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Synthesis, crystal structure, and luminescent properties of metal complexes bearing 2,6-pyridine-diacylhydrazide ligands: supramolecular assemblies via intermolecular interactions

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Abstract Four metal complexes of *N*,*N*′-bis(salicyl)-2,6-pyridine-dicarbohydrazide ligand (H_6L), $[Co^{II}(H_4L)(H_2O)_2]\cdot 2DMF$ (**1**), $[Zn^{II}(H_4L)(H_2O)_2]\cdot 2DMF$ (**2**), $[Cd^{II}(H_4L)(Py)_2]\cdot DMF\cdot Py$ (**3**), and $[Co^{II}Co^{III}_2(H_4L)_4(H_2O)_4]\cdot DMF\cdot H_2O$ (**4**), were synthesized and characterized by elemental analysis, IR, and single-crystal X-ray diffraction analysis. Structural studies revealed that complexes **1–3** present discrete mononuclear structures and complex **4** displays a centrosymmetric mixed-valence trinuclear structure. All four complexes are further extended into interesting two- or three-dimensional supramolecular frameworks. The luminescent properties of **2** and **3** were studied, which show emissions with maxima at 485 nm upon excitation at 396 nm for **2** and 476 nm upon excitation at 397 nm for **3**, respectively.

Introduction

Much effort has been paid to the design and synthesis of supramolecular frameworks because of their versatile architectures as well as potential applications in the fields of catalysis, electronics, nonlinear optics, magnetic material, porous materials, and other technologies [1–10]. The process of the self-assembly of a supramolecular framework is based on the extension of individual molecules by noncovalent or weak covalent interactions, including Van der Waals, electrostatic and hydrophobic interactions, hydrogen bonds, as well as π–π and ion-π stacking [11–21]. Among these, hydrogen bonding and π–π stacking interactions have been considered to play active roles in the formation of ordered supramolecular chains, layers, and three-dimensional frameworks, the research on which is of great interest for the development of supramolecular chemistry [22–29].

To date, many ligands have been used in the syntheses of metal complexes as molecular building blocks for the further self-assemblies of supramolecules. Among these ligands, aromatic carboxylate-containing or amide-containing ligands are often employed due to their facile coordination to metal ions and inclination to form H-bonds of COOH···N, COOH···O, and N–H···O, etc., as well as the potential π–π stacking interaction between the aromatic rings [14, 17, 19, 23, 30, 31]. *N*,*N*′-bis(salicyl)-2,6-pyridine-dicarbohydrazide (H_6L) ligand possesses eleven potential donor groups (one pyridine group, four carbonyl groups, two phenolic groups, and four amide moieties). It provides not only sufficient metal binding sites, but also the favorable conditions to generate intermolecular interactions such as hydrogen bonding and π–π stacking interaction. Thus, it is an excellent ligand for the construction of supramolecules from its corresponding metal complexes. Herein, we present the syntheses and structures of four metal complexes with H_6L ligand, $[Co^{II}(H_4L)(H_2O)_2]\cdot 2DMF$ (**1**), $[Zn^{II}(H_4L)(H_2O)_2]\cdot 2DMF$ (**2**), $[Cd^{II}(H_4L)(Py)_2]\cdot DMF\cdot Py$ (**3**), and $[Co^{II}Co^{III}_2(H_4L)_4(H_2O)_4]\cdot DMF\cdot H_2O$ (**4**). Complexes **1–3** possess similar mononuclear units, and

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complex **4** displays a centrosymmetric mixed-valence trinuclear structure. With the aid of diverse intermolecular interactions, they are further extended into interesting two- or three-dimensional supramolecular frameworks. The Photoluminescence properties of **2** and **3** were investigated.

Experimental

All reagents and solvents were purchased commercially as reagent grade and used without further purification. Elemental analyses were performed on a Perkin-Elmer 2400 II elemental analyzer. IR spectra were obtained in KBr pellets on a Nicolet 360 FTIR spectrometer in the range 4,000–400 cm^{-1}. Solid-state luminescence spectra were measured at room temperature on a FL3-PTCSPC spectrophotometer with a xenon lamp as the light source.

Preparation of *N*,*N*′-bis(salicyl)-2,6-pyridine-dicarbohydrazide (**H_6L**)

The reaction of 2,6-pyridinedicarbonyl dichloride (1.70 g, 10 mmol) with salicyloyl hydrazide (3.3 g, 22 mmol) in THF for 3 days gave a white precipitate of H_6L, which was isolated by filtration and recrystallized from methanol solution (yield 85%). Anal. Calc. for $C_{21}H_{17}N_5O_6$ (%): C, 57.93; H, 3.93; N, 16.08. Found: C, 57.79; H, 3.79; N, 15.96. IR (KBr pellet, cm^{-1}): 3,340(m), 3,236(m), 1,706(m), 1,640(m), 1,608(s), 1,547(m), 1,508(s), 1,489(s), 1,307(m), 1,238(m), 759(m).

Preparation of $[Co^{II}(H_4L)(H_2O)_2]\cdot 2DMF$ (**1**) and $[Zn^{II}(H_4L)(H_2O)_2]\cdot 2DMF$ (**2**)

A methanol solution (5 mL) of $CoCl_2\cdot 6H_2O$ (0.0714 g, 0.3 mmol) was slowly added to a DMF solution (5 mL) of H_6L (0.0435 g, 0.1 mmol). The resulting solution was further stirred at ambient temperature for 9 h and then filtered. The filtrate was allowed to evaporate at room temperature, giving orange block crystals of **1** suitable for single-crystal X-ray diffraction after 30 days (yield 45%). Anal. Calc. for $C_{27}H_{33}CoN_7O_{10}$: C, 48.08; H, 4.93; N, 14.54. Found: C, 47.94; H, 5.07; N, 14.38. FT-IR (cm^{-1}): 3,481(s, br), 3,334(m), 3,322(m), 1,648(s), 1,603(s), 1,592(s), 1,566(s), 1,540(s), 1,494(s), 1,385(s), 1,307(m), 1,282(m), 1,100(m), 759(m).

Complex **2** was prepared in a method similar to that for **1** using $Zn(NO_3)_2\cdot 6H_2O$ (0.0892 g, 0.3 mmol) instead of $CoCl_2\cdot 6H_2O$. Colorless block crystals were obtained in a yield of 42% by slow evaporation of the filtrate at room temperature for 40 days. Anal. Calc. for $C_{27}H_{33}ZnN_7O_{10}$: C, 47.62; H, 4.88; N, 14.40. Found: C, 47.74; H, 5.01; N, 14.29. FT-IR (cm^{-1}): 3,454(s, br), 3,336(m), 3,321(m), 1,651(s), 1,605(s), 1,543(s), 1,492(s), 1,381(s), 1,306(m), 1,282(m), 1,101(m), 759(m).

Preparation of $[Cd^{II}(H_4L)(Py)_2]\cdot DMF\cdot Py$ (**3**)

H_6L (0.0218 g, 0.05 mmol), $Cd(NO_3)_2\cdot 4H_2O$ (0.0463 g, 0.15 mmol), pyrazine (0.012 g, 0.15 mmol), DMF (0.5 mL), pyridine (0.5 mL), and CH_3OH (0.2 mL) were placed in a thick Pyrex tube (ca 20 cm long). The tube was frozen using liquid N_2, evacuated under vacuum and flame-sealed. Subsequently, it was allowed to warm to room temperature and heated at 90 °C for 3 days, giving yellow block crystals of **3** in a yield of 56%. Anal. Calc. for $C_{39}H_{37}CdN_9O_7$: C, 54.71; H, 4.36; N, 14.72. Found: C, 54.57; H, 4.45; N, 14.87. FT-IR (cm^{-1}): 3,417(s, br), 3,342(m), 3,268(m), 1,636(s), 1,607(s), 1,531(s), 1,491(s), 1,375(s), 1,307(m), 1,282(m), 1,101(m), 750(m).

Preparation of $[Co^{II}Co_2^{III}(H_4L)_4(H_2O)_4]\cdot DMF\cdot H_2O$ (**4**)

A methanol solution (5 mL) of $Co(NO_3)_2\cdot 6H_2O$ (0.0873 g, 0.3 mmol) was slowly added to a methanol solution (5 mL) of H_6L (0.0435 g, 0.1 mmol). The resulting solution was further stirred at ambient temperature for 9 h and then filtered. The filtrate was allowed to evaporate at room temperature, giving dark brown block crystals of **4** suitable for single-crystal X-ray diffraction after 40 days (yield 38%). Anal. Calc. for $C_{90}H_{86}Co_3N_{22}O_{32}$: C, 49.94; H, 4.00; N, 14.24. Found: C, 49.78; H, 4.11; N, 14.09. FT-IR (cm^{-1}): 3,371(s, br), 3,254(m), 1,644(s), 1,623(s), 1,599(s), 1,514(s), 1,489(m), 1,371(m), 1,300(m), 1,248(m), 1,103(m), 760(m).

X-ray crystallography study

Suitable single crystals of complexes **1**–**4** were selected and mounted onto thin glass fibers. The single-crystal X-ray diffraction studies of **1**, **2**, and **4** were performed at 187(2) K and **3** at 185(2) K, using a Bruker CCD Area Detector with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The program SAINT was used for integration of the diffraction profiles. The structures were solved by direct methods using the *SHELXS-97* program package and refined against F^2 by full-matrix least-squares methods with *SHELXL-97* [32, 33]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms on C atoms were set in calculated positions and refined as riding atoms. The crystallographic data are summarized in Table 1, and the selected bond lengths and angles are listed in Table 2.

Table 1 Crystallographic data and refinement summary for **1**–**4**

	1	**2**	**3**	**4**
Empirical formula	$C_{27}H_{33}CoN_7O_{10}$	$C_{27}H_{33}ZnN_7O_{10}$	$C_{39}H_{37}CdN_9O_7$	$C_{90}H_{86}Co_3N_{22}O_{32}$
Formula weight	674.53	680.97	856.18	2164.60
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a (Å)	16.6766 (11)	16.698 (5)	14.0912 (5)	13.2440 (5)
b (Å)	7.2424 (5)	7.205 (5)	20.0980 (6)	13.9350 (10)
c (Å)	24.4485 (17)	24.289 (5)	28.1697 (9)	14.6847 (6)
α (°)	90	90	90	103.8260 (10)
β (°)	98.3980 (10)	98.308 (5)	104.3230 (10)	112.7820 (10)
γ (°)	90	90	90	98.7340 (10)
V (Å^3)	2,921.2 (3)	2,892 (2)	7,729.8 (4)	2,334.2 (2)
Z	4	4	8	1
D_{Calc} (g cm^{-3})	1.534	1.564	1.471	1.540
μ (Mo-Kα) (mm^{-1})	0.658	0.920	0.627	0.625
θ (°)	1.68–25.00	1.23–25.00	2.03–25.09	1.56–25.00
Reflections collected/unique (R_{int})	16,734/5,154 (0.0554)	16,791/5,096 (0.0943)	55,911/13,733 (0.0465)	16,880/8,203 (0.0158)
Goodness-of-fit on F^2	1.047	0.931	1.040	1.067
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0515$, $wR_2 = 0.1319$	$R_1 = 0.0455$, $wR_2 = 0.0947$	$R_1 = 0.0384$, $wR_2 = 0.0899$	$R_1 = 0.0319$, $wR_2 = 0.0912$
R indices (all data)	$R_1 = 0.0894$, $wR_2 = 0.1450$	$R_1 = 0.1083$, $wR_2 = 0.1242$	$R_1 = 0.0539$, $wR_2 = 0.0986$	$R_1 = 0.0366$, $wR_2 = 0.0937$
Largest diff. peak and hole (e A^{-3})	0.916, −0.703	0.422, −0.522	1.220, −0.969	0.597, −0.460

Table 2 Selected bond distances (Å) and bond angles (°) for **1**–**4**

1					
Co1–O7	2.143 (3)	Co1–N5	2.164 (3)	Co1–N1	2.218 (3)
Co1–N3	2.144 (3)	Co1–O1	2.217 (2)	Co1–O3	2.252 (2)
Co1–O8	2.153 (3)				
O7–Co1–N3	91.72 (10)	N3–Co1–O1	71.77 (10)	O1–Co1–N1	141.59 (10)
O7–Co1–O8	174.63 (9)	O8–Co1–O1	87.77 (10)	O7–Co1–O3	86.79 (9)
N3–Co1–O8	89.21 (10)	N5–Co1–O1	148.55 (10)	N3–Co1–O3	149.90 (11)
O7–Co1–N5	90.67 (11)	O7–Co1–N1	92.25 (10)	O8–Co1–O3	89.76 (9)
N3–Co1–N5	139.68 (11)	N3–Co1–N1	69.85 (10)	N5–Co1–O3	70.42 (10)
O8–Co1–N5	92.05 (11)	O8–Co1–N1	93.03 (10)	O1–Co1–O3	78.13 (9)
O7–Co1–O1	87.49 (10)	N5–Co1–N1	69.84 (10)	N1–Co1–O3	140.23 (10)
2					
Zn1–O7	2.111 (3)	Zn1–N5	2.181 (4)	Zn1–O1	2.240 (3)
Zn1–O8	2.119 (3)	Zn1–N1	2.221 (3)	Zn1–O3	2.333 (3)
Zn1–N3	2.150 (3)				
O7–Zn1–O8	171.73 (11)	O8–Zn1–N1	94.92 (12)	N1–Zn1–O1	141.80 (12)
O7–Zn1–N3	91.88 (12)	N3–Zn1–N1	70.07 (13)	O7–Zn1–O3	86.80 (11)
O8–Zn1–N3	90.46 (12)	N5–Zn1–N1	70.17 (13)	O8–Zn1–O3	87.24 (11)
O7–Zn1–N5	90.79 (13)	O7–Zn1–O1	86.58 (12)	N3–Zn1–O3	150.27 (12)
O8–Zn1–N5	92.48 (13)	O8–Zn1–O1	86.62 (12)	N5–Zn1–O3	69.49 (12)
N3–Zn1–N5	140.24 (13)	N3–Zn1–O1	71.75 (12)	N1–Zn1–O3	139.66 (12)
O7–Zn1–N1	93.33 (12)	N5–Zn1–O1	148.00 (12)	O1–Zn1–O3	78.52 (10)

Table 2 continued

3					
Cd1–N4	2.333 (3)	Cd1–O5	2.468 (2)	Cd2–N13	2.366 (3)
Cd1–N12	2.348 (3)	Cd1–O2	2.529 (2)	Cd2–O8	2.394 (2)
Cd1–N11	2.355 (3)	Cd2–N9	2.328 (3)	Cd2–N8	2.465(3)
Cd1–N2	2.356 (3)	Cd2–N7	2.350 (3)	Cd2–O11	2.504 (2)
Cd1–N3	2.460 (3)	Cd2–N14	2.357 (3)		
N4–Cd1–N12	98.40 (10)	N3–Cd1–O5	131.22 (8)	N7–Cd2–O8	67.61 (9)
N4–Cd1–N11	92.04 (10)	N4–Cd1–O2	164.51 (9)	N14–Cd2–O8	83.70 (9)
N12–Cd1–N11	163.33 (10)	N12–Cd1–O2	83.18 (9)	N13–Cd2–O8	84.27 (10)
N4–Cd1–N2	129.42 (9)	N11–Cd1–O2	83.34 (9)	N9–Cd2–N8	65.19 (9)
N12–Cd1–N2	91.32 (10)	N2–Cd1–O2	65.70 (8)	N7–Cd2–N8	64.23 (9)
N11–Cd1–N2	92.03 (10)	N3–Cd1–O2	130.29 (8)	N14–Cd2–N8	95.64 (9)
N4–Cd1–N3	64.85 (9)	O5–Cd1–O2	98.48 (7)	N13–Cd2–N8	100.09 (10)
N12–Cd1–N3	99.43 (10)	N9–Cd2–N7	129.41 (9)	O8–Cd2–N8	131.84 (8)
N11–Cd1–N3	96.76 (9)	N9–Cd2–N14	95.68 (10)	N9–Cd2–O11	66.42 (8)
N2–Cd1–N3	64.61 (9)	N7–Cd2–N14	89.88 (10)	N7–Cd2–O11	164.16 (8)
N4–Cd1–O5	66.40 (8)	N9–Cd2–N13	92.81 (10)	N14–Cd2–O11	87.73 (9)
N12–Cd1–O5	85.80 (9)	N7–Cd2–N13	95.06 (10)	N13–Cd2–O11	83.41 (9)
N11–Cd1–O5	86.53 (9)	N14–Cd2–N13	164.14 (10)	O8–Cd2–O11	96.56 (8)
N2–Cd1–O5	164.17 (8)	N9–Cd2–O8	162.97 (9)	N8–Cd2–O11	131.59 (8)
4					
Co1–N1	1.8571 (15)	Co1–N7	1.9554 (16)	Co2–O14	2.1279 (15)
Co1–N2	1.8638 (15)	Co2–O13^{i}	2.0654 (15)	Co2–O14^{i}	2.1279 (15)
Co1–N3	1.9267 (16)	Co2–O13	2.0654 (15)	O1–C1	1.246 (2)
Co1–N5	1.9314 (15)	Co2–O1	2.0973 (14)	N3–C1	1.328 (3)
Co1–N9	1.9391 (16)	Co2–O1^{i}	2.0973 (14)		
N1–Co1–N2	178.15 (7)	N1–Co1–N7	99.42 (6)	O1–Co2–O1^{i}	180.000 (1)
N1–Co1–N3	81.21 (7)	N2–Co1–N7	81.24 (6)	O13^{i}–Co2–O14	90.81 (6)
N2–Co1–N3	97.09 (7)	N3–Co1–N7	88.87 (7)	O13–Co2–O14	89.19 (6)
N1–Co1–N5	81.36 (6)	N5–Co1–N7	94.33 (7)	O1–Co2–O14	91.29 (6)
N2–Co1–N5	100.33 (7)	N9–Co1–N7	162.26 (7)	O1^{i}–Co2–O14	88.71 (6)
N3–Co1–N5	162.56 (7)	O13^{i}–Co2–O13	180.0	O13^{i}–Co2–O14^{i}	89.19 (6)
N1–Co1–N9	98.31 (7)	O13^{i}–Co2–O1	86.42 (6)	O13–Co2–O14^{i}	90.81 (6)
N2–Co1–N9	81.03 (7)	O13–Co2–O1	93.58 (6)	O1–Co2–O14^{i}	88.71 (6)
N3–Co1–N9	94.00 (7)	O13^{i}–Co2–O1^{i}	93.58 (6)	O1^{i}–Co2–O14^{i}	91.29 (6)
N5–Co1–N9	88.16 (7)	O13–Co2–O1^{i}	86.42 (6)	O14–Co2–O14^{i}	180.00 (7)

Symmetry codes: (i) $-x + 2, -y, -z + 1$

Results and discussion

Structure descriptions of complexes 1 and 2

The isostructural complexes **1** and **2**, which present mononuclear structures, crystallize in the monoclinic space group $P2_1/c$. Co^{II} ion in **1** and Zn^{II} ion in **2** are both seven-coordinated in pentagonal bipyramidal geometries. The divalent anionic H_4L^{2-} in **1** and **2** behaves a pentadentate chelating ligand. It coordinates to one Co^{II} or Zn^{II} ion using one $N_{pyridyl}$ atom (N1), two $N_{pyridyl\text{-}acylamide}$ atoms (N3 and N5), and two $O_{benzyl\text{-}acylamide}$ atoms (O1 and O3) to form a mononuclear molecule as shown in Fig. 1. The $O_{pyridyl\text{-}acylamide}$, $N_{benzyl\text{-}acylamide}$, and $O_{phenolic}$ atoms of the ligand are free from coordination. The five coordinating atoms of H_4L^{2-} complete the equatorial plane and the mean deviations are 0.0132 Å for **1** and 0.0107 Å for **2**, indicating that the five atoms are nearly coplanar. Such planarity was

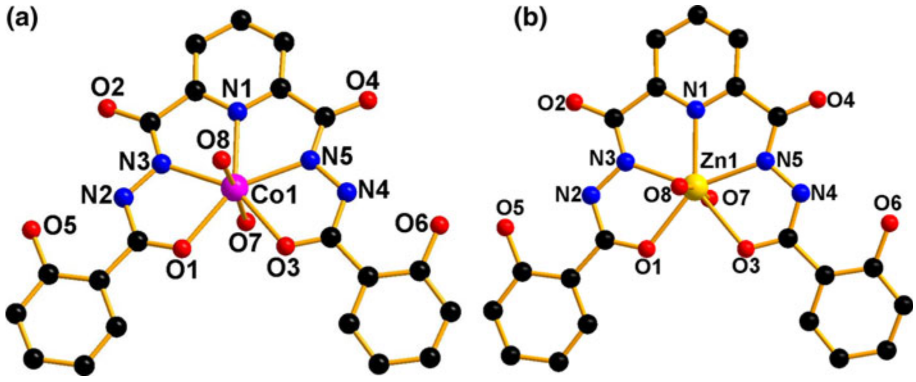

Fig. 1 The perspective views of the structures of **1** (**a**) and **2** (**b**). H atoms and guest DMF molecules are omitted for clarity

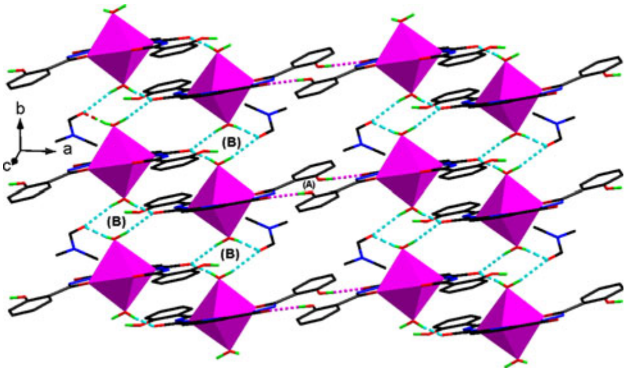

Fig. 2 2D network formed by type A and type B hydrogen bonds indicated by *broken lines* of **1**

observed in the reported complex $[Cd(C_{15}H_{11}N_5O_8)(H_2O)_2]\cdot 2C_3H_7NO$ ($C_{15}H_{11}N_5O_8$ = *N*,*N*′-bis(3-carboxy-*cis*-propenoyl)-2, 6-picolyldihydrazide) [34]. The remaining axial sites of the Co^{II} or Zn^{II} are occupied by two oxygen atoms (O7 and O8) from two water ligands.

Complexes **1** and **2** exhibit similar hydrogen bonds. Thus, only the hydrogen bonds of **1** are discussed here in detail. As shown in Fig. 2, one uncoordinated phenolic group forms hydrogen bonds O6–H6A···O4^{i} (i $= -x + 1, -y + 1, -z + 1$) with an $O_{pyridyl\text{-}acylamide}$ atom from the adjacent unit, composing type A hydrogen bonds with the O···O distance of 2.592 Å. The two water ligands at axial positions of **1** form hydrogen bonds simultaneously with the oxygen atom of one guest DMF molecule and one $O_{pyridyl\text{-}acylamide}$ atom (O7–H7A···O2^{ii}, O7–H7B···O10, O8–H8A···O2^{iii} and O8–H8B···O10^{iv}, ii $= -x, -y + 1, -z + 1$; iii $= -x, -y, -z + 1$; iv $= x, y - 1, z$), composing type B hydrogen bonds with the O···O distances and O–H···O angles in the ranges of 2.69–2.88 Å and 169°–175°, respectively (Table 3). As a result, complex **1** is further extended into a two-dimensional supramolecular network by type A and type B hydrogen bonds.

Structure description of complex 3

Complex **3** crystallizes in the monoclinic space group $P2_1/c$ and presents two discrete mononuclear units $[Cd^{II}(H_4L)(Py)_2]$, which are similar to the mononuclear unit $[M^{II}(H_4L)(H_2O)_2]$ of complexes **1** and **2**. The structural difference of **3** from **1** and **2** is that the two axial sites of the metal are occupied by two pyridine ligands in **3**, rather than the two water ligands in **1** and **2**. This might be due to the strong coordinating ability of pyridine solvent used in the synthesis of **3**. The five coordinated atoms (one $N_{pyridyl}$, two $N_{pyridyl\text{-}acylamide}$, and two $O_{benzyl\text{-}acylamide}$ atoms) of H_4L^{2-} are nearly coplanar with the mean deviations of 0.0120 and 0.0331 Å for the two mononuclear units.

There are π–π stacking interactions between the benzyl rings from the two mononuclear molecules in **3** (Fig. 3). The dihedral angles and centroid-to-centroid distances of adjacent benzyl rings are 2.716° and 3.570 Å (rings a and b), 3.119° and 3.634 Å (rings c and d), respectively. Furthermore, the adjacent units of **3** form hydrogen bonds O1–H1A···O10^{i}, O6–H6A···O9^{ii}, O7–H7A···O4^{iii}, O12–H12B···O3^{iv} (i $= x, -y + 1/2, z + 1/2$; ii $= x + 1$, y, z; iii $= x - 1, y, z$; iv $= x, -y + 1/2, z - 1/2$) between the phenolic groups from one unit and the $O_{pyridyl\text{-}acylamide}$ atoms from the adjacent units, with the O···O distances and O–H···O angles in the ranges of 2.54–2.61 Å and 169°–177°, respectively (Table 3). With the aid of these π–π stacking and hydrogen bonding interactions, complex **3** is extended into a two-dimensional supramolecular network as shown in Fig. 4.

Structure description of complex 4

The single-crystal X-ray structural analysis reveals that complex **4** has a centrosymmetric mixed-valence trinuclear structure, which crystallizes in the triclinic space group $P\bar{1}$. There are one Co^{II} and two Co^{III} ions in **4**, as established by charge balance considerations and bond

Table 3 Hydrogen bonds (Å and °) for **1**–**4**

D–H···A	D–H	H···A	D···A	∠D–H···A	Symmetry code on A
1 (**2** exhibits similar hydrogen bonds)					
N2–H2A···O5	0.88	1.97	2.633	131.0	
N4–H4B···O6	0.88	2.02	2.678	130.4	
O5–H5B···O9	0.84	1.76	2.590	170.4	$-x, y - 1/2, -z + 1/2$
O6–H6A···O4	0.84	1.75	2.592	175.8	$-x + 1, -y + 1, -z + 1$
O7–H7A···O2	0.85	1.85	2.697	174.1	$-x, -y + 1, -z + 1$
O7–H7B···O10	0.84	2.04	2.865	169.6	
O8–H8A···O2	0.84	1.93	2.766	172.0	$-x, -y, -z + 1$
O8–H8B···O10	0.85	1.99	2.832	167.9	$x, y - 1, z$
3					
N10–H10···O12	0.88	1.89	2.592	135.5	
N6–H6···O7	0.88	1.92	2.608	133.9	
N5–H5···O6	0.88	1.91	2.607	134.4	
N1–H1···O1	0.88	1.89	2.590	135.7	
O12–H12B···O3	0.84	1.75	2.584	171.0	$x, -y + 1/2, z - 1/2$
O7–H7A···O4	0.84	1.71	2.546	176.9	$x - 1, y, z$
O6–H6A···O9	0.84	1.77	2.602	169.9	$x + 1, y, z$
O1–H1A···O10	0.84	1.73	2.567	170.6	$x, -y + 1/2, z + 1/2$
4					
N4–H4B···O1 W	0.88	1.95	2.768	153.4	$-x + 2, -y, -z + 1$
N6–H6B···O7	0.88	2.03	2.844	154.3	$-x + 1, -y - 1, -z + 1$
N8–H8A···O4	0.88	2.62	3.190	123.0	
N10–H10B···O12	0.88	2.09	2.679	123.7	
N10–H10B···O3	0.88	2.25	2.962	137.5	
O5–H5B···O3	0.84	1.81	2.553	146.1	
O6–H6A···O4	0.84	1.86	2.601	146.7	
O11–H11B···O9	0.84	1.86	2.598	145.8	
O12–H12B···O2	0.84	1.74	2.577	174.8	$-x + 1, -y - 1, -z$
O13–H13A···O10	0.85	1.86	2.708	174.4	
O13–H13B···O15	0.85	1.88	2.690	159.2	
O14–H14A···O15	0.85	2.00	2.797	155.9	
O14–H14B···O1 W	0.85	1.92	2.756	166.3	
O1 W–H1 WA···O10	0.85	1.89	2.719	166.4	$-x + 2, -y, -z + 1$
O1W–H1WB···O8	0.85	1.85	2.693	173.6	$x, y + 1, z$

valence sum (BVS) calculations (BVS for the Co^{II} and Co^{III} ions were 2.014 and 3.108, respectively) as shown in Table 4 [35–37]. The central divalent Co2 is six-coordinated in a regular octahedral geometry by two O$_{pyridyl\text{-}acylamide}$ atoms (O1 and O1A) from two H$_4$L^{2-} ligands and four oxygen atoms (O13, O13A, O14, and O14A) from four water molecules. The bond distances of C–O and C–N in pyridyl-acylamide groups of H$_4$L^{2-} are 1.246 and 1.328 Å, respectively, suggesting that the CO and CN groups coordinate to cobalt in the enolic form [38]. Co1 and Co1A are both trivalent and six-coordinated in distorted octahedral geometries. The six coordinating sites of Co1 (Co1A) are all occupied by nitrogen atoms, that is, two N$_{pyridyl}$ atoms (N1 and N2) and four N$_{pyridyl\text{-}acylamide}$ atoms (N3, N5, N7, and N9) from two H$_4$L^{2-} ligands (Fig. 5).

The H$_4$L^{2-} ligands in **4** present two kinds of coordination modes. One is tridentate chelating mode coordinating to Co1^{III} ion using its N$_{pyridyl}$ atom and two N$_{pyridyl\text{-}acylamide}$ atoms. The other one is μ_2-η^4-bridging mode linking Co1^{III} and Co2^{II} via the coordination of three nitrogen atoms mentioned above to Co1^{III} and the coordination of O$_{pyridyl\text{-}acylamide}$ to Co2^{II}, resulting in the formation of a trinuclear structure of **4** as shown in Fig. 5. All of the O$_{benzyl\text{-}acylamide}$, N$_{benzyl\text{-}acylamide}$, and O$_{phenolic}$ atoms of H$_4$L^{2-} in **4** are free from coordination.

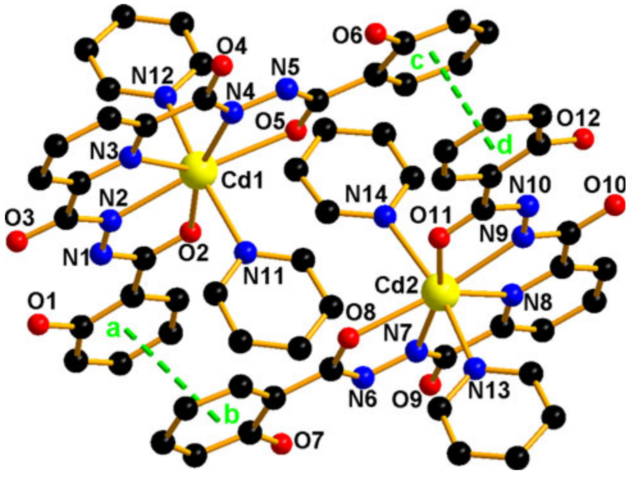

Fig. 3 The perspective view of two mononuclear units in **3**, showing the π–π stacking interactions indicated by *broken lines*. H atoms, guest pyridine and DMF molecules are omitted for clarity

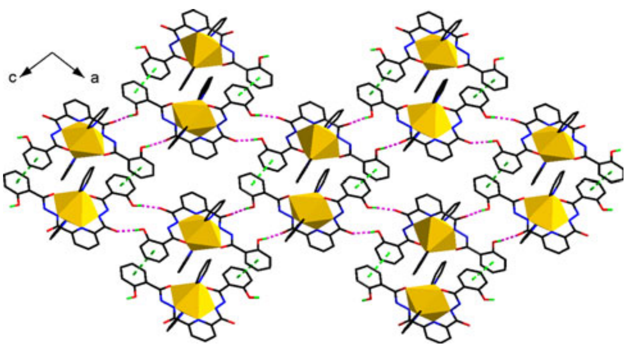

Fig. 4 2D network formed by the π–π stacking and hydrogen bonding interactions (indicated by *broken lines*) of **3**

Table 4 Bond Valence Sum[a] (BVS) calculations for the cobalt ions in **4**

	Co^{II}	Co^{III}
Co1 (Co1A)	3.788	$\underline{3.108}$
Co2	$\underline{2.014}$	2.058

[a] The underlined value is the one closest to the charge for which it was calculated. The oxidation state of a particular atom can be taken as the nearest whole number to the underlined value [39]

As depicted in Fig. 6 and Table 3, trinuclear units of **4** are linked into 1D chains via intermolecular hydrogen bonds between the uncoordinated benzyl-acylamide group and the $O_{pyridyl\text{-}acylamide}$ atom from the neighboring trinuclear unit (N6–H6B···O7^{i} with an O···O distance of 2.844 Å, i = $-x + 1$, $-y - 1$, $-z + 1$). These 1D chains are further connected into a 2D network by interchain H-bonds O12–H12B···O2^{ii} (ii = $-x + 1$, $-y - 1$, $-z$) between the phenolic group and the $O_{pyridyl\text{-}acylamide}$ atom from the adjacent chains (Fig. 6). The guest water molecule in **4** forms hydrogen bonds with one water ligand on Co2^{II} and the $O_{benzyl\text{-}acylamide}$, $N_{benzyl\text{-}acylamide}$ atoms of H_4L^{2-} ligands from one 2D sheet (O14–H14B···O1W, O1W–H1WA···O10^{iii} and N4–H4B···O1W^{iii}, iii = $-x + 2$, $-y$, $-z + 1$), and the $O_{pyridyl\text{-}acylamide}$ atom from the adjacent sheet (O1W–H1WB···O8^{iv} at O···O = 2.844 Å, iv = x, $y + 1$, z). These hydrogen bonds connect the 2D networks into a 3D supramolecular framework of **4** as shown in Fig. 7.

Structural discussion

The doubly deprotonated *N*,*N'*-bis(salicyl)-2,6-pyridinedicarbohydrazide (H_4L^{2-}) in **1**–**3** chelates to one metal atom as a pentadentate ligand to form similar mononuclear structures. However, the four H_4L^{2-} ligands in **4** coordinate to Co1^{III} or Co1A^{III} in a tridentate chelating mode with two of them further binding to Co2^{II} using the $O_{pyridyl\text{-}acylamide}$ atom, resulting in the formation of a trinuclear structure for **4**. Complexes **1**–**4** are further extended into interesting two- or three-dimensional supramolecular frameworks via diverse intermolecular interactions.

In complexes **1** and **2**, the mononuclear units are both linked into 2D supramolecular networks by type A hydrogen bonds between the phenolic group and $O_{pyridyl\text{-}acylamide}$ atom of neighboring H_4L^{2-} ligands, and type B hydrogen bonds between water ligands, guest DMF molecules, and $O_{pyridyl\text{-}acylamide}$ ligand atoms. The presence of abundant hydrogen bonds in **1** and **2** is attributed to the water ligands and guest DMF molecules. Different from **1** and **2**, the presence of coordinated and guest pyridine molecules in **3** blocks the formation of hydrogen bonds from the solvent molecules. As a result, hydrogen bonds in complex **3** are formed only between the phenolic group and $O_{pyridyl\text{-}acylamide}$ atom of neighboring H_4L^{2-} ligands. However, there are π–π stacking interactions between the two discrete mononuclear units in **3**, which, together with hydrogen bonds, helps to construct a 2D supramolecular network of **3** different from those of **1** and **2**. In the case of complex **4**, the trinuclear units are linked into 1D chains via hydrogen bonds between the uncoordinated benzyl-acylamide group and the $O_{pyridyl\text{-}acylamide}$ atom of H_4L^{2-} ligands. These 1D chains are further connected into a 2D network by hydrogen bonds involving the phenolic group and the $O_{pyridyl\text{-}acylamide}$ atom of H_4L^{2-} ligands. Due to the presence of a guest water molecule, which forms hydrogen bonds with the water ligand on central Co2^{II} and the $O_{benzyl\text{-}acylamide}$, $N_{benzyl\text{-}acylamide}$, and $O_{pyridyl\text{-}acylamide}$ atoms of H_4L^{2-} ligands, the 3D supramolecular framework of **4** is built.

Luminescent properties

The solid-state luminescent properties of complexes **2** and **3**, as well as the free H_6L ligand, were investigated at room

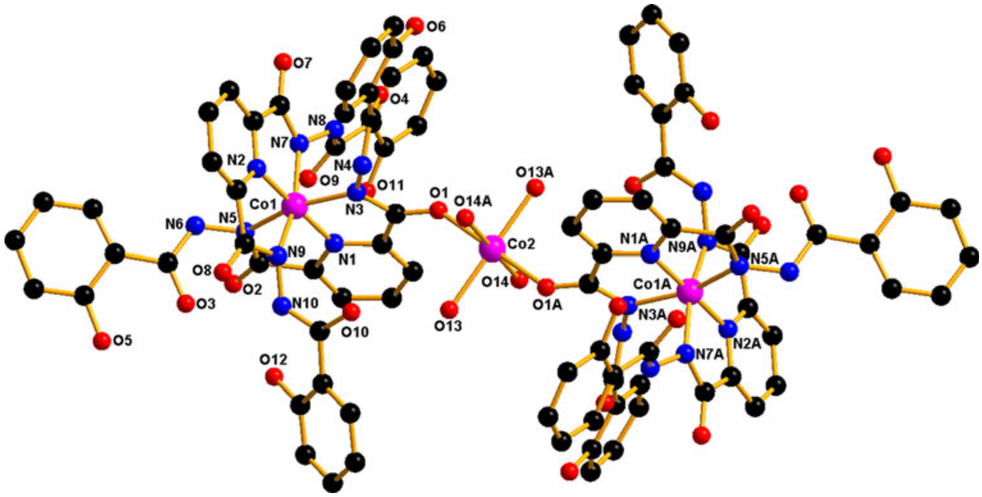

Fig. 5 The perspective view of the trinuclear structure of **4**. H atoms, guest H_2O, and DMF molecules are omitted for clarity. Symmetry codes: A) $-x + 2, -y, -z + 1$

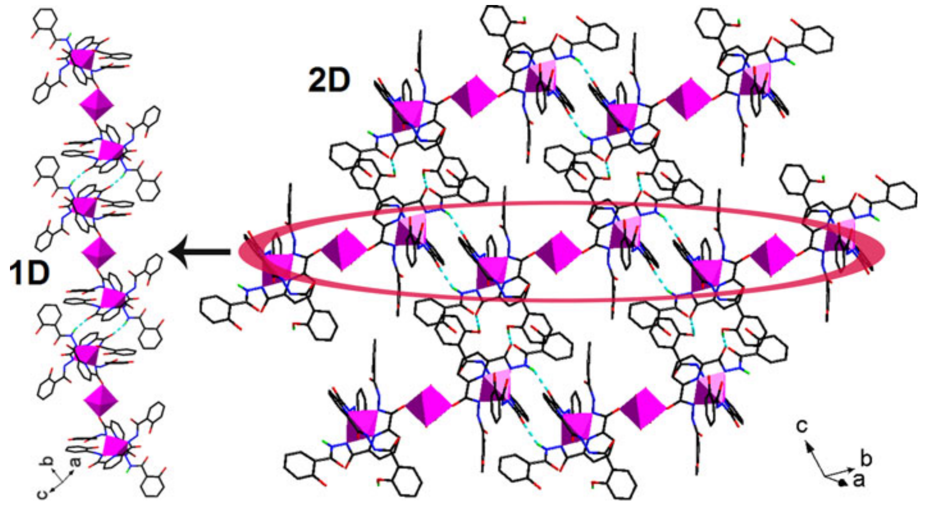

Fig. 6 1D chain and 2D network formed by hydrogen bonds (indicated by *broken lines*) of **4**

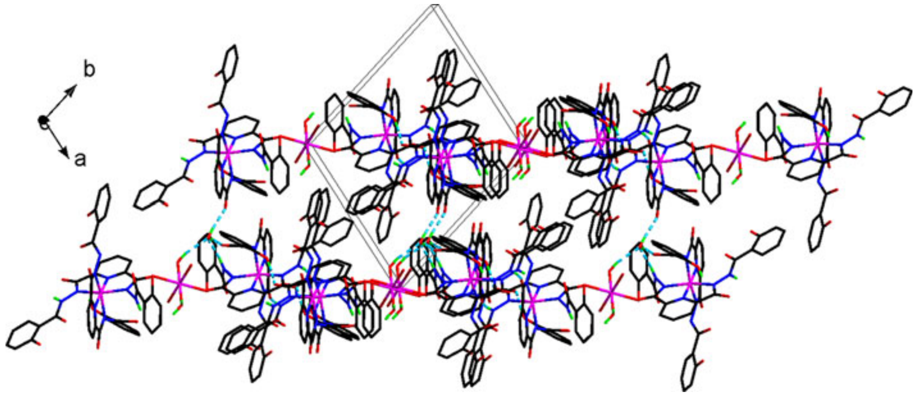

Fig. 7 3D hydrogen-bonded framework of **4**

temperature as shown in Fig. 8. The emission spectrum of the free ligand displays a band with a maximum at 446 nm when excited at 372 nm, which corresponds to the $\pi \rightarrow \pi^*$ transition of the ligand. The complexes exhibit characteristic luminescence with maximum at 485 nm upon excitation at 396 nm for **2** and 476 nm upon excitation at 397 nm for **3**, respectively, which are assigned to intraligand transitions. These emissions are slightly disturbed by the coordination of H_4L^{2-} to metal ions [40].

The emission decay profiles of complexes **2** and **3** in the solid state were obtained at room temperature. The lifetime

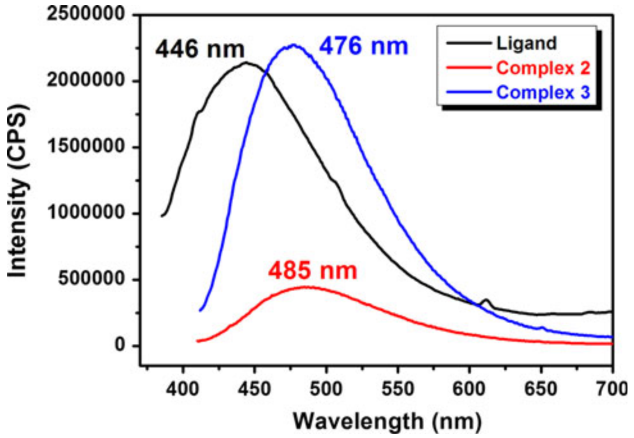

Fig. 8 Fluorescence emission spectra of complexes **2** (*red*) and **3** (*blue*) and the free ligand (*black*) in the solid state at room temperature

of the 485 nm emission for **2** is 0.61 ns, longer than that of the 476 nm emission for **3** (0.32 ns).

Conclusion

In this work, *N*,*N*′-bis(salicyl)-2,6-pyridine-dicarbohydrazide-containing metal complexes **1**–**4** were synthesized and structurally characterized. Complexes **1**–**3** exhibit similar mononuclear unit, and complex **4** presents a centrosymmetric mixed-valence trinuclear structure. All complexes are further extended into interesting two- or three-dimensional supramolecular frameworks. Complexes **1** and **2** present 2D supramolecular networks formed by the assembly of mononuclear units via two types of H-bonds. Complex **3** shows a 2D supramolecular network built by hydrogen bonds and π–π stacking interactions, which is different from those of **1** and **2** due to the presence of coordinated and guest pyridine molecules in **3** instead of the coordinated water ligands and guest DMF molecules in **1** and **2**. Complex **4** displays a 3D supramolecular framework constructed via hydrogen bonding interaction with the participation of guest water molecule. The fluorescence measurements revealed emissions with maximum at 485 nm upon excitation at 396 nm for **2** and 476 nm upon excitation at 397 nm for **3**, respectively.

Supplementary material

CCDC 797380–797383 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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