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# Structures of Co, Pd and Ni complexes with iminopyridine ligands having an hydroxymethyl or acrylate pendant group

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# ABSTRACT

Co(II), Pd(II) and Ni(II) complexes with iminopyridine ligands have different coordination structures in the solid state, depending on the metal, pendant group of the pyridyl ring and recrystallization conditions. The iminopyridine ligand having an acrylate group, Ar–N=CH-2,6-C<sub>5</sub>H<sub>3</sub>N–CH<sub>2</sub>–OCO–CH=CH<sub>2</sub> (**L**<sup>1</sup>: Ar = 2,6-diisopropylphenyl), forms a Co(II) complex whose metal center has a trigonal pyramidal coordination with two chloride ligands and an *N*,*N*-bidentate ligand **L**<sup>1</sup>. Both **L**<sup>1</sup> and the iminopyridine ligand with a CH<sub>2</sub>OH pendant on the pyridyl ring, Ar–N=CH-2,6-C<sub>5</sub>H<sub>3</sub>N–CH<sub>2</sub>–OH (**L**<sup>2</sup>: Ar = 2,6-diisopropylphenyl), coordinate to the PdCl<sub>2</sub> moiety, giving complexes with a square–planar coordination. The reaction of **L**<sup>1</sup> with [NiBr<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>] and recrystallization of the products forms crystals which contain mono- and dinuclear complexes with aqua ligands and the *N*,*N*'-bidentate ligand. **L**<sup>2</sup> is coordinated to the Ni(II) center as an *N*,*N*,*O*-tridentate ligand. Recrystallization of the products of the reaction of **L**<sup>2</sup> with [NiBr<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>] with and without excess H<sub>2</sub>O in the solution yields crystals of the cationic octahedral complex with two aqua ligands [NiBr(H<sub>2</sub>O)<sub>2</sub>(**L**<sup>2</sup>)]Br and the neutral square pyramidal complex [NiBr<sub>2</sub>(**L**<sup>2</sup>)], respectively.

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## 1. Introduction

Iminopyridine derivatives have been extensively employed as ligands of transition metal complexes. The aromatic ligands whose conformation is fixed by coordination to a metal center act as a mesogen of liquid crystalline molecules, and Cu complexes with such ligands are expected to be liquid crystalline materials [1]. Iminopyridine ligands provide convenient building blocks of supramolecules, partly because ligands with various functional groups can be obtained easily by simple condensation reactions of amines and 2-formylpyridine derivatives, forming a new C=N bond [2-4]. Introduction of a polar hydroxy group on the iminopyridine ligand allows the formation of supramolecular assemblies with the molecules having a hydrogen-bond acceptor group, via hydrogen bonds [3,4]. Catalysis is another important research topic for transition metal complexes with iminopyridine ligands [5]. In particular, bis(imino)pyridine complexes of Fe and Co exhibit high activity for olefin polymerization [6,7]. Recently, we reported the synthesis of heterobimetallic complexes having Co, Pd and Ni metal centers and iminopyridine ligands, and their unique behavior as catalysts

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for polymerization [8]. During the study, we characterized mononuclear Co(II), Pd(II) and Ni(II) complexes which were prepared as intermediates for dinuclear complexes, and found different coordination modes of the ligand depending on the metal and the ligand. Herein, we report the syntheses and crystal structures of Co(II), Pd(II) and Ni(II) complexes having iminopyridine ligands with hydroxy or acrylate groups, and the interaction between the metal centers and these groups in the crystalline state.

### 2. Results and discussion

Iminopyridine ligands having an acrylate group, Ar–N=CH-2,6-C<sub>5</sub>H<sub>3</sub>N–CH<sub>2</sub>–OCO–CH=CH<sub>2</sub> (**L**<sup>1</sup>; Ar = 2,6-diisopropylphenyl) [8], and a hydroxy group, Ar–N=CH-2,6-C<sub>5</sub>H<sub>3</sub>N–CH<sub>2</sub>–OH (**L**<sup>2</sup>), were synthesized by the condensation reactions of 2,6-diisopropylaniline with the corresponding aldehyde (Chart 1). The reaction of









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Scheme 1.



**Fig. 1.** ORTEP drawing of **1** with thermal ellipsoids shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

 $L^1$  with CoCl<sub>2</sub> afforded the Co-iminopyridine complex **1** (Scheme 1). The crystal structure of **1** is shown in Fig. 1. Table 1 summarizes selected bond parameters. Sum of the N1–Co–Cl1, N1–Co–Cl2 and

 Table 1

 Selected bond distances (Å) and angles (°) for complexes 1–5b

Cl1–Co–Cl2 angles (353.46°) is close to 360°, and the coordination is recognized to be distorted trigonal pyramidal with the N2 atom at the apical position. The ether oxygen atom (O1) of the acrylate group seems to occupy the remaining apical site by a weak interaction with the Co center, with a distance of 2.690 Å. The Zr–Co bimetallic complex, with a similar coordination of the iminopyridine to Co, has a slightly longer Co–O distance (2.774 Å). Co complexes with acetyl- or ester-substituted iminopyridine ligands have a penta-coordinated structure with coordination of the carbonyl group (Co–O lengths = 2.327 and 2.374 Å) [9,10]. The bond parameters around Co are similar between CoCl<sub>2</sub>(Ar–N=CH-2,6-C<sub>5</sub>H<sub>3</sub>N–CO–CH<sub>3</sub>) (Ar = 2,6-diisopropylphenyl) and **1**, with the exception of the short Co–O bond in the former complex.

The reactions of  $L^1$  and  $L^2$  with  $[PdCl_2(cod)]$  (cod = 1,5-cyclooctadiene) afforded complexes **2** and **3**, respectively (Scheme 2). Fig. 2 shows the crystal structures of the Pd complexes with the *N*,*N*-bidentate iminopyridine ligands. Each Pd center has a distorted square–planar geometry without any remarkable interaction with the acrylate or hydroxy pendant group. The square

	<b>1</b> (M=Co, X=Cl)	<b>2</b> (M=Pd, X=Cl)	<b>3</b> (M=Pd, X=Cl)	<b>4a</b> (M=Ni, X=Br)	<b>4b</b> (M=Ni, X=Br)	<b>5a</b> (M=Ni, X=Br)	<b>5b</b> (M=Ni, X=Br)			
M-X1	2.2420(6)	2.2819(6)	2.302(2)	2.4408(5)	2.5085(6)	2.3935(7)	2.4690(7)			
M-X2	2.2290(7)	2.2625(7)	2.258(2)	2.4296(5)	2.4338(6)	2.4134(9)				
M-N1	2.063(2)	2.121(2)	2.096(7)	2.094(3)	2.078(3)	2.005(3)	2.006(2)			
M-N2	2.105(2)	2.009(2)	2.021(6)	2.025(3)	2.043(3)	2.135(3)	2.127(3)			
M-01						2.137(4)	2.248(2)			
M-02							2.049(3)			
M-03				2.107(3)			2.089(2)			
X1-M-X2	113.13(2)	86.61(2)	86.99(9)	139.55(2)	144.94(2)	107.86(3)				
X1-M-N1	129.51(6)	101.86(5)	101.0(2)	91.97(9)	89.10(9)	150.7(2)	172.8(1)			
X1-M-N2	100.44(5)	175.33(6)	172.3(2)	108.70(9)	104.70(9)	102.33(9)	106.23(9)			
X2-M-N1	110.82(6)	171.43(5)	172.0(2)	93.95(9)	91.40(8)	100.8(1)				
X2-M-N2	117.66(5)	91.12(6)	92.0 (2)	111.73(9)	109.97(9)	100.6(1)				
N1-M-N2	79.66(7)	80.53(8)	80.1(3)	80.0(2)	80.7(2)	77.9(2)	79.2(2)			

In the case of 4b (dimer complex), X1, X2, N1 and N2 indicate Br3, Br4, N3 and N4, respectively.



Scheme 2.



**Fig. 2.** ORTEP drawing of (a) **2** and (b) **3**·1.5CHCl<sub>3</sub> with thermal ellipsoids shown at the 30% probability level. Hydrogen atoms are omitted for clarity. Hydrogen atoms and solvating CHCl<sub>3</sub> molecules are omitted for clarity.

plane is orthogonally-oriented to the 2,6-diisopropylphenyl group owing to the sterically bulky isopropyl groups [6,7]. The CH<sub>2</sub>–OH bond is orientated towards the Cl ligand with the distance Cl1– O1 = 3.046 Å, which indicates intramolecular hydrogen bonding in the crystal structure (Fig. 2b). The <sup>1</sup>H NMR spectrum of **3** (25 °C, CDCl<sub>3</sub>) exhibits a triplet ( $J_{HH}$  = 8 Hz) assigned to the OH hydrogen at 4.67 ppm, which is at a much lower magnetic field than that of **L**<sup>2</sup>. Appearance of H–H coupling between the OH and CH<sub>2</sub> hydrogen of **3**, as well as the shift of the OH peak position, upon coordination of the ligand suggests Pd–Cl…H–O intramolecular hydrogen bonding in solution [11–13]. Fig. 3 shows the variable temperature <sup>1</sup>H NMR spectra of **3** in ClCD<sub>2</sub>CD<sub>2</sub>Cl. The triplet signal of the OH hydrogen shifts downfield by ca 0.17 ppm on raising the temperature from 25 to 100 °C. The OH and CH<sub>2</sub> hydrogen signals became somewhat broadened at 100 °C. The temperature-depen-



Fig. 3.  $^1H$  NMR spectra of the hydroxymethyl region of 3 at 25–100  $^\circ C$  in  $C_2D_2Cl_4$  (8.2 mM).

dent change of the spectra may also suggest  $O\text{-}H\text{-}\text{\cdot}\text{\cdot}\text{Cl}$  hydrogen bonds in solution.

Elemental analysis of the product from the reaction of L<sup>1</sup> and [NiBr<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>] indicates the formation of the aqua complex, [NiBr<sub>2</sub>(H<sub>2</sub>O)L<sup>1</sup>] (**4a**) [8], but X-ray crystallography of the crystals obtained from CHCl<sub>3</sub> revealed the presence of 4a and a dinuclear complex with two bridging Br ligands,  $[NiBr(\mu-Br)L^1]_2$ , (4b) in a 1:1 ratio (Scheme 3). Fig. 4 shows the structure of the mononuclear and dinuclear complexes contained in the crystal lattice. Complex 4a undergoes partial dissociation of the aqua ligand to yield the anhydrous dinuclear complex 4b during the recrystallization. Chart 2 lists the penta-coordinated Ni(II) complexes with two Br, one aqua and one iminopyridine ligand, similar to 4a [14,15]. The coordination of **4a** resembles that of a complex with an iminopyridine ligand with a methyl group next to the pyridine group (right in Chart 2), although the other complex (left) has different ligand positions. The reaction of an iminopyridine ligand with [NiBr<sub>2</sub>(dme)] (dme = 1,2-dimethoxyethane) gives dinuclear com-





**Fig. 4.** ORTEP drawing of **4a** and **4b** with thermal ellipsoids shown at the 30% probability level. Hydrogen atoms except for O–H hydrogens are omitted for clarity. Atoms with asterisks are crystallographically equivalent to those having the same number without asterisks.



plexes with two bridging Br ligands (Chart 3) [16,17]. In the crystal structures of **4a** and **4b**, the acrylate group of the ligand does not interact with the Ni(II) centers.

The reaction of the ligand with the CH<sub>2</sub>OH pendant,  $L^2$ , with [NiBr<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>] yielded a Ni complex, **5a**, having an *N*,*N'*,*O*-coordination (Scheme 4). The crystal structure of **5a** shows a five-coordinate square pyramidal geometry with a Br atom (Br2) at the apical position (Fig. 5a). The Ni center lies 0.43 Å out of the basal plane composed of the N1, N2, Br1 and O1 atoms. A similar *N*,*N'*,*O*-coordination was observed in Ni(II) complexes with Ar-N=CCH<sub>3</sub>-2,6-C<sub>5</sub>H<sub>3</sub>N-COCH<sub>3</sub> (Ar = 2,6-diisopropylphenyl) and Ar-N=CCH<sub>3</sub>-2,6-C<sub>5</sub>H<sub>3</sub>N-COOCH<sub>2</sub>CH<sub>3</sub> (Ar = 2,6-dimethylphenyl) [10,14], which have longer Ni–O bonds (2.334 and 2.402 Å) than that of **5a** (2.137 Å) (Chart 4). Recently, Gibson and co-workers reported a Fe(II) complex with a similar ligand to  $L^2$ , Ar–N=CCH<sub>3</sub>-2,6-C<sub>5</sub>H<sub>3</sub>N-C(CH<sub>3</sub>)<sub>2</sub>OH





Chart 3.





Scheme 4.

(Ar = 2,6-diisopropylphenyl), in which the OH group is coordinated to Fe with a Fe-O bond distance of 2.173 Å (Chart 4) [18]. The bond length of the Ni and imine nitrogen (N2) is 0.13 Å longer than that of Ni and the pyridine nitrogen (N1). In contrast, 4a and 4b have shorter Ni-imine bonds than Ni-pyridine bonds. Therefore, coordination of the hydroxy group is likely to elongate the Ni-imine bond due to the trans influence of the O-ligand [19,20]. Other Ni-iminopyridine complexes with N,N',O-tridentate coordination have Ni-imine bonds approximately 0.1 Å longer than the Ni-pyridine bonds (Chart 4) [10,14,18]. Recrystallization of **5a** in the presence of an excess amount of H<sub>2</sub>O caused dissociation of a Br ligand, resulting in the formation of the cationic aqua complex **5b** (Fig. 5b). The structure has a distorted octahedral geometry with two agua ligands at trans positions. In analogy to 5a, 5b has longer Ni-imine bonds (2.127 Å) than Ni-pyridine bonds (2.006 Å). A similar replacement of a Br ligand with an agua ligand was reported in a Ni(II) complex with the bidentate diphenvl(dipvrazolvl)methane ligand [21].

Intermolecular hydrogen bonding was observed in the aqua complexes **4a** and **5b**, as shown in Fig. 6. In the structure of **4a**, the short distance of H1…Br1\* (2.596 Å) and the angle of H1–Br1\*–Ni\* (105.8°) indicate hydrogen bonding [22]. The distance H2…O2\* (2.451 Å) is also related to an intermolecular interaction,



**Fig. 5.** ORTEP drawing of (a) **5a**C<sub>4</sub>H<sub>8</sub>O and (b) **5b**C<sub>4</sub>H<sub>8</sub>O with thermal ellipsoids shown at the 30% probability level. Hydrogen atoms except for O–H hydrogens and solvating THF molecules are omitted for clarity.

although the non-linear O3-H2-O2<sup>\*</sup> bonding (139.8°) suggests that the contribution of the H2-O2<sup>\*</sup> hydrogen bond is minor. The structure of **5b** shows that H1 in the hydroxy group and H2 in the aqua ligand have an interaction with the free Br anion (Br2)



**Fig. 6.** Association of (a) **4a** and (b) **5b** via hydrogen bonding. Hydrogen atoms except for O–H hydrogens and solvating THF molecules are omitted for clarity. Selected angles for **4a** (°): H1–Br1\*–Ni\* 105.7, O3–H1–Br1\* 160.2, O3–H2–O2\* 138.9, Ni–O3–Br1\* 102.8, Ni–O3–O2\* 138.6. Selected angles for **5b** (°): H4–Br1\*–Ni 86.1, O1–H1–Br2 177.4, O2–H2–Br2 160.2, O3–H4–Br1\* 155.5, O3–H5–O1\* 150.9, Ni–O1–Br2 105.8, Ni–O2–Br2 105.8, Ni–O3–Br1\* 120.6, Ni–O3–O1\* 125.7.



with distances of 2.289 and 2.398 Å, respectively. The other aqua ligand shows hydrogen bonding with the Br1\* and O1\* atoms in the neighboring molecule in the crystal packing.

# 3. Conclusions

The crystal structures of iminopyridine complexes with an acrylate or a hydroxy pendant group were revealed by single-crystal X-ray diffraction studies. The weak interaction of the acrylate pendant group to the metal center was observed only in the case of the Co(II) complex. Coordination of the carbonyl oxygen atoms is unfavorable partly because it requires the formation of unstable 7-membered metallacycles. In the iminopyridine complexes with an hydroxy pendant group ( $L^2$ ), the ligand coordinates to the Ni(II) center in an *N*,*N'*,*O*-tridentate coordination fashion. Since coordination of an aqua ligand to Ni(II) caused the dissociation of the Br ligand in the presence of the coordinated hydroxy group, the coordination of the hydroxy group is presumably stronger than that of Br because of the chelate effect.

## 4. Experimental

# 4.1. General

6-Hydroxymethyl-2-pyridinecarboxaldehyde [23], [PdCl<sub>2</sub>(cod)] [24], **1** (green solid), **2** (yellow solid) and **4** (orange solid) were prepared according to the literature methods [8]. [NiBr<sub>2</sub>·(H<sub>2</sub>O)<sub>3</sub>] and other chemicals were used as received from commercial suppliers. NMR spectra (<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H}) were recorded on Varian Mercury 300 and JEOL JNM LA-500 spectrometers. Elemental analyses were carried out with a Yanaco MT-5 CHN autocorder.

## 4.2. Synthesis of 2-hydroxymethyl-6-[(2,6-diisopropylphenyl)iminomethyl]pyridine (**L**<sup>2</sup>)

A mixture of 6-hydroxymethyl-2-pyridinecarboxaldehyde (141.0 mg, 1.0 mmol), 2,6-diisopropylaniline (0.200 mL, 1.1 mmol)

Table 2Crystal data and details of structure refinement of complexes 1–5b.

and acetic acid (1 drop) in EtOH (3 mL) was stirred for 14 h at room temperature. After the volatiles were evaporated under reduced pressure, the residue was washed with hexane  $(2 \text{ mL} \times 4)$  and dried under reduced pressure to give 2-hydroxymethyl-6-[(2,6diisopropylphenyl)iminomethyl]pyridine as a pale yellow solid (275.6 mg, 90%). Anal. Calc. for C<sub>19</sub>H<sub>24</sub>N<sub>2</sub>O: C, 76.99; H, 8.16; N, 9.45. Found: C, 76.30; H, 7.99; N, 9.30%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.31 (s, 1H, N=CH), 8.19 (d, 1H,  $J^3$  = 8 Hz, CH in pyridyl group), 7.78 (t, 1H,  $J^3 = 8$  Hz, CH in pyridyl group), 7.38 (d, 1H,  $J^3 = 8$  Hz, CH in pyridyl group), 7.20-7.11 (m, 3H, CH in aromatic group), 4.85 (s, 2H, CH<sub>2</sub>), 3.90 (br, 1H, OH), 2.96 (quint, 2H, J<sup>3</sup> = 7 Hz, CH), 1.18 (d, 12H,  $\int_{-1}^{3} = 7 \text{ Hz}$ , CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>): δ162.9 (s, N=CH), 159.2 (s, ipso), 153.8 (s, ipso), 148.6 (s, ipso), 137.7 (s, CH in pyridyl group), 137.4 (s, *ipso*), 124.8 (s, CH in pyridyl group). 123.3 (s, CH in aromatic group), 122.4 (s, CH in aromatic group), 120.1 (s, CH in pyridyl group), 64.2 (s, CH<sub>2</sub>), 28.2 (s, CH), 23.7 (s. CH<sub>3</sub>).

# 4.3. Synthesis of dichloro{2-hydroxymethyl-6-[(2,6-diisopropylphenyl)iminomethyl]pyridine}palladium(II) (**3**)

A mixture of 2-hydroxymethyl-6-[(2,6-diisopropylphenyl)iminomethyl]pyridine (68.0 mg, 0.23 mmol) and [PdCl<sub>2</sub>(cod)] (65.3 mg, 0.23 mmol) in THF (20 mL) was stirred for 12 h at room temperature. After the volatiles were evaporated under reduced pressure, the residue was extracted with THF. Crystallization from THF/Et<sub>2</sub>O gave 3 as yellow solid (91.9 mg, 78%). Anal. Calc. for C<sub>19</sub>H<sub>24</sub>N<sub>2</sub>OCl<sub>2</sub>Pd: C, 48.17; H, 5.11; N, 5.91; Cl, 14.97. Found: C, 47.92; H, 5.32; N, 5.92; Cl, 15.38% <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta 8.17$  (t, 1H,  $J^3 = 8$  Hz, CH in pyridyl group), 8.07 (s, 1H, N=CH), 7.84 (d, 1H,  $J^3 = 8$  Hz, CH in pyridyl group), 7.80 (d, 1H,  $J^3 = 8$  Hz, CH in pyridyl group), 7.36 (t, 1H,  $J^3 = 8$  Hz, CH in aromatic group), 7.20 (d, 2H,  $J^3 = 8$  Hz, CH in aromatic group), 5.15 (d, 2H,  $J^3 = 8$  Hz,  $CH_2$ ), 4.67 (t, 1H,  $J^3 = 8$  Hz, OH), 3.31 (double quartet, 2H,  $J^3 = 7$  Hz, CH), 1.41 (d, 6H,  $J^3 = 7$  Hz, CH<sub>3</sub>), 1.14 (d, 6H,  $J^3 = 7$  Hz,  $CH_3$ ). The low solubility of the complex made it impossible to obtain a <sup>13</sup>C{<sup>1</sup>H} NMR spectrum.

	1	2	<b>3</b> ·1.5CHCl <sub>3</sub>	4	<b>5a</b> ·C <sub>4</sub> H <sub>8</sub> O	<b>5b</b> ·C <sub>4</sub> H <sub>8</sub> O
Chemical formula	C22H26Cl2CoN2O2	$C_{22}H_{26}Cl_2N_2O_2Pd$	2C <sub>19</sub> H <sub>24</sub> Cl <sub>2</sub> N <sub>2</sub> OPd·3CHCl <sub>3</sub>	C44H54Br4N4Ni2O5	C <sub>19</sub> H <sub>24</sub> Br <sub>2</sub> N <sub>2</sub> NiO·C <sub>4</sub> H <sub>8</sub> O	C19H28Br2N2NiO3·C4H8O
Formula weight	480.30	527.77	1303.55	1155.95	587.03	623.06
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$ (No. 14)	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (No. 19)	P2 <sub>1</sub> 2 <sub>1</sub> 2 (No. 18)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	<i>P</i> 1 (No. 2)
a (Å)	9.200(2)	12.022(3)	12.435(2)	10.216(2)	9.468(2)	9.9948(4)
b (Å)	15.087(2)	12.905(3)	21.765(2)	22.678(3)	13.707(3)	10.1121(4)
c (Å)	16.460(3)	14.881(4)	9.974(2)	20.599(3)	19.654(5)	13.9053(5)
α (°)						78.734(2)
β (°)	91.980(3)			97.398(2)	93.247(4)	85.777(2)
γ (°)						76.073(2)
V (Å <sup>3</sup> )	2283.3(6)	2308.7(9)	2699.6(5)	4733(1)	2547(1)	1337.27(1)
Ζ	4	4	2	4	4	2
$\mu$ (cm <sup>-1</sup> )	10.054	10.552	13.463	42.294	39.299	37.520
F(000)	996	1072	1304	2328	1192	636
$D_{\text{calc}}$ , (g cm <sup>-3</sup> )	1.397	1.518	1.604	1.622	1.531	1.547
Crystal size (mm)	$0.40 \times 0.12 \times 0.10$	$0.20 \times 0.20 \times 0.20$	$0.45 \times 0.20 \times 0.12$	$0.20 \times 0.17 \times 0.15$	$0.12 \times 0.10 \times 0.10$	$0.50 \times 0.15 \times 0.15$
Exposure rate sec. (°)	20.0	10.0	40.0	80.0	80.0	60.0
Number of date	16 961	15 716	20 296	34 856	18 884	13 241
Number of unique date	5070	5194	6161	10 775	5771	6040
Number of used reflections $(I > 2\sigma(I))$	4249	5076	5848	8917	3832	4635
Number of variables	263	263	243	541	276	310
$R (I > 2\sigma(I))$	0.042	0.026	0.085	0.049	0.057	0.044
R (All reflections)	0.054	0.027	0.088	0.065	0.088	0.065
R <sub>W</sub> (All reflections)	0.113	0.068	0.230	0.118	0.168	0.128
Goodness-of-fit (GOF)	1.07	1.13	1.07	1.13	1.08	1.11

#### 4.4. Synthesis of dibromo{2-hydroxymethyl-6-[(2,6-diisopropylphenyl)iminomethyl]pyridine}nickel(II) (**5a**)

 $[NiBr_2(H_2O)_3]$  (54.5 mg, 0.20 mmol) was added to a solution of 2-hydroxymethyl-6-[(2,6-diisopropylphenyl)iminomethyl]pyridine (59.3 mg, 0.20 mmol) in THF (10 mL). After stirring at room temperature for 18 h, the solvent was reduced under vacuum. Et<sub>2</sub>O was added to the solution to cause the separation of**5a**as an orange solid (68.9 mg, 67%).*Anal.*Calc. for C<sub>19</sub>H<sub>24</sub>Br<sub>2</sub>N<sub>2</sub>NiC<sub>4</sub>H<sub>8</sub>O: C, 47.06; H, 5.49; N, 4.77; Br, 27.22. Found: C, 46.91; H, 5.52; N, 4.77; Br, 27.26%.

# 4.5. Synthesis of bisaqua(bromo){2-hydroxymethyl-6-[(2,6-diisopropylphenyl) iminomethyl]pyridine}nickel(II) bromide (**5b**)

Complex **5a** (19.1 mg, 0.037 mmol) was stirred in a mixture of THF and H<sub>2</sub>O (30/1) for 20 h. After the solution was dried with MgSO<sub>4</sub>, the solvent was slowly evaporated to cause the separation of **5b** as green crystals (11.5 mg, 59%). *Anal.* Calc. for  $C_{19}H_{28}Br_2N_2O_3NiC_4H_8O$ : C, 44.34; H, 5.82; N, 4.50; Br, 25.65. Found: C, 44.12; H, 6.06; N, 4.40; Br, 25.63%.

#### 4.6. Crystal structure determination

Intensity data were collected on a Rigaku Saturn CCD area detector or a Rigaku R-AXIS Rapid diffractometer with Mo K $\alpha$  radiation. Crystals of **1–5b** suitable for an X-ray diffraction study were mounted on glass capillary tubes. Crystallographic data and details of refinement of the complexes are summarized in Table 2. A full matrix least-squares refinement was used for non-hydrogen atoms with the anisotropic thermal parameters method by the SHELXL-97 program. In the structure of **3**·1.5CHCl<sub>3</sub>, disordered CHCl<sub>3</sub> molecules, C1 and O1 atoms were refined isotropically. The positional parameters for O–H hydrogen atoms, except for those in **3**·1.5CHCl<sub>3</sub>, were refined isotropically, but other hydrogens were located by assuming an ideal geometry and were included in the structure calculation without further refinement of the parameters [25].

#### Supplementary data

CCDC 719682, 719683, 719684, 719685, 719686, 719687 contains the supplementary crystallographic data for **1**, **2**, **3**, **4**, **5a** and **5b**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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