Linear and Helical Chains in Hydrothermally Synthesized Coordination Polymers [Co(bpdc)(H_2O)$_2$] and [Ni(bpdc)(H_2O)$_3$]·H_2O Involving in situ Ligand Synthesis

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Hydrothermal treatment of M($MeCO_2$)$_2$ (M = Co or Ni) and 1,10-phenanthroline-5,6-dione (pdon) resulted in two chain-like coordination polymers [Co(bpdc)(H_2O)$_2$] and [Ni(bpdc)(H_2O)$_3$]·H_2O. X-ray single-crystal structural analysis revealed that the organic reagent pdon was transformed in situ into 2,2′-bipyridine-3,3′-dicarboxylate (bpdc). The different coordination modes concomitant with the difference of the dihedral angles between two bpdc pyridine rings results in simple linear chains and helical chains in **1** and **2**, respectively. The one-dimensional coordination chains of **1** and **2** are further extended into two-dimensional supramolecular arrays by hydrogen-bond interactions. A possible mechanism for the new hydrolysis reaction with the formation of bpdc under hydrothermal conditions was also discussed.

Introduction

The self-assembled construction of coordination polymers has become the subject of many current studies,[1−15] due to their potential optoelectronic,[16−19] magnetic,[20,21] microporous,[22−25] and catalytic applications.[26] The design of coordination polymers takes certain factors into account such as the coordination nature of the metal ion, structural features of the polydentate organic ligand, metal/ligand ratio, and possible counterion influence. A subtle alteration to any of these factors may lead to new extended network structures. Although most of these insoluble solids have been synthesized by controlled mixing of suitable soluble molecular components, hydro(solvo)thermal conditions have demonstrated increasing success in providing alternative pathways to the preparation of crystalline supramolecular solids, including metal-organic coordination networks and hydrogen-bonded systems. Hydro(solvo)thermal syntheses carried out in superheated solvent systems provide ideal conditions for the crystal growth owing to the enhanced transport ability of the solvents.[4] Besides, recent studies revealed that crystal growth under hydrothermal conditions occasionally involves in situ ligand synthesis which not only provides a powerful synthesis method for organic ligands that are difficult to synthesise but also represents a potential new direction for novel inorganic−organic hybrid network construction through crystal engineering.[16−19,27−32] Examples of in situ ligand syntheses under hydrothermal conditions include hydrolysis of −CN and −COOR groups,[16−19] hydroxylation,[27−29] carbon−carbon bond formation by reductive coupling or oxidative coupling,[30,31] and replacement of $-CO_2^-$ with $-SO_3^-$.[32]

We have paid considerable interest to the reactivity of chelate ligands such as 2,2′-bipyridine and 1,10-phenanthroline under hydrothermal conditions and found that their hydroxylation reactivity was promoted by copper(II) ions.[27,28] As an extension of our previous work, we are paying attention to 1,10-phenanthroline-5,6-dione (pdon) because of its peculiar reactivity (Scheme 1) in organic chemistry.[33,34] Two nucleophilic centers (nitrogen and oxygen lone pairs) are contained in the quinone-like pdon molecule with all the non-hydrogen atoms being sp^2-hybridized. The presence of two electronegative heteroatoms not only creates the basic properties in the Lewis sense but also, because of conjugation, makes it possible to alter the electron density in different parts of the molecule. As a result, a dramatic change in reactivity can occur, which is not observed in the case of the corresponding aromatic homocyclic analogue, phenanthrenequinone. We report herein on the in situ hydrothermal synthesis of 2,2′-bipyridine-3,3′-dicarboxylate (bpdc) from pdon and its two coordination polymers [Co(bpdc)(H_2O)$_2$] and [Ni(bpdc)(H_2O)$_3$]·H_2O.

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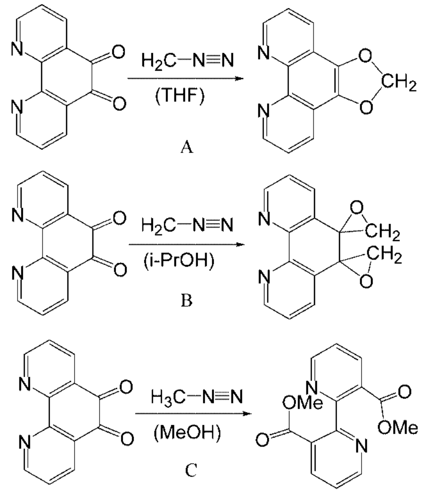


Scheme 1. Schematic representation of some known organic reactions of pdon

Results and Discussion

IR Spectra

The infrared spectra of the two compounds show strong broad bands at 3344 (**1**) or 3390 (**2**) cm^{-1} that are attributable to the stretching modes of hydrogen-bonded H_2O groups. The $\nu_{as}(COO)$ vibration is identified by the strong bands at 1566 (**1**) or 1568 (**2**), and the $\nu_s(COO)$ bands at 1394 (**1**) and 1392 (**2**) cm^{-1}. The separations $\Delta(COO)$ between the $\nu_{as}(COO)$ and $\nu_s(COO)$ bands, in both compounds, imply that the carboxylate groups act in a monodentate coordination mode.[35]

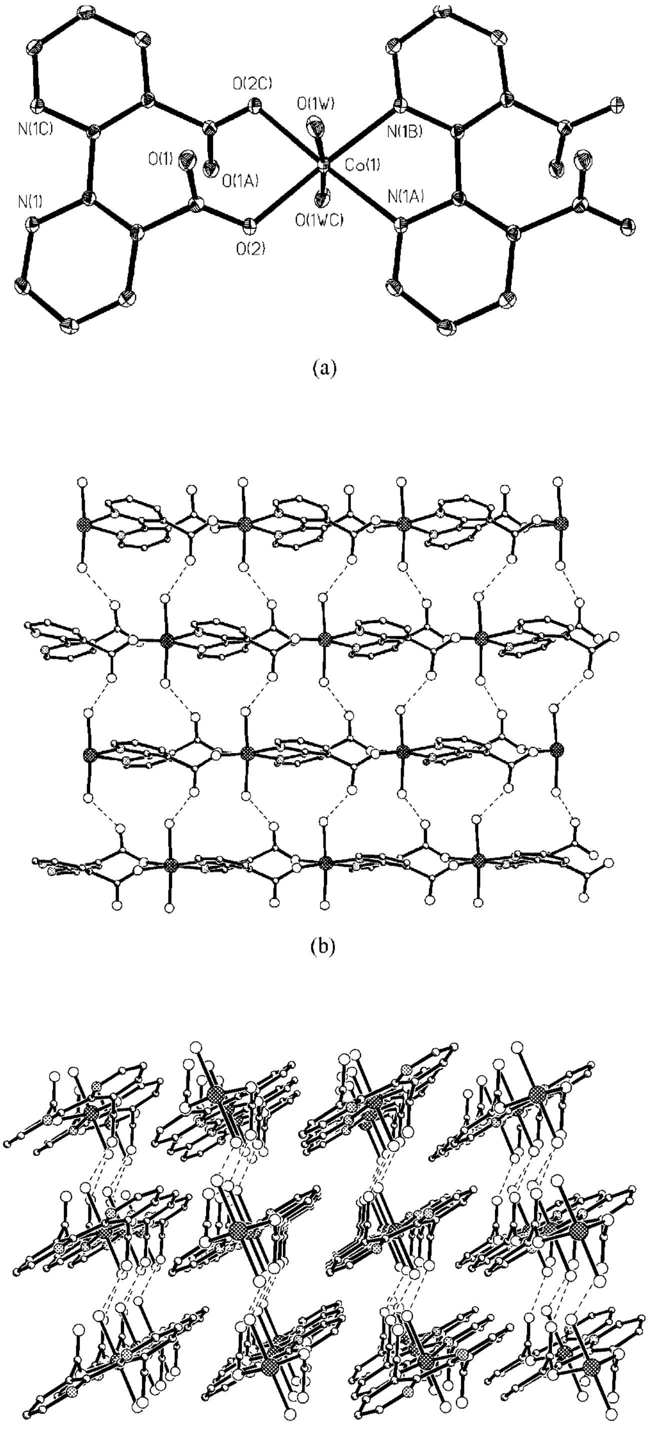
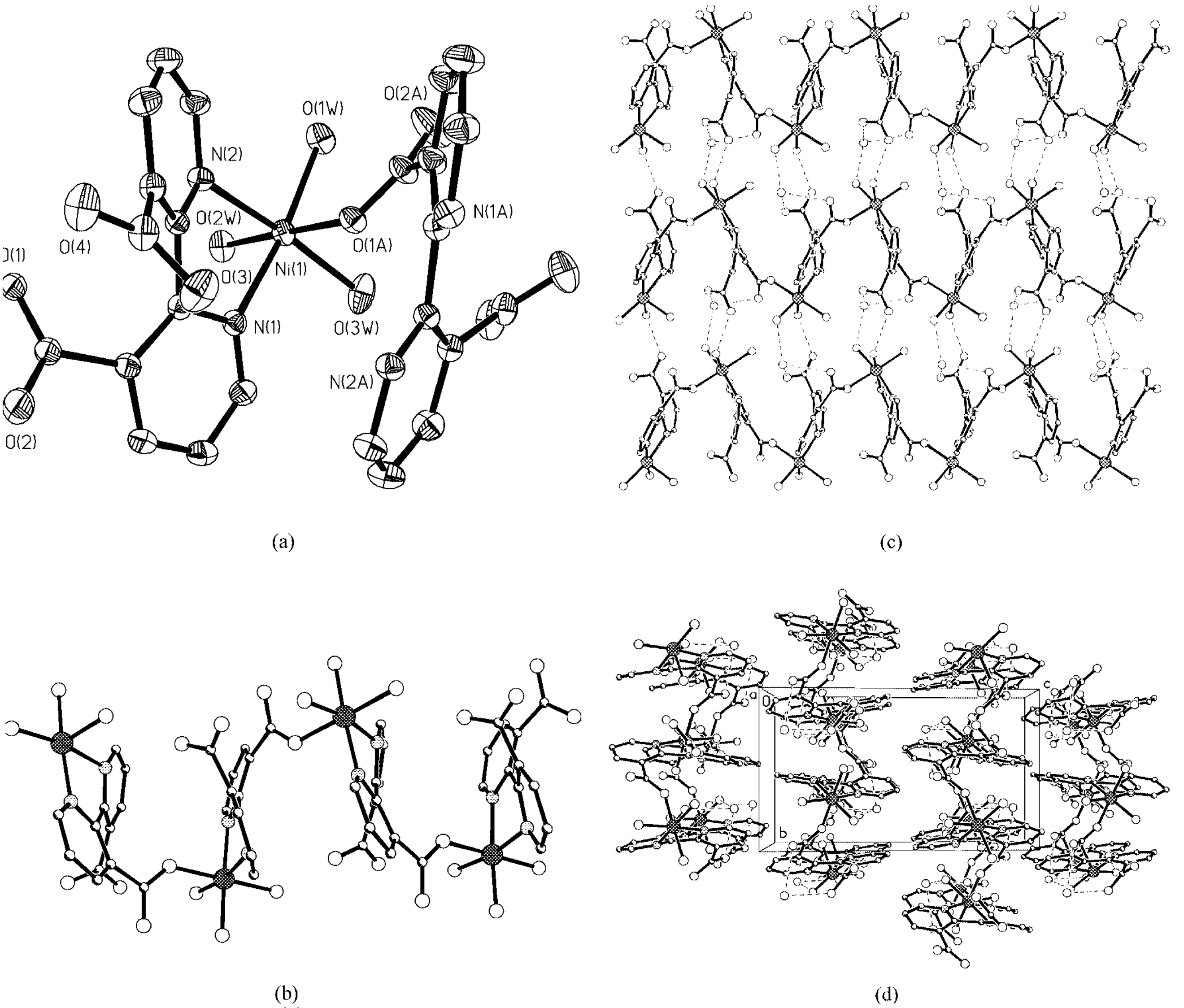


Figure 1. Perspective views of the coordination environment of the cobalt(II) atom (a), two-dimensional supramolecular network (b) and stacking array (c) in **1**

Structural Description

X-ray single-crystal structural analysis revealed that compound **1** crystallizes in the monoclinic space group *C*2/*c* and that the pdon ligand was transformed in situ into bpdc during the hydrothermal process. The asymmetric unit in **1** consists of 0.5 Co^{II}, 0.5 bpdc and 1 H_2O. The Co^{II} atom lies on a crystallographic twofold axis, which bisects one bpdc. The Co^{II} site shows a distorted octahedral geometry, being coordinated by two nitrogen atoms of one bpdc in a chelate mode and two oxygen atoms of two carboxylate groups in the equatorial plane, as well as two aqua ligands in the axial positions, as shown in Figure 1. The Co−N(1), Co−O(2) and Co−O(1w) distances are 2.123(2), 2.133(2) and 2.151(3) Å, respectively. The *cis*-L−Co−L angles are in the range of 76.70(11)−99.37(9)° and the *trans*-L−Co−L angles are 168.02(7) and 174.85(9)°. The dihedral angle between two bydc pyridine rings is 20.5°, indicating a slight non-coplanarity, which may reduce mutual repulsion between the two carboxy groups in each bpdc. Metal complexes synthesized directly from the bpdc ligand,[36,37] show the tridentate bridging and bis(monodentate) bridging coordination modes in $[Cu(bpdc)(H_2O)_2]$ and $[Mn(bpdc)(H_2O)_4]$, respectively. In contrast, each bpdc ligand utilizing the pair of nitrogen atoms and two oxygen atoms of two carboxylate groups bridge two Co^{II} atoms in **1** to generate one-dimensional chains (Figure 1, b) in which all cobalt atoms are located linearly at a twofold axis. It should be noted that the aqua O(1W) atom forms a donor hydrogen bond with the uncoordinated carboxy oxygen atom O(1) [O(1W)···O(1) 2.786 Å], which extend the one-dimensional chains into two-dimensional supramolecular networks. Such two-dimensional networks are arranged in a repeated ···AAA··· fashion in the lattice, as shown in Figure 1, c.

In contrast to **1**, compound **2** crystallizes in the monoclinic space group $P2_1/n$ and each asymmetric unit consists of 1 Ni^{II}, 1 bpdc, 3 H_2O and one lattice H_2O. All atoms are located at general positions. The Ni^{II} site shows a distorted octahedral geometry, being ligated by two nitrogen atoms of one bpdc in a chelate mode, one carboxylate oxygen atom and three *cis*-related aqua ligands (Figure 2, a). The Ni−N and Ni−O distances are in the range of 2.080(3)−2.118(3) and 2.071(3)−2.110(3) Å, respectively, which are slightly shorter than the Co−N and Co−O distances observed in **1**. The *cis*-L−Co−L angles are in the range of 78.53(11)−96.26(12) and *trans*-L−Co−L angles are 169.35(11)−178.94(10)°, indicating that the Ni^{II} site has a more regular octahedron than the Co^{II} center in **1**. The two pyridine rings of bpdc in **2** are more twisted with a larger dihedral angle of 31.6° than that in **1**. Besides, with only one carboxylate group utilizing one oxygen atom to ligate a nickel(II) atom, the coordination mode of the bpdc molecule in **2** is different from that in **1**, in which each bpdc has two carboxylate groups coordinated, but similar to that found in [Cu(bpdc)$(H_2O)_2$].[36] Different from the linear chain-like structure in **1**, the coordination modes of the bpdc ligand and the configuration of the Ni^{II} atom with three *cis*-related aqua ligands in **2** result in helical chains in which equivalent atoms are related by a 2_1-screw axis (Figure 2, b). This fact implies that the tridentate coordination mode of bpdc may play an important role in the



(a) (c)

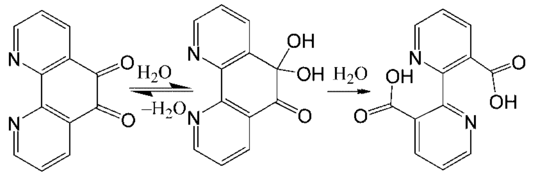
(b) (d)

Figure 2. Perspective views of the coordination environments of the nickel atom (a), helical chain (b), and two-dimensional supramolecular network (c) and stacking array (d) in **2**

formation of the chiral helical chains in **2**. On the other hand, there are a number of hydrogen bonds [O(1W)···O(4), 2.674; O(2W)···O(3), 2.744; O(3W)···O(4W), 2.716; O(4W)···O(3), 2.891; O(4W)···O(3W), 2.71 Å] which extend the helical chains into two-dimensional supramolecular networks (Figure 2, c). Such networks are arranged in an ···ABAB··· fashion as shown in Figure 2, d. Within each layer, all helical chains have the same chirality. However, helical chains of opposite chiralities construct adjacent layers and thus **2** crystallizes in the centrosymmetric space group.

Synthesis Chemistry

Although pdon was used as the original organic reagent in the preparation of **1** and **2** the bipyridine-3,3′-dicarboxylate ligand was unexpectedly found in the final products, which indicates an in situ transformation of pdon into bpdc during the course of hydrothermal treatment. As shown in our previous investigation[27−29] on ligand reactions under hydrothermal conditions in the presence of metal ions, the ligation of the metal ion will cause some decrease of electron density on the aromatic ring of the organic ligand, hence promote nucleophilic attack by water molecules or hydroxy groups. In this case, it seems most probable that the solvent aqua molecules act effectively as nucleophiles, attacking the carbonyl carbon atoms of pdon. As a result, the hydration of carbonyl groups of pdon furnishes an intermediate diol or even a double diol. When the sp^2 carbonyl carbon atoms become sp^3-hybridized, the carbon−carbon bond is then cleaved probably because of the crowdedness, resulting in the formation of bpdc. A recent study, indeed revealed that there is a tautomerism between a pdon complex of Co^{II} and its corresponding diol complex in aqueous solution.[38] The formation mechanism of bpdc in **1** and **2** shows some similarity to that of dimethyl 2,2′-bipyridine-3,3′-dicarboxylate in a previously reported pure organic reaction (Scheme 1, C).[34] Although the exact mechanism of ligand transformation is not yet proved, slow hydrolysis of the carbonyl groups ensures that an excess of metal ions remains in solution, thereby promoting the formation of less soluble polymeric networks. Equally important, the in situ slow bpdc formation also ensures the growth of large single crystals that are suitable for X-ray structure determination.



Scheme 2. Schematic representation of the possible transformation mechanism of pdon to bpdc

Conclusion

A new hydrolysis reaction of 1,10-phenanthroline-5,6-dione to 2,2′-bipyridine-3,3′-dicarboxylate has been achieved under hydrothermal conditions in the presence of metal acetates, resulting in the formation of two chain-like coordination polymers $[Co(bpdc)(H_2O)_2]$ and $[Ni(bpdc)(H_2O)_3]\cdot H_2O$. The different coordination modes concomitant with the difference of the dihedral angles between two pyridine rings of bpdc results in simple linear and helical chains, respectively.

Experimental Section

General Remarks: Elemental analyses were performed with a Perkin−Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range of 400−4000 cm^{-1} with a Nicolet 5DX spectrometer.

Synthesis

$[Co(bpdc)(H_2O)_2]$ (1): A mixture of $Co(MeCO_2)_2\cdot 4H_2O$ (0.25 g, 1.0 mmol), 1,10-phenanthroline-5,6-dione (pdon) (0.208 g, 1.0 mmol), methanol (3 mL) and water (5 mL) in a molar ratio of 1:1:74:278 was stirred for 10 min in air, then transferred and sealed in a 23-ml Teflon-lined stainless steel container, which was heated to 140 °C for 72 h. After cooling to room temperature at the rate of 5 °C per hour, 0.34 g (ca. 50% yield) of brown block crystals of **1** was recovered. $C_{24}H_{20}Co_2N_4O_{12}$ (674.3): calcd. C 42.75, H 2.99, N 8.31; found C 42.67, H 3.08, N 8.23. IR (KBr): $\tilde{\nu}$ = 3751 w cm^{-1}, 3344 bs, 3102 m, 1796 w, 1566 s, 1438 m, 1394 s, 1227 w, 1152 w, 1096 wm, 826 w, 783 m, 750 m, 662 m, 518 w, 447 m.

$[Ni(bpdc)(H_2O)_3]\cdot H_2O$ (2): A mixture of $Ni(MeCO_2)_2\cdot 4H_2O$ (0.25 g, 1 mmol), pdon (0.208 g, 1 mmol), methanol (3 mL) and water (5 mL) in a molar ratio of 1:1:74:278 was stirred for 10 min in air, then transferred and sealed in a 23-ml Teflon-lined stainless steel container, which was heated to 140 °C for 72 h. After cooling to room temperature at a rate of 5 °C per hour, 0.373 g (35% yield) of blue block crystals of **1** were recovered. $C_{24}H_{28}N_4Ni_2O_{16}$ (745.9): calcd. C 38.65, H 3.78, N 7.51; found C 38.60, H 3.82, N 7.44. IR (KBr): $\tilde{\nu}$ = 3673 w cm^{-1}, 3390 bs, 1603 w, 1568 s, 1392 s, 1158 w, 1122 w, 1097 m, 772 m, 699 w, 442 w.

X-ray Crystallography: Diffraction intensities were collected at 293 K with a Siemens R3 diffractometer (Mo-K_{α}, λ = 0.71073 Å). Lorentz-polarization and absorption corrections were applied. The structure was solved with direct methods (SHELXS-97) and refined with a full-matrix least-squares technique (SHELXL-97).[39] Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. In all cases, all non-hydrogen atoms were refined anisotropically and hydrogen atoms of organic ligands were geometrically placed. CCDC-200013 and -200014 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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

	1	**2**
Empirical formula	$C_{24}H_{20}Co_2N_4O_{12}$	$C_{24}H_{28}N_4Ni_2O_{16}$
Molecular mass	674.30	745.92
Temperature [K]	293(2)	293(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/n$
a [Å]	11.573(14)	10.045(10)
b [Å]	7.965(7)	9.285(7)
c [Å]	13.368(8)	16.155(10)
β [°]	101.21(2)	96.60(2)
V [Å^3]	1208.7(19)	1497(2)
Z	2	2
Density (calcd.) [Mg/m^3]	1.853	1.655
Absorption coefficient [mm^{-1}]	1.452	1.340
F(000)	684	768
Crystal size [mm]	0.50 × 0.26 × 0.06	0.82 × 0.64 × 0.57
Theta range for data collection [°]	3.11 to 26.68	2.28 to 27.02
Index ranges	$-14 \leq h \leq 10$, $-9 \leq k \leq 10$, $-16 \leq l \leq 16$	$0 \leq h \leq 12$, $0 \leq k \leq 11$, $-20 \leq l \leq 20$
Reflections collected	3283	3451
Independent reflections	1261 (R_{int} = 0.0227)	3268 (R_{int} = 0.0403)
Max. and min. transmission	0.9179 and 0.5304	0.5154 and 0.4061
Refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2
Data/restrains/parameters	1261/0/97	3268/0/209
Goodness-of-fit on F^2	1.082	1.028
Final R indices [$I > 2\sigma(I)$]	0.0309, 0.0767	0.0464, 0.1207
R indices (all data)	0.0361, 0.0789	0.0620, 0.1307
Largest diff. Peak and hole [e·A^{-3}]	0.403 and −0.268	0.571 and −0.680

Table 2. Selected Bond lengths [Å] and angles [°] for complexes **1** and **2**

Complex **1**		Complex **2**	
Co(1)−N(1)[a]	2.123(2)	Ni(1)−O(3W)	2.065(3)
Co(1)−N(1)[b]	2.123(2)	Ni(1)−O(1W)	2.071(3)
Co(1)−O(2)[c]	2.133(2)	Ni(1)−O(1)[a]	2.078(3)
Co(1)−O(2)	2.133(2)	Ni(1)−N(1)	2.080(3)
Co(1)−O(1W)[c]	2.151(3)	Ni(1)−O(2W)	2.110(3)
Co(1)−O(1W)	2.151(3)	Ni(1)−N(2)	2.118(3)
N(1)[a]−Co(1)−N(1)[b]	76.70(11)	O(3W)−Ni(1)−O(1W)	95.26(13)
N(1)[a]−Co(1)−O(2)[c]	168.02(7)	O(3W)−Ni(1)−O(1)[a]	88.54(12)
N(1)[b]−Co(1)−O(2)[c]	99.37(9)	O(1W)−Ni(1)−O(1)[a]	90.51(10)
N(1)[a]−Co(1)−O(2)	99.37(9)	O(3W)−Ni(1)−N(1)	93.06(13)
N(1)[b]−Co(1)−O(2)	168.02(7)	O(1W)−Ni(1)−N(1)	171.47(11)
O(2)[c]−Co(1)−O(2)	86.65(10)	O(1)[a]−Ni(1)−N(1)	87.84(10)
N(1)[a]−Co(1)−O(1W)[c]	85.01(8)	O(3W)−Ni(1)−O(2W)	90.47(12)
N(1)[b]−Co(1)−O(1W)[c]	99.05(8)	O(1W)−Ni(1)−O(2W)	89.95(11)
O(2)[c]−Co(1)−O(1W)[c]	84.46(7)	O(1)[a]−Ni(1)−O(2W)	178.94(10)
O(2)−Co(1)−O(1W)[c]	91.79(7)	N(1)−Ni(1)−O(2W)	91.84(11)
N(1)[a]−Co(1)−O(1W)	99.05(8)	O(3W)−Ni(1)−N(2)	169.35(11)
N(1)[b]−Co(1)−O(1W)	85.01(8)	O(1W)−Ni(1)−N(2)	92.99(12)
O(2)[c]−Co(1)−O(1W)	91.79(7)	O(1)[a]−Ni(1)−N(2)	84.66(11)
O(2)−Co(1)−O(1W)	84.46(7)	N(1)−Ni(1)−N(2)	78.53(11)
O(1W)[c]−Co(1)−O(1W)	174.85(9)	O(2W)−Ni(1)−N(2)	96.26(12)

Symmetry codes for **1**: [a] $x, y + 1, z$; [b] $-x + 1, y + 1, -z + 1/2$. [c] $-x + 1, y, -z + 1/2$. Symmetry codes for **2**: $-x + 3/2, y + 1/2, -z + 1/2$.

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