

Synthesis and Crystal Structures of Fluorinated β -Diketonate Metal (Al^{3+} , Co^{2+} , Ni^{2+} , and Cu^{2+}) Complexes

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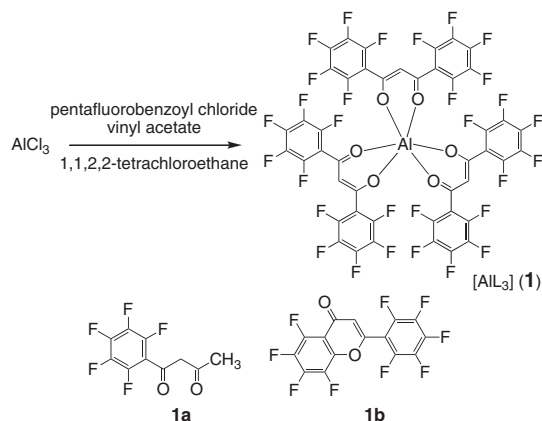
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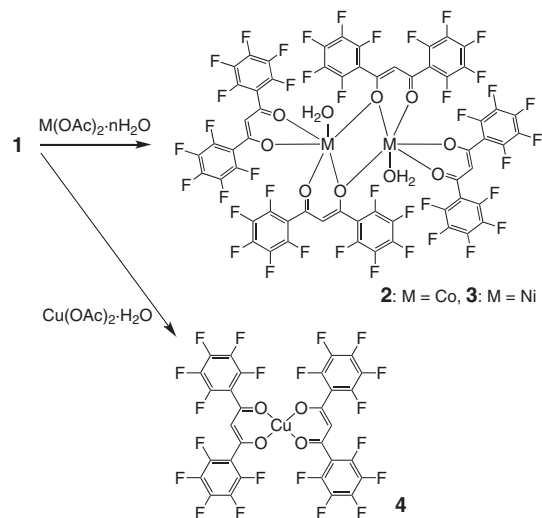
Co^{2+} , Ni^{2+} , and Cu^{2+} complexes with bis(pentafluorobenzoyl)methanide (L, $\text{C}_6\text{F}_5\text{COCHCOC}_6\text{F}_5^-$) were prepared from $[\text{Al}(\text{L})_3]$, which was directly synthesized from AlCl_3 , pentafluorobenzoyl chloride, and vinyl acetate under N_2 atmosphere. The complexation of L with Co^{2+} and Ni^{2+} ions gave $[\text{M}_2(\text{L})_4(\text{OH}_2)_2]$ ($\text{M} = \text{Co}$ and Ni) and that with Cu^{2+} ion gave $[\text{Cu}(\text{L})_2]$.

Fluorine-attached coordination complexes have been widely investigated to control their spectroscopic and redox properties due to their potentially unique properties; high electrophilicity and polarization.^{1,2} Especially, fully fluorinated aromatic substituents, e.g., $-\text{C}_6\text{F}_5$ or $-\text{C}_6\text{F}_4-$, show unique interactions with aromatic hydrocarbons because of the reversion of charge orientation of the quadrupole moments;³ benzene and hexafluorobenzene have alternately layered stacks.⁴ This is now well known as the arene–perfluoroarene interaction to develop self-assembled supramolecular motifs.^{5,6} However, the synthesis of perfluorinated β -diketones fundamentally shows poor yields and instability because of the possibility of intramolecular cyclization reactions; e.g., bis(pentafluorobenzoyl)methane (HL) is transformed into 5,6,7,8-tetrafluoro-2-(pentafluorophenyl)-4H-chromen-4-one (**1b**).⁷ Thus, we attempted a metal-exchange reaction to develop a synthesis of fluorinated β -diketonate metal complexes. In this paper we report the unique synthesis and crystal structures of fluorinated complexes, $[\text{Co}_2(\text{L})_4(\text{OH}_2)_2]$ **2**, $[\text{Ni}_2(\text{L})_4(\text{OH}_2)_2]$ **3**, and $[\text{Cu}(\text{L})_2]$ **4** from $[\text{Al}(\text{L})_3]$ **1**.

Starting material of Al^{3+} complex **1** was directly prepared as colorless block crystals during the preparation of its ligand, bis(pentafluorobenzoyl)methane (HL), as previously reported via the vinyl acetate.⁹ The reaction of pentafluorobenzoyl chloride and vinyl acetate in 1,1,2,2-tetrachloroethane in the presence of anhydrous AlCl_3 gave **1** with two by-products: 1-(pentafluorophenyl)-1,3-butanedione (**1a**) and 5,6,7,8-tetrafluoro-2-(pentafluorophenyl)-4H-chromen-4-one (**1b**) (Scheme 1). In spite of the description in Ref. 9, the free ligand HL was not obtained under these conditions. Typically, the reaction was employed under N_2 atmosphere and was precisely kept at 35°C to give the desired complex **1** (yield



Scheme 1. Synthesis of **1** and by-products **1a** and **1b**.



Scheme 2. Syntheses of **2**, **3**, and **4** from **1** with metal acetate in CH_2Cl_2 -ethanol solution at rt.

37%). ^1H NMR spectrum gave only one singlet peak at δ 6.29, showing clearly a highly symmetric structure. The result of elemental analysis shows the isolation of **1** as a pure product: Calcd for $\text{C}_{45}\text{H}_3\text{AlF}_{30}\text{O}_6$ (%): C, 43.71; H, 0.24. Found: C, 43.79; H, 0.34. The crystal structure of **1** was deposited in CCDC 699193. The yield of **1** decreased in air and the formation of by-product **1b** increased when the reaction was conducted at high temperature.

Al^{3+} complex **1** is useful as a starting material for the complexation with valuable transition metals, in this case, Co^{2+} , Ni^{2+} , and Cu^{2+} ions (Scheme 2).

$\text{M}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ ($\text{M} = \text{Co}$ and Ni) and **1** were combined in an ethanol/ CH_2Cl_2 solution to give dinuclear complexes $[\text{Co}_2(\text{L})_4(\text{OH}_2)_2]$ **2** and $[\text{Ni}_2(\text{L})_4(\text{OH}_2)_2]$ **3**. The results of elemental analyses showed the formation of **2** (Calcd for $\text{C}_{60}\text{H}_8\text{Co}_2\text{F}_{40}\text{O}_{10}$ (%): C, 40.79; H, 0.46. Found: C, 40.85; H, 0.56) and **3** (Calcd for $\text{C}_{60}\text{H}_8\text{F}_{40}\text{Ni}_2\text{O}_{10}$ (%): C, 40.81; H, 0.46. Found: C, 40.98; H, 0.47). These complexes were crystallized from CH_2Cl_2 with the gas-phase diffusion of benzene to give red block crystals of **2**· $2\text{C}_6\text{H}_6$ and green block crystals of **3**· $2\text{C}_6\text{H}_6$. The same products **2** and **3** were obtained when 10% water was added to the reaction mixture, irrespective of the polarity of the solvents. This fact is in contrast to the general tendency that

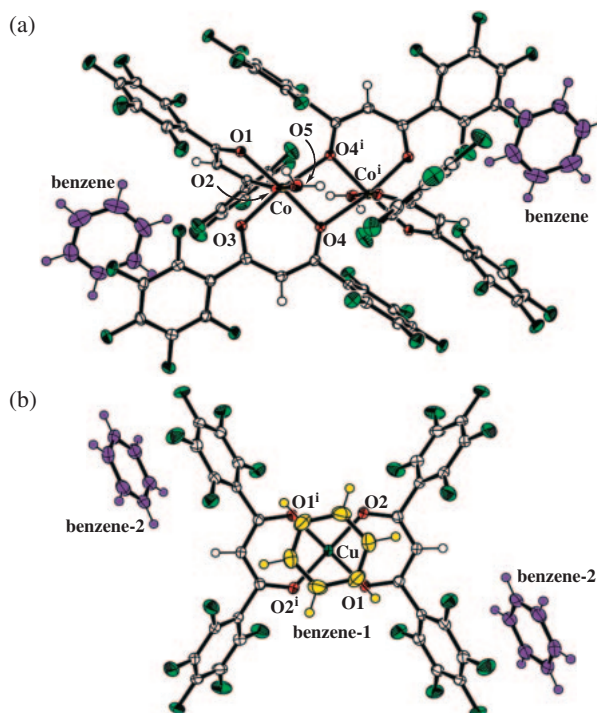


Figure 1. ORTEP drawings of the crystal structure of (a) $2 \cdot 2\text{C}_6\text{H}_6$ and (b) $4 \cdot 3\text{C}_6\text{H}_6$ at 100 K with 50% probability thermal ellipsoids. For (a) and (b), symmetry transformations used to generate equivalent atoms show i ($-x + 1, -y, -z$) and i ($-x + 2, -y + 1, z$), respectively.

mononuclear complexes are obtained with bulky diketonate ligands or in polar media.^{10,11} For example, when $\text{M}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ ($\text{M} = \text{Co}$ and Ni) and dibenzoylmethane (DBM, non-fluorinated ligand) were combined in the same procedure, mononuclear complexes were obtained and it was thought that the large phenyl groups sterically hindered dinucleation and two polar solvent molecules sited on axial positions.¹¹ Thus, structures of **2** and **3** are unique objects, being thought to result from the influence of fluorine-substitutions.

The crystal structure of complex **2** is shown in Figure 1a and the crystal structure of **3** resembles that of **2**. Complex **2** comprises two Co^{2+} ions, four ligands (L), and two water molecules to give the dinuclear complex. Complex **3** also comprises two Ni^{2+} ions, four ligands (L), and two water molecules. Both of the geometries around metal centers are pseudo octahedral. The metal...metal separations are 3.182 Å (**2**) and 3.139 Å (**3**). The M–O(L) distances are 2.0132(11), 2.0407(11), 2.0496(11), 2.0465(11), and 2.1628(11) Å for **2** and 1.9842(11), 2.0138(12), 2.0087(12), 2.0231(11), and 2.1224(12) Å for **3**. The Co–O5(water) and Ni–O5(water) distances are 2.1127(13) and 2.0829(13) Å, respectively. The average of the O=C bond distances are the same, 1.27 Å, for **2** and **3**. The pentafluorophenyl groups of **2** are highly twisted with respect to the coordination plane and 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)°, respectively (Figure 2). Those of **3** are similarly twisted with respect to the coordination plane. Two pentafluorophenyl groups (C1–C2–C3–C4–C5–C6 and C25ⁱ–C26ⁱ–C27ⁱ–C28ⁱ–

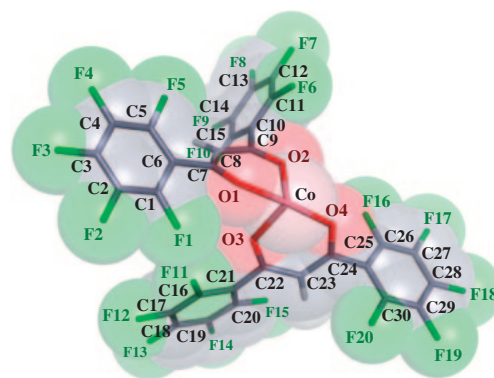


Figure 2. A part of the structure around Co^{2+} ion of **2**.

C29ⁱ–C30ⁱ) in **2** have further intramolecular π – π stacks with a distance of nearly 3.3 Å and the closest atom...atom distance is 2.949 Å (F5...F19ⁱ). Thus, the pentafluorophenyl rings have a twisted conformation with the coordination plane, leading to the efficient overlapping of the ligands for dinuclear complexes. This feature is in contrast to the case of the complexes of DBM,¹¹ where phenyl rings and the coordination plane are essentially planar due to the expanding π -conjugation, which causes a steric hindrance and hence mononucleation. Furthermore, both crystals of **2** and **3** were well grown in benzene atmosphere and two benzenes behave as crystal solvents. The benzenes are located close to the pentafluorophenyl groups and the average $\text{C}_6\text{H}_6 \cdots \text{C}_6\text{F}_5$ intermolecular distance is around 3.4 Å, showing the arene–perfluoroarene interaction.^{4–6}

On the other hand, complex **1** and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ gave the mononuclear complex $[\text{Cu}(\text{L})_2]$ **4** as bluish green crystals of $4 \cdot 3\text{C}_6\text{H}_6$ under the same conditions as those of **2** and **3**.⁸ Complex **4** comprises one Cu^{2+} and two L to give the mononuclear complex (Figure 1b). The geometry around the metal is essentially planar. The average of the Cu–O(L) and O=C bond distances are 1.92 and 1.27 Å, respectively. The pentafluorophenyl groups are also highly twisted with respect to the coordination plane and the torsion angles C5–C6–C7–C8 and C8–C9–C10–C15 are 58.9(3) and 57.9(3)°, respectively.¹²

In the crystal of **4**, three benzenes are sited in unique positions in the crystal. Benzene-1 closely interacts with Cu^{2+} ion and two benzene-2 interact with pentafluorophenyl groups of **4**. Benzene-1 is observed at the axial position of Cu and the intermolecular distance between **4** and benzene-1 is approximately 3.4 Å. Benzene-1 is stabilized by cation– π interaction¹³ with Cu^{2+} and by the CH...F interaction¹⁴ with pentafluorophenyl groups. The cavity effects surrounding pentafluorophenyl rings of **4** also stabilized the position of benzene-1. Benzene-2 is located close to the pentafluorophenyl group of **4** and the average $\text{C}_6\text{H}_6 \cdots \text{C}_6\text{F}_5$ intermolecular distance is 3.4 Å. All crystals show good affinity for benzene molecules and sufficiently large crystals are grown in benzene atmosphere.

In conclusion, remarkably different complexes, dinuclear complexes with the fluorinated ligand and mononuclear complexes¹¹ with DBM, have been obtained for Co^{2+} and Ni^{2+} with octahedral geometry, while mononuclear complexes have been obtained for Cu^{2+} with square-planar geometry. These facts result from the steric hindrance due to fluorine substitutions and electrostatic interactions.

Experimental

All chemicals were of reagent grade and used without further purification. ^1H NMR spectral data were recorded on a Bruker DRX600 spectrometer. Infrared and electronic absorption spectra were recorded on a Shimadzu IR 8400s and JASCO V-570 spectrometer, respectively. Cyclic voltammetry (CV) was performed with a BAS CV-100W potentiostat using tetrabutylammonium perchlorate (TBAP) solution. CV of fluorine-attached compound **2–4** was only irreversible. The results of elemental analysis of C and H were collected by Perkin-Elmer PE2400 analyzer.

[Al(L)₃] 1. Anhydrous AlCl_3 (2.93 g, 22 mmol) and pentafluorobenzoyl chloride (5.00 g, 22 mmol) in 1,1,2,2-tetrachloroethane (20 mL) was stirred at 45 °C for 1 h under N_2 . Vinyl acetate (1.89 g, 0.022 mmol) was added dropwise into the reaction mixture at 25 °C over 60 min. The mixture was stirred at 35 °C for 12 h and was then poured into 10% hydrochloric acid (50 mL) at 0 °C. The mixture was steam distilled to remove the solvent and the residue was extracted with diethyl ether. The residue was distilled to remove **1a** at 80 °C under vacuum (around 1 mmHg). The residue was purified by column chromatography (alumina, benzene); the first product ($R_f = 0.8$) was complex **1** and the second product ($R_f = 0.5$) was characterized as **1b**. Complex **1** was further purified by crystallization in benzene/hexane. Yield 37%. mp 194 °C. ^1H NMR (600 MHz, CDCl_3): δ 6.29 (s). ^{13}C NMR (150 MHz, CDCl_3): δ 178.4 (CO), 145.0 (d, $J = 256$ Hz, CF), 142.9 (d, $J = 256$ Hz, CF), 137.8 (d, $J = 256$ Hz, CF), 113.5 (t, $J = 14.8$ Hz), 107.2 (CH). UV-vis [CH_2Cl_2 , λ_{nm} ($\epsilon \text{ M}^{-1} \text{ cm}^{-1}$)]: 337 (74600), 254 (29000). IR (KBr disk, cm^{-1}): 1653, 1591, 1501, 1437, 1397, 1342, 1116, 999, 938, 825.

[Co₂(L)₄(OH)₂] 2. A solution of **1** (1.00 g, 0.8 mmol) in 1:1 ethanol- CH_2Cl_2 solution (20 mL) was added to a solution of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.30 g, 1.2 mmol) in ethanol (10 mL). The mixture was stirred for 2 h at rt. The reaction mixture was evaporated to give red powder. The powder was extracted with CH_2Cl_2 and crystallized in CH_2Cl_2 /benzene to give complex **2**. Yield 70%. mp 126 °C. UV-vis [CH_2Cl_2 , λ_{nm} ($\epsilon \text{ M}^{-1} \text{ cm}^{-1}$)]: 546sh (100), 512sh (130), 319 (62200), 232 (40300). IR (KBr disk, cm^{-1}): 3675, 1653, 1589, 1498, 1436, 1412, 1330, 1212, 1111, 998, 819, 629. CV (0.1 M TBAP/ CH_2Cl_2 , V): E_{pa1} 1.194, E_{pa2} 1.178, E_{pc} 0.25.

[Ni₂(L)₄(OH)₂] 3. This was obtained as green crystals by the same procedure as **2** with $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$. Yield 75%. mp 153 °C. UV-vis [CH_2Cl_2 , λ_{nm} ($\epsilon \text{ M}^{-1} \text{ cm}^{-1}$)]: 631 (20), 331 (55100), 280 (21300), 230 (42300). IR (KBr disk, cm^{-1}): 3671, 1653, 1589, 1500, 1411, 1331, 1216, 1113, 999, 821. CV (0.1 M TBAP/ CH_2Cl_2 , V): E_{pa1} 1.50, E_{pa2} 1.75.

[Cu(L)₂] 4. This was obtained as bluish green crystals by the same procedure as **2** with $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$. Yield 94%. mp 216 °C. UV-vis [CH_2Cl_2 , λ_{nm} ($\epsilon \text{ M}^{-1} \text{ cm}^{-1}$)]: 662 (40), 330 (36000), 258 (26400); $[\text{Cu}(\text{dbm})_2]$: 646 (50), 350 (47100), 266 (35400).¹² IR (KBr disk, cm^{-1}): 1652, 1568, 1510, 1502, 1426, 1406, 1342, 1228, 1117, 999, 934, 816, 648.

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

Crystal data for (a) **1**: $\text{C}_{45}\text{H}_3\text{AlF}_{30}\text{O}_6$, MW 1236.45, monoclinic, $P2_1$, $a = 12.9098(13) \text{ \AA}$, $b = 12.3912(12) \text{ \AA}$, $c = 14.0452(14) \text{ \AA}$,

$\beta = 107.770(1)^\circ$, $V = 2139.6(4) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calcd}} = 1.919 \text{ g cm}^{-3}$, GOF = 1.062, $R(I) > 2\sigma(I) = 0.0399$, $wR(F_o^2) = 0.1096$, CCDC 699193; (b) **2**: $\text{C}_{72}\text{H}_{20}\text{Co}_2\text{F}_{40}\text{O}_{10}$, MW 1922.74, monoclinic, $P2_1/n$, $a = 11.5519(6) \text{ \AA}$, $b = 16.1859(9) \text{ \AA}$, $c = 18.0976(10) \text{ \AA}$, $\beta = 98.961(1)^\circ$, $V = 3342.5(3) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calcd}} = 1.910 \text{ g cm}^{-3}$, GOF = 1.066, $R(I) > 2\sigma(I) = 0.0293$, $wR(F_o^2) = 0.0887$, CCDC 699194; (c) **3**: $\text{C}_{72}\text{H}_{20}\text{F}_{40}\text{Ni}_2\text{O}_{10}$, MW 1922.30, monoclinic, $P2_1/n$, $a = 11.5848(5) \text{ \AA}$, $b = 16.1079(6) \text{ \AA}$, $c = 18.0508(7) \text{ \AA}$, $\beta = 99.050(1)^\circ$, $V = 3326.5(2) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calcd}} = 1.919 \text{ g cm}^{-3}$, GOF = 1.086, $R(I) > 2\sigma(I) = 0.0293$, $wR(F_o^2) = 0.0866$, CCDC 699196; (d) **4**: $\text{C}_{48}\text{H}_{20}\text{CuF}_{20}\text{O}_4$, MW 1104.18, orthorhombic, $Fdd2$, $a = 26.7956(13) \text{ \AA}$, $b = 47.077(2) \text{ \AA}$, $c = 6.7294(3) \text{ \AA}$, $V = 8488.8(7) \text{ \AA}^3$, $Z = 8$, $\rho_{\text{calcd}} = 1.728 \text{ g cm}^{-3}$, GOF = 1.140, $R(I) > 2\sigma(I) = 0.0246$, $wR(F_o^2) = 0.0829$, CCDC 699195. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

This work was supported by a Grant-in-Aid for Young Scientists B (No. 19750052) of MEXT and a Kitasato University Research Grant for Young Researchers. A.H thanks the Hayashi Memorial Foundation for Female Natural Scientists.

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