5A–Cd1–N3	82.99(9)
O2–Cd1–O1	95.15(8)	O8–Cd1–O1	160.35(9)
O5A–Cd1–O1	91.15(8)	N3–Cd1–O1	76.38(8)
O2–Cd1–O4A	86.63(8)	O8–Cd1–O4A	112.69(9)
O5A–Cd1–O4A	54.66(8)	N3–Cd1–O4A	134.20(9)
O1–Cd1–O4A	86.88(8)	O2–Cd1–O3	52.78(8)
O8–Cd1–O3	85.44(9)	O5A–Cd1–O3	165.90(8)
N3–Cd1–O3	83.69(8)	O1–Cd1–O3	81.19(9)
O4A–Cd1–O3	135.87(8)		

[a] Symmetry transformations used to generate equivalent atoms: A, $x+1/2$, $-y+1/2$, $-z+1$.

described as a distorted pentagonal-bipyramidal geometry, in which $\mathrm{Cd^{II}}$ deviates from the least-squares plane generated by O2–O3–O4A–O5A toward N3 by only ca 0.1690 Å. The Cd–O bond distances fall in the range of 2.257(2) ~ 2.624(3) Å, and the bond angles around each $\mathrm{Cd^{II}}$ range from 54.66(8)° to 165.90(8)° (table 3).

Different from **1**, the NIP dianion in **2** is chelating bi-bidentate bridging, connecting the metal centers to generate a 1-D chain along [1 0 0] (figure 4). The separations of adjacent Cd ⋯ Cd centers is 10.050(1) Å, much longer than that in complex **1**. Also, the neutral AAP provides its exocyclic ketonic oxygen and amino-group nitrogen atoms to coordinate with $\mathrm{Cd^{II}}$ centers in an asymmetrically chelating bidentate fashion, locating at one side of the chain as a terminal ligand. The bond lengths of Cd–O and Cd–N are consistently longer than the corresponding values in **1**, which result from the relatively larger atomic radius of $\mathrm{Cd^{II}}$ than $\mathrm{Co^{II}}$. The phenyl ring C1–C6 of the antipyrine moiety is tilted by 41.3° with respect to the central five-member rings.

In addition, there exist two types of strong O–H ⋯ O and N–H ⋯ O hydrogen bonds and $\pi \cdots \pi$ stacking interactions, which link 1-D arrays into a 2-D layered network (figure 5 and table 4). Two N–H ⋯ O hydrogen bonds form between amino-group

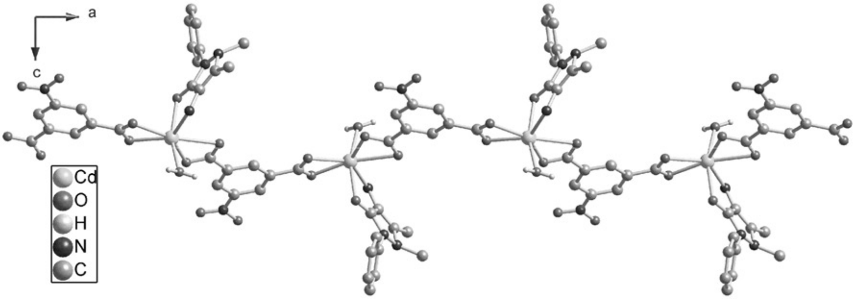

Figure 4. 1-D chain of **2** along [1 0 0] direction.

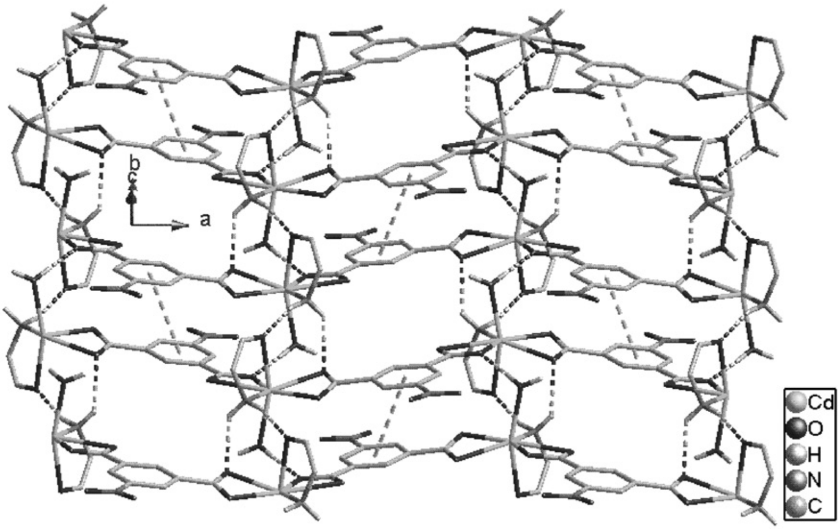

Figure 5. 2-D supramolecular network of **2** formed by hydrogen bonds and π–π stacking interactions. (Some atoms of AAP uncoordinated with Cd ion are omitted for clarity).

Table 4. Hydrogen bond geometries for **1** and **2**.[a]

D–H $\cdots$ A	d(D $\cdots$ A) (Å)	d(H $\cdots$ A) (Å)	∠(D–H $\cdots$ A) (°)
1			
O24–H24^{A} $\cdots$ O11	2.701	1.809	153.14
O25–H25^{A} $\cdots$ O16	2.733	1.861	149.51
O27–H27^{B} $\cdots$ O18	2.635	1.749	151.87
O30–H30^{B} $\cdots$ O12	2.854	1.930	160.56
2			
N3–H3^{A} $\cdots$ O4	3.012	2.321	134
N3–H3^{B} $\cdots$ O1	3.047	2.173	164
O8–H8^{B} $\cdots$ O2	2.719	1.871	175

[a] Symmetry transformations used to generate equivalent atoms: for **1**: (A) $-x+1, -y+1, -z$; (B) $x, y+1, z$; for **2**: (A) $-x+1, -y+1, -z+1$; (B) $-x+3/2, y+1/2, z$.

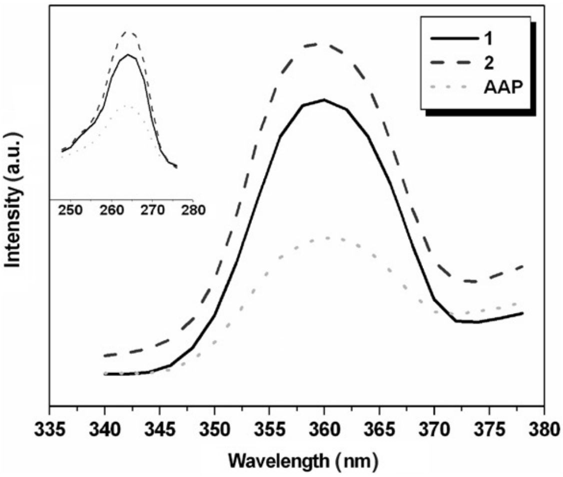

Figure 6. The solid excited (insert) and emission spectra of **1**, **2** and free AAP ligand at room temperature.

nitrogen atoms of AAP and the carboxylate oxygen of NIP (N3–H3A ··· O4) as well as exocyclic ketonic oxygen of AAP (N3–H3B ··· O1). One oxygen atom of coordinated H_2O also takes part in formation of O8–H8B ··· O2 hydrogen bond. A $\pi \cdots \pi$ stacking interaction is formed between the inter-chain benzene rings with the center to center distance being 3.783 Å. Thus, similar to **1**, abundant hydrogen bonds formed between coordinated water molecular and amino-group of AAP and $\pi \cdots \pi$ interactions corporately contribute to the stability of **2**.

3.4. *Fluorescence properties*

Luminescent compounds are of great current interest because of their various applications in chemical sensors, photochemistry, and electroluminescent displays [27]. To establish the relationship between the crystal structure and the fluorescence properties, the solid fluorescence spectra of **1** and **2** as well as the free AAP for comparison were measured at room temperature (figure 6). The similar fluorescence emission peaks around 360 nm are observed for both complexes upon excitation at 266 nm for **1** and 264 nm for **2**, analogous to that of free AAP ($\lambda_{ex} = 264$ nm, $\lambda_{em} = 360$ nm). Therefore, the fluorescence emissions originate from transitions between the energy levels of the coordinated AAP.

Supplementary material

Crystallographic data (excluding structure factors) for the crystal structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center (CCDC Nos. 634184–634185). This material can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk).

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