Preparation, crystal structures, properties, and time-dependent density functional theory of two cobalt complexes with 3-hydroxy-2-methyl-quinoline-4-carboxylate

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Abstract
One organic compound [HMCA]2 (1) and two novel cobalt complexes [Co(MCA)(bipy)(H2O)](H2O) (2), [Co2(MCA)2(Phen)]3(H2O) (3) are synthesized by a solvothermal approach and are structurally determined by single-crystal X-ray diffraction. Compound 1 exhibits a two-dimensional structure by hydrogen bond and π...π stacking interaction. The complexes exhibit a three-dimensional and one-dimensional metal-organic framework. Solid-state photoluminescence spectrums reveal that they show blue emission bands at 449 nm, and theoretical calculation results of time-dependent density functional theory show that all belong to ligand-to-ligand charge transfer. Solid-state diffuse reflectance spectrums reveal the presence of a narrow optical band gap of 1.72 and 1.60 eV in the complexes 2 and 3, respectively.

Keywords
Crystal structure, photoluminescence, semiconductor, time-dependent density functional theory

Date received: 10 May 2020; accepted: 18 July 2020

Introduction
In recent years, in the field of chemistry and materials, inorganic–organic hybrid materials have attracted increasing attention from chemists and material scientists, due to their potential applications in semiconductors,1 optics,2 magnetism,3 solar cells,4 medical materials,5 and so on. Quinoline compounds are widely used in many fields such as in the coordination of metal ions,6 for selective recognition of anions,7 for printing and dyeing auxiliaries,8 as antimalarial,9 and so on, because of their unique conjugated structure, good spectral properties, high thermal stability, and excellent biological activity. Quinoline is a type of nitrogen-containing heterocyclic naphthalene compound, which can react with many raw materials to form quinoline derivatives. Quinoline derivatives are heterocyclic compounds that are widely used as antibacterial, bactericidal, anti-allergic, antidepressant, antihypertensive, antitumor, and antimalarial agents.10–13 Quinoline carboxylic acid derivatives are multidentate organic ligands containing nitrogen atoms and carboxyl oxygen atoms which can coordinate with metal ions. The coordination modes of the carboxyl groups vary at different pH values, resulting in more coordination modes. The coordination mode can exhibit various structures and unique properties.

Based on the interest in quinoline carboxylic acids, a series of transition and lanthanide metal complexes with 3-hydroxy-2-methylquinoline-4-carboxylate (HMCA) as the main ligand were synthesized and reported by Yi’s group.14–19 In this work, all of the complexes are mononuclear complexes with monodentate or bidentate chelated coordination. In continuation of our work, we report here the solvothermal synthesis, X-ray crystal structure, solid-state photoluminescence, solid-state diffuse reflectance and magnetic properties, as well as the time-dependent density functional theory (TDDFT) calculations for three complexes, namely, [HMCA]2 (1),

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[Co(MCA)(bipy)(H2O)]·(H2O) (2), and [Co,(MCA),(Phen)], 3(H2O) (3). In this paper, complex 3 is the first reported binuclear cobalt complex with HMCA as the main ligand, in which the carboxylate exhibits both monodentate and bidentate chelation.

Results and discussion

Synthesis and crystal structures

The synthesis of HMCA is based on relevant references. 20 Complexes 2 and 3 are prepared by cobalt salt, HMCA, Bipy/Phen, Et3N, and distilled water under solvothermal conditions.

[HMCA]2(1): Single-crystal X-ray diffraction analysis revealed that compound 1 adopts a monoclinic system with the $P2_1/c$ space group and contains two HMCA molecules in a cell. From the point of view of charge balance, in situ protonation occurs at the nitrogen atom. As shown in Figure 1, there are strong intermolecular and intramolecular hydrogen bonds (N(2)–H(2). . .O(2); N(1)–H(1A). . .O(4)i; O(1)–H(1). . .O(3); C(7)–H(7). . .O(2), and weak intramolecular hydrogen bonds (C(7)–H(7). . .O(2) and C(18)–H(18). . .O(4)) in 1. A one-dimensional (1D) chain structure is formed by intermolecular hydrogen bonding as shown in Figure 2. In addition, there are abundant offset face-to-face π...π stacking interactions between Cg1...Cg2; Cg2...Cg2; Cg2...Cg3; Cg4...Cg4 (symmetry codes Cg2: 1–x, y, 1–z; Cg3: 1–x, –y, 1–z; Cg4: x, 1–y, 1–z). Cg1 is ring of C6 to C11, Cg2 is N1–C2–C3–C4–C6–C11, Cg3 is C17 to C22, Cg4 is N2–C13–C14–C15–C17–C22), and thus forms a two-dimensional (2D) supramolecular structure as shown in Figure 3. The centroid–centroid distance of Cg1...Cg2 is 3.851 Å, with a slippage distance of 1.721 Å and a dihedral angle of 3.415°. The analogous data for other stacking interactions are as follows: Cg2...Cg2: 3.678 Å, 1.289 Å, 0°, Cg2...Cg3: 3.748 Å, 1.488 Å, 2.880°, Cg4...Cg4: 3.853 Å, 1.058 Å, 0°.

[Co(MCA)(bipy)(H2O)]·(H2O) (2): Single-crystal X-ray diffraction analysis revealed that complex 2 is a neutral molecule that crystallizes in the space group $Pbca$, orthorhombic system. The Co2+ ion is located at the inversion center and is pentacoordinated by HMCA, bipy, and a water molecule, yielding a rectangular pyramidal geometry. The Co2+ ion is coordinated by three oxygen atoms and two nitrogen atoms, of which two oxygen atoms are from the HMCA ligand, one oxygen atom is from a coordinated water molecule, and the two nitrogen atoms are from the bipy ligand. Quinolinecarboxylate (MCA–) and bipy act as the bidentate ligands, and a water molecule acts as the monodentate ligand coordinated to the cobalt metal center as shown in Figure 4. The following bond distances were observed: Co(1)–O(1) 1.9929(14) Å, Co(1)–O(3) 1.9323(13) Å, Co(1)–O(4) 2.0204(15) Å, Co(1)–N(1) 2.1279(17) Å, and Co(1)–N(2) 2.0828(16) Å. These are comparable with those reported in the literature. 21 22 An intramolecular hydrogen bond can be found between the C–H bond and the carboxyl oxygen atom (C(11)–H(11) . . .O(1)). Many intermolecular hydrogen bonds are present in the crystal structure in the form O–H . . .O or O–H . . .N, such as O(4)–H(4A). . .O(1)i; O(4)–H(4B). . .O(5); O(5)–H(5A). . .O(1)ii; O(5)–H(5A). . .N(3)iii (symmetry code: i = 1/2 + x, ½–y, 1–z; ii = 1 + x, y, z; iii = 1/2 + x, y, 1/2–z), and thus form a three-dimensional (3D) supramolecular structure as shown in Figure 5. In addition, there are abundant offset face-to-face π...π stacking interactions between Cg1...Cg4 (symmetry codes: –1/2 + x, +y, 1/2–z), Cg2...Cg2 (symmetry codes: 2–x, 1–y, 1–z), Cg3...Cg3 (symmetry codes: 1–x, 1–y, 1–z) as shown in Figure 6. (Cg1 is the ring consisting of C6 to C11, Cg2 is N1 and C17 to C21, Cg3 is N2 and C12 to C16, and Cg4 is N3, C2, C3 C4, C6, C7.) The centroid–centroid distance of Cg1...Cg4 is 3.818 Å, with a slippage distance of 1.354 Å and a dihedral angle of 177.253°. The centroid–centroid distance of Cg2...Cg2 is 3.868 Å, with a slippage distance of 1.425 Å and a dihedral angle of 0°, and thus forms a 2D supramolecular structure.

Figure 1. The molecular structure of the HMCA ligand.

Figure 2. One-dimensional structure of the hydrogen bonds in the HMCA ligand.
Single-crystal X-ray diffraction analysis revealed that complex 3 is a neutral molecule that crystallizes in the space group $P2_1/n$, monoclinic system. The Co$^{2+}$ ions are located at the inversion center and are pentacoordinated by the two HMCA molecules and three Phen molecules, yielding two slightly deformed octahedral geometries. The Co$^{2+}$(1) ion is coordinated by two oxygen atoms and four nitrogen atoms, of which the two oxygen atoms are from one HMCA ligand, and the four nitrogen atoms are from two Phen ligands. The Co$^{2+}$(2) ion is coordinated by four oxygen atoms and two nitrogen atoms, of which four oxygen atoms are from two HMCA ligands, and two nitrogen atoms are from one Phen ligand. Quinolinecarboxylate (MCA–) and Phen act as the bidentate ligands coordinated to the cobalt metal center as shown in Figure 7. The following bond distances were observed:

- Co(1)–O(1) 2.050(2) Å, Co(1)–O(3) 1.987(3) Å, Co(2)–O(1) 2.264(2) Å, Co(2)–O(2) 2.126(2) Å, Co(2)–O(4) 2.051(2) Å, Co(2)–O(6) 1.984(2) Å, Co(1)–N(3) 2.136(3) Å, Co(1)–N(4) 2.121(3) Å, Co(1)–N(5) 2.218(3) Å, Co(1)–N(6) 2.142(3) Å, Co(2)–N(7) 2.117(3) Å, and Co(2)–N(8) 2.107(3) Å. These are comparable with those reported in the literature.23,24

There are three groups of intermolecular hydrogen bonds in the crystal structure of the form O–H-. . .O, for example, O(7)–H(7A). . .O(5); O(8)–H(8A). . .O(7); O(9)–H(9B). . .O(7), and also two interactions between C–H. . .Cg (π. . .ring) in the crystal structure (there are C24–H24. . .Cg(N2/C13/C14/C15/C17/C22; −1 + x, y, z) and
C30–H30⋯Cg(N1/C2/C3/C4/C6/C11; 1/2 + x, −1/2 + y, 3/2 − z), forming a 1D supramolecular structure as shown in Figure 8. In addition, there are abundant offset face-to-face π⋯π stacking interactions between Cg1⋯Cg3 (symmetry codes: x, y, z), Cg1⋯Cg5 (symmetry codes: x, y, z), Cg4⋯Cg1 (symmetry codes: −x, 1 − y, 1 − z), Cg4⋯Cg2 (symmetry codes: x, y, z), Cg4⋯Cg5 (symmetry codes: x, y, z), Cg5⋯Cg3 (symmetry codes: 1 − x, 1 − y, 1 − z) as shown in Figure 9. (The Cg1 is the ring consisting of N8 and C41 to C45; Cg2 is N7 and C53 to C57; Cg3 is N8, C47 to C50 and C58; Cg4 is C38 to C41, C45 and C46; Cg5 C50 to C53, C57 and C58.) The centroid–centroid distance of Cg1⋯Cg3 is 3.723(2) Å, with a slippage distance of 1.383 Å and a dihedral angle of 1.28(19)°; for the Cg1⋯Cg5 is 3.728(2) Å, 1.354 Å and 1.61(19)°; for the Cg4⋯Cg1 is 3.980(3) Å, 1.715 Å and 1.2(2)°; for the Cg4⋯Cg2 is 3.670(3) Å, 0.691 Å and 4.6(2)°; for the Cg4⋯Cg5 is 3.601(2) Å, 1.230 Å and 0.34(17)°, respectively. There are π⋯π stacking interactions and van de Waals attraction yielding the 1D supramolecular structure, and the crystal packing is presented in Figure 10 (see Table S1).

Photoluminescence

In recent years, increasing attention has been paid to the photoluminescence of coordination complexes. Coordination complexes containing transition elements and lanthanides have abundant 3/4d and 4f orbital electronic configurations because of their luminescent properties. The luminescent properties of the transition state complexes and lanthanide complexes have been studied. Some studies have shown that the complexes containing Co(II) ions have interesting photoluminescence properties. Based on the above considerations, we conducted photoluminescence spectral analysis on solid samples of 2 and 3 at room temperature and the results are shown in Figure 11. The photoluminescent spectra of the Co(II) complexes 2 and 3 display the same effective energy absorption in the range of 225–335 nm. When the emission is 449 nm, the excitation spectra of the Co(II) complexes 2 and 3 show the same band at 277 nm. Furthermore, we measured the corresponding photoluminescence emission spectra of the
Co(II) complexes 2 and 3. Upon excitation at 277 nm, the blue region of the spectra showed a similar peak of 449 nm. The Commission International De l’Eclairage (CIE) 1931 chromaticity coordinates under the emission were calculated for the Co(II) complexes. The estimated CIE values were found to be \( x = 0.1365 \); \( y = 0.087 \) for complex 2 and \( x = 0.1358 \); \( y = 0.0982 \) for complex 3 (Figure 12). Therefore, we deem that complexes 2 and 3 are both promising blue light–emitting diode materials.

**TDDFT calculations**

Based on the B3LYP function with basis set SDD for Co and 6-31-G* for C, H, O, and N elements to reveal the fluorescence innate character of the title Co (II) complexes, we calculated them with the Gaussian09 program using the TDDFT. The ground state geometry was truncated from them single-crystal X-ray data without optimization. The characteristics of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the complexes 2 and 3 are given in Figure 13(a) and (b), respectively. The results show that the electron density distribution of the HOMO totally resided on the coordinating \( \pi \)-orbital of HMCA, the HMCA of Co(2), and the three Phen ligands with the energies of \(-0.161900\) Hartree and \(-0.112989\) Hartree, respectively, whereas the electron density distribution of the LUMO totally resided on the coordinating \( \pi \)-orbital of bipy and the two Phen ligands of Co(1) with the energy of \(-0.104960\) Hartree and \(-0.090100\) Hartree, respectively. Based on this observation, the nature of the photoluminescence of complexes 2 and 3 could be attributed to the charge transfer from ligand to ligand (LLCT; from the HOMO of the \( \pi \)-orbital of the HMCA ligand to the LUMO of the \( \pi \)-orbital of the bipy ligand in the complex 2; from the HOMO of the \( \pi \)-orbital of the HMCA and Phen ligands to the LUMO of the \( \pi \)-orbital of the Phen ligand). This calculated results are in good agreement with the experimental results.

**Solid-state UV-Vis diffuse reflectance spectroscopy**

Diffuse reflectance spectroscopy (DRS) can be helpful to understand the conductance properties of materials; therefore, a study was carried out with the title Co(II) complexes. The solid-state UV-Vis diffuse reflectance spectra of power samples of the title Co(II) complexes 2 and 3 were measured at room temperature on the basis of barium sulfate as a reference giving 100% reflectivity. DRS was performed in the range 200–900 nm. After measuring the diffuse reflectance spectra of the solid state, the Kubelka–Munk function was used to process the data, that is, \( F = \alpha / S = (1 - R^2) / (2R) \). The vertical coordinate is transformed from the Kubelka–Munk equation and the horizontal coordinate is transformed from the energy formula \( E_g = hc/\lambda \). As shown in Figure 14, for this function, the parameter \( \alpha \) refers to the absorption coefficient, \( S \) refers to the scattering coefficient, \( R \) refers to the reflection coefficient, and \( \lambda \) refers to the absorption wavelength. When the size of the particle is larger than 5 \( \mu \)m, the reflection coefficient is actually independent of the wavelength. From the plot of \( \alpha / S \) vs energy gap, we can obtain the value of the optical band gap, which can be extrapolated from the linear part of the absorption edge. The solid-state UV-Vis diffuse reflectance spectra show the band widths of complexes 2 and 3 are 1.72 and 1.60 eV, respectively. The energy band

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**Figure 11.** The solid-state excitation and emission spectra of the Co(II) complexes 2 and 3.

**Figure 12.** CIE chromaticity diagrams and chromaticity coordinates of the emission spectra of the Co(II) complexes 2 and 3.
gap of complexes 2 and 3 is obviously larger than those of GaAs (1.4 eV),29 CdTe (1.5 eV),30 and CuInS2 (1.55 eV),31 which are well known as highly efficient band gap photovoltaic materials. Therefore, we deem that the title Co(II) complexes may represent highly efficient band gap photovoltaic materials.

Conclusion

In conclusion, we have reported the preparation of two novel cobalt complexes with HMCA, bipy, and Phen as mixed ligands under the solvothermal conditions and which have been structurally characterized by single-crystal X-ray diffraction. The complexes exhibit 2D, 3D and 1D chain-like structures, respectively. Solid-state photoluminescence reveals that the complexes 2 and 3 display an emission (449 nm) in the blue region which is due to LLCT, as shown by TDDFT calculation. Solid-state DRS revealed the presence of narrow optical band gaps of 1.72 and 1.60 eV, indicating that complexes 2 and 3 are potential narrow band gap organic semiconductor materials. Further investigations on the relationship between the structures and the properties of cobalt crystalline complexes are in progress in our laboratory.

Experimental section

Measurements

The infrared spectra were recorded using a Nicolet iS10 spectrometer as KBr pellets. 1H NMR spectra were measured on a Bruker Avance 400 MHz instrument with DMSO-d6 as the solvent. The photoluminescence of solid-state samples was investigated using an FX-97XP fluorescence spectrometer. The solid-state UV-Vis DRS was recorded using a TU-1901 UV-Vis spectrometer with an integrating sphere in the wavelength range of 200–900 nm. TDDFT investigations were carried out using the Gaussian 09 suite of program packages.
Syntheses

Commercially available reagents and chemicals that were used to synthesize the title compound are analytical reagent grade.

HMCA (1) Ligand

The synthesis of HMCA is based on relevant references Boudet et al.\textsuperscript{20} as shown in Scheme 1.

Isatin: Yield: 116 g (90%); m.p.: 210 °C; HRMS m/z (ESI): calcd. for C\textsubscript{14}H\textsubscript{12}N\textsubscript{2}O\textsubscript{3} ([M + H]\textsuperscript{+}): 203.0548; 1H NMR (400 MHz, DMSO): Co(CH\textsubscript{3}COO)\textsubscript{2}·4H\textsubscript{2}O (1.0 mmol, 249 mg), HMCA (1) Ligand

Final indexes \[I\begin{array}{c}1.064 \\
1.059 \\
1.032 \end{array}\]

Data/restraints/parameters 3373/0/283 4583/0/284 12518/0/693

2

4

1241 (vs), 1161 (m), 906 (m), 861 (vs), 766 (m), 687 (m).

Table 1. Crystal parameters of complexes 1, 2, and 3.

Table: |
| Compound | 1 | 2 | 3 |
|----------|---|---|---|
| Formula  | C\textsubscript{22}H\textsubscript{18}N\textsubscript{2}O\textsubscript{6} | C\textsubscript{21}H\textsubscript{19}CoN\textsubscript{3}O\textsubscript{5} | C\textsubscript{58}H\textsubscript{44}Co\textsubscript{2}N\textsubscript{8}O\textsubscript{9} |
| Fw       | 406.38 | 452.32 | 1144.87 |
| T (K)     | 292(2) | 293(2) | 293(2) |
| Crystal system | Monoclinic | Orthorhombic | Monoclinic |
| Space group | P2\textsubscript{1}/c | Pbc\textsubscript{a} | P2\textsubscript{1}/n |
| a (Å)     | 12.6155(7) | 9.9021(4) | 14.1963(4) |
| b (Å)     | 8.8221(5) | 17.5262(6) | 16.6714(3) |
| c (Å)     | 16.8945(11) | 22.5494(7) | 22.2616(7) |
| α (deg)   | 90 | 90 | 90 |
| β (deg)   | 90 | 90 | 90 |
| γ (deg)   | 90 | 90 | 90 |
| V (Å\textsuperscript{3}) | 1812.6(2) | 3913.2(2) | 5242.6(2) |
| Z         | 4 | 8 | 4 |
| d\textsubscript{calc} (g/cm\textsuperscript{3}) | 1.489 | 1.535 | 1.412 |
| μ (mm\textsuperscript{-1}) | 0.110 | 0.917 | 0.699 |
| F(000)    | 848.0 | 1864.0 | 2296.0 |
| Crystal size (mm\textsuperscript{3}) | 0.410.29, 0.15 | 0.310.21, 0.18 | 0.42, 0.310.29 |
| ω (deg)   | 6.578 to 50.99 | 7.142 to 58.658 | 6.918 to 58.744 |
| Reflections collected | 10,608 | 13,563 | 36,364 |
| Independent reflections (R\textsubscript{int}) | 3373 (0.0237) | 4583 (0.0256) | 12518 (0.0320) |
| Data/restraints/parameters | 3373/0/283 | 4583/0/284 | 12518/0/693 |
| S         | 1.064 | 1.059 | 1.032 |
| Final R indexes [I≥2σ(I)] | R\textsubscript{1} = 0.0502 | R\textsubscript{1} = 0.0376 | R\textsubscript{1} = 0.0589 |
| wR\textsubscript{2} = 0.1134 | wR\textsubscript{2} = 0.0843 | wR\textsubscript{2} = 0.1453 |
| Δρ (max, min) (e Å\textsuperscript{-3}) | 0.23, −0.15 | 0.27, −0.45 | 0.67, −0.40 |

X-ray crystallographic studies

The diffraction data were collected on a SuperNova CCD X-ray diffractometer using carefully selected single crystals of complexes 1, 2, 3. The X-ray source was graphite monochromated Mo-Kα radiation (λ=0.71073 Å), and the ω scan method was employed. The reduction and empirical absorption correction of the diffraction data were carried out with the CrystalClear software. Using Olex2,\textsuperscript{32} the structures of the title complexes were solved with the ShelXT,\textsuperscript{33} the structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package\textsuperscript{34} using least squares minimization. All of the non-hydrogen atoms were generated based on the subsequent Fourier difference maps and were refined anisotropically. The hydrogen atoms, except for the lattice water, were located theoretically and ride on their parent atoms. Crystallographic data and structural refinements for the complexes are summarized in Table 1. Selected bond lengths and bond angles for the crystal structure are displayed in Table 2. The hydrogen bonding interactions are presented in Table 3. CCDC: 1988957 (1), 1988958 (2), 1988959 (3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center (CCDC) via http://www.ccdc.cam.ac.uk/data_request/cif.
Table 2. Selected bond lengths (Å) and bond angles (°) for the complexes 1, 2, and 3.

**Compound 1**

| Bond          | Distance | Bond          | Distance |
|---------------|----------|---------------|----------|
| O(1)–C(3)     | 1.331(2) | N(2)–C(22)    | 1.375(3) |
| O(2)–C(5)     | 1.242(3) | N(2)–C(13)    | 1.315(3) |
| O(3)–C(5)     | 1.264(3) | N(1)–C(11)    | 1.373(3) |
| O(4)–C(16)    | 1.240(3) | N(1)–C(2)     | 1.314(3) |
| O(6)–C(14)    | 1.327(3) | O(5)–C(16)    | 1.267(3) |
| Angle         | (°)      | Angle         | (°)      |
| C(13)–N(2)–C(22) | 124.47(17) | C(2)–N(1)–C(11) | 124.55(18) |

**Compound 2**

| Bond          | Distance | Bond          | Distance |
|---------------|----------|---------------|----------|
| Co(1)–O(2)   | 1.9929(14) | Co(1)–N(1)   | 2.1279(17) |
| Co(1)–O(3)   | 1.9323(13) | Co(1)–N(2)   | 2.0828(16) |
| Co(1)–O(4)   | 2.0204(15) | Co(1)–N(4)   | 2.051(2)   |
| Angle         | (°)      | Angle         | (°)      |
| O(2)–Co(1)–O(4) | 97.50(7)  | O(3)–Co(1)–N(1) | 87.64(6)   |
| O(2)–Co(1)–N(1) | 167.98(7) | O(3)–Co(1)–N(2) | 131.17(7) |
| O(2)–Co(1)–N(2) | 95.61(7)  | O(4)–Co(1)–N(1) | 93.94(7)   |
| O(3)–Co(1)–O(2) | 90.30(6)  | O(4)–Co(1)–N(2) | 109.49(7) |
| O(3)–Co(1)–O(4) | 117.69(6) | N(2)–Co(1)–N(1) | 77.01(7)   |

**Compound 3**

| Bond          | Distance | Bond          | Distance |
|---------------|----------|---------------|----------|
| Co(1)–O(1)   | 2.050(2) | Co(2)–O(1)    | 2.264(2) |
| Co(1)–O(3)   | 1.987(3) | Co(2)–O(2)    | 2.126(2) |
| Co(1)–N(3)   | 2.136(3) | Co(2)–O(4)    | 2.051(2) |
| Co(1)–N(4)   | 2.121(3) | Co(2)–O(6)    | 1.984(2) |
| Co(1)–N(5)   | 2.218(3) | Co(2)–N(7)    | 2.117(3) |
| Co(1)–N(6)   | 2.142(3) | Co(2)–N(8)    | 2.107(3) |
| Angle         | (°)      | Angle         | (°)      |
| O(1)–Co(1)–N(3) | 165.29(10) | O(2)–Co(2)–O(1) | 59.34(18) |
| O(1)–Co(1)–N(4) | 91.49(10)  | O(4)–Co(2)–O(1) | 89.80(9)  |
| O(1)–Co(1)–N(5) | 96.85(9)   | O(4)–Co(2)–O(2) | 91.45(10) |
| O(1)–Co(1)–N(6) | 97.49(10)  | O(4)–Co(2)–N(7) | 172.25(11)|
| O(3)–Co(1)–O(1) | 87.37(10)  | O(4)–Co(2)–N(8) | 93.97(11) |
| O(3)–Co(1)–N(3) | 85.79(11)  | O(6)–Co(2)–O(1) | 155.06(9) |
| O(3)–Co(1)–N(4) | 104.25(11) | O(6)–Co(2)–O(2) | 95.74(9)  |
| O(3)–Co(1)–N(5) | 166.58(11) | O(6)–Co(2)–O(4) | 89.99(10) |
| O(3)–Co(1)–N(6) | 91.25(11)  | O(6)–Co(2)–N(7) | 91.37(11) |
| N(3)–Co(1)–N(5) | 92.77(10)  | O(6)–Co(2)–N(8) | 99.04(10) |
| N(3)–Co(1)–N(6) | 95.66(11)  | N(7)–Co(2)–O(1) | 92.17(10) |
| N(4)–Co(1)–N(3) | 77.64(11)  | N(7)–Co(2)–O(2) | 96.01(10) |
| N(4)–Co(1)–N(5) | 88.42(11)  | N(8)–Co(2)–O(1) | 105.85(10)|
| N(4)–Co(1)–N(6) | 162.46(11) | N(8)–Co(2)–O(2) | 164.24(10)|
| N(6)–Co(1)–N(5) | 75.60(12)  | N(8)–Co(2)–N(7) | 78.27(12) |
Table 3. Hydrogen bond lengths (Å) and bond angles (°) for the complexes 1, 2, and 3.

### Compound 1

| D–H . . A | D–H (Å) | H . . A (Å) | D . . A (Å) | D–H . . A (°) |
|-----------|---------|-------------|-------------|---------------|
| O(1)–H(1)...O(3) | 0.82    | 1.72        | 2.449(2)    | 146.7         |
| N(1)–H(1A)...O(4)i | 0.96(3) | 1.74(3)     | 2.697(3)    | 170(2)        |
| N(2)–H(2)...O(2) | 0.96(3) | 1.71(3)     | 2.651(2)    | 167(2)        |
| O(6)–H(6)...O(5) | 0.82    | 1.70        | 2.431(3)    | 147.3         |
| C(7)–H(7)...O(2) | 0.93    | 2.24        | 2.852(3)    | 122.4         |
| C(18)–H(18)...O(4) | 0.93    | 2.24       | 2.852(3)    | 122.9         |

Symmetry codes: i = 1 + x, −1 + y, z

### Compound 2

| D–H . . A | D–H (Å) | H . . A (Å) | D . . A (Å) | D–H . . A (°) |
|-----------|---------|-------------|-------------|---------------|
| O(4)–H(4A)...O(1)i | 0.86    | 1.82        | 2.683(2)    | 177           |
| O(4)–H(4B)...O(5) | 0.82(3) | 1.89(3)     | 2.694(2)    | 165(3)        |
| O(5)–H(5A)...O(1)ii | 0.85    | 1.92        | 2.742(2)    | 163           |
| O(5)–H(5A)...N(3)iii | 0.85    | 2.00        | 2.847(2)    | 176           |
| C(11)–H(11)...O(1) | 0.93    | 2.27        | 2.863(3)    | 121           |

Symmetry codes: i = 1/2 + x, 1/2 − y, 1 − z; ii = 1 + x, y, z; iii = 1/2 + x, y, 1/2 − z

### Compound 3

| D–H . . A | D–H (Å) | H . . A (Å) | D . . A (Å) | D–H . . A (°) |
|-----------|---------|-------------|-------------|---------------|
| O(7)–H(7A)...O(5) | 0.85    | 2.00        | 2.711(6)    | 140.9         |
| O(8)–H(8A)...O(7) | 0.85    | 2.00        | 2.727       | 143.1         |
| O(9)–H(9B)...O(7) | 0.85    | 2.00        | 2.604       | 127.5         |

### Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

### Funding

The author(s) disclosed receipt of the following financial support for the research, authorship, and/or publication of this article: This work was supported by the NSF of China (51363009), Jiangxi Provincial Department of Education’s Item of Science and Technology (GJJ190550), and Doctoral Research Startup Foundation of Jinggangshan University (JZB1905).

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### Supplemental material

Supplemental material for this article is available online.

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