Syntheses, Structures and Characterization of Two Ni(II) and Pb(II) Coordination Polymers Constructed by 2-(4-Fluorophenyl)-1*H*-imidazo[4,5-*f*][1,10]phenanthroline and Flexible 4,4'-Oxybis(benzoate) Ligands

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Two coordination polymers, [Ni(H$_2$O)(L)(OBA)] (**1**) and [Pb(L)$_2$(OBA)]·3H$_2$O (**2**) [L = 2-(4-fluorophenyl)-1*H*-imidazo[4,5-*f*][1,10]phenanthroline and OBA = 4,4'-oxybis(benzoate)], have been synthesized under hydrothermal conditions, and characterized by elemental analysis, and IR and UV/Vis spectra. Crystal data for **1**: C$_{33}$H$_{21}$FN$_4$NiO$_6$, triclinic, space group $P\bar{1}$, a = 13.8490(10), b = 14.932(2), c = 14.993(3) Å, α = 107.534(4), β = 94.670(4), γ = 103.836(5)°, V = 2830.9(7) Å^3, Z = 4. Crystal data for **2**: C$_{52}$H$_{36}$F$_2$N$_8$O$_8$Pb, orthorhombic, space group $Pna2_1$, a = 16.256(4), b = 16.085(5), c = 17.810(3) Å, V = 4657 (2) Å^3, Z = 4. In **1**, OBA dianions bridge Ni(II) atoms to form two crystallographically distinct chains. These chains are further extended into a 2D supramolecular architecure through π-π interactions. In **2**, each OBA dianion links neighboring Pb(II) atoms to yield a helical chain. Further, π-π interactions among adjacent chains give rise to a 3D supramolecular architecture.

Key words: Crystal Structure, Coordination Polymer, 2-(4-Fluorophenyl)-1*H*-imidazo[4,5-*f*]phenanthroline, 4,4'-Oxybis(benzoate)

Introduction

In recent years, the design and synthesis of coordination polymers has attracted much attention from chemists, not only for their great potential for a wide range of applications, such as in catalysts and sensors, and in gas storage and separation, but also owing to their intriguing framework architectures and topologies [1 – 6]. Usually, the structure of a coordination polymer can be controlled and modified by selecting the coordination geometry preferred by the metal ion and the chemical structure of the organic ligand [7 – 9]. In this regard, dicarboxylate and *N*-containing chelating ligands are excellent candidates for the construction of coordination polymers [10 – 12]. The 4,4'-oxybis(benzoate) dianion (L) is an example of a flexible dicarboxylate owing to the presence of an ether linkage between the two rigid phenylene rings. On the other hand, *N*-containing chelating ligands have been intensely investigated as auxiliary ligands for the construction of novel coordination polymers [13].

For example, 1,10-phenanthroline (phen) has been widely used to construct supramolecular architectures because of its excellent coordination ability and large conjugated system that can easily form π-π interactions [14]. However, less attention has been paid to its derivative 2-(4-fluorophenyl)-1*H*-imidazo[4,5-*f*]1,10phenanthroline (L) [13 – 15].

In this work, two coordination polymers, [Ni(H$_2$O)(L)(OBA)] (**1**) and [Pb(L)$_2$(OBA)]·3H$_2$O (**2**), have been synthesized under hydrothermal conditions. Their structures have been determined by single-crystal X-ray diffraction analyses, and the compounds characterized by IR and UV/Vis spectra, elemental analyses, and magnetic susceptibility data.

Results and Discussion

Structure description of *1*

Selected bond lengths and angles for [Ni(H$_2$O)(L)(OBA)] (**1**) and [Pb(L)$_2$(OBA)]·3H$_2$O (**2**)
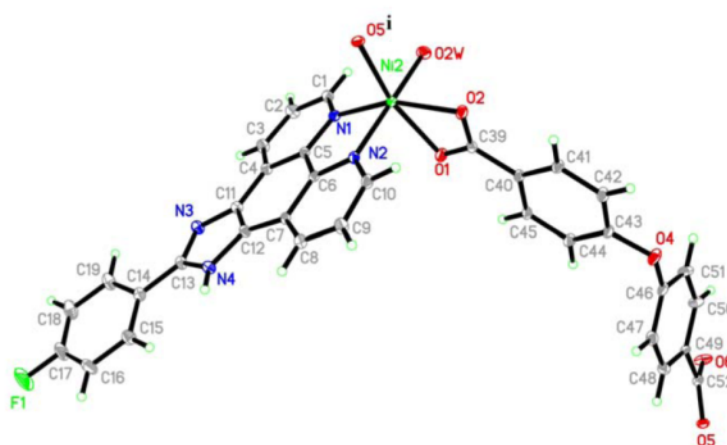
(a)
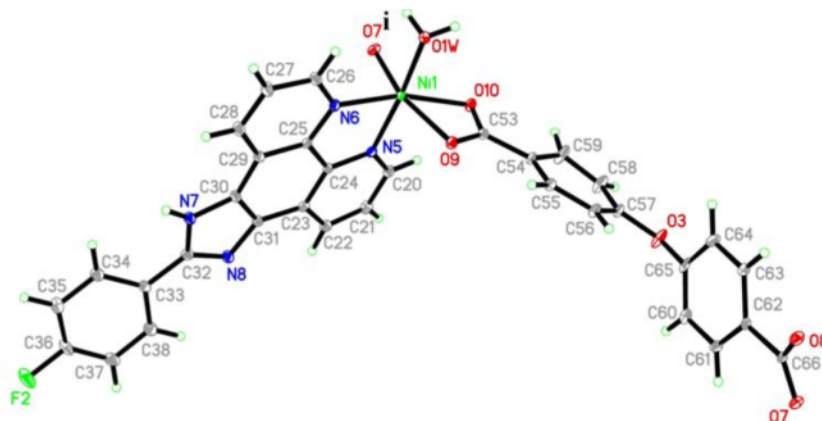
(b)

Fig. 1 (color online). OR-TEP view of the two crystallographically independent molecular entities of **1** showing the local coordination environment of the Ni(II) centers (15 % probability displacement ellipsoids).

are listed in Table 1. The asymmetric unit of **1** contains two crystallographically independent Ni(II) atoms, two unique OBA dianions, two unique L ligands, and two unique coordinated water molecules (Fig. 1). Each Ni(II) atom is six-coordinated by three oxygen atoms from two different OBA anions and one water molecule, and two nitrogen atoms from one L ligand in a distorted octahedral environment. Two nitrogen atoms (N5, N6 for Ni1 and N1, N2 for Ni2) and two oxygen atoms (O10, O1W for Ni1 and O2, O2W for Ni2) constitute the equational plane, while two oxygen atoms (O9, O7^i for Ni1 and O1, O5^i for Ni2) occupy the axial positions. The Ni–O bond lengths range from 2.015(3) to 2.145(3) Å, and the Ni–N distances vary from 2.06(4) to 2.075(4) Å. Each OBA anion bridges two neighboring Ni(II) atoms to yield two crystallographically independent chains (Fig. 2). It is
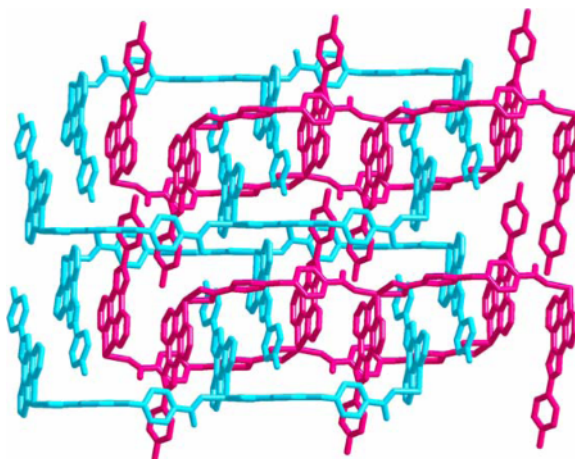

Fig. 2 (color online). View of the 2D supramolecular architecture of **1** formed by π-π interactions.

Table 1. Selected bond lengths (Å) and angles (deg) for **1** and **2** with estimated standard deviations in parentheses[a].

Compound **1**			
Distances			
Ni(1)–O(7)[i]	2.015(3)	Ni(2)–O(5)[i]	2.093(3)
Ni(1)–O(10)	2.105(3)	Ni(2)–O(1)	2.111(3)
Ni(1)–O(9)	2.127(3)	Ni(2)–O(2)	2.145(3)
Ni(1)–O(1W)	2.064(3)	Ni(2)–O(2W)	2.081(3)
Ni(1)–N(5)	2.075(4)	Ni(2)–N(1)	2.072(3)
Ni(1)–N(6)	2.062(3)	Ni(2)–N(2)	2.060(4)
Angles			
O(7)[i]–Ni(1)–N(6)	95.91(12)	N(2)–Ni(2)–O(5)[i]	93.65(12)
O(7)[i]–Ni(1)–O(1W)	93.15(11)	O(2W)–Ni(2)–O(5)[i]	91.78(12)
O(7)[i]–Ni(1)–N(5)	88.53(12)	N(1)–Ni(2)–O(5)[i]	98.58(12)
O(1W)–Ni(1)–N(5)	172.95(13)	N(2)–Ni(2)–O(2W)	171.47(12)
N(6)–Ni(1)–O(10)	163.59(11)	N(1)–Ni(2)–O(2)	159.52(12)
N(5)–Ni(1)–O(10)	93.66(12)	N(2)–Ni(2)–O(1)	89.39(13)
N(6)–Ni(1)–O(9)	102.58(11)	N(1)–Ni(2)–O(1)	98.53(12)
N(5)–Ni(1)–O(9)	93.69(12)	O(2)–Ni(2)–N(2)	93.10(13)
O(10)–Ni(1)–O(9)	62.42(10)	O(1)–Ni(2)–O(2)	61.89(10)
N(6)–Ni(1)–O(1W)	92.90(13)	N(1)–Ni(2)–O(2W)	92.72(13)
N(6)–Ni(1)–N(5)	80.12(13)	N(2)–Ni(2)–N(1)	79.97(14)
O(7)[i]–Ni(1)–O(10)	99.11(11)	O(5)[i]–Ni(2)–O(2)	101.10(11)
O(1W)–Ni(1)–O(10)	92.83(12)	O(2W)–Ni(2)–O(2)	92.31(12)
O(7)[i]–Ni(1)–O(9)	161.49(11)	O(5)[i]–Ni(2)–O(1)	162.89(11)
O(1W)–Ni(1)–O(9)	86.88(11)	O(2W)–Ni(2)–O(1)	87.35(12)
Compound **2**			
Distances			
Pb(1)–O(4)[i]	2.458(4)	Pb(1)–O(1)	2.770(4)
Pb(1)–O(5)[i]	2.86(2)	Pb(1)–N(1)	2.519(6)
Pb(1)–N(2)	2.509(5)	Pb(1)–N(5)	2.778(5)
Pb(1)–N(6)	2.773(6)		
Angles			
O(4)[i]–Pb(1)–N(2)	79.53(15)	N(6)–Pb(1)–N(5)	59.81(17)
O(4)[i]–Pb(1)–N(1)	75.61(16)	N(2)–Pb(1)–N(1)	64.77(17)
O(4)[i]–Pb(1)–N(6)	157.16(17)	N(2)–Pb(1)–N(6)	79.79(17)
N(1)–Pb(1)–N(6)	86.86(17)	O(4)[i]–Pb(1)–N(5)	130.05(15)
N(2)–Pb(1)–N(5)	129.13(14)	N(1)–Pb(1)–N(5)	82.31(16)
O(4)[i]–Pb(1)–O(1)	73.17(15)	N(2)–Pb(1)–O(1)	77.07(15)
N(1)–Pb(1)–O(1)	134.12(17)	O(1)–Pb(1)–N(6)	111.27(17)
O(1)–Pb(1)–N(5)	143.47(14)		

[a] Symmetry transformations used to generate equivalent atoms for **1**: [i] $x, y, z-1$; for **2**: [i] $-x-2, -y, z-1/2$.
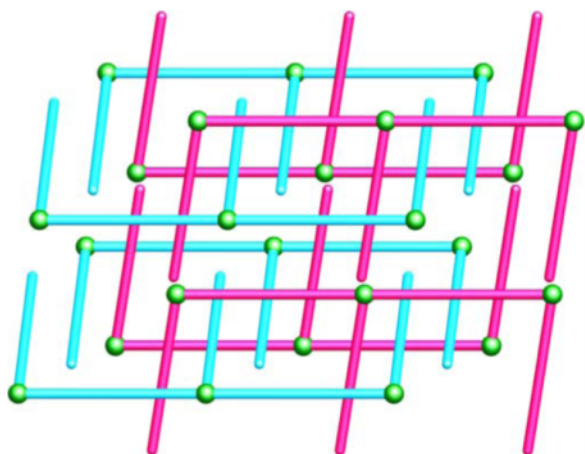

Fig. 3 (color online). Schematic representation of the 2D supramolecular architecture of **1** formed by π-π interactions.

noteworthy that the L ligands are only located on one side of the chain, with π-π stacking interactions between neighboring chains (with a centroid-to-centroid distance of 3.710 Å and a face-to-face distance of 3.524 Å). Through these π-π stacking interactions, neighboring chains are interlinked to generate a 2D supramolecular layer (Figs. 2 and 3). It is noted that a large number of 1D coordination polymers have been reported so far, however, examples with two crystallographically independent chains are rarely observed in this system [13 – 15].

Structure description of 2

As shown in Fig. 4, the asymmetric unit of **2** contains one Pb(II) atom, one OBA dianion, two L ligands, and three water molecules. Each Pb(II) atom is seven-coordinated by three carboxylate oxygen atoms from two different OBA dianions, and four nitrogen atoms from two L ligands. The Pb–N distances range from 2.458(4) to 2.778(5) Å, and the Pb–O distances are 2.458(4) and 2.86(2) Å. These distances are close to those reported for [Pb(L)(1,3-bdc)]·2.5H$_2$O (1,3-bdc = 1,3-benzenedicarboxylate) [16]. The OBA anions are in a bidentate bridging mode and link two neighboring Pb(II) atoms to form a fascinating helical chain with a Pb···Pb distance of 15.632 Å (Fig. 5). Different from those of **1**, in **2**, the L ligands are attached on both sides of the helical chains. π-π Stacking interactions among neighboring chains (with a centroid-centroid distance of 3.459 Å and a face-to-face distance of 3.361 Å) extend the adjacent helical chains into a 3D supramolecular architecture (Fig. 6).

Generally, the geometries of Pb(II) complexes can be classified as holo- and hemidirected [15]. Hemidirected refers to Pb(II) complexes where the bonds to the ligand atoms are directed through only part of
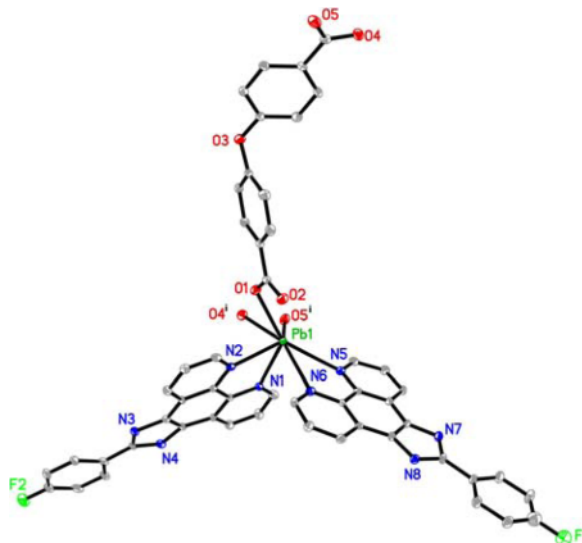

Fig. 4 (color online). ORTEP view of **2** showing the local coordination environment of the Pb(II) center with hydrogen atoms and non-coordinated water molecules omitted for clarity (15 % probability displacement ellipsoids).

an encompassing sphere, however, holodirected refers to those cases where the bonds to the ligand atoms are located throughout the surface of an encompassing sphere. In compound **2**, the arrangement of three O and four N atoms for the seven-coordinated Pb(II) atom suggests a gap or hole in the coordination geometry around this atom. Thus, its coordination sphere is hemidirected [16].

It is noteworthy that the structure of **2** is entirely different from that of [Pb(L)(1,3-bdc)]·2.5H$_2$O [16], where the Pb(II) atoms are bridged by the 1,3-bdc ligands to yield a linear chain structure. The ligands L are only located on one side of the chain, where π-π interactions among neighboring chains
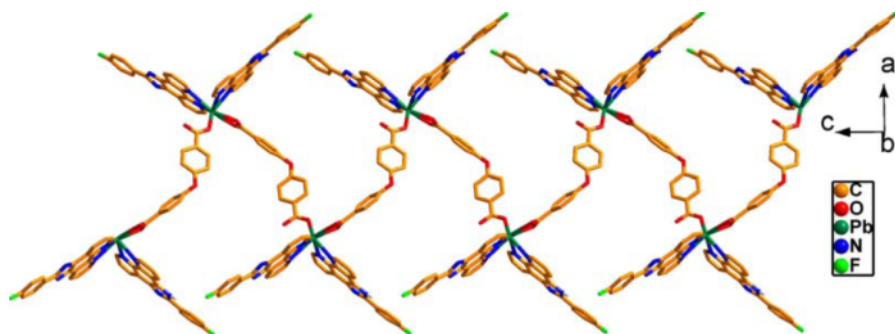

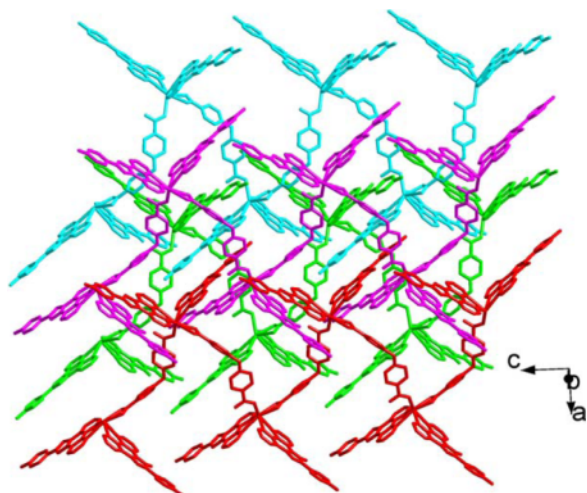Fig. 5 (color online). View of the helical chain structure of **2**.

Fig. 6 (color online). View of the 3D supramolecular architecture of **2** formed by π-π interactions.

Fig. 7. Plot of the temperature dependence of $\chi_m T$ (open squares) and χ_m^{-1} (open triangles) for compound **1**.

result in a supramolecular ladder. It should be pointed out that compound **2** and the related compound [Pb(OBA)(L')$_2$]·2H$_2$O (L' = 4-(1*H*-1,3,7,8-tetraazacyclopenta[*l*]phenanthren-2-yl)phenol) have similar *N*-donor ligands [17], but they show different chain structures. Compound **2** displays a helical chain structure with a Pb···Pb···Pb angle of 69.45°, whereas the other reported compound shows a more linear chain structure with the Pb···Pb···Pb angle of 155.98°.

IR spectra

The OH stretching vibrations of water molecules in complexes **1** and **2** are observed at 3364–3437 and 3071–3454 cm^{-1}, respectively. The strong peaks at 1684 and 1596 cm^{-1} for **1** and at 1691 and 1526 cm^{-1} for **2** are assigned to the asymmetric and symmetric stretching vibrations of the OBA carboxylate groups. The bands at 1160 and 1408 cm^{-1} can be attributed to the C=N and C-N stretching vibrations of the L ligands [18].

UV/Vis absorption spectra

The UV/Vis absorption spectra of compounds **1** and **2** were measured in the crystalline state at room temperature. The absorption bands of compound **1** from 550 to 700 nm may result from the *d-d* spin-allowed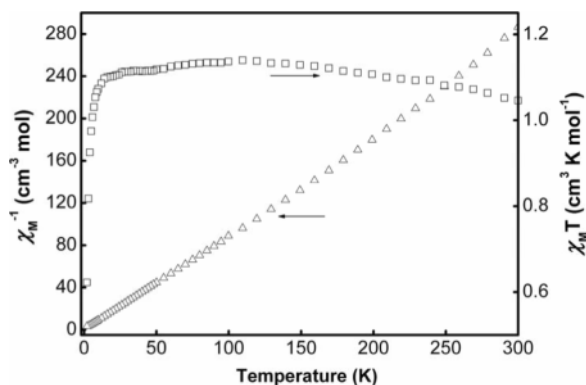 transition of the d^8 (Ni^{2+}) ion. The bands from 200 to 380 nm for **1** and from 200 to 400 nm for **2** probably originate from the $\pi \rightarrow \pi^*$ transitions of the ligands [18].

Magnetic properties

The temperature-dependent magnetic susceptibility of compound **1** has been measured at an applied magnetic field of 1 kOe (1 kOe = 7.96×10^4 A m^{-1}) in the temperature range of 2–300 K (Fig. 7). For **1**, the $\chi_m T$ value at 300 K is 1.046 cm^3 mol^{-1} K, which is corresponding to the expected value of non-interacting Ni(II) ions [19]. Upon cooling, the values of $\chi_m T$ gradually increase, exhibit a maximum value of 1.138 cm^3 mol^{-1} K at 100 K, and then keep almost constant from 100 to 26 K before going down quickly to a minimum value of 0.622 cm^3 mol^{-1} K at 2 K. This feature shows the occurrence of a weak ferromagnetic coupling between the Ni(II) ions [20]. The magnetic susceptibility in the temperature range of 300–26 K obeys the Curie-Weiss law with the Curie constant $C = 1.067$ cm^3 mol^{-1} K, and the Weiss constant $\Theta = 3.738$ K.

Experimental Section

General

All materials were of analytical or reagent grade and used as received without further purification. Elemental analysis was carried out with a Perkin-Elmer 240C analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. Diffuse reflectance UV/Vis spectra were measured from 200

Compound	1	2	
Formula	$C_{33}H_{21}FN_4NiO_6$	$C_{52}H_{36}F_2N_8O_8Pb$	Table 2. Crystal structure data for **1** and **2**.
M_r	647.25	1146.08	
Crystal size, mm^3	$0.27 \times 0.22 \times 0.17$	$0.29 \times 0.23 \times 0.19$	
Crystal system	triclinic	orthorhombic	
Space group	$P\bar{1}$	$Pna2_1$	
a, Å	13.8490(10)	16.256(4)	
b, Å	14.932(2)	16.085(5)	
c, Å	14.993(3)	17.810(3)	
α, deg	107.534(4)	90	
β, deg	94.670(4)	90	
γ, deg	103.836(5)	90	
V, Å^3	2830.9(7)	4657(2)	
Z	4	4	
D_{calcd}, g cm^{-3}	1.52	1.64	
$\mu(MoK_\alpha)$, mm^{-1}	0.7	3.7	
$F(000)$, e	1328	2272	
hkl range	$-16 \rightarrow 12, -17 \rightarrow 15, \pm 17$	$-15 \rightarrow 19, -15 \rightarrow 19, -21 \rightarrow 17$	
θ range, deg	$1.44 - 25.03$	$1.71 - 25.03$	
Refl. collect. / unique /R_{int}	17788 / 9987 / 0.0383	18132 / 7623 / 0.0268	
Data / ref. parameters	9987 / 818	7623 / 589	
$R1$ / $wR2$ [$I > 2\sigma(I)$]	0.0406 / 0.0846	0.0263 / 0.0619	
$R1$ / $wR2$ (all data)	0.0832 / 0.0904	0.0396 / 0.0633	
GoF (F^2)	0.810	0.923	
x (Flack)	–	$-0.003(5)$	
$\Delta\rho_{max/min}$, e Å^{-3}	0.87 / -0.88	0.66 / -0.75	

to 800 nm using barium sulfate as standard on a Varian Cary 500 spectrometer. Temperature-dependent magnetic susceptibility data for compound **1** were obtained on a Quantum Design MPMSXL SQUID magnetometer under an applied field of 1 kOe over the temperature range of $2 - 300$ K.

Syntheses of compounds 1 and 2

NiCl$_2$·6H$_2$O (1 mmol), L (1 mmol) and H$_2$OBA (1 mmol) were dissolved in 10 mL distilled water, followed by addition of triethylamine until the pH value of the system was adjusted to between 5 and 6. The resulting solution was stirred for about 30 min at r. t., sealed in a 23 mL Teflon-lined stainless-steel autoclave and heated at 421 K for 3 d under autogeneous pressure. After the mixture had been cooled to room temperature at a rate of 10 $^\circ$C·h^{-1}, blue crystals of **1** were obtained. Yield: 19 % based on Ni(II). − Anal. for C$_{33}$H$_{21}$FN$_4$NiO$_6$ (%): calcd. C 61.24, H 3.27, N 8.66; found C 61.53, H 3.40, N 8.29. − IR (KBr, cm^{-1}): $\nu = 3437$m, 3364w, 1773w, 1684m, 1596s, 1533s, 1496m, 1408s, 1243s, 1160s, 1065w, 1000w, 954w, 877w, 800w, 776w, 723w, 641w. The preparation of **2** was similar to that of **1** except that Pb(NO$_3$)$_2$ (0.5 mmol) was used instead of NiCl$_2$·6H$_2$O (0.1 mmol). Crystals of **2** suitable for single-crystal X-ray diffraction analysis were collected by filtration, washed several times with distilled water and dried in air at ambient temperature. Yield 39 % based on Pb(II). − Anal. for C$_{52}$H$_{36}$F$_2$N$_8$O$_8$Pb (%): calcd. C 54.49, H 3.17, N

9.78; found C 54.62, H 3.01, N 10.33. − IR (KBr, cm^{-1}): $\nu = 3454$w, 3071w, 1684w, 1691s, 1608m, 1526s, 1484s, 1390s, 1289s, 1243s, 1148s, 1072m, 1025w, 947w, 842s, 806m, 730m, 618m.

X-Ray structure determinations

Single-crystal X-ray diffraction data for **1** and **2** (Table 2) were recorded on an Oxford Diffraction Gemini R Ultra diffractometer with graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å) at 293 K. The structures were solved by Direct Methods with SHELXS-97 [21] and refined by full-matrix least-squares techniques using the SHELXL-97 [22] program. Non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms attached to the carbon atoms were generated geometrically. Some water H atoms of **1** and **2** were not located in difference Fourier maps.

CCDC 875856 (**1**) and 875857 (**2**) 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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