

Syntheses, Structures and Photoluminescent Properties of Two New Pb(II) and Cd(II) Coordination Polymers Constructed from 1,10-Phenanthroline-derived and 1,4-Naphthalenedicarboxylate Ligands

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Two new related coordination polymers, namely, [Pb(L)(1,4-ndc)] · 0.5H₂O (**1**) and [Cd(L)(1,4-ndc)] · 0.5H₂O (**2**), where L = 2-(3-fluorophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline and 1,4-ndc = 1,4-naphthalenedicarboxylate, were synthesized under hydrothermal conditions. Crystal data for **1**: C₆₂H₃₆F₂N₈O₉Pb₂, monoclinic space group *C2/c*, *a* = 15.874(3), *b* = 19.982(4), *c* = 16.045(3) Å, β = 94.26(3), *V* = 5075.3(18) Å³, *Z* = 4. Crystal data for **2**: C₆₂H₃₆Cd₂F₂N₈O₉, monoclinic space group *P2₁/n*, *a* = 12.622(2), *b* = 14.038(3), *c* = 14.938(3) Å, β = 100.81(2), *V* = 2600.0(8) Å³, *Z* = 2. In compound **1**, the 1,4-ndc ligands connect the Pb(II) atoms to yield a chain structure. The L ligands are attached on the same side of the chain. The π - π interactions between L ligands of neighboring chains result in a 2D supramolecular architecture of **1**. In compound **2**, 1,4-ndc ligands link the Cd(II) atoms to generate a layer structure. The L ligands from adjacent layers are paired to furnish strong π - π interactions. Further, these layers are extended into 3D supramolecular architectures through these π - π interactions. The structural differences of **1** and **2** suggest the importance of the metal centers in the construction of the coordination polymers. The luminescent properties of the compounds were also investigated.

Key words: Coordination Polymer, Crystal Structure, 2-(3-Fluorophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline, 1,4-Naphthalenedicarboxylate

Introduction

Research on the design and synthesis of coordination polymers has attracted much attention, not only for their functional material purposes, but also for their fascinating structures and topologies [1–3]. Consequently, a number of coordination polymers with various topological architectures and properties have been constructed and reported [4–6]. It is well-known that there are several factors that can influence the self-assembly of coordination polymers, such as the chemical structure of the ligands, the metal centers, the anions, reaction temperature and pH value [7]. In this regard, the selection of the ligands is a vital subject in the construction of the coordination polymers [8]. Up to now, nitrogen-containing rigid polydentate ligands, such as pyrazine, 4,4'-bipyridine, 2,2'-bipyridine, and 1,10-phenanthroline (phen), have been extensively in-

vestigated [9, 10]. The phen ligand is particularly interesting because of its excellent coordinating ability and the large conjugated system that can easily form π - π interactions [11]. On this basis, a number of coordination polymers have been prepared from covalently bonded chains or layers, yielding extended 2D or 3D supramolecular structures through these interactions [11]. However, investigations on phen-derived ligands have been lacking [12].

In recent years, we have investigated the coordination chemistry of phen-derived ligands [13]. The results have shown that these ligands are good candidates for the construction of coordination polymers with interesting supramolecular architectures [14, 15]. As a continuation of the investigation of the new phen derivatives, two related Pb(II) and Cd(II) coordination polymers with different structures and topologies were synthesized under hydrothermal conditions,

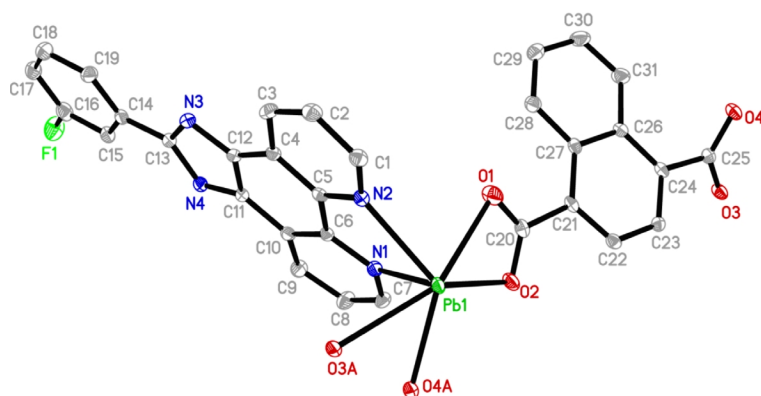


Fig. 1 (color online). ORTEP view of the molecular structure of **1** in the crystal showing the local coordination environment of the Pb(II) center (hydrogen atoms and water molecules omitted for clarity; displacement ellipsoids at the 30 % probability level; of the disordered fluorine atoms only one alternative is shown).

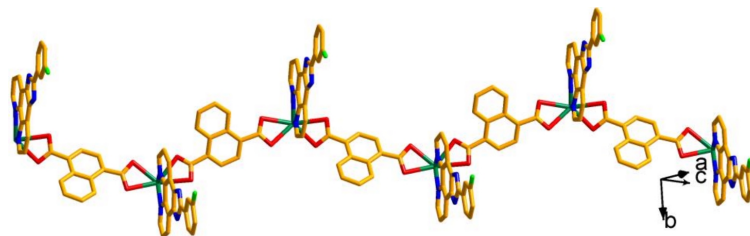


Fig. 2 (color online). View of the chain structure of **1** in the crystal.

namely, $[\text{Pb}(\text{L})(1,4\text{-ndc})] \cdot 0.5\text{H}_2\text{O}$ (**1**) and $[\text{Cd}(\text{L})(1,4\text{-ndc})] \cdot 0.5\text{H}_2\text{O}$ (**2**), where $\text{L} = 2\text{-(3-fluorophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline}$ and $1,4\text{-ndc} = 1,4\text{-naphthalenedicarboxylate}$. Both compounds have been characterized by elemental analysis and X-ray crystallography. In addition, their photoluminescent properties in the solid state have also been investigated.

Results and Discussion

Structure description of **1**

The crystal structures of $[\text{Pb}(\text{L})(1,4\text{-ndc})] \cdot 0.5\text{H}_2\text{O}$ (**1**) and $[\text{Cd}(\text{L})(1,4\text{-ndc})] \cdot 0.5\text{H}_2\text{O}$ (**2**) have been determined by single-crystal X-ray diffraction. Selected bond lengths and angles for both structures are listed in Table 1. There are one crystallographically independent Pb(II) atom, one L ligand, one 1,4-ndc anion, and one half water molecule in the asymmetric unit of **1**. As shown in Fig. 1, each Pb(II) atom is six-coordinated by two nitrogen atoms from one L ligand, and four carboxylate oxygen atoms from two different 1,4-ndc anions in a severely distorted, irregular coordination geometry. The Pb–O bond lengths range from 2.526(2) to 2.682(2) Å, and the Pb–N bond lengths are 2.465(3) and 2.557(3) Å. Each carboxylate group of a 1,4-ndc ligand chelates one Pb(II) atom. In this way, the 1,4-ndc ligands link neighboring Pb(II) atoms to yield a unique chain structure with

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

<i>Compound 1:</i>			
Pb(1)–N(1)	2.465(3)	Pb(1)–N(2)	2.557(3)
Pb(1)–O(1)	2.558(3)	Pb(1)–O(2)	2.528(2)
Pb(1)–O(4) ⁱ	2.526(2)	Pb(1)–O(3) ⁱ	2.682(2)
N(1)–Pb(1)–O(4) ⁱ	76.17(9)	N(1)–Pb(1)–O(2)	78.50(9)
O(4) ⁱ –Pb(1)–O(2)	88.18(8)	O(4) ⁱ –Pb(1)–O(1)	137.54(9)
O(4) ⁱ –Pb(1)–N(2)	124.21(9)	N(1)–Pb(1)–O(1)	82.64(10)
N(1)–Pb(1)–O(3) ⁱ	71.43(9)	O(2)–Pb(1)–O(3) ⁱ	132.97(8)
O(1)–Pb(1)–O(3) ⁱ	149.99(10)	N(1)–Pb(1)–N(2)	65.37(9)
O(2)–Pb(1)–O(1)	51.37(8)	O(2)–Pb(1)–N(2)	119.68(9)
N(2)–Pb(1)–O(1)	76.52(9)	O(4) ⁱ –Pb(1)–O(3) ⁱ	50.36(8)
N(2)–Pb(1)–O(3) ⁱ	79.05(8)		
<i>Compound 2:</i>			
Cd(1)–N(1)	2.304(2)	Cd(1)–N(2)	2.342(2)
Cd(1)–O(1)	2.2975(19)	O(3) ⁱ –Cd(1)	2.300(3)
Cd(1)–O(1) ⁱⁱ	2.3425(19)	Cd(1)–O(4) ⁱ	2.419(2)
O(1)–Cd(1)–O(3) ⁱ	95.87(12)	O(1)–Cd(1)–N(1)	111.97(8)
O(3) ⁱ –Cd(1)–N(1)	92.78(11)	O(1)–Cd(1)–N(2)	169.25(10)
O(3) ⁱ –Cd(1)–N(2)	98.68(13)	N(1)–Cd(1)–N(2)	71.83(8)
O(1)–Cd(1)–O(1) ⁱⁱ	70.58(7)	O(3) ⁱ –Cd(1)–O(1) ⁱⁱ	145.26(10)
N(1)–Cd(1)–O(1) ⁱⁱ	121.89(8)	N(2)–Cd(1)–O(1) ⁱ	94.74(7)
O(1)–Cd(1)–O(4) ⁱ	95.42(9)	O(3) ⁱ –Cd(1)–O(4) ⁱ	53.89(10)
N(1)–Cd(1)–O(4) ⁱ	139.52(9)	N(2)–Cd(1)–O(4) ⁱ	89.59(9)
O(1) ⁱⁱ –Cd(1)–O(4) ⁱ	94.56(8)		

Symmetry transformations used to generate equivalent atoms for **1**: (i) $x - 1/2, -y + 1/2, z - 1/2$; for **2**: (i) $-x + 3/2, y - 1/2, -z + 3/2$; (ii) $-x + 1, -y + 1, -z + 1$.

Pb···Pb distances of 11.587 Å (Fig. 2). Notably, the L ligands extend only from one side of the chain, and

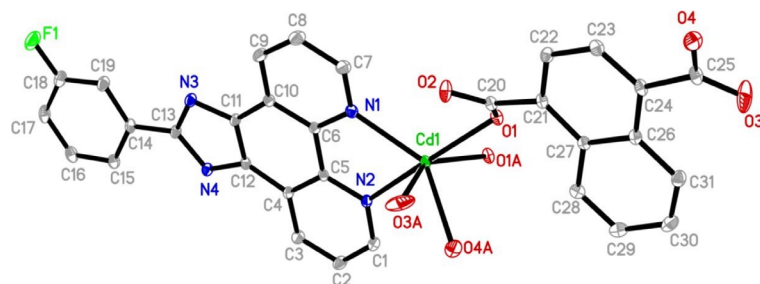


Fig. 4 (color online). ORTEP view of the molecular structure of **2** in the crystal showing the local coordination environment of the Cd(II) center (hydrogen atoms and water molecules omitted for clarity; displacement ellipsoids at the 30 % probability level; of the disordered fluorine atoms only one alternative is shown).

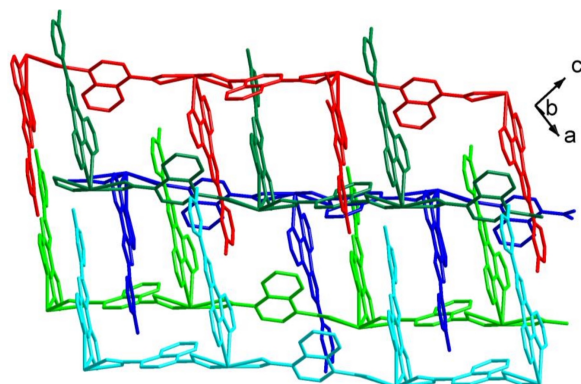


Fig. 3 (color online). View of the 2D supramolecular architecture of **1** formed by π - π interactions.

the planes of adjacent L ligands in the same chain are nearly parallel. The L ligands are paired to furnish strong arene π - π stacking interactions (centroid-to-centroid distance of *ca.* 3.51 Å and face-to-face distance of *ca.* 3.43 Å), which extend the chains into a 2D supramolecular architecture (Fig. 3). O-H \cdots O and N-H \cdots O hydrogen bonding interactions further stabilize the 2D supramolecular architecture of **1**.

Structure description of **2**

Compound **2** has a 2D supramolecular network structure in the crystal. As shown in Fig. 4, the asymmetric unit of **2** contains one crystallographically independent Cd(II) atom, one ligand L, one 1,4-ndc anion, and one half water molecule. Each Cd(II) atom is six-coordinated by two nitrogen atoms from one L ligand and four carboxylate oxygen atoms from three different 1,4-ndc anions in a distorted octahedral coordination geometry. The Cd-O bond lengths range from 2.298(2) to 2.419(2) Å, and the Cd-N distances vary from 2.304(2) to 2.342(2) Å, which are near to the data reported for [Cd₂(DFDA)₂(L1)₂] (DFDA = 9,9-dipropylfluorene-2,7-dicarboxylate anion; L1 = 1,4-bis(imidazol-1-ylmethyl)benzene) [16]. Notably, one

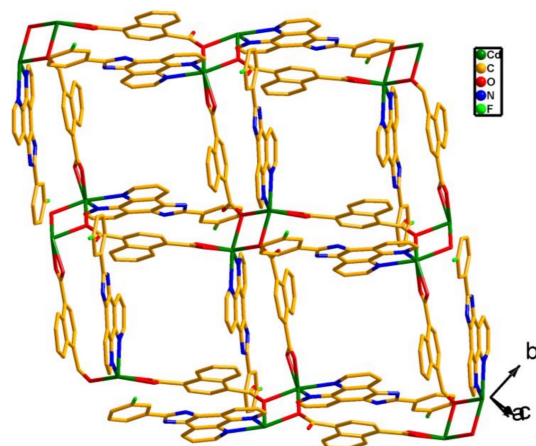


Fig. 5 (color online). View of the layer structure of **2** in the crystal.

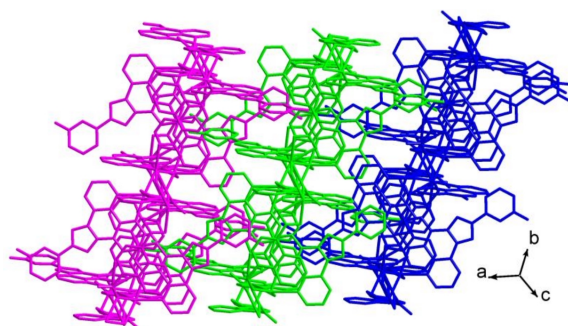


Fig. 6 (color online). View of the 3D supramolecular architecture of **2** formed by π - π interactions.

carboxylate group of each 1,4-ndc anion bridges two Cd(II) atoms to form a dimer with Cd \cdots Cd separations of 3.787 Å. Interestingly, the backbone of the 1,4-ndc ligands further links the dimers to yield a unique layer structure (Fig. 5). As shown in Fig. 6, the ligands L from adjacent layers are paired to furnish strong π - π interactions (centroid-to-centroid distance of *ca.* 3.61 Å and face-to-face distance of *ca.* 3.50 Å). Therefore, these layers are extended into

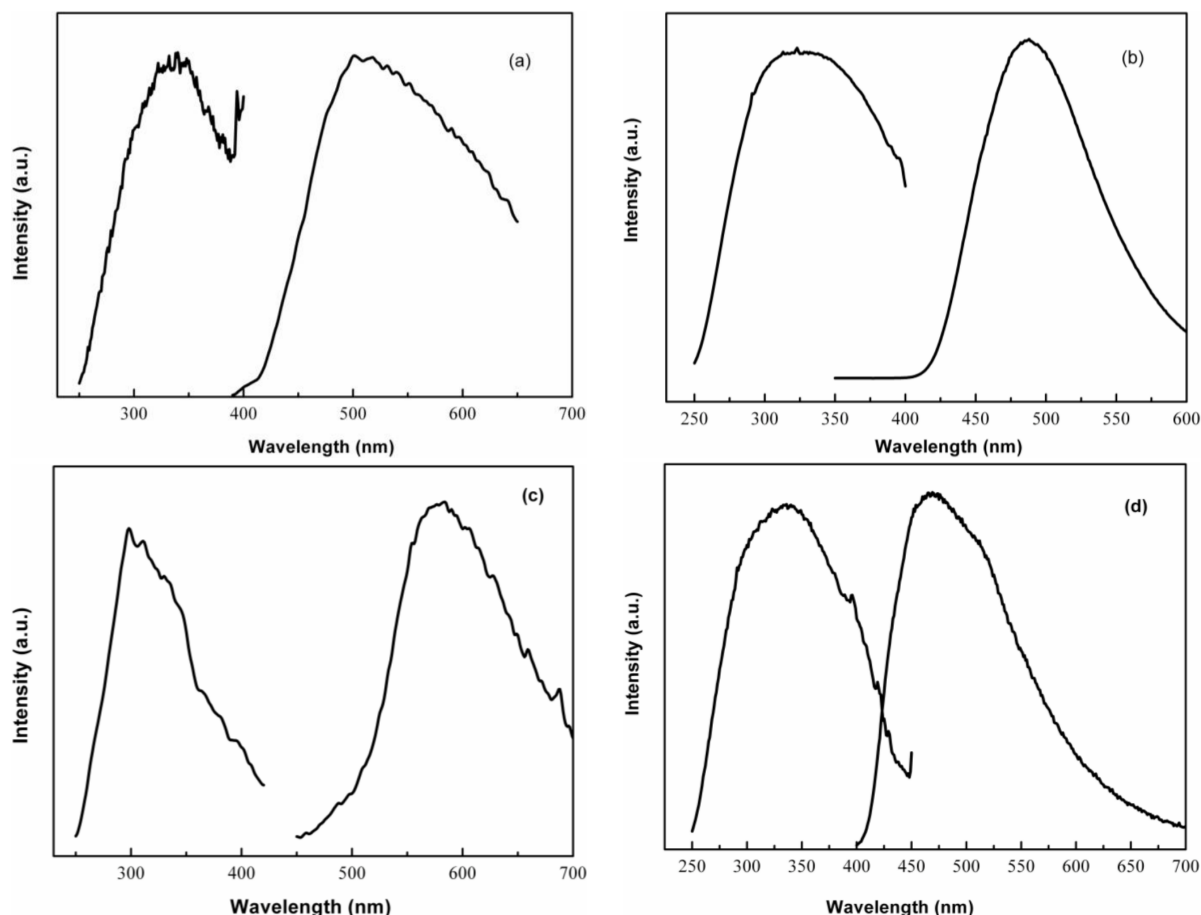


Fig. 7. Photoluminescence excitation and emission spectra of **L** (a), 1,4-ndcH₂ (b), **1** (c), and **2** (d) at r. t.

a 3D supramolecular architecture through π - π interactions (Fig. 6). Clearly, the π - π stacking interactions play a key role in the formation and stabilization of the supramolecular architecture of **2**. Moreover, N-H \cdots O hydrogen bonding interactions further stabilize the 3D supramolecular structure of **2**.

Clearly, the structural differences between **1** and **2** are mainly attributed to the central metals. Compared with the Cd(II) centers in **2** (without lone pairs of electrons), the irregular coordination geometry of the Pb(II) centers in **1** clearly points to a stereochemically active lone pair located in the empty space opened up by the coordinated carboxylate oxygen atoms opposite to the ligand **L**. With respect to the stereochemical activity of the lone pairs, the geometries of Pb(II) complexes can be classified as holo- and hemi-directed [13]. In compound **1**, the coordination of the ligands at Pb(II) leaves room for the lone pair of elec-

trons. Therefore, this coordination environment can be considered to be somewhat hemi-directed [13].

Luminescent properties

The photoluminescence of Cd(II) and Pb(II) complexes has been attracting intensive research interest because of their potential applications in chemical sensors and photochemistry. However, little attention has been paid to the luminescence of Pb(II) coordination polymers so far [17]. To examine the photoluminescent properties of complexes **1** and **2**, their luminescence spectra were measured in the solid state at room temperature (Fig. 7). **L** and 1,4-ndcH₂ show emissions at about 513 ($\lambda_{\text{ex}} = 336$ nm) and 486 nm ($\lambda_{\text{ex}} = 324$ nm), which may be attributed to the $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ transitions as previously reported [18]. Compound **1** exhibits an emission at about 587 nm ($\lambda_{\text{ex}} = 304$ nm).

Compound	1	2
Formula	C ₆₂ H ₃₆ F ₂ N ₈ O ₉ Pb ₂	C ₆₂ H ₃₆ Cd ₂ F ₂ N ₈ O ₉
<i>M_r</i>	1489.37	1299.79
Crystal size, mm ³	0.22 × 0.17 × 0.11	0.20 × 0.17 × 0.10
Crystal system	monoclinic	monoclinic
Space group	C2/c	P2 ₁ /n
<i>a</i> , Å	15.874(3)	12.622(2)
<i>b</i> , Å	19.982(4)	14.038(3)
<i>c</i> , Å	16.045(3)	14.938(3)
β, deg	94.26(3)	100.81(2)
<i>V</i> , Å ³	5075.3(18)	2600.0(8)
<i>Z</i>	4	2
<i>D</i> _{calcd} , g cm ^{−3}	1.95	1.66
μ(MoK _α), mm ^{−1}	6.7	0.9
<i>F</i> (000), e	2872	1300
<i>hkl</i> range	±20, ±25, −20 → 19	±16, ±18, ±19
θ range, deg	3.11–27.48	3.29–27.48
Refl. collect. / unique / <i>R</i> _{int}	23989 / 4735 / 0.0388	24910 / 5151 / 0.0270
Data / ref. parameters	5798 / 387	5935 / 361
<i>R</i> 1 / <i>wR</i> 2 [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0262 / 0.0463	0.0349 / 0.0873
<i>R</i> 1 / <i>wR</i> 2 (all data)	0.0391 / 0.0502	0.046 / 0.0905
GoF (<i>F</i> ²)	1.025	1.053
Δρ _{max/min} , e Å ^{−3}	0.079 / −0.85	0.98 / −0.73

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

The emissions of the Pb(II) compound **1** in the solid state originate from the ³P₁ level (³P₁ → ¹S, ³P₂ → ¹S, and ¹P₁ → ¹S) [10]. Compound **2** shows an emission at about 473 nm (λ_{ex} = 335 nm). The solid-state luminescence of the Cd(II) compound **2** may be attributed to the intraligand charge transfer of the coordinated 1,4-ndc ligand which is similar to that of 1,4-ndcH₂.

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 photoluminescence properties of the ligands and compounds were measured on a Perkin-Elmer FLS-920 spectrometer.

Syntheses of compounds **1** and **2**

A mixture of Pb(NO₃)₂ (0.5 mmol), L (0.5 mmol), 1,4-ndcH₂ (0.5 mmol), and water (10 mL) was placed in a Teflon reactor (15 mL) and heated at 445 K for 7 d. After the mixture had cooled to r. t. at a rate of 10 °C h^{−1}, pale-yellow crystals of **1** were obtained. Yield: 22 % based on Pb(II). – Anal. for C₆₂H₃₆F₂N₈O₉Pb₂ (%): calcd. C 50.07, H 2.30, N 7.53; found C 50.31, H 2.58, N 7.70. The preparation of **2** was similar to that of **1** except that CdCl₂ · 2H₂O (0.5 mmol) was used instead of Pb(NO₃)₂. Yield: 19 % based on Cd(II). – Anal. for C₆₂H₃₆Cd₂F₂N₈O₉: calcd. C 57.38, H 2.64, N 8.63; found C 57.22, H 2.59, N 8.48. It should be mentioned that when the pH values of the preparations of **1**

and **2** are adjusted to about 5–6 by addition of a suitable base, products **1** and **2** can probably be obtained in higher yields.

X-Ray structure determination

Single-crystal X-ray diffraction data for **1** and **2** were recorded on a Rigaku RAXIS-RAPID image plate diffractometer with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) at 293 K. The structures were solved by Direct Methods with SHELXS-97 [19] and refined by full-matrix least-squares techniques using the program SHELXL-97 [20]. Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms of the ligands were refined as part of rigid groups. Water H atoms of **1** were located in a difference Fourier map and refined as riding atoms with *d*(O–H) = 0.85–0.89 Å and *U*_{iso} = 1.5 *U*_{eq}(O). The F atoms of **1** and **2** were found to be disordered about the two *meta*-positions of the phenyl rings [C(16)/C(18)] and refined as split atom model with half occupancy each. Table 2 summarizes the crystal data as well as numbers pertinent to data collection and structure refinement.

CCDC 844728 and 844729 for **1** and **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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