

Construction of Various Supramolecules by π – π Interactions: Self-Assembly of Nickel(II) Macrocyclic Complexes Containing Pyridine Pendant Arms with Bidentate Ligands

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The supramolecular compounds, $[\text{Ni}(\text{C}_{20}\text{H}_{32}\text{N}_8)(\text{en})](\text{ClO}_4)_2 \cdot 2 \text{H}_2\text{O}$ (**1**), $[\text{Ni}(\text{C}_{20}\text{H}_{32}\text{N}_8)(\text{isonicotinate})_2]$ (**2**), and $[\text{Ni}(\text{C}_{20}\text{H}_{32}\text{N}_8)(\text{BQDC})] \cdot 3 \text{H}_2\text{O}$ (**3**), have been constructed by the self-assembly of a nickel(II) macrocyclic complex containing pyridyl pendant rings, $[\text{Ni}(\text{C}_{20}\text{H}_{32}\text{N}_8)](\text{ClO}_4)_2 \cdot 2 \text{H}_2\text{O}$, with ethylenediamine (hereafter noted en), isonicotinic acid, and potassium 2,2'-biquinoline-4,4'-dicarboxylate, ($\text{K}_2\text{BQDC} \cdot 3 \text{H}_2\text{O}$), respectively, in MeCN/ H_2O . The X-ray crystal structure of **1** indicates that one en coordinates a nickel(II) macrocyclic complex to form a folded macrocyclic complex, which ends up with a stacking dimer via C–H $\cdots\pi$ and offset face-to-face π – π interactions between the pyridine pendant groups. The X-ray crystal structure of **2** indicates that two isonicotinate ions coordinate a nickel(II) macrocyclic complex at the axial positions and the pyridine groups of the

coordinated isonicotinates are involved in offset face-to-face π – π interactions, which gives rise to a 1D chain. The 1D chains are linked together via the offset face-to-face π – π interactions between the pyridine groups of the macrocycle to generate a 2D network. The X-ray crystal structure of **3** indicates that each BQDC^{2-} ion coordinates two nickel(II) macrocyclic complexes and each nickel(II) macrocyclic unit binds two BQDC^{2-} ions at the axial positions to form a 1D chain. The 1D chains experience the intramolecular hydrogen bonding as well as the interchain offset face-to-face π – π interactions between the pyridyl pendant rings of the macrocycle and the BQDC^{2-} ions, which gives rise to a 2D sheet. Between the 2D sheets herringbone π – π interactions exist, which results in a 3D framework.

Introduction

Self-assembly of organic molecules and metal-ion building blocks may yield a new generation of multidimensional supramolecular networks. In the assembly of the supramolecules, hydrogen bonding,^[1] π – π stacking interaction,^[2] and C–H $\cdots\pi$ interaction^[3], besides the metal–ligand coordination, are utilized to induce intermolecular interactions.^[4] In particular, supramolecules built by noncovalent interactions between aromatic rings are of great importance because of the potential applications for molecular recognition,^[5] catalysis,^[6] stabilizing protein structure,^[7] and molecular devices.^[8] To become a new class of solid materials, the supramolecules should be insoluble and the frameworks should be maintained, even after the removal of the guest molecules or restored upon reintroduction of the guest molecules. For this purpose, extensive intermolecular interactions, hopefully multidimensional ones, should exist in the solid. In particular, the control of dimensionality of the supramolecules is a challenging subject in the self-assembly since the ancillary ligation by solvent or anion may result in low dimensionality.

To obtain insoluble supramolecules which are constructed by the extensive π – π stacking interactions as well as the metal–ligand coordination, we have employed in the self-assembly the nickel(II) macrocyclic complex containing pyridine pendants (**A**) as a metal building block and the bidentate ligands such as en, isonicotinate, and 2,2'-biquinoline-4,4'-dicarboxylate (BQDC^{2-}) as the organic building blocks (Figure 1). We have obtained a dimer $[\text{Ni}(\text{C}_{20}\text{H}_{32}\text{N}_8)(\text{en})](\text{ClO}_4)_2 \cdot 2 \text{H}_2\text{O}$ (**1**), a 2D sheet $[\text{Ni}(\text{C}_{20}\text{H}_{32}\text{N}_8)(\text{isonicotinate})_2]$ (**2**), and a 3D network $[\text{Ni}(\text{C}_{20}\text{H}_{32}\text{N}_8)(\text{BQDC})] \cdot 3 \text{H}_2\text{O}$ (**3**), respectively, from the self-assembly. Here, we report X-ray crystal structures and properties of these supramolecules.

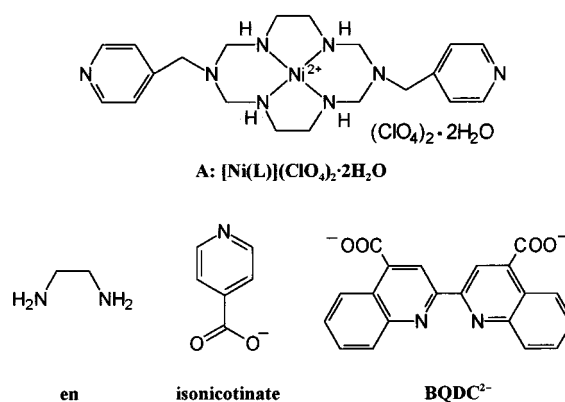


Figure 1. Building blocks employed in the self-assembly of **1–3**

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Results and Discussion

Properties and X-ray Crystal Structure of $[\text{Ni}(\text{C}_{20}\text{H}_{32}\text{N}_8)(\text{en})](\text{ClO}_4)_2 \cdot 2 \text{H}_2\text{O}$ (**1**)

Compound **1** was prepared in MeCN/H₂O by the self-assembly of nickel(II) macrocyclic complex **A** with en. It is soluble in DMF, DMSO, and MeNO₂/MeOH. The infrared spectrum (Nujol mull) shows $\nu_{\text{C}=\text{N}}$ of pyridine pendant rings at 1605 cm⁻¹, ν_{NH} of the primary amines of en at 3335 and 3270 cm⁻¹, and ν_{NH} of the secondary amines of macrocycle at 3182 cm⁻¹. The value of molar conductance (Λ_{M}) measured in DMSO is 70 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$, which corresponds to a 1:2 electrolyte.^[9] The electronic absorption spectrum shows a d–d transition band at 532 nm ($\epsilon = 9$), which corresponds to the characteristic chromophore of a nickel(II) ion coordinated with an N₄ macrocycle and an N₂ bidentate ligand.^[10]

An ORTEP drawing of **1** is shown in Figure 2a and the selected bond lengths and angles are listed in Table 1. The

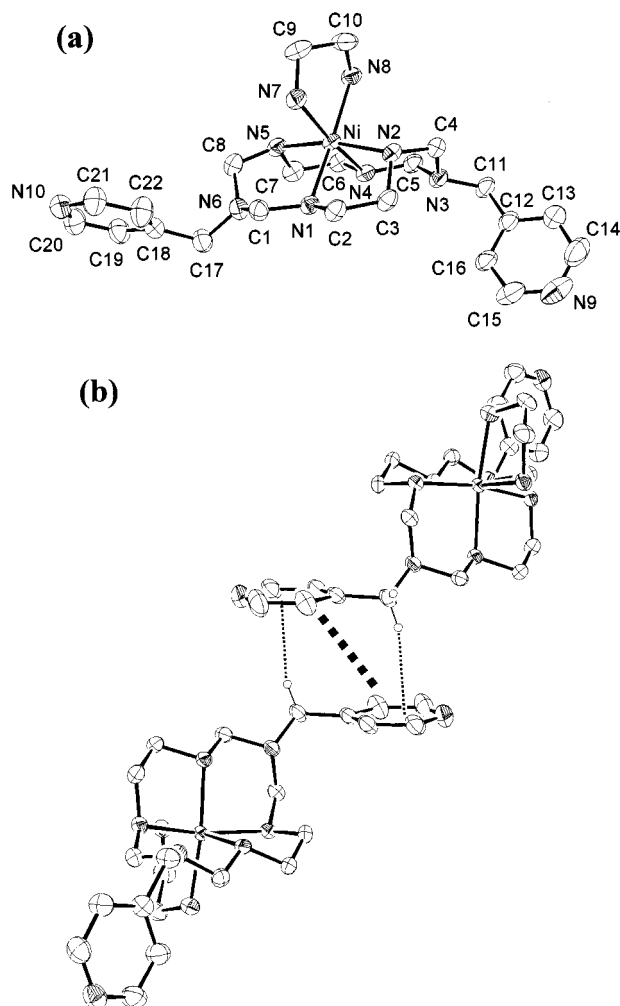


Figure 2. (a) ORTEP drawing of **1** with atomic numbering scheme; the atoms are represented by 40% probable thermal ellipsoids; (b) perspective view of **1**, showing a dimer; the C–H... π interactions are indicated as $\cdots$; the offset face-to-face π – π interaction between pyridine groups leading to a dimer is indicated as $\blacksquare$

nickel(II) ion displays distorted octahedral coordination geometry by coordination with the four secondary amine nitrogen atoms of the macrocycle in a folded conformation and the two nitrogen atoms of en in the *cis* positions. The average Ni–N bond length is 2.136(1) Å, which is longer than that for octahedral nickel(II) complex coordinated with N₄O₂ donors.^[11] In the structure, one pyridine pendant group of the macrocyclic complex experiences C–H... π interaction^[3] as well as offset face-to-face π – π interaction^[2,12] with a pyridine pendant group belonging to a neighboring macrocyclic complex, which leads to a stacked dimer (Figure 2b). For the C–H... π interaction, the distance between the centroid of the pyridine pendant ring and the nearest carbon atom of the pendant group is 3.579 Å (H11A...centroid 2.699 Å, C11–H11A...centroid 159.4°).^[13] For the π – π stacking interaction, the interplanar separation of the aromatic rings is 3.63–3.65 Å (centroid...centroid 4.741 Å) and the dihedral angle between the ring planes is 0.0°. The lattice water molecules form hydrogen bonds with the nitrogen atoms of the pyridine pendant groups: O9...N9 2.875(5) Å, O10...N10 2.789(5) Å. In addition, the oxygen atoms of the perchlorate anion form hydrogen bonds with a secondary amine of the macrocycle [O8...N4(–*x* + 1, –*y* + 1, –*z* + 1) 3.172(5) Å, O8–H4–N4 171.2°] and the primary amines of en [O3...N7(–*x*, –*y* + 1, –*z*) 3.155(6) Å, O3–H7A–N7 162.1°; O1...N8(*x*, *y* – 1, *z*) 3.202(6) Å, O1–H8B–N8 170.2°].

Table 1. Selected bond lengths [Å] and angles [°] for **1**–**3**

$[\text{Ni}(\text{C}_{20}\text{H}_{32}\text{N}_8)(\text{en})](\text{ClO}_4)_2 \cdot 2 \text{H}_2\text{O}$ (**1**)

Ni–N1	2.124(3)	Ni–N5	2.138(3)
Ni–N2	2.151(3)	Ni–N7	2.140(3)
Ni–N4	2.115(3)	Ni–N8	2.146(3)
N1–Ni–N2	82.21(10)	N2–Ni–N8	95.91(12)
N1–Ni–N4	94.44(11)	N4–Ni–N5	82.64(11)
N1–Ni–N5	88.63(11)	N4–Ni–N7	171.88(12)
N1–Ni–N7	93.47(12)	N4–Ni–N8	91.98(11)
N1–Ni–N8	173.26(11)	N5–Ni–N7	95.73(13)
N2–Ni–N4	88.79(11)	N5–Ni–N8	94.22(13)
N2–Ni–N5	166.95(11)	N7–Ni–N8	80.18(12)
N2–Ni–N7	94.10(13)		

$[\text{Ni}(\text{C}_{20}\text{H}_{32}\text{N}_8)(\text{isonicotinate})_2]$ (**2**)

Ni–N1	2.062(5)	O1–C11	1.247(8)
Ni–N2	2.021(6)	O2–C11	1.255(8)
Ni–O1	2.135(4)	N3–C1 ^[a]	1.421(9)
N1–Ni–N2	86.8(2)	O1–C11–O2	127.7(5)
N1–Ni–O1	91.94(16)	O1–C11–C12	116.4(7)
N2–Ni–O1	92.60(17)	O2–C11–C12	115.9(6)

$[\text{Ni}(\text{C}_{20}\text{H}_{32}\text{N}_8)(\text{BQDC})] \cdot 3 \text{H}_2\text{O}$ (**3**)

Ni–N1	2.048(5)	O1–C11	1.238(7)
Ni–N2	2.080(5)	O2–C11	1.251(7)
Ni–O1	2.110(4)	C14–C14 ^[b]	1.410(12)
N1–Ni–N2	84.91(18)	O1–C11–O2	125.1(7)
N1–Ni–O1	93.50(18)	O1–C11–C12	114.6(6)
N2–Ni–O1	91.6(2)	O2–C11–C12	120.2(6)

^[a] Marked atoms are generated by symmetry operations: –*x*, –*y*, –*z*. ^[b] –*x* – 1, –*y*, –*z*.

Properties and X-ray Crystal Structure of $[\text{Ni}(\text{C}_{20}\text{H}_{32}\text{N}_8)(\text{isonicotinate})_2] \cdot (2)$

Compound **2** was prepared in MeCN/H₂O by the self-assembly of nickel(II) macrocyclic complex **A** with isonicotinate. It is insoluble in any solvents. The infrared spectrum (Nujol mull) shows $\nu_{\text{C}=\text{N}}$ of pyridine pendant groups at 1596 cm⁻¹, $\nu_{\text{C}=\text{O}}$ of the carboxylate groups coordinating the macrocyclic complex at 1547 cm⁻¹, and ν_{NH} of the secondary amines of macrocycle at 3213 and 3140 cm⁻¹. Two split secondary amine peaks of the nickel(II) complex indicate that the compound has two kinds of secondary amines, which is attributed to the hydrogen bonding interactions of the two secondary amines of the macrocycle as revealed by the X-ray crystal structure. The diffuse reflectance spectrum shows maximum absorption at 510 nm, which corresponds to the characteristic chromophore for the nickel(II) ion coordinated with N₄O₂ donors.^[10]

An ORTEP drawing of **2** is shown in Figure 3a and the selected bond lengths and angles are listed in Table 1. The coordination geometry around the nickel(II) ion is a tetragonally distorted octahedron in which the nickel(II) ion is coordinated with the four secondary amine nitrogen atoms of the macrocycle in the square-planar fashion and two oxygen atoms from two isonicotinate ions at the axial sites. The average Ni–N and Ni–O bond lengths are 2.053(2) and 2.130(3) Å, respectively. All pyridine groups of the isonicotinate ions coordinating nickel(II) ions are involved in offset face-to-face π - π interactions by themselves (centroid...centroid 3.673 Å),^[12] which leads to a supramolecular 1D polymer propagating along the *c* axis (Figure 3b). The interplanar separation and the offset angle between the ring planes of isonicotinate ions are 3.46–3.47 Å and 11.2°, respectively. Within a 1D chain, the free carbonyl oxygen atom of the coordinated carboxylate ion forms an intramolecular hydrogen bond with the secondary amine of the macrocycle [O2...N2 2.883(6) Å, O2–H2–N2 155.6°]. Therefore, two C–O bond lengths of the carboxylate group are not significantly different although one is coordinated [1.247(8) Å] and the other is uncoordinated [1.255(8) Å] to the nickel(II) ion. The 1D polymers are linked together via offset face-to-face π - π interactions between the pyridine rings of the macrocycle, which leads to a 2D network extending along the [110] plane (Figure 3c). The pyridine rings are positioned completely parallel to each other with the dihedral angle of 0.0°. The intercentroid distance and the offset angle between the ring planes are 4.847 Å and 47.6°, respectively.

Properties and X-ray Crystal Structure of $[\text{Ni}(\text{C}_{20}\text{H}_{32}\text{N}_8)(\text{BQDC})] \cdot 3 \text{H}_2\text{O} \cdot (3)$

Compound **3** was prepared in MeCN/H₂O by the self-assembly of nickel(II) macrocyclic complex **A** with 2,2'-biquinoline-4,4'-dicarboxylate (BQDC²⁻). It is stable and does not lose guest water molecules upon exposure to the atmosphere. The compound is insoluble in any solvents.

The infrared spectrum (Nujol mull) of **3** shows ν_{NH} of the secondary amines of macrocycle at 3276 and 3181 cm⁻¹, $\nu_{\text{C}=\text{N}}$ of pyridine pendant groups at 1600 cm⁻¹, and $\nu_{\text{C}=\text{O}}$ of the carboxylate groups of BQDC²⁻ at 1579 cm⁻¹. Two split secondary amine peaks of the nickel(II) complex indicate that the macrocycle has two kinds of secondary amines due to the hydrogen bonding interactions, which is revealed by the X-ray crystal structure. The diffuse reflectance spectrum shows maximum absorption at 502 nm, which corresponds to the characteristic chromophore for the nickel(II) ion coordinated with N₄O₂ donors.^[10] The TGA trace of **3** (Figure S1, Supporting Information) shows a weight loss of 5.65% at 80 °C, corresponding to the loss of three guest water molecules per unit formula. No chemical decomposition was observed up to 250 °C.

An ORTEP drawing of **3** is shown in Figure 4a and the selected bond lengths and angles are listed in Table 1. Each nickel(II) ion of macrocyclic complex **A** is coordinated by two carboxylate oxygen atoms of BQDC²⁻ ion at the axial positions as well as the N₄ macrocycle to display a distorted octahedral coordination geometry. Since each BQDC²⁻ ion binds two metal ions in an *exo*-bidentate mode, **3** becomes a linear coordination polymer (Figure 4b). The average Ni–N and Ni–O bond lengths are 2.064(3) and 2.110(3) Å, respectively. The aromatic ring of BQDC²⁻ ion is tilted [dihedral angle = 67.5(2)°] with respect to the square coordination plane of the macrocycle. The BQDC²⁻ bridging ligand is not planar since the dihedral angle between the carboxylate group and the aromatic ring of BQDC²⁻ ion is 30.6(3)°. The dihedral angle between the carboxylate plane and the macrocyclic coordination plane involving nickel atom is 87.4(6)°. Within a 1D chain, intramolecular hydrogen bonding interactions exist between the uncoordinated oxygen atoms of carboxylate and the secondary amines of the macrocycle to form stable six-membered rings [O2...N1 2.915(7) Å, O2–H1–N1 150.7°]. Compound **3** has two kinds of 1D chains. The linear chains are linked by the offset face-to-face π - π interactions^[12] between the aromatic groups of the BQDC²⁻ ions belonging to a chain, and the pyridine pendant groups of the macrocycle belonging to the adjacent linear chains, which leads to a 2D network extending along the (002) plane (Figure 4c). The interplanar separation and the dihedral angle between the aromatic ring of BQDC²⁻ ion and the pyridine pendant group of macrocyclic complex are 3.32–3.55 Å and 5.87°, respectively. Between the layers, there exist the herringbone π - π interactions between the BQDC²⁻ ion and the pyridine pendant ring of macrocycle, which gives rise to a 3D network (Figure 4d). The distance between the centroids is 5.237 Å, and the dihedral angle between the pendant pyridine group and the aromatic ring of BQDC²⁻ ion is 75.1(1)°. The separation between the layers is 10.697 Å. The shortest Ni...Ni distance within a linear chain is 13.451(5) Å and that between the linear chains is 12.968(4) Å. The lattice water molecules are located in the cavities created by the packed chains. The void volume of cavities per unit cell is 648 Å³ (15.4%) as estimated by PLATON.^[14] In addition, the lattice water molecules form hydrogen bonds with the uncoor-

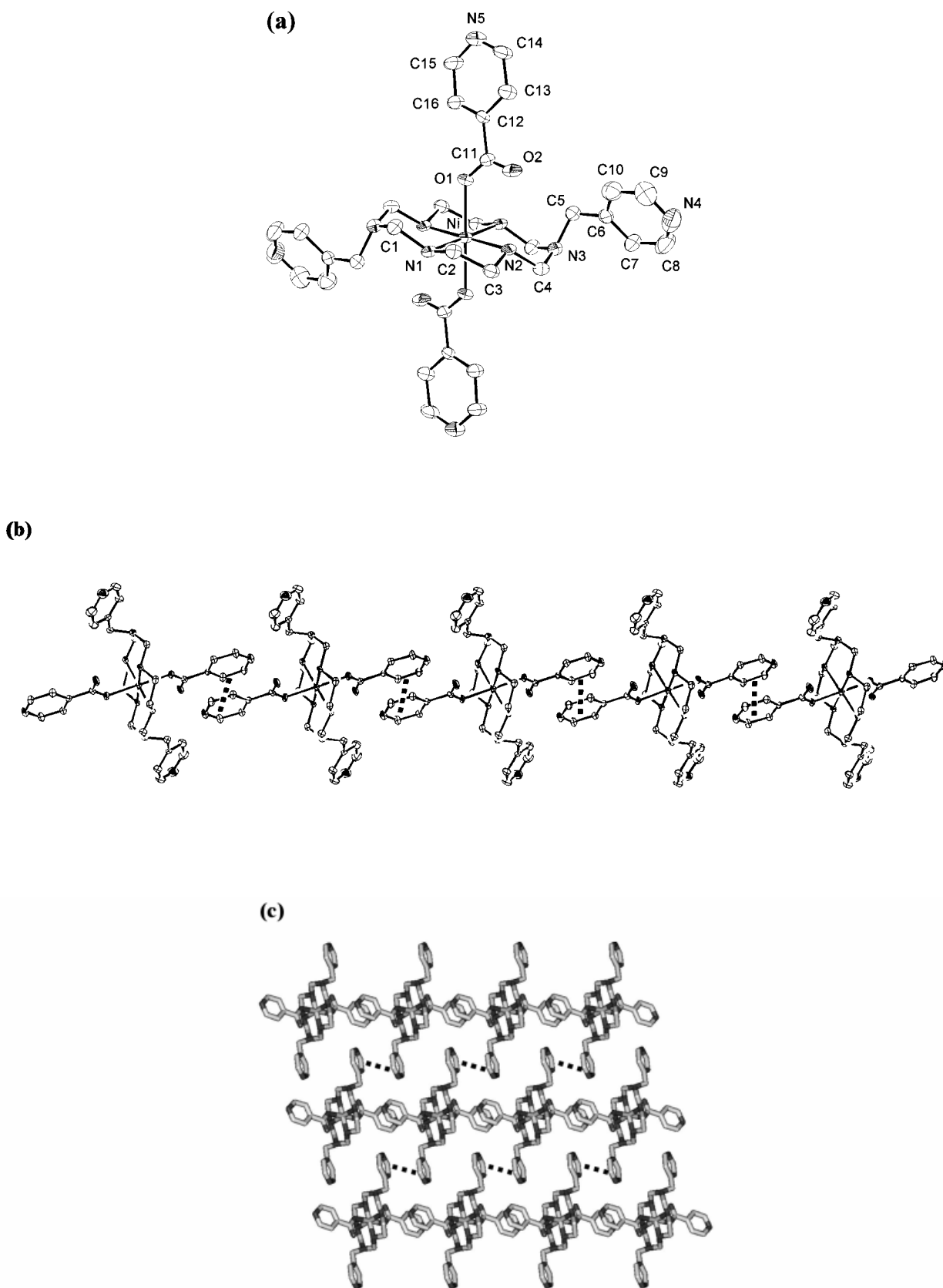


Figure 3. (a) ORTEP drawing of **2** with atomic numbering scheme; the atoms are represented by 40% probable thermal ellipsoids; (b) perspective view of **2** showing a 1D chain; the offset face-to-face π - π interactions between the coordinated isonicotinate ions are indicated as ■■■; (c) extended 2D structure of **2**; the interchain offset face-to-face π - π interactions are indicated as ■■■

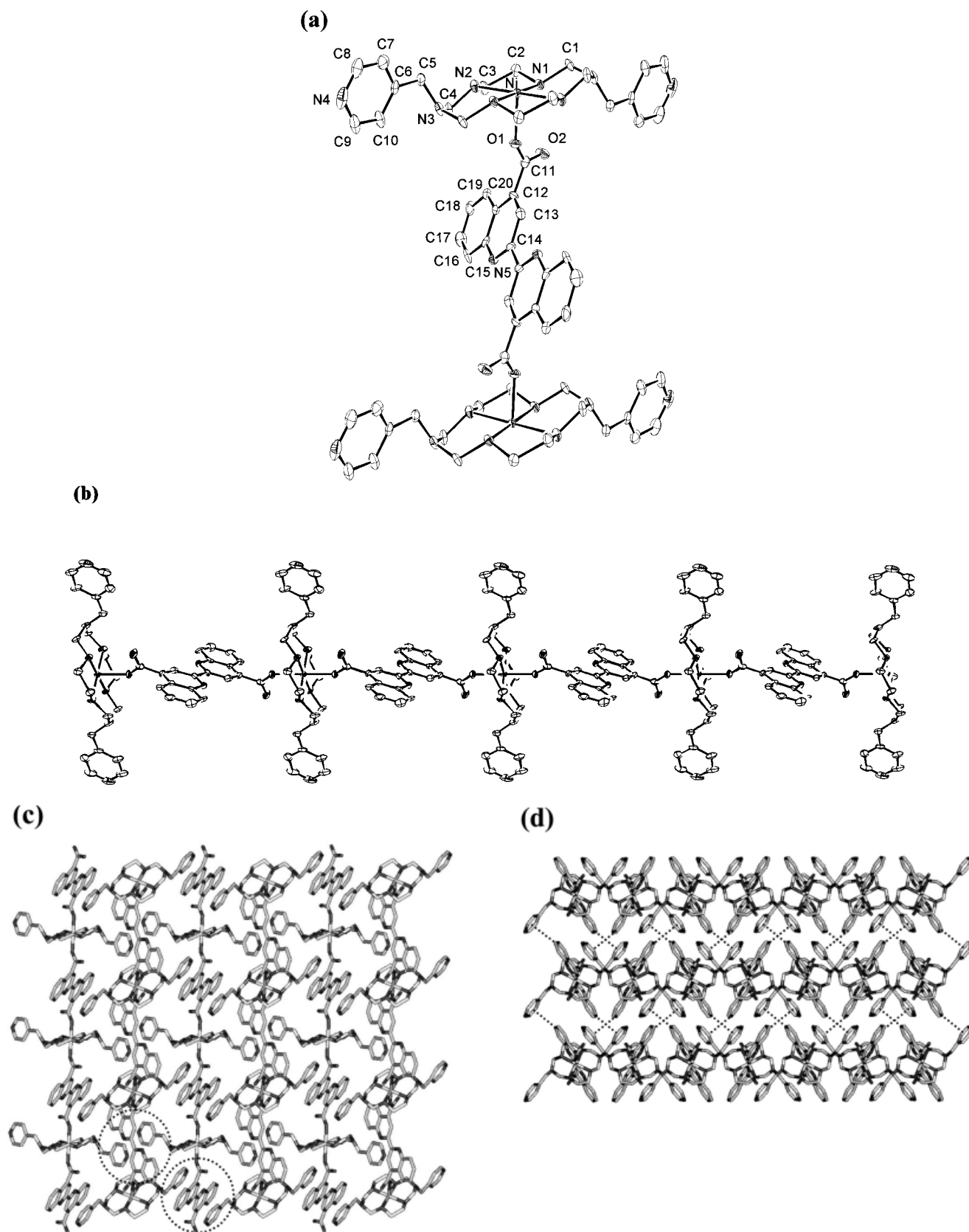


Figure 4. (a) ORTEP drawing of **3** with atomic numbering scheme; the atoms are represented by 20% probable thermal ellipsoids; (b) perspective view of **3** showing a 1D chain; (c) extended 2D structure of **3**; the interchain offset face-to-face π - π interactions are indicated as dotted circles; (d) side view of the packed structure of **3** showing the herringbone π - π interactions between the 2D layers, which are indicated as ●●●

minated carboxylate oxygen atom $[O2 \cdots O3(-1 + x, y, z) = 2.757(8) \text{ \AA}]$, with the pyridine nitrogen atom of the macrocycle $[O3 \cdots N4(1 + x, -0.5 - y, 0.5 + z) = 3.041(11) \text{ \AA}]$, and with the other lattice water molecule ($O3 \cdots O4 = 2.754(7) \text{ \AA}$).

Conclusion

We have constructed several supramolecules having structures of dimer, 2D sheet, and 3D framework by the self-assembly of a nickel(II) macrocyclic complex containing pyridyl pendant rings (**A**) with organic bidentate ligands such as en, isonicotinate, and 2,2'-biquinoline-4,4'-dicarboxylate, respectively. The supramolecules are assembled by the π - π stacking interactions involving aromatic rings of the organic ligand and the pyridine pendant groups attached to the macrocyclic ligand.

Experimental Section

General: All chemicals and solvents used in the synthesis were of reagent grade and used without further purification. – Infrared spectra were recorded with a Perkin–Elmer 2000 FT-IR spectrophotometer. – Elemental analyses were performed by the analytical laboratory of Seoul National University. – UV/Vis diffuse reflectance spectra were recorded with a Cary 300 Bio UV/Vis spectrophotometer. – Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed at a scan rate of $5^\circ\text{C}/\text{min}$ using a DuPont TGA 2050 TA instrument and a DuPont DSC 2100 TA instrument, respectively.

Safety Note: Although we have experienced no problem with the compounds reported in this work, perchlorate salts of metal complexes with organic ligands are often explosive and should be handled with great caution!

$[\text{Ni}(\text{C}_{20}\text{H}_{32}\text{N}_8)](\text{ClO}_4)_2 \cdot 2 \text{H}_2\text{O}$ (A**):**^[15] To a stirred methanol solution (75 mL) of $\text{Ni}(\text{OAc})_2 \cdot 4 \text{H}_2\text{O}$ (12.4 g, 0.05 mol), were slowly added ethylenediamine (6.8 mL, 0.10 mol), paraformaldehyde (6.0 g, 0.20 mol), and 4-(aminomethyl)pyridine (10.8 g, 0.10 mol). The mixture was heated at reflux for 24 h. The solution was filtered while hot and the filtrate was concentrated to ca. 1/5 of the original volume. HClO_4 (60%, 20 mL) was added to the yellow-brown solution and the solution was allowed to stand in a refrigerator until yellow crystals of $[\text{Ni}(\text{L} + 2 \text{H})](\text{ClO}_4)_4 \cdot 2 \text{H}_2\text{O}$ formed, these were filtered off, washed with methanol, and dried in air. Yield: 35%. To an MeCN suspension (40 mL) of $[\text{Ni}(\text{L} + 2 \text{H})](\text{ClO}_4)_4 \cdot 2 \text{H}_2\text{O}$ (2.5 g), was added an excess amount of triethylamine (2 mL). The complex went into the solution and yellow crystals of $[\text{Ni}(\text{L})](\text{ClO}_4)_2 \cdot 2 \text{H}_2\text{O}$ (**A**) formed in a few minutes. The crystals were filtered off, washed with water, and dried in air. – FT IR (Nujol mull, cm^{-1}): $\tilde{\nu} = 3590$ (s, br.), 3195 (s), 1650 (m), 1605 (s), 1565 (m), 1100 (s), 625 (s). – UV/Vis (MeNO_2): λ_{max} [nm] (ϵ [$\text{M}^{-1} \text{cm}^{-1}$]) = 450 (68). – $\text{C}_{20}\text{H}_{36}\text{Cl}_2\text{N}_8\text{NiO}_{10}$ (678.2): calcd. C 35.42, H 5.35, N 16.52; found C 35.24, H 4.93, N 16.59.

$[\text{Ni}(\text{C}_{20}\text{H}_{32}\text{N}_8)(\text{en})](\text{ClO}_4)_2 \cdot 2 \text{H}_2\text{O}$ (1**):** To an MeCN/ H_2O (v/v; 1:1, 20 mL) solution of **A** (0.50 g, 0.74 mmol), was added dropwise an MeCN solution (5 mL) of ethylenediamine (0.044 g, 0.74 mmol) at room temperature. The color of the solution turned from yellow to purple. The solution was allowed to stand at room temperature.

The purple crystals formed, which were filtered off, washed with MeOH, and dried in air. Yield: 83%. – FT IR (Nujol mull, cm^{-1}): $\tilde{\nu} = 3650$ (s), 3335 (s), 3270 (s), 3182 (s), 1605 (s), 1565 (s), 1100 (s). – UV/Vis (DMSO): λ_{max} [nm] (ϵ [$\text{M}^{-1} \text{cm}^{-1}$]) = 339 (14), 532 (9). – Molar conductance (DMSO): Λ_{M} [$\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$] = 70. – $\text{C}_{22}\text{H}_{44}\text{Cl}_2\text{N}_{10}\text{NiO}_{10}$ (738.3): calcd. C 35.79, H 6.01, N 18.97; found C 35.38, H 5.62, N 19.27.

$[\text{Ni}(\text{C}_{20}\text{H}_{32}\text{N}_8)(\text{isonicotinate})_2]$ (2**):** To an MeCN/ H_2O (v/v; 1:1, 20 mL) solution of **A** (0.50 g, 0.74 mmol), was added dropwise an MeCN solution (10 mL) containing isonicotinic acid (0.18 g, 1.48 mmol) and excess triethylamine (0.30 g, 2.96 mmol) at room temperature. The color of the solution turned from yellow to pale pink. The solution was allowed to stand at room temperature. The pale pink crystals formed, which were filtered off, washed with water, and dried in air. Yield: 85%. – FT IR (Nujol mull, cm^{-1}): $\tilde{\nu} = 3213$ (s), 3140 (s), 1596 (s), 1565 (s), 1547 (s). – UV/Vis (diffuse reflectance): λ_{max} [nm] = 260, 510, 650. – $\text{C}_{32}\text{H}_{40}\text{N}_{10}\text{NiO}_4$ (687.4): calcd. C 55.91, H 5.87, N 20.38; found C 55.24, H 5.87, N 20.58.

$[\text{Ni}(\text{C}_{20}\text{H}_{32}\text{N}_8)(\text{BQDC})] \cdot 3 \text{H}_2\text{O}$ (3**):** To an MeCN/ H_2O (v/v; 1:1, 20 mL) solution of **A** (0.50 g, 0.74 mmol), was added dropwise an aqueous solution (10 mL) containing potassium 2,2'-biquinoline-4,4'-dicarboxylate ($\text{K}_2\text{BQDC} \cdot 3 \text{H}_2\text{O}$) (0.35 g, 0.74 mmol) at room temperature. The color of the solution turned from yellow to pale yellow. The solution was allowed to stand at room temperature. The pale yellow crystals formed, which were filtered off, washed with water, and dried in air. Yield: 79%. – FT IR (Nujol mull, cm^{-1}): $\tilde{\nu} = 3392$ (s), 3277 (s), 3183 (s), 3074 (m), 1600 (s), 1579 (s), 1546 (m), 1492 (m), 1026 (s). – UV/Vis (diffuse reflectance): λ_{max} [nm] = 257, 334, 502, 682. – $\text{C}_{40}\text{H}_{42}\text{N}_{10}\text{NiO}_7$ (833.5): calcd. C 57.22, H 5.76, N 16.68; found C 56.41, H 5.68, N 16.76.

X-ray Diffraction Measurements: Single crystals of **1** ($0.5 \times 0.5 \times 0.2 \text{ mm}$), **2** ($0.2 \times 0.2 \times 0.06 \text{ mm}$), and **3** ($0.6 \times 0.7 \times 0.08 \text{ mm}$) were mounted on an Enraf–Nonius CAD4 diffractometer. The unit cell parameters were determined from 25 machine-centered reflections with $22^\circ \leq 2\theta \leq 28^\circ$ for **1**, $19^\circ \leq 2\theta \leq 29^\circ$ for **2**, and $22^\circ \leq 2\theta \leq 28^\circ$ for **3**. Intensities were collected with graphite-monochromated Mo-K_α radiation, using the ω - 2θ scan mode. For **1**, among 5835 reflections measured in the range $3.30^\circ \leq 2\theta \leq 49.96^\circ$, 4460 were assumed to be observed [$F > 4\sigma(F)$]. For **2**, among 2206 reflections measured in the range $3.84^\circ \leq 2\theta \leq 50.16^\circ$, 1278 were assumed to be observed [$F > 4\sigma(F)$]. For **3**, among 3404 reflections measured in the range $3.80^\circ \leq 2\theta \leq 49.90^\circ$, 1322 were assumed to be observed [$F > 4\sigma(F)$]. Three standard reflections were measured every 2 h as orientation and intensity control and no significant intensity decay was observed. Lorentz and polarization corrections were made. No absorption correction was made. The crystal structure was solved by direct methods^[16] for **1** and **3** and by Patterson synthesis^[16] for **2**, and refined by full-matrix least-squares methods using the SHELXL97 computer program.^[17] For **1–3**, the positions of all non-hydrogen atoms were refined with anisotropic displacement factors. In **1**, all hydrogen atoms were located and refined with isotropic thermal parameters except those of the lattice water molecules. In **2** and **3**, all hydrogen atoms were allowed to ride on their bonded atoms with the isotropic displacement factors fixed with values of 1.2 times those of the bonded atoms, except those of the lattice water molecules. The crystallographic data of **1–3** are summarized in Table 2. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-143549 to -143551. Copies of the data can be obtained free of

Table 2. Crystallographic data for **1**–**3**

	1	2	3
Empirical formula	C ₂₂ H ₄₄ Cl ₂ N ₁₀ NiO ₁₀	C ₃₂ H ₄₀ N ₁₀ NiO ₄	C ₄₀ H ₄₂ N ₁₀ NiO ₇
Molecular mass	738.25	687.42	839.60
Crystal system	triclinic	triclinic	orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>Pccn</i>
<i>a</i> [Å]	9.287(1)	8.386(3)	13.451(5)
<i>b</i> [Å]	12.363(2)	8.856(1)	14.662(5)
<i>c</i> [Å]	14.598(2)	10.941(4)	21.393(9)
α [°]	94.84(1)	103.37(2)	90
β [°]	93.75(1)	93.11(3)	90
γ [°]	91.12(1)	92.27(2)	90
<i>V</i> [Å ³]	1666.0(4)	788.3(4)	4219(3)
<i>Z</i>	2	1	4
<i>D</i> _{calcd.} [g cm ^{−3}]	1.472	1.448	1.322
<i>T</i> [K]	293(2)	293(2)	293(2)
λ [Å]	0.71069	0.71069	0.71069
μ [mm ^{−1}]	0.808	0.671	0.520
<i>F</i> (000)	776	362	1768
Collected	6348	2375	3426
Unique	5835	2103	3404
Observed	4460	1411	1322
Parameters	566	214	264
GOF	1.033	1.020	0.954
<i>R</i> ₁ ^[a] (4 σ data)	0.0468	0.0607	0.0731
<i>wR</i> ₂ ^[b] (4 σ data)	0.1284	0.1473	0.1380

$$^{[a]} R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|, \quad ^{[b]} wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}.$$

charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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