Syntheses and Crystal Structures of Two Novel Zinc(II) Coordination Polymers

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Two novel zinc(II) coordination polymers, $[Zn_3(\mu_3\text{-}OH)_2(nip)_2]$ (**1**) and $[Zn_2(nip)_2(4,4'\text{-}bpy)_3{\cdot}(OH_2)]$ (**2**) (H_2nip = 5-nitroisophthalic acid, 4,4′-bpy = 4,4′-bipyridyl), were obtained by the hydrothermal reactions of zinc nitrate, 5-nitroisophthalate (nip) (for **1**) and zinc nitrate, 5-nitroisophthalate and 4,4′-bipyridyl (for **2**). Complex **1** displays a two-dimensional structure that is built from $[Zn_3(\mu_3\text{-}OH)_2]_n$ chains, while complex **2** is a three-dimensional structure formed by the interpenetration of two-dimensional hydrogen-bonded bilayers. The photoluminescent properties of complex **1** have also been investigated.

Introduction

Recently, coordination polymer frameworks have attracted great attention not only owing to their fascinating applications in the areas of magnetism, optics, electronics, catalysis and sorption,[1−5] but also to their interesting topologies.[6] Among the frameworks reported so far, two types of interactions — coordinate covalent bonds and non-covalent intermolecular forces such as hydrogen bonding and π-π stacking — play major roles in constructing and stabilizing these polymers. Currently, the direct mixing of metal ions and a single organic ligand by means of coordinative covalent and/or hydrogen-bonding interactions has produced a great variety of such frameworks. One of our research interests has focused on a systematic study of the construction of coordination polymers by using mixed organic ligands under hydrothermal conditions,[7] and recently we have been investigating the influences of substituted isophthalate derivatives, such as 5-nitroisophthalate (nip), in which the two carboxylate groups can form covalent bonds with metal centers while the nitro group acts as a hydrogen-bond acceptor and can form strong hydrogen bonds, on the assembly process of coordination polymers.[8] Here we report the syntheses and crystal structures of two novel zinc(II) coordination polymers with the 5-nitroisophthalate ligand (nip), namely $[Zn_3(\mu_3\text{-}OH)_2(nip)_2]$ (**1**) and $[Zn_2(nip)_2(4,4'\text{-}bpy)_3{\cdot}(OH_2)]$ (**2**). Interestingly, the nitro groups in complex **1** play important roles in the formation of the hydrogen bonds, while in complex **2** the 4,4′-bpy ligands act as hydrogen-bond acceptors.

Results and Discussion

The structures of $[Zn_3(\mu_3\text{-}OH)_2(nip)_2]$ (**1**) and $[Zn_2(nip)_2(4,4'\text{-}bpy)_3{\cdot}H_2O]$ (**2**) were determined by single-crystal X-ray crystallography. Selected bond lengths and angles for **1** and **2** are listed in Table 1 and 2, respectively,

Table 1. Selected bond lengths [Å] and angles [deg] for **1**[a]

Zn1−O1	1.997(1)	Zn1−O2	1.920(1)
Zn2−O1	2.086(1)	Zn2−O3	2.135(1)
O1−Zn1−O1A	85.25(7)	O1−Zn1−O2	110.65(7)
O2−Zn1−O1A	129.14(2)	O2−Zn1−O2B	96.08(6)
O1−Zn2−O3	97.18(5)	O1−Zn2−O1D	180.00(10)
O1−Zn2−O3D	82.82(5)	O3−Zn2−O3E	88.46(6)

[a] Symmetry codes: A $x, -y, z + 1$; B $-x, -y, -z + 1$; C $- x, y, z$; D $-x, -y, -z$; E $-x, y, -z$.

Table 2. Selected bond lengths [Å] and angles [deg] for **2**[a]

Zn1−O1	2.245(6)	Zn1−O2	2.386(6)
Zn1−O4A	2.076(4)	Zn1−N1	2.164(5)
Zn1−N3	2.179(5)	Zn1−N5	2.208(4)
Zn2−O7	2.280(4)	Zn2−O8	2.140(4)
Zn2−O1W	2.058(5)	Zn2−O10B	2.033(4)
Zn2−N2	2.181(5)	Zn2−N4C	2.177(5)
O4A−Zn(1)−O1	86.52(19)	O4A−Zn1−O2	142.33(18)
N1−Zn1−N5	91.07(17)	N1−Zn1−N3	175.41(19)
O4A−Zn1−N1	89.59(18)	N1−Zn1−O1	88.93(18)
O8−Zn2−O7	60.23(15)	O1W−Zn2−O7	164.30(18)
O10B−Zn2−O1W	102.0(2)	O10B−Zn2−O8	153.66(17)
O1W−Zn2−N4C	90.3(2)	O8−Zn2−N4C	88.27(18)
O1W−Zn2−N2	91.7(2)	N4C−Zn2−N2	178.01(19)

[a] Symmetry codes: A $x + 1, y, z$; B $x -1, y, z$; C $x, y, z + 1$.

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Table 3. Crystallographic data for complex **1** and **2**

	1	**2**
Chemical formula	$C_{16}H_8N_2O_{14}Zn_3$	$C_{46}H_{32}N_8O_{13}Zn_2$
Mol. wt.	648.35	1035.54
Space group	$C2/m$	$P\bar{1}$
a (Å)	14.7847(16)	10.1001(8)
b (Å)	10.2014(11)	11.0760(8)
c (Å)	6.2298(7)	22.919(2)
α (°)	90	99.774(4)
β (°)	91.797(6)	91.441(4)
γ (°)	90	115.304(4)
V (Å^3)	939.15(18)	2270.5(3)
Z	2	2
D_c (g·cm^{-3})	2.293	1.515
μ (mm^{-1})	3.889	1.132
R_1, wR_2 (all data)	0.0512, 0.0971	0.0665, 0.1787

with crystallographic and refinement data in Table 3. As shown in Figure 1, compound **1** contains two-dimensional sheets constructed from $[Zn_3(\mu_3\text{-}OH)_2]_n$ chains and nip ligands, in which the crystallographically equivalent unit is one half of a nip ligand, one half of a Zn1 center, one quarter of a Zn2 center and one half of a μ3-hydroxy group. The Zn1 center has pseudo-tetrahedral coordination symmetry, and is ligated by two oxygen atoms from two crystallographically equivalent μ3-hydroxy groups [Zn1−O1 = 1.997(1) Å] and two oxygen atoms from two carboxylate groups [Zn1−O2 = 1.902(1) Å] of two symmetry-related nip ligands. The Zn2 atom is bound to four oxygen atoms from four different nip ligands in the equatorial plane and two oxygen atoms from two μ3-hydroxy groups to give a pseudo-octahedral center [Zn2−O1 = 2.086(1) Å and Zn2−O3 = 2.135(1) Å]. The average Zn−O(H)−Zn angle (108.26°) in **1** is close to those found in typical tetrahedral Zn complexes containing μ3-hydroxy groups, rather than the trigonal-planar one generally observed for μ3-hydroxy groups.[9] The infinite $[Zn_3(\mu_3\text{-}OH)_2]_n$ chain-like structural motif shown in Figure 2 is also observed in the structures of three-dimensional basic zinc 4,4′-biphenyldicarboxylate and discrete basic zinc crotonate.[9a,10]

The infinite $[Zn_3(\mu_3\text{-}OH)_2]_n$ chains are stacked in parallel and connected by the nip ligands to give a two-dimensional undulating sheet. Viewed along the crystallographic *a* axis (Figure 3), the resulting two-dimensional framework is reminiscent of the shape of a compressed square, and obviously contains the C_{2h} point group. The nitro groups are found on the wave crest of both sides of the sheet, and the μ3-hydroxy groups point away from the $[Zn_3(\mu_3\text{-}OH)_2]_n$ chains and into the trough. These undulating two-dimensional sheets are stacked in a parallel fashion with the wave crests coinciding with the troughs of adjacent sheets, and vice versa. The whole three-dimensional structure is then stabilized by inter-layer moderate hydrogen bonds (O1···O4 = 3.109 Å) between the μ3-hydroxy groups in one

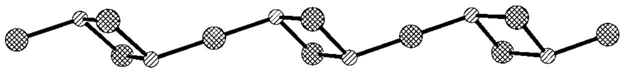

Figure 2. Perspective view of the one-dimensional $[Zn_3(\mu_3\text{-}OH)_2]_n$ structural motif

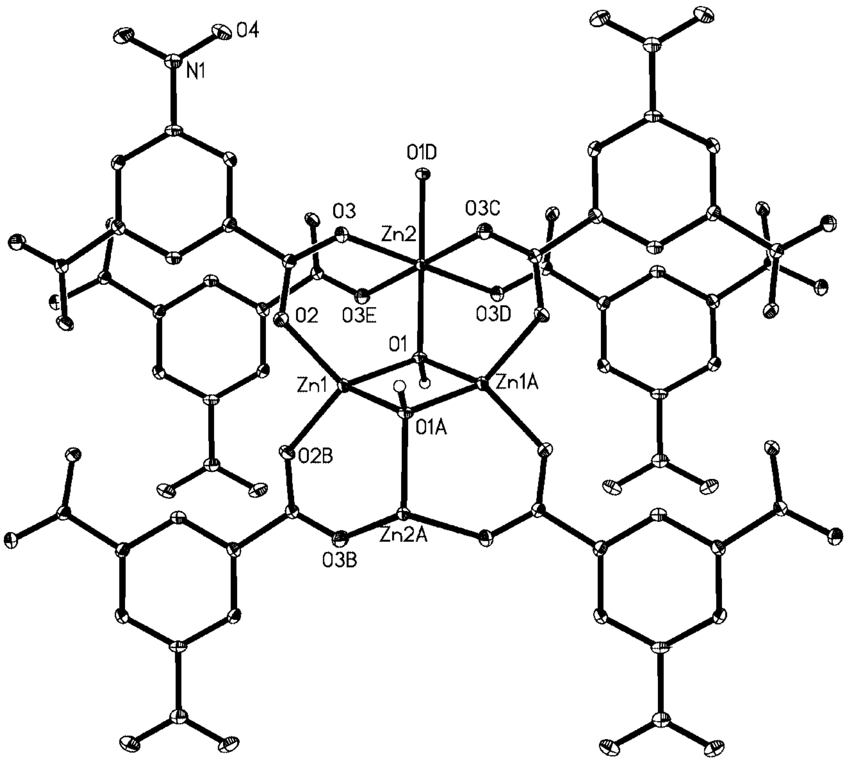

Figure 1. The coordination environments of zinc atoms in **1** with the atomic labeling scheme (30% probability)

sheet and the nitro oxygen atoms in the adjacent sheet (Figure 4); they are bifurcated hydrogen bonds with $d_1 = d_2$.[11]

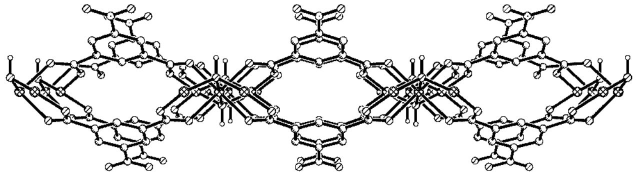

Figure 3. The two-dimensional structure of **1** viewed along the *a* axis

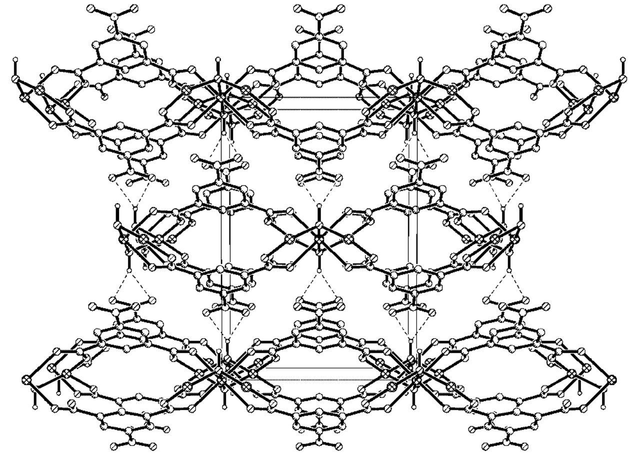

Figure 4. The hydrogen-bonded three-dimensional structure of **1** packed along the *a* axis

The crystal structure of **2** consists of hydrogen-bonded two-dimensional bilayered cuboids as the fundamental building unit. In the asymmetric unit there are two crystallographically unique Zn atoms, three 4,4′-bpy ligands, two nip ligands and one water molecule. The immediate coordination arrangement around the zinc centers in **2** is shown in Figure 5. The Zn1 atom lies in a slightly distorted octahedral environment, consisting of three nitrogen atoms from three different 4,4′-bpy ligands and three oxygen atoms from two symmetry-related nip carboxylate groups. The Zn2 atom, slightly different from Zn1 in its coordination environment, is ligated by two nitrogen atoms from two different 4,4′-bpy ligands, three oxygen atoms from two symmetry-related nip carboxylate groups and one water molecule, completing an octahedral coordination at Zn2. It is interesting to note that the 4,4′-bpy ligand containing the N5 and N6 atoms is linked to the Zn1 atom through only one of the nitrogen ends (N5), while the other end (N6) is hydrogen bonded to the coordinated water molecule in the adjacent layer [O1W···N6D = 2.758(7) Å], the water molecule is also hydrogen-bonded to the oxygen atom [O1W···O9B 2.653(7) Å] of a nip carboxylate group. Even more interesting is the fact that the three crystallographically unique 4,4′-bpy ligands are all non-coplanar, as can be seen from their different dihedral angles (N1−N2 = 36.4°, N3−N4 = 20.6° and N5−N6 = 29.6°).

The distinctive feature of **2** is that the alternating $[Zn(nip)(4,4'\text{-}bpy)]_n$ and $[Zn(nip)(H_2O)]_n$ chains are covalently linked by μ_2-4,4′-bpy bridges, resulting in an interesting two-dimensional (4,4) coordination sheet with 4,4′-bpy ligands (N5−N6) suspended on one side (Figure 6). Two such sheets, located at an inversion center, are linked into a

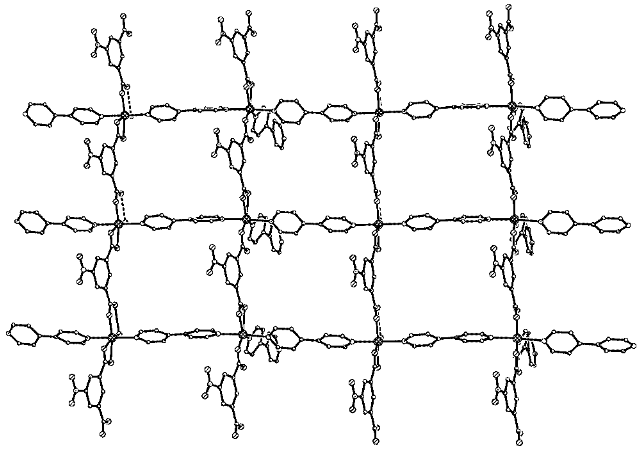

Figure 6. Perspective view of the two-dimensional (4,4) sheet of **2**

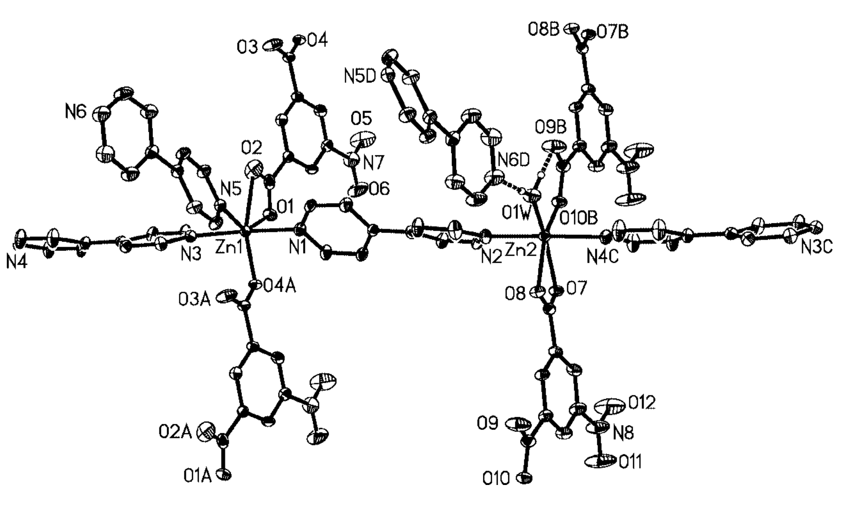

Figure 5. The coordination environments of zinc atoms in **2** with the atomic labeling scheme (30% probability)

two-dimensional bilayer by inter-layer hydrogen bonds [O1W···N6 = 2.758(7) Å] in a face-to-face fashion, whereas the nitro groups adopt an orientation that can be regarded as being *trans* to one another on either side of the bilayer, as shown in Figure 7. To the best of our knowledge, although several coordination bilayers having been reported,[7c,12] this is the first example of a bilayer connected through hydrogen bonds in coordination polymers. The cuboidal $[Zn_8(nip)_8(4,4'\text{-bpy})_8]$ building block with dimensions of ca. 10.100 × 11.456 × 13.971 Å^3 in the bilayer is significantly different from those in other bilayer structures or three-dimensional structures.[7b,7c,12]

Although large void spaces exist within a single bilayer, there are no encapsulated guest molecules because of interpenetration. As shown in Figure 8, each bilayer is interpenetrated by two adjacent identical ones in a parallel fashion, the resulting extended array is therefore an infinite catenane of 2D architecture, as reported previously.[7c,12a] This is consistent with the fact that crystal structures with large cavities are inclined to self-interpenetrate.

As we previously reported, zinc oxide or hydroxide coordination polymers exhibit photoluminescent properties,[7a,7d] and we have also investigated the photoluminescent properties of **1** (Figure 9). In the solid state, **1** exhibits intense photoluminescence upon photoexcitation at 308 nm, the emission of **1** (λ_{max} = 354 nm) might be attributable to the formation of $[Zn_3(\mu_3\text{-OH})_2]_n$ chains and/or ligand-to-metal charge transfer (LMCT).[7a,7d,13]

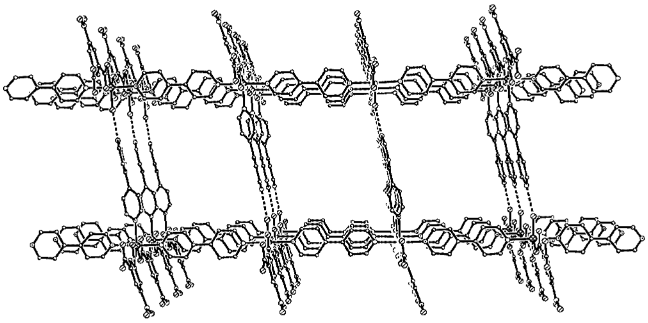

Figure 7. Perspective view of the two-dimensional bilayer of **2**

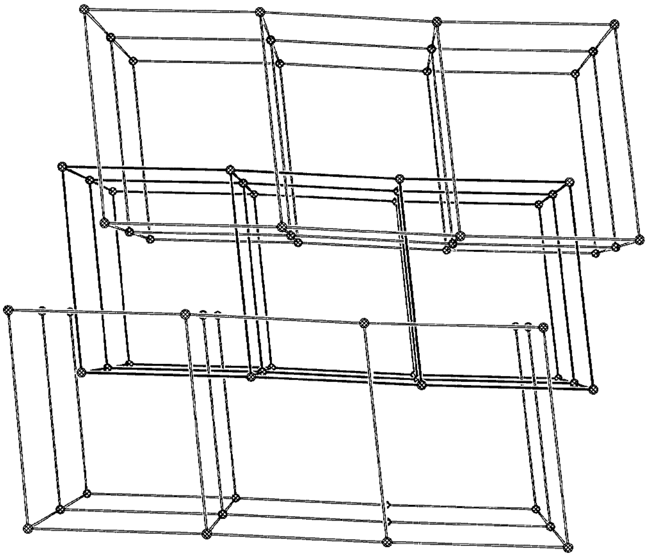

Figure 8. Perspective view of the twofold interpenetrated framework of **2**

Thermogravimetric analyses (TGA) of complexes **1** and **2** performed on polycrystalline samples reveal that **1** and **2** are thermally stable up to ca. 295 and 300 °C, respectively, indicating that even hydrogen-bonded frameworks can also be thermally stable at high temperatures.

In summary, two novel zinc(II) coordination polymers $[Zn_3(\mu_3\text{-OH})_2(nip)_2]$ (**1**) and $[Zn_2(nip)_2(4,4'\text{-bpy})_3\cdot(OH_2)]$ (**2**) have been hydrothermally synthesized. Their structures are both two-dimensional with inter-layer hydrogen bonds, and **2** is the first hydrogen-bonded bilayer in coordination polymers.

Experimental Section

General Remarks: All starting materials were reagent grade and used as purchased. The elemental analyses were performed on a

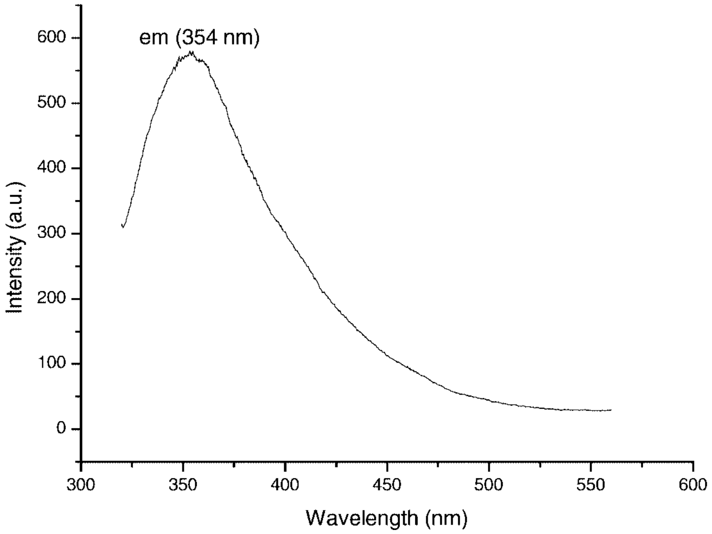

Figure 9. The solid-state photoluminescent spectrum of **1** at room temperature

Perkin−Elmer 240 elemental analyzer. The infrared spectra were recorded on a Nicolet 5DX spectrometer with KBr pellets. Thermal gravimetric analyses were performed in dinitrogen on a Perkin−Elmer 7 thermogravimetric analyzer with a heating rate of 10 °C/min.

Synthesis of 1: An aqueous mixture of $Zn(NO_3)_2{\cdot}6H_2O$ (0.158 g, 0.5 mmol), H_2nip (0.106 g, 0.5 mmol) and NaOH (0.04 g, 1 mmol) in a molar ratio of 1:1:2 was placed in a Teflon-lined stainless vessel, then the mixture was heated at 180 °C for 80 h. Colorless plate-like crystals were obtained in 50% yield based on zinc after the mixture was cooled to room temperature. $C_{16}H_8N_2O_{14}Zn_3$ (648.35): calcd. C 29.64, H 1.24, N 4.32; found C 30.01, H 1.40, N 4.22. IR (KBr): $\tilde{\nu}$ = 3538(m), 3084(w), 2925(w), 1636(s), 1614(vs), 1571(s), 1522(m), 1425(m), 1385(s), 1352(vs), 1206(w), 1127(s), 1065(w), 1027(w), 835(w), 785(m), 556(w) cm^{-1}.

Synthesis of 2: This compound was prepared as colorless plate-like crystals by the procedure described above for **1** except for the addition of 4,4′-bpy (H_2nip:4,4′-bpy = 1:2). Yield: 65% based on zinc. $C_{46}H_{32}N_8O_{13}Zn_2$ (1035.54): calcd. C 53.35, H 3.11, N 10.82; found C 53.10, H 2.83, N 11.01. IR (KBr): $\tilde{\nu}$ = 3427(s), 3090(w), 2924(w), 1610(vs), 1566(m), 1531(s), 1414(s), 1368(vs), 1345(s), 1219(m), 1073(m), 1064(w), 821(m), 789(w), 542(w) cm^{-1}.

Crystallographic Analysis: Data collection (single crystal with dimensions of 0.37 × 0.12 × 0.05 mm^3 for **1** and 0.40 × 0.20 × 0.05 mm^3 for **2**) was performed at 296(2) K on a Bruker APEX CCD-based diffractometer equipped with Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods using SHELXS-97[14] and refined with full-matrix least-squares technique using SHELXL-97.[15] All non-hydrogen atoms were refined anisotropically and the hydrogen atoms of the organic ligands were placed geometrically. The H atom of the hydroxyl group in **1** was located in the calculated position, and the H atoms of the coordinated water in **2** were found by Fourier syntheses. Selected crystallographic data and structure determination parameters for complexes **1** and **2** are presented in Table 3.
CCDC-201058 (**1**) and -201059 (**2**) contain the supplementary crystallographic data for this paper. The structure of **2** was re-refined after the data were deposited to CCDC. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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