

Research Article

Synthesis and Crystal Structure Differences between Fully and Partially Fluorinated β -Diketonate Metal (Co^{2+} , Ni^{2+} , and Cu^{2+}) Complexes

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Coordination complexes, $[\text{Co}_2(\mathbf{1})_4(\text{H}_2\text{O})_2]$ (**2**), $[\text{Ni}_2(\mathbf{1})_4(\text{H}_2\text{O})_2]$ (**3**), and $[\text{Cu}(\mathbf{1})_2]$ (**4**), by using an asymmetric and partially fluorinated 3-hydroxy-3-pentafluorophenyl-1-phenyl-2-propen-1-one (**H1**) have been prepared, and the structures were investigated to compare with the corresponding fully fluorinated complexes of $[\text{Co}_2(\mathbf{5})_4(\text{H}_2\text{O})_2]$ (**6**), $[\text{Ni}_2(\mathbf{5})_4(\text{H}_2\text{O})_2]$ (**7**), and $[\text{Cu}(\mathbf{5})_2]$ (**8**) with bis(pentafluorobenzoyl)methane (**H5**) and to understand the fluorine-substituted effects. While the coordination mode of the partially fluorinated complexes was quite similar to the fully fluorinated complexes, the intra- and intermolecular π -interactions of the ligand moieties were highly influenced by the fluorination effects; the arene-perfluoroarene interactions were observed in complexes **2** and **3** as a reason of the dinucleation. In this paper, we describe detail structures of the protonated form of the ligand, **H1**, and complexes **2–4** by X-ray crystallographic studies.

1. Introduction

While π - π interactions are observed in various aromatic compounds in chemistry and biology [1–7], the control of the interaction is still challenging because of their repulsion of the electron charge of the aromatic moieties. For example, a benzene molecule has a negative quadrupole moment, $-29.0 \times 10^{-40} \text{ C m}^2$ [8] stabilizing a rectangular orientation of $\text{CH} \cdots \pi$ interaction [9] and a sliding orientation of π - π stacking. The negative charge of aromatic center also interacts the cationic source through cation $\cdots \pi$ interactions [10–12]. On the other hand, the electron charge of aromatic compounds can be controlled by fluorination (e.g., a hexafluorobenzene molecule which shows positive quadrupole moment, $31.7 \times 10^{-40} \text{ C m}^2$) [8] and unique electrostatic interactions, such as arene-perfluoroarene [13–18] and anion- π [19–21] interactions, which have attracted interests in a couple of decades. We have also synthesized several fluorinated compounds to control the electrostatic

interactions and to design the metal \cdots metal [22] and metal $\cdots \pi$ [23] arrangements through the interactions [24–28]. In these studies, the fluorination into the aromatic moieties on coordination complexes has potentially shown three unique effects: (1) fluorinated π -planes show unique molecular recognition through the electrostatic interactions; (2) an electron-density of a metal is controlled by the fluorination; (3) fluorinated π -planes of the molecules are twisted with the whole molecular planes by the steric hindrance of the fluorine substituents in several cases [23, 24]. Such effects give rise to several unique guest-recognitions of the coordination complexes based on the crystal engineering.

In this paper, we show the crystal structures of partially fluorinated **H1** (Scheme 1) and its three coordination complexes, $[\text{Co}_2(\mathbf{1})_4(\text{H}_2\text{O})_2]$ (**2**), $[\text{Ni}_2(\mathbf{1})_4(\text{H}_2\text{O})_2]$ (**3**), and $[\text{Cu}(\mathbf{1})_2]$ (**4**) (Scheme 2). The corresponding coordination complexes $[\text{M}(\text{DBM})_2]$ ($\text{M} = \text{Co}^{2+}$, Ni^{2+} , Cu^{2+}) with dibenzoylmethanide ligand (**DBM**, $\text{C}_6\text{H}_5\text{COCHCOC}_6\text{H}_5^-$) [29–34] and $[\text{Co}_2(\mathbf{5})_4(\text{H}_2\text{O})_2]$ (**6**), $[\text{Ni}_2(\mathbf{5})_4(\text{H}_2\text{O})_2]$ (**7**), and

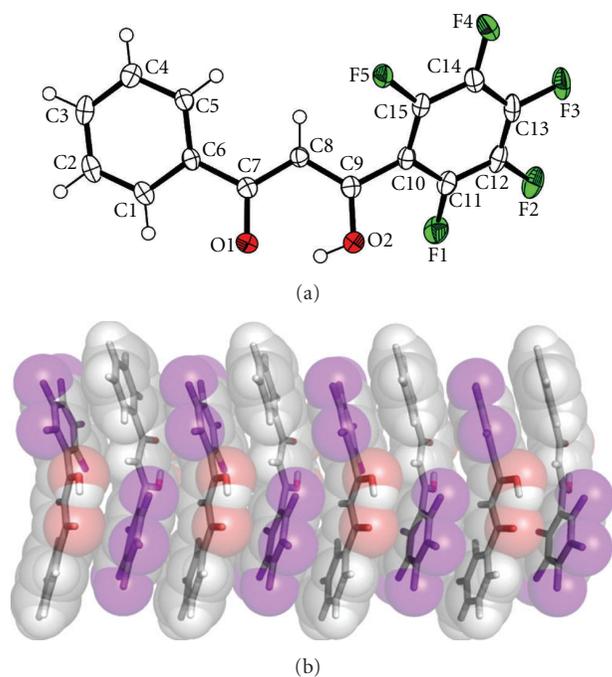


FIGURE 1: (a) ORTEP drawing of the crystal structure with 50% probability thermal ellipsoids and (b) a part of packing structure of H1 at 100 K (color scheme: C: gray; F: purple; O: red).

calcd. for $C_{66}H_{34}Co_2F_{20}O_{10}$ ($2 \cdot C_6H_6$): C 53.39, H 2.31; found: C 53.02, H 2.41.

$[Ni_2(1)_4(OH_2)_2]$ (**3**). This was obtained as green powder by the same procedure as **2** with $Ni(OAc)_2 \cdot 4H_2O$. The single crystals of $3 \cdot 2H_2O \cdot 3C_6H_6$ were obtained from a CH_2Cl_2 /benzene solution suitable for X-ray crystallographic studies. The compound was dried by vacuum conditions for measurement of physical properties. Yield 85%. mp $260^\circ C$. UV-Vis [CH_2Cl_2 , λ nm ($\epsilon M^{-1} cm^{-1}$)]: 640 (20), 339 (62400), 253 sh (35200). IR (KBr disk, cm^{-1}): 3443(broad), 3336(broad), 3071, 1654, 1599, 1568, 1509, 1488, 1450, 1433, 1424, 1405, 1322, 1261, 1064, 988, 715. Elemental analysis: calcd. for $C_{60}H_{28}Ni_2F_{20}O_{10}$ (**3**): C 51.25, H 2.01; found: C 51.38, H 2.33.

$[Cu(1)_2]$ (**4**). This was obtained as bluish green crystals by the same procedure as **2** with $CuCl_2 \cdot 2H_2O$ and NaOMe. The single crystals of **4** were obtained from a CH_2Cl_2 /benzene solution suitable for X-ray crystallographic studies. Yield 97%. mp $319^\circ C$. IR (KBr disk, cm^{-1}): 1655, 1591, 1559, 1514, 1485, 1451, 1410, 1329, 1269, 986754, 710. Elemental analysis: calcd. for $C_{30}H_{12}CuF_{10}O_4$: C 52.22, H 1.75; found: C 52.17, H 1.71.

2.3. Crystal Structure Determination. Single crystal X-ray structures were determined on a Bruker SMART APEX CCD diffractometer with graphite monochromated $MoK\alpha$ ($\lambda = 0.71073 \text{ \AA}$) generated at 50 kV and 35 mA. All crystals were coated by paratone-N and were measured at 100 K.

Crystal data for H1: $C_{15}H_7F_5O_2$, Mw = 314.21, monoclinic, $P2_1/c$, $a = 7.1675(10) \text{ \AA}$, $b = 7.1980(10) \text{ \AA}$, $c =$

$24.239(3) \text{ \AA}$, $\beta = 93.086(2)^\circ$, $V = 1248.7(3) \text{ \AA}^3$, $Z = 4$, $\rho_{calcd} = 1.671 \text{ g cm}^{-3}$, GOF = 1.022, $R(I) > 2\sigma(I) = 0.0354$, $wR(F_o^2) = 0.1027$, CCDC 805820; $2 \cdot 2H_2O \cdot 3C_6H_6$: $C_{78}H_{50}Co_2F_{20}O_{12}$, Mw = 1677.04, triclinic, $P-1$, $a = 9.7381(5) \text{ \AA}$, $b = 13.7690(7) \text{ \AA}$, $c = 14.5108(7) \text{ \AA}$, $\alpha = 114.060(1)^\circ$, $\beta = 93.870(1)^\circ$, $\gamma = 96.571(1)^\circ$, $V = 1750.92(15) \text{ \AA}^3$, $Z = 1$, $\rho_{calcd} = 1.590 \text{ g cm}^{-3}$, GOF = 1.097, $R(I) > 2\sigma(I) = 0.0285$, $wR(F_o^2) = 0.0852$, CCDC 805821; $3 \cdot 2H_2O \cdot 3C_6H_6$: $C_{78}H_{50}F_{20}Ni_2O_{12}$, Mw = 1676.60, triclinic, $P-1$, $a = 9.7085(9) \text{ \AA}$, $b = 13.7652(13) \text{ \AA}$, $c = 14.5171(13) \text{ \AA}$, $\alpha = 114.385(1)^\circ$, $\beta = 93.688(1)^\circ$, $\gamma = 96.484(1)^\circ$, $V = 1742.4(3) \text{ \AA}^3$, $Z = 1$, $\rho_{calcd} = 1.598 \text{ g cm}^{-3}$, GOF = 1.052, $R(I) > 2\sigma(I) = 0.0296$, $wR(F_o^2) = 0.0773$, CCDC 805822; **4**: $C_{30}H_{12}CuF_{10}O_4$, Mw = 689.94, monoclinic, $P2_1/c$, $a = 11.958(5) \text{ \AA}$, $b = 6.273(3) \text{ \AA}$, $c = 17.310(8) \text{ \AA}$, $\beta = 107.549(5)^\circ$, $V = 1237.9(10) \text{ \AA}^3$, $Z = 2$, $\rho_{calcd} = 1.851 \text{ g cm}^{-3}$, GOF = 0.998, $R(I) > 2\sigma(I) = 0.0387$, $wR(F_o^2) = 0.0939$, CCDC 805823. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via http://www.ccdc.cam.ac.uk/data_request/cif/.

3. Results and Discussion

3.1. Preparation and Structure of H1. The protonated form of the ligand, H1, was prepared by previously reported procedure [35] and characterized by 1H NMR, EI-MS, and elemental analysis. Colorless needle crystals of H1 were obtained from an ethanol solution, suitable for X-ray crystallography. The ORTEP drawing and a part of packing structures of crystal H1 are shown in Figure 1. The OH proton was located into the side of the pentafluorophenyl group, based on the difference Fourier density map and refined as riding on its idealized position, O2-H = 0.84 \AA . The bond distances of the O1-C7 and O2-C9 are 1.2841(18) and 1.2918(19) \AA , respectively. The r.m.s deviation of the β -diketonato plane, O1-C7-C8-C9-O2, is 0.008 \AA . The pentafluorophenyl group is more twisted to the plane of O1-C7-C8-C9-O2 than the phenyl group; the dihedral angle between O1-C7-C8-C9-O2 and the pentafluorophenyl group of C10-C11-C12-C13-C14-C15 is $41.42(4)^\circ$ and that between O1-C7-C8-C9-O2 and the phenyl group of C1-C2-C3-C4-C5-C6 is $16.23(6)^\circ$. Interestingly, the H1 shows head-to-tail stacking through arene-perfluoroarene interactions to give an alternate layered structure; the closest intermolecular distance and the corresponding perpendicular distance of $Cg(\text{Ph}) \cdots Cg(C_6F_5)^i$ ($i: -x+1, y-0.5, -z+0.5$) are 3.6838(10) and 3.4529(6) \AA , respectively, where $Cg(\text{Ph})$ is the centroid of the phenyl ring and $Cg(C_6F_5)$ is the centroid of the pentafluorophenyl ring. The carbonyl moiety also closely interacts to pentafluorophenyl group, and the intermolecular distance of $C7-O1 \cdots Cg(C_6F_5)^{ii}$ ($ii: -x+1, y+0.5, -z+0.5$) is 3.2981(14) \AA . This π -stacked structure including the interaction of phenyl and pentafluorophenyl groups prompted us to investigate of the synthesis and crystallographic studies for its coordination complexes.

3.2. Preparation and Structures of Co^{2+} and Ni^{2+} Complexes. Co^{2+} and Ni^{2+} complexes with the partially fluorinated

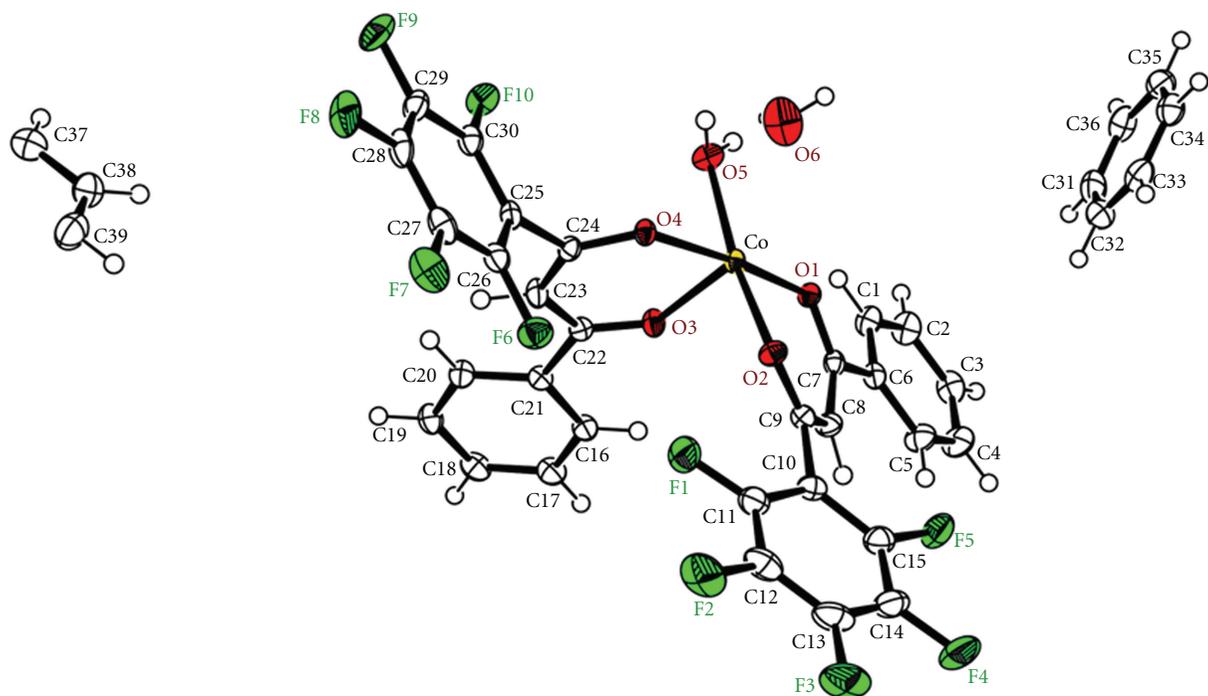


FIGURE 2: Numbering scheme of an asymmetric unit of the crystal structure of $2 \cdot 2\text{H}_2\text{O} \cdot 3\text{C}_6\text{H}_6$ at 100 K. ORTEP drawing is shown with 50% probability thermal ellipsoids.

ligand **1** were obtained as dinuclear complexes (Scheme 2), which are the same tendency of the fully fluorinated complexes of **6** and **7** [24]. Typically, $\text{M}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ ($\text{M} = \text{Co}, \text{Ni}$) and **H1** were combined in an ethanol/ CH_2Cl_2 solution to give $[\text{Co}_2(\text{I})_4(\text{OH}_2)_2]$ **2** and $[\text{Ni}_2(\text{I})_4(\text{OH}_2)_2]$ **3**. These complexes were crystallized from CH_2Cl_2 with vapor-phase diffusion of benzene to give red block crystals of $2 \cdot 2\text{H}_2\text{O} \cdot 3\text{C}_6\text{H}_6$ and green block crystals of $3 \cdot 2\text{H}_2\text{O} \cdot 3\text{C}_6\text{H}_6$. Fundamentally, the reaction of DBM and $\text{Co}^{2+}/\text{Ni}^{2+}$ ions formed mononuclear complexes, $[\text{M}(\text{DBM})_2(\text{X})_2]$ ($\text{M} = \text{Co}^{2+}$ or Ni^{2+} , $\text{X} = \text{solvent}$ or water), and the DBM ligands were sited in equatorial planes [30]. Thus, the dinucleation of the complexes with partially and fully fluorinated ligands, **1** and **5**, are quite unique motifs, which are useful to understand the intramolecular interaction of the coordination complexes.

The crystal structure of $2 \cdot 2\text{H}_2\text{O} \cdot 3\text{C}_6\text{H}_6$ is shown in Figures 2 and 3(a), and $2 \cdot 2\text{H}_2\text{O} \cdot 3\text{C}_6\text{H}_6$ and $3 \cdot 2\text{H}_2\text{O} \cdot 3\text{C}_6\text{H}_6$ are isomorphs. The selected bond distances and angles of $2 \cdot 2\text{H}_2\text{O} \cdot 3\text{C}_6\text{H}_6$, $3 \cdot 2\text{H}_2\text{O} \cdot 3\text{C}_6\text{H}_6$, $6 \cdot 2\text{C}_6\text{H}_6$, and $7 \cdot 2\text{C}_6\text{H}_6$ are summarized in Table 1. The detail structure of $2 \cdot 2\text{H}_2\text{O} \cdot 3\text{C}_6\text{H}_6$ is as follows. Complex **2** comprises two Co^{2+} ions, four ligands **1**, and two water molecules to give the dinuclear complex. The complex lies across crystallographic inversion center. Both of the geometries around the metal centers are pseudo-octahedral. The two ligands are chelate coordinated to each metal by the O1 and O2 (x, y, z) and O1ⁱⁱⁱ and O2ⁱⁱⁱ (iii: $-x + 2, -y + 1, -z + 1$) atoms. Two metal centers are linked through the O4 and O4ⁱⁱⁱ atoms forming a lozenge geometry of the dinuclear core, and the remaining O3 and O3ⁱⁱⁱ atoms are coordinated to each metal. The O5

and O5ⁱⁱⁱ atoms of two water molecules are coordinated to each metal and two water solvates, O6 and O6ⁱⁱⁱ, and linked to the coordinated water through hydrogen bonds; the intermolecular distance of $\text{O5} \cdots \text{O6}$ is 2.6888(19) Å and the angle of O5-H40B-O6 is 174(2)°, as shown in Figure 2. The metal \cdots metal separations are 3.2061(3) Å for **2**. The M–O(ligand) distances are 2.0265(10), 2.0159(10), 2.0422(10), 2.0529(10), and 2.1492(10) Å for **2** (av. 2.06 Å). The Co–O5(water) distances of **2** is 2.0755(11), and the average of the O=C bond distances is 1.27 Å. The r.m.s deviations of O1–C7–C8–C9–O2 and O3–C22–C23–C24–O4 in **2** are 0.0231 and 0.0112 Å, respectively. The pentafluorophenyl groups, C10–C11–C12–C13–C14–C15 and C25–C26–C27–C28–C29–C30, of **2** are highly twisted to the coordination plane; the dihedral angles between O1–C7–C8–C9–O2 and C10–C11–C12–C13–C14–C15 is 36.75(5)° and that between O1–C7–C8–C9–O2 and C25–C26–C27–C28–C29–C30 is 82.47(5)°. The dihedral angles between O1–C7–C8–C9–O2 and two phenyl groups, C1–C2–C3–C4–C5–C6 and C16–C17–C18–C19–C20–C21, are 17.19(5)° and 18.93(9)°, respectively. The dihedral angle for C25–C26–C27–C28–C29–C30 is remarkably twisted because of the intramolecular stacking of the phenyl group of C1ⁱⁱⁱ–C2ⁱⁱⁱ–C3ⁱⁱⁱ–C4ⁱⁱⁱ–C5ⁱⁱⁱ–C6ⁱⁱⁱ through the arene-perfluoroarene interaction; the intramolecular distance and the corresponding perpendicular distance of $\text{Cg}(\text{C}_6\text{F}_5) \cdots \text{Cg}(\text{Ph})^{\text{iii}}$ are 4.3461(10) and 3.3637(7) Å, respectively. This intramolecular stacking leading to the efficient overlapping of the ligands gives efficient stabilization of the dinuclear framework (Figure 3(a)).

The similar structure was observed in Ni^{2+} complex, $3 \cdot 2\text{H}_2\text{O} \cdot 3\text{C}_6\text{H}_6$. Complex **3** also comprises two Ni^{2+} ions,

TABLE 1: Selected bond distances and angles of Co and Ni complexes.

Complex	2·2H ₂ O·3C ₆ H ₆	3·2H ₂ O·3C ₆ H ₆	6·2C ₆ H ₆ [24]	7·2C ₆ H ₆ [24]
M···M ^{iii/iv}	3.2061(3) Å	3.1638(4)	3.1822(3)	3.1385(3)
M-O1	2.0265(10)	1.9891(10)	2.0132(11)	1.9842(11)
M-O2	2.0159(10)	1.9952(10)	2.0407(11)	2.0138(12)
M-O3	2.0422(10)	2.0051(10)	2.0496(11)	2.0087(12)
M-O4	2.0529(10)	2.0348(10)	2.0465(11)	2.0231(11)
M-O4 ^{iii/iv}	2.1492(10)	2.1101(10)	2.1628(11)	2.1224(12)
M-O5	2.0755(11)	2.0567(11)	2.1127(13)	2.0828(13)
O1-C7	1.2685(17)	1.2687(17)	1.2616(19)	1.266(2)
O2-C9	1.2774(18)	1.2739(18)	1.2722(19)	1.271(2)
O3-C22	1.2596(17)	1.2573(18)	1.2506(19)	1.252(2)
O4-C24	1.2850(17)	1.2831(17)	1.2931(19)	1.293(2)
O1-M-O2	89.23(4)	91.13(4)	89.61(4)	91.74(5)
O3-M-O4	88.45(4)	90.01(4)	89.27(4)	90.79(5)
O4-M-O4 ^{iii/iv}	80.57(4)	80.51(4)	81.82(4)	81.61(5)
M-O4-M ^{iii/iv}	99.43(4)	99.49(4)	98.18(4)	98.39(5)
O2-M-O5	169.54(4)	171.49(4)	171.63(5)	172.70(5)

four **1**, and two water molecules. Both of the geometries around the metal centers are pseudo-octahedral. The coordination bond distances between the oxygen atoms and Ni²⁺ are also summarized in Table 1 and the average M-O(ligand) distance of 3·2H₂O·3C₆H₆ is slightly shorter than that of 2·2H₂O·3C₆H₆, as depends on the size of metal ions. The pentafluorophenyl group of **3** interacts phenyl group through the same intramolecular interactions.

While the molecular structures of the complexes **2** and **3** are resembled to the corresponding complexes **6** and **7** (see Figure 3), the crystal solvates are different; two water molecules and three benzene molecules are included for the partially fluorinated complexes and two benzene molecules are included for the fully fluorinated complexes [24]. The structures of **2** and **6** are discussed as follows. The average of M–O(ligand) distances is the same, 2.06 Å, for **2** and **6**, and the average of the O=C bond distances is the same, 1.27 Å, for **2** and **6**. The Co–O5(water) distances of **2** [2.0755(11) Å] are shorter than those of **6** [2.1127(13) Å]. The metal···metal separation of **2** [3.2061(3) Å] is slightly longer than that of **6** [3.1822(3) Å]. The Ni²⁺ complexes **3** and **7** have also the same difference; the average O=C bond distances and metal···metal separation of **3** are shorter and longer, respectively, than those of **7**. It is pointed out that the pentafluorophenyl groups of **6** (and **7**) are also highly twisted with respect to the coordination plane (the torsion angles C5–C6–C7–C8, C8–C9–C10–C15, C20–C21–C22–C23, and C23–C24–C25–C30 are 38.9(2), 63.6(2), 35.7(2), and 68.2(2)°, resp.) and the intramolecular stacking is dominant between the two rings, C25–C26–C27–C28–C29–C30 and C1^{iv}–C2^{iv}–C3^{iv}–C4^{iv}–C5^{iv}–C6^{iv} (iv: $-x + 1, -y, -z$); the intramolecular distance and the corresponding perpendicular distance of Cg(C₆F₅)···Cg(C₆F₅)^{iv} are 4.4373(10) and 3.3253(7) Å, respectively. The pentafluorophenyl groups have a twisted conformation with the coordination plane,

leading to the efficient overlapping of the ligands for dinuclear complexes (Figure 3(b)). This feature is in contrast to the case of the complexes of DBM [30], where phenyl groups and the coordination plane are essentially planar due to the expanding π -conjugation, which causes a steric hindrance and hence mononucleation.

In the packing structures of 2·2H₂O·3C₆H₆ and 3·2H₂O·3C₆H₆, three benzene molecules (two C31–C32–C33–C34–C35–C36 and one C37–38–C39–C37^v–C38^v–C39^v (v: $-x + 2, -y + 2, -z$)) are included in the crystals and these benzenes interact with the pentafluorophenyl groups through arene-perfluoroarene interactions. This encapsulated solvate through the interactions was also observed in the fully fluorinated complexes of 6·2C₆H₆ and 7·2C₆H₆ [24]. Especially, the crystals of **7** show unique pseudopolymorphs of 7·2C₆H₆ and 7·4C₆H₆ [25]. In our examinations, when no benzene solvent was used in the crystallization, single crystals were not grown as suitable for X-ray crystallography. These results indicate that the crystals of the partially and fully fluorinated Co²⁺ and Ni²⁺ complexes are stabilized by benzene molecules through arene-perfluoroarene interactions.

3.3. Preparation and Structure of Cu²⁺ Complex. The Cu²⁺ complex with the ligand **1** was obtained as a mononuclear complex (Scheme 2). Typically, an MeOH (10 mL) solution of H1 (0.10 g, 0.30 mmol) and NaOMe (16 mg, 0.3 mmol) was combined into an MeOH (5 mL) solution of CuCl₂·2H₂O (30 mg, 0.15 mmol). Then, the mixture was stirred for 2 h at r.t. to give a green precipitates of [Cu(**1**)₂] **4**. In this case, the structure of **4** is mononuclear complex and no influences are observed by fluorine substitutions because the DBM and H5 are also mononuclear complexes [24]. This result is expected from the fact that the ligands are only

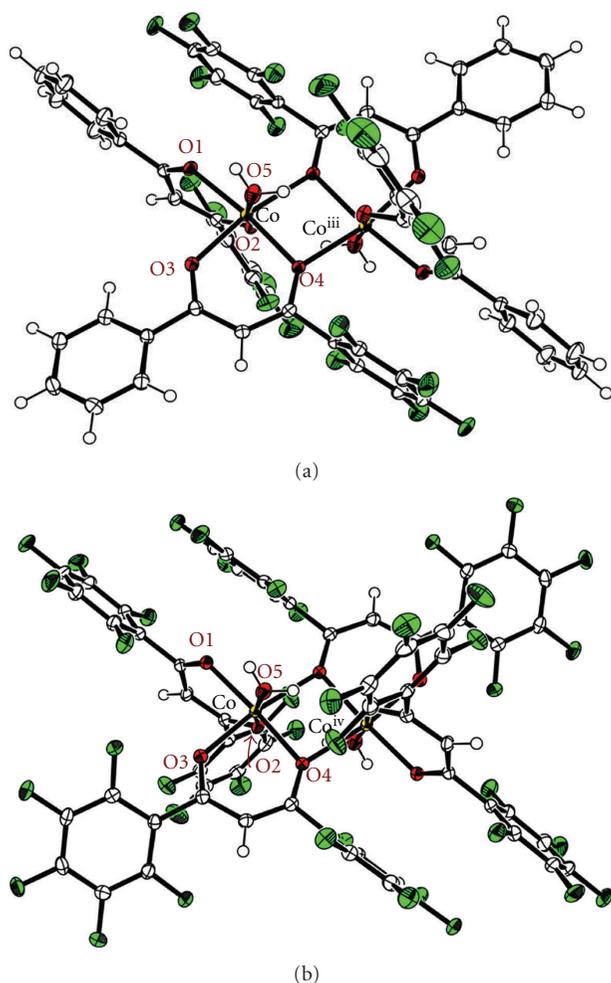


FIGURE 3: ORTEP drawings of the dinuclear complexes of (a) $2 \cdot 2\text{H}_2\text{O} \cdot 3\text{C}_6\text{H}_6$ and (b) $6 \cdot 2\text{C}_6\text{H}_6$ at 100 K with 50% probability thermal ellipsoids. For (a) and (b), symmetry transformations used to generate equivalent atoms show iii $(-x + 2, -y + 1, -z + 1)$ and iv $(-x + 1, -y, -z)$, respectively.

sited in equatorial planes of Cu^{2+} ions by Jahn-Teller effect. The Crystallization by diffusion of benzene into a CH_2Cl_2 solution of **4** yielded the pure product. The crystallization of three Cu^{2+} complexes, the target complex **4**, $[\text{Cu}(\text{DBM})_2]$, and the fully fluorinated complex **8** in $\text{CH}_2\text{Cl}_2/\text{benzene}$ conditions gave single crystals, **4**, $[\text{Cu}(\text{DBM})_2]$, and **8**· $3\text{C}_6\text{H}_6$ [24]. While crystals of the fully fluorinated Cu^{2+} complex capsulated 21 w% of benzene molecules, no solvate crystals were obtained for partially fluorinated Cu^{2+} complex **4**, as well as $[\text{Cu}(\text{DBM})_2]$.

In the crystal, complex **4** comprises one Cu^{2+} and two ligand **1** (Figure 4), that the composition and the packing structure was similar to $[\text{Cu}(\text{DBM})_2]$. The complex lies across crystallographic inversion center. The geometry around the metal is essentially planar, forming a square-planar. The r.m.s deviation of O1-C7-C8-C9-O2 is 0.016 Å showing the flat plane of the chelate moiety of the β -diketonate framework. The bond distances of the Cu-O1, Cu-O2, O1-C7, and O2-C9 are 1.9100(19), 1.9216(18), 1.271(3), and 1.271(3) Å,

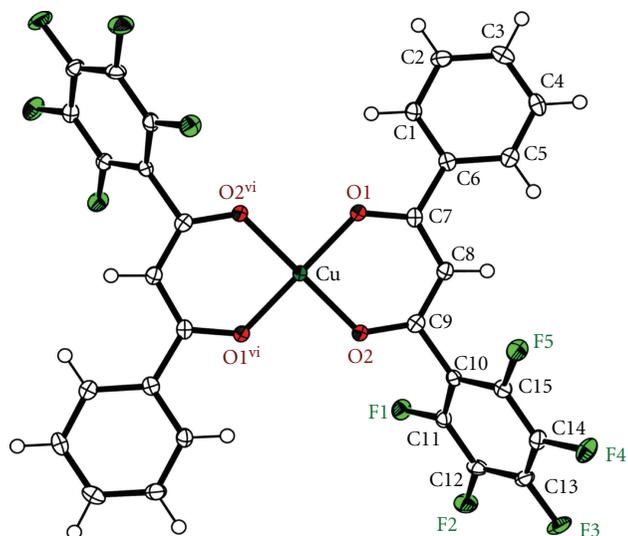


FIGURE 4: ORTEP drawings of the crystal structure of **4** with 50% probability thermal ellipsoids. Symmetry transformation used to generate equivalent atoms is vi $(-x, -y + 1, -z)$.

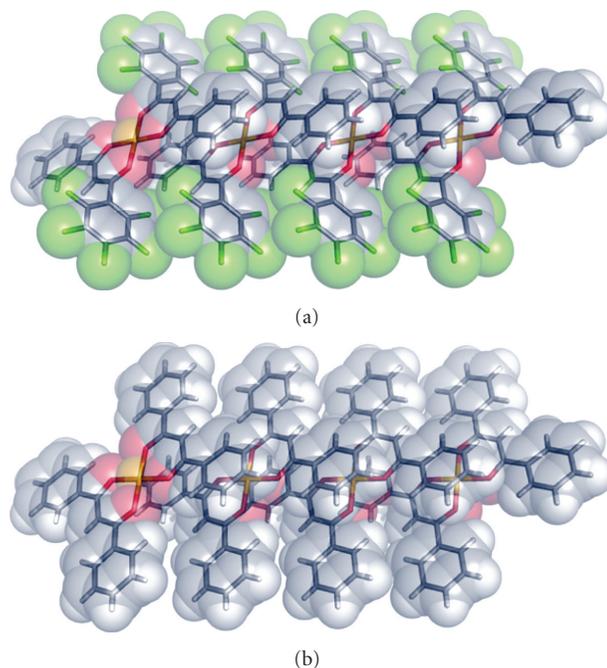


FIGURE 5: Parts of packing structures of (a) **4** and (b) $[\text{Cu}(\text{DBM})_2]$.

respectively. The phenyl and pentafluorophenyl groups are clearly different orientation in **4**. The phenyl group is flat with respect to the coordination plane (the dihedral angle between O1-C7-C8-C9-O2 and C1-C2-C3-C4-C5-C6 is $6.82(16)^\circ$), and the pentafluorophenyl group is highly twisted (that between O1-C7-C8-C9-O2 and C10-C11-C12-C13-C14-C15 is $56.76(8)^\circ$). On the other hand, the crystal structure of $[\text{Cu}(\text{DBM})_2]$ at 293 K is highly flat [31, 32]. The phenyl groups of $[\text{Cu}(\text{DBM})_2]$ are also flat with respect to the coordination plane, and the dihedral angles between O1-C7-C8-C9-O2 and two phenyl rings are $9.96(30)$ and $4.98(33)^\circ$,

showing the π -delocalization of the whole complex. The averages of the Cu-O and O=C bond distances are 1.90 Å and 1.27 Å, respectively. The fully fluorinated Cu²⁺ complex **8** was obtained as **8**·3C₆H₆ under the same crystallization procedure of CH₂Cl₂/benzene [23, 24]. The averages of the Cu-O(5) and O=C bond distances of **8** are 1.92 Å and 1.27 Å, respectively. The pentafluorophenyl groups of **8** are also highly twisted with respect to the coordination plane [24], giving the benzene capsulated cavities.

Parts of the crystal packing of **4** and [Cu(DBM)₂] were shown in Figures 5(a) and 5(b), respectively. A common intermolecular electrostatic interaction is found in both crystals, such as a cation- π interaction. The phenyl groups in **4** interact with Cu²⁺ ion and the pentafluorophenyl groups of another molecule through the cation- π and arene-perfluoroarene interactions, respectively. The closest intermolecular distances of Cg(Ph) ··· Cu^{vii} (vii: $x, y + 1, z$) and Cg(Ph) ··· Cg(C₆F₅)^{viii} (viii: $-x, y + 0.5, -z + 0.5$) are 3.270 Å and 3.631 Å, respectively. This cation- π interaction is only observed in Cu²⁺ complexes because of the free apical sites of the Cu²⁺ ions. The CF ··· π interaction is also observed between the two pentafluorophenyl groups, and the distance of F4 atom in the pentafluorophenyl group and Cg(C₆F₅)ⁱⁱ is 3.109 Å, which is a reversed version of the charge orientation of the CH ··· π interaction.

In crystal of **8**, one benzene molecule closely interacts with the Cu²⁺ ion through the cation- π interaction, and two benzenes interact with the pentafluorophenyl groups through the arene-perfluoroarene interaction. This result indicates, that the Cu²⁺ ion preferably recognized π -molecules and the cation- π interaction is required for the molecular packing. The crystallographic study of **4** also indicates that the cation- π interaction takes priority in crystal packing in the mononuclear complex and no alternately layered packing structure through arene-perfluoroarene interactions was obtained, in contrast to the case of H1.

In conclusion, we show three crystal structures of the complexes **2–4**, using the partially fluorinated ligand **1**. The octahedral geometry of the Co²⁺ and Ni²⁺ ions gives dinuclear complexes **2** and **3**, as well as the corresponding fully fluorinated complexes **6** and **7**, which are caused by intramolecular stacking of the pentafluorophenyl groups. On the other hand, the square planar geometry of the Cu²⁺ ion gives mononuclear complexes for all of the partially, fully, and nonfluorinated ligands (**1**, **5**, and DBM) because of the Jahn-Teller effect, which gives free cavity spaces above the Cu²⁺ ions. Thus, the phenyl group interacts to the Cu²⁺ ions through the cation- π interaction for **4**, as well as [Cu(DBM)₂]. The arene-perfluoroarene and cation- π interactions are clearly shown as key electrostatic interactions in the complexation behaviors and crystal structures of the partially fluorinated complexes.

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