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A unique chair–shaped hexanuclear Cu(I) metallamacrocyclic C_2H_4 adduct encapsulating a BF_4^- anion

Masahiko Maekawa,[*a] Atsuhiro Nabei,[b] Toshi Tominaga,[b] Kunihisa Sugimoto,[c] Toshie Minemastu,[d] Takashi Okubo,[b] Takayoshi Kuroda–Sowa,[b] Megumu Munakata[b] and Susumu Kitagawa[*e,f]

[a] *Research Institute for Science and Technology, Kinki University, Kowakae, Higashi–Osaka, Osaka 577–8502, Japan. E–mail: maekawa@ rist.kindai.ac.jp*

[b] *Department of Chemistry, Kinki University, Kowakae, Higashi–Osaka, Osaka 577–8502, Japan*

[c] *Research and Utilization Division, Japan Synchrotron Radiation Research Institute, Kouto, Sayo–cho, Sayo–gun, Hyogo 679–5198, Japan.*

[d] *School of Pharmaceutical Science, Kinki University, Kowakae, Higashi–Osaka, Osaka 577–8502, Japan*

[e] *Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo–ku, Kyoto 615–8510, Japan. E–mail: kitagawa@sbchem.kyoto–u.ac.jp*

[f] *Institute for Integrated Cell–Material Sciences, Kyoto University, Yoshida, Sakyo–ku, Kyoto 606–8501, Japan.*

(1) The detailed preparations of complexes 1–3.

(a) *Preparation of $[Cu_2(pprd)(C_2H_4)_2(NO_3)]NO_3$* (**1**). The precursor Cu(I)–C_2H_4 complex $[Cu(C_2H_4)_n]NO_3$ was prepared by the reductive reaction of $Cu(NO_3)_2 \bullet 3H_2O$ (0.0604g, 0.25 mmol) with Cu wire in Me_2CO (5 ml) under C_2H_4. A 5 ml Me_2CO solution of pprd (0.0393 mg, 0.25 mmol) was added to the Cu(I)–C_2H_4 solution described above. The C_2H_4 gas was moreover bubbled for 1 hour. The dark brown suspension was filtered and the filtrates were sealed in 7 mmϕ glass tubes under C_2H_4. The reaction solution was allowed to stand at –20 °C for two weeks and yellowish brown crystals of **1** were collected. Anal. Calcd. for $C_{13}H_{15}Cu_2N_5O_6$: C, 33.62; H, 3.26; N, 15.08. Found: C, 33.75; H, 3.41; N, 14.95. ^{1}H NMR (δ, CD_3OD, 23 °C): {9.42(H^2), 9.20(H^5) and 8.59(H^6)} for pyrimidine ring, {8.68($H^{3'}$), 8.31($H^{4'}$), 7.87($H^{5'}$) and 8.84($H^{6'}$)} for pyridine ring, 4.55 for C_2H_4. IR (KBr, cm^{-1}): 1525 [$\nu_{C=C}(C_2H_4)$]. After complex **1** was dried by the flow of C_2H_4 gas, complex **1** was immediately used to measure elementary analysis, IR, ^{1}H NMR and TG–DTA. The isolated complex **1** is relatively stable in air.

(b) *Preparation of $[Cu_3(pprd)_2(MeCN)_2(C_2H_4)_2](BF_4)_3$* (**2**). $[Cu(MeCN)_4]BF_4$ (0.1573 g, 0.50 mmol) and pprd (0.0393 g, 0.25 mmol) were reacted in Me_2CO (10 ml) under Ar. The C_2H_4 gas was bubbled into dark brown solution to form the yellowish brown solution. The reaction solution was filtered and the filtrates were sealed in 7 mmϕ glass tubes under C_2H_4. The reaction solution was allowed to stand for one month at –20 °C. The reddish brown crystals of **2** were collected. Anal. Calcd. for

$C_{26}H_{28}B_3Cu_3F_{12}N_8$: C, 34.56; H, 3.12; N, 12.40. Found: C, 34.13; H, 3.12; N, 12.29. ^{1}H NMR (δ, 23 °C): {9.81(H^2), 9.34(H^5) and 8.79(H^6)} for pyrimidine ring, {8.81($H^{3'}$), 8.38($H^{4'}$), 7.97($H^{5'}$) and 9.02($H^{6'}$)} for pyridine ring, 4.83 for C_2H_4 in $(CD_3)_2CO$; {9.51(H^2), 9.10(H^5) and 8.59(H^6)} for pyrimidine ring, {8.65($H^{3'}$), 8.27($H^{4'}$), 7.85($H^{5'}$) and 8.85($H^{6'}$)} for pyridine ring, 4.48 for C_2H_4 in CD_3OD. IR (KBr, cm^{-1}): 1529 [$\nu_{C=C}(C_2H_4)$]. After complex **2** was dried by the flow of C_2H_4 gas, complex **2** was immediately used to measure elementary analysis, IR, ^{1}H NMR and TG–DTA. The isolated complex **2** is unstable in air.

(c) *Preparation of* $\{[Cu_6(pprd)_6(C_2H_4)_6](BF_4)_6\}_2 \cdot 6H_2O$ (**3**). $[Cu(MeCN)_4]BF_4$ (0.629 g, 0.20 mmol) and pprd (0.0157 g, 0.10 mmol) were reacted in MeOH (10 ml) under Ar. The C_2H_4 gas was bubbled into the dark brown solution to produce pale yellow solution. The reaction solution was filtered and the filtrates were sealed in 7 mmϕ glass tubes under C_2H_4. The reaction solution was kept to stand for two weeks at –20 °C and yellowish brown crystals of **3** were collected. Anal. Calcd. for $C_{132}H_{144}B_{12}Cu_{12}F_{48}N_{36}O_6$: C, 38.34; H, 3.51; N, 12.19. Found: C, 38.45; H, 3.37; N, 12.00. ^{1}H NMR (δ, 23 °C): {9.85(H^2), 9.31(H^5) and 8.78(H^6)} for pyrimidine ring, {8.81($H^{3'}$), 8.37($H^{4'}$), 7.96($H^{5'}$) and 9.06($H^{6'}$)} for pyridine ring, 4.88 for C_2H_4 in $(CD_3)_2CO$; {9.41 (H^2), 9.19(H^5) and 8.59(H^6)} for pyrimidine ring, {8.68($H^{3'}$), 8.32($H^{4'}$), 7.87($H^{5'}$) and 8.83($H^{6'}$)} for pyridine ring, 4.86 for C_2H_4 in CD_3OD. IR (KBr, cm^{-1}): 1543 [$\nu_{C=C}(C_2H_4)$]. After complex **3** was dried by the flow of C_2H_4 gas, complex **3** was immediately used to measure elementary analysis, IR ^{1}H NMR and TG–DTA. The isolated complex **3** is unstable in air.

(2) X–ray crystallography of complexes 1–3.

All measurements of Cu(I)–pprd–C_2H_4 adducts **1**–**3** were made on a Rigaku Mercury CCD diffractometer made with graphite monochromated Mo–K_α radiation (λ=0.71070 Å). The diffraction data were collected at –123 ºC for complexes **1** and **2**, and –163 ºC for complex **3** by the ω scan mode. Of the 22732, 11828 and 33514, reflections which were collected, 5351, 3847 and 6725 were unique (R_{int}=0.0895, 0.0944 and 0.0456) for complexes **1**–**3**, respectively. Data were collected and processed using Crystal Clear program (Rigaku). The linear absorption coefficient, μ, for Mo–K_α radiation is 25.08, 19.84, and 15.29 cm^{-1} for complexes **1**–**3**, respectively. The data were corrected for Lorentz and polarization effects.

The structures were solved by direct methods (*SIR*–97 for **1**, *SHELXS*–97 for **2** and **3**) and expanded using Fourier techniques. The non–hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. In complex **1**, the disordered nitrate was restrained as the ideal bond lengths and angles using the DFIX and DANG commands on SHELXL–97. The NO_3^- moiety of chelate configuration is disordered, which lead to the short O(8)•••C(10) contact consequently. In complexes **2** and **3**, all disordered BF_4^- anions were restrained on structure refinement, assuming ideal bond lengths and angles by DFIX and DANG command on SHELXL–97. In complex **3**, the large U_{eq}(max)/U_{eq}(min) ratio of the C(10), C(11) and C(22) atoms is due to the C_2H_4 molecule being slightly disordered as a result of the

flexibility of the Cu–C_2H_4 bond. The bond lengths of C(10)–C(11) and C(21)–C(22) were restrained using DFIX command in SHELXL–97. The hydrogen atoms of disordered water molecules are not located. The final cycle of full–matrix least squares refinement was based on {5351, 3065}, {3847, 2845} and {6725, 4036} observed reflections (all data, $I>2\sigma(I)$) for complexes **1**–**3**, respectively. The unweighted and weighted agreement factors of $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, $R1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ ($F_o>4\sigma(F_o)$) and $wR2=[\Sigma(w(F_o^2-F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$ are used. The *R*, *R1* and *wR2* values were {0.1511, 0.0767 and 0.1333}, {0.1137, 0.0880 and 0.2434} and {0.1500, 0.1063 and 0.3483} for complexes **1**–**3**, respectively. All calculations were performed using the *Crystal Structure 3.8* Crystal Structure Analysis Package (Rigaku and Rigaku Americas).

CCDC 695266 – 695268 for complexes **1**–**3**, respectively.

For crystallographic data in CIF or other electroformat see DOI: 10.1039/b000000x.

(3) Crystal data of complexes 1–3.

(a) *Crystal data for complex **1***. Formula $C_{13}H_{15}N_5O_6Cu_2$, M=464.38, Monoclinic, $P2_1/n$, a=13.7587(11), b=8.1512(6), c=15.7527(13) Å, β=102.603(2) °, V=1724.1(2) Å^3, Z=4, D_c=1.789 g/cm^3, μ (Mo–K_α)=25.08 cm^{-1}, T=150 K, Observed reflections; 22732 (Total); 5351 (Unique, R_{int}=0.0895), Refined reflections; 5351 (all data); 3065 ($I>2\sigma(I)$), R=0.1511 (all data), $R1$=0.0767 ($I>2\sigma(I)$), $wR2$(all data)=0.1333. GOF=1.073. CCDC–695266.

(b) *Crystal data for complex **2***. Formula $C_{26}H_{28}B_3Cu_3F_{12}N_8$, M=903.61, Monoclinic, $P2_1/m$, a=8.6904(8), b=23.414(2), c=8.8729(1) Å, β=111.645(2) °, V=1678.1(3) Å^3, Z=2, D_c=1.788 g/cm^3, μ (Mo–K_α)=19.84 cm^{-1}, T=150 K, Observed reflections; 11828 (Total); 3847 (Unique, R_{int}=0.0944), Refined reflections; 3847 (all data); 2845 ($I>2\sigma(I)$), R=0.1137 (all data), $R1$=0.0880 ($I>2\sigma(I)$), $wR2$(all data)=0.2434. GOF=1.253. CCDC–695267.

(c) *Crystal data for complex **3***. Formula $C_{66}H_{72}B_6Cu_6F_{24}N_{18}O_3$, M=2067.52, Trigonal, $R3(-)$, a=27.6972(15), c=19.8549(16) Å, V=13190.8(15) Å^3, Z=6, D_c=1.562 g/cm^3, μ (Mo–K_α)=15.29 cm^{-1}, T=110 K, Observed reflections; 33514 (Total); 6725 (Unique, R_{int}=0.0456), Refined reflections; 6725 (all data); 4036 ($I>2\sigma(I)$), R=0.1500 (all data), $R1$=0.1063 ($I>2\sigma(I)$), $wR2$(all data)=0.3483, GOF=1.895. CCDC–695268.