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Structures of Bimetallic Assemblies Derived from a Macrocyclic Dinuclear Copper(II) Complex and $[Cr(ox)_3]^{3-}$ or $[Co(CN)_6]^{3-}$

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A dinuclear copper(II) complex, $[Cu_2(L)](ClO_4)_2$, of the macrocyclic ligand (H_2L) derived from the [2:2] condensation of 2,6-diformyl-4-methylphenol and 1,3-diaminopropane, was reacted with $[Cr(ox)_3]^{3-}$ and $[Co(CN)_6]^{3-}$ to produce $[Cu_2(L)]_3[Cr(ox)_3]_2\cdot 6MeOH$ (**1**) of a discrete octanuclear structure and $[Cu_2(L)]_3[Co(CN)_6]_2\cdot 6MeOH\cdot 2DMF$ (**2**) of a 2-D grid structure, respectively.

Metal-condensed compounds are the current subject of many studies because of great interest in ther physicochemical properties and functions arising from the interaction or interplay of metal ions in close proximity.[1] In order to produce metal-condensed compounds, the reaction between a "complex metal" having one or more vacant (or labile) sites for accepting donation and a "complex bridge" having two or more groups capable of donating to another metal ion is generally adopted. $[M(ox)_3]^{3-}$ (ox^{2-} = oxalate) and $[M(CN)_6]^{3-}$ are important molecules as a "complex bridge" because the former coordinates to metal ion with a monodentate or a bidentate chelate,[2] and the latter forms from one-dimensional (1-D) to three-dimensional (3-D) structure with various bridging modes.[3,4] Recent attention is directed to a search of a novel function by combining polynuclear "complex metals" and "complex bridges" into a metal-condensed system.[5–7]

Dinuclear metal complexes of the macrocyclic ligand (H_2L) (Fig. 1), derived from the [2:2] condensation of 2,6-diformyl-4-methylphenol and 1,3-diaminopropane, are expected to act as "complex metals," since their dinuclear core is stabilized by the macrocyclic effect and the apical positions of the dinuclear core are available for accepting a donation from a "complex bridge." In this work, a dinuclear copper(II) complex, $[Cu_2(L)](ClO_4)_2$, as a polynuclear "complex metal" was used in reactions with $[Cr(ox)_3]^{3-}$ and $[Co(CN)_6]^{3-}$ as "complex bridges." Compounds **1** ($[Cu_2(L)]_3[Cr(ox)_3]\cdot 6MeOH$) and **2** ($[Cu_2(L)]_3[Co(CN)_6]_2\cdot 6MeOH\cdot 2DMF$) were obtained from the reaction of $[Cu(L)]^{2+}$ with $[Cr(ox)_3]^{3-}$ or $[Co(CN)_6]^{3-}$ in the 3:2 molar ratio in a DMF/MeOH solution, respectively. The single crystals for suitable X-ray crystallography of these compounds were obtained by standing a mixture of a methanol solution of $[Cu_2(L)](ClO_4)_2$ and a DMF solution of $(NEt_4)_3[Cr(ox)_3]$ or $(NEt_4)_3[Co(CN)_6]$ for two weeks.

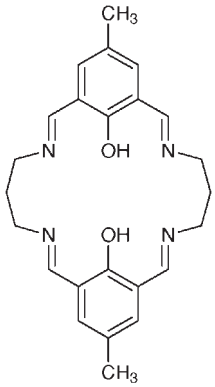

Fig. 1. Chemical structure of the dinucleating macrocyclic ligand (H_2L).

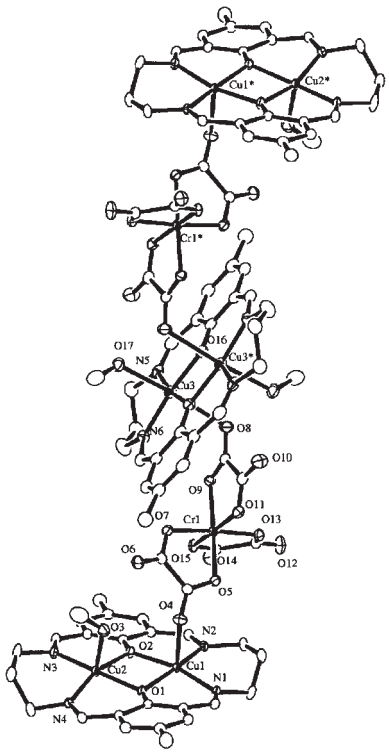

Fig. 2. An octanuclear structure of **1**. The lattice MeOH molecules hydrogen-bonded to $[Cr(ox)_3]^{3-}$ are omitted for clarity.

An ORTEP view of **1** is shown in Fig. 2 together with selected atom numberings. The asymmetric unit consists of one $[Cu_2(L)(MeOH)_2]^{2+}$ cation, two $[Cu_2(L)(MeOH)]^{2+}$ cations, two $[Cr(ox)_3]^{3-}$ anions, and two MeOH molecules captured in the crystal lattice. Complex **1** is a discrete octanuclear cluster comprised of two terminal $[Cu_2(L)(MeOH)]^{2+}$ cations, the central $[Cu_2(L)(MeOH)_2]^{2+}$ cation, and two μ_2-[Cr-

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$(ox)_3]^{3-}$ anions. The terminal $[Cu_2(L)(MeOH)]^{2+}$ cations and the central $[Cu_2(L)(MeOH)_2]^{2+}$ cation are connected by a μ_2-$[Cr(ox)_3]^{3-}$ anion through the donation of O(4) to Cu(1) and the donation of O(8) to Cu(3). The $[Cu_2(L)(MeOH)_2]^{2+}$ existing at the center of molecule forms a $\{Cu_2(L)(MeOH)_2(\underline{O})_2\}$ unit together with two oxygen atoms ($\underline{O}$) from separate μ_2-$[Cr(ox)_3]^{3-}$ bridges, and each $[Cu_2(L)(MeOH)]^{2+}$ existing at the terminal forms a $\{Cu_2(L)(MeOH)(\underline{O})\}$ unit together with one oxalate oxygen atom (O(4)). The $\{Cu_2(L)(MeOH)_2(\underline{O})_2\}$ unit has the center of symmetry, and each Cu ion has a pseudo-octahedral environment with a methanol oxygen atom (O(17)) and an oxalate oxygen atom (O(8)) at axial positions. The Cu(3)···Cu(3*) separation is 3.116 Å and the average of the in-plane bond distances is 1.98 Å. The axial Cu–O(8) and Cu–O(17) bond distances are elongated (2.643(2) and 2.360(2) Å, respectively) due to the Jahn–Teller effect. In the terminal $\{Cu_2(L)(MeOH)(\underline{O})\}$ unit, Cu(1) has a square-pyramidal geometry with the oxalate oxygen atom ($\underline{O}$ = O(4)) at the axial site, and Cu(2) also has a square-pyramidal geometry with a methanol oxygen atom (O(3)) at the axial site. The $\{Cu_2(L)(MeOH)(\underline{O})\}$ unit has a *cis* configuration with respect to the axial Cu(1)–O(4) and Cu(2)–O(3) bonds. The Cu(1)···Cu(2) separation is 3.076 Å and the average of the in-plane bond distances is 1.96 Å. The axial Cu(1)–O(4) and Cu(2)–O(3) bond distances are 2.307(2) and 2.273(3) Å, respectively. The Cr(1)···Cu(1) and Cr(1)···Cu(3) separations are 5.302 and 5.593 Å, respectively. The methanol oxygen atom O(17) in the central $\{Cu_2(L)(MeOH)_2(\underline{O})_2\}$ unit is hydrogen-bonded to the oxygen atoms O(8*) and O(10*) of the adjacent $[Cr(ox)_3]^{3-}$; the O(17)···O(8*) and O(17)···O(10*) separations are 3.184 and 2.686 Å, respectively. The methanol oxygen atom O(3) in the terminal $\{Cu_2(L)(MeOH)(\underline{O})\}$ unit is hydrogen-bonded to the oxygen atoms O(4) and O(6) of the adjacent $[Cr(ox)_3]^{3-}$; the O(3)···O(4) and O(3)···O(6) separations are 2.983 and 2.844 Å, respectively. The lattice methanol molecules are also concerned with hydrogen bonding with the $[Cr(ox)_3]^{3-}$ ion in the O(18)···O(12) and O(18)···O(14) separations of 3.042 and 3.015 Å, respectively.

An ORTEP view of **2** with selected atom numberings is shown in Fig. 3. The asymmetric unit consists of three $[Cu_2(L)]^{2+}$ cations, two $[Co(CN)_6]^{3-}$ anion, six MeOH molecules, and two DMF molecules. Each $[Co(CN)_6]^{3-}$ makes a bond to three separate $[Cu_2(L)]^{2+}$ cations through three cyanide groups in the meridional mode, affording a $\{Cu_2(L)(\underline{N})_2\}$ unit together with two nitrogen atoms ($\underline{N}$) from adjacent $[Co(CN)_6]^{3-}$ ions. In the $\{Cu_2(L)(\underline{N})_2\}$ unit, each Cu has a square-pyramidal geometry with a cyanide nitrogen atom at the axial site and the unit has a *trans* configuration with respect to two axial Cu–$\underline{N}$ bonds. The average Cu···Cu separation in the $\{Cu_2(L)(\underline{N})_2\}$ unit is 3.13 Å. The average of the in-plane Cu to the donor distances is 1.98 Å and the average of the Cu–$\underline{N}$ bond distances is 2.26 Å. A 1-D chain is formed by an alternate array of $[Cu_2(L)]^{2+}$ and $[Co(CN)_6]^{3-}$ through –{Cu(2)-Cu(1)}–Co(1)–{Cu(4)-Cu(5)}–Co(2)–{Cu(2)-Cu(1)}– linkage, and the 1-D chains are combined by –Co(1)–{Cu(3)-Cu(3*)}–Co(1*)– and –Co(2)–{Cu(6)-Cu(6*)}–Co(2*)– linkages affording a two-dimensional (2-D) grid structure (Fig. 4). The nearest Co···Cu separation along the 1-D chain is 5.01 Å and that between the 1-D chains is 4.95 Å. The C–N–Cu angle in the 1-D chain is 141.8° and that between 1-D chains is 142.7°. The methanol and DMF molecules are free from coordination and being captured in the crystal lattice.

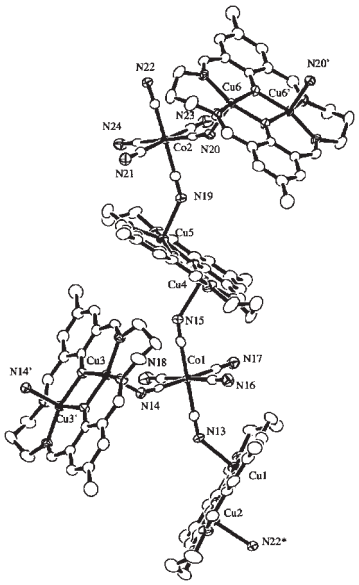

Fig. 3. Asymmetric unit for **2**. The crystal solvents are omitted for clarity.

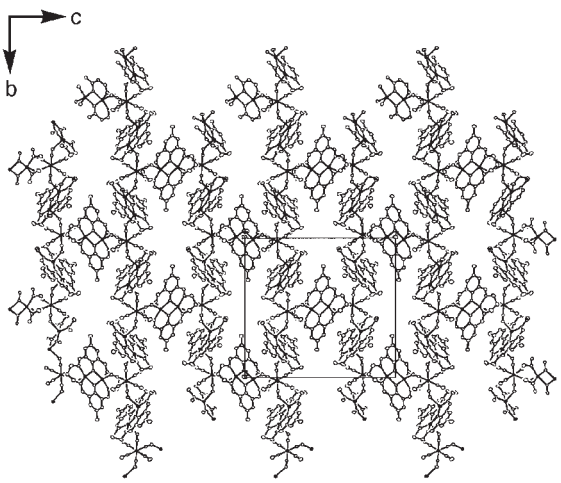

Fig. 4. The 2-D grid structure for **2** onto *bc* plane. The crystal solvents are omitted for clarity.

It is interesting that **1** has a discrete octanuclear structure, whereas **2** has a 2-D grid structure. Oxalate groups of $[M(ox)_3]^{3-}$ commonly coordinate to another metal ion as bidentate chelate. However, those of $[Cr(ox)_3]^{3-}$ of **1** coordinate to each copper as monodentate, since copper ions are located in the N_2O_2 plane of L^{2-}. The terminal dicopper(II) unit, $\{Cu_2(L)(MeOH)(\underline{O})\}$, of **1** forms a *cis* configuration with respect to the axial Cu(1)–O(4) and Cu(2)–O(3) bonds with the hydrogen bond to adjacent methanol molecules (O(3)···O(4) and O(3)···O(6)), like bidentate chelate. It seems that the hydrogen bond to MeOH promotes the *cis* configuration for the terminal unit. It is suggested that the octanuclear structure of **1** is formed by connecting two terminal dicop-

per(II) units to a central *trans*-$[Cu_2(L)(MeOH)_2]^{2+}$ cation due to satisfying the electroneutrality over the molecule. The bond distance of Cu(3)–O (2.643(2) Å) at the central $\{Cu_2(L)(MeOH)_2(O)_2\}$ unit is longer than the methanol-to-copper(II) distance (Cu–O(17): 2.360(2) Å) despite the fact that O is an anion donor. Further extension of the octanuclear core to a 1-D or 2-D network is inhibited due to the *cis* configuration of the terminal dicopper(II) unit. On the other hand, each $\{Cu_2(L)(N)_2\}$ unit of **2** has a *trans* configuration with respect to two axial Cu–N bonds and all methanol molecules as crystal solvent do not coordinate to the copper(II) ion. The *trans* configuration for the suquared-pyramidal dicopper(II) complex with L^{2-} is the most preferred configuration.[8–10] Thus, a 1-D chain is formed by an alternate array of $[Cu_2(L)]^{2+}$ and $[Co(CN)_6]^{3-}$ through the Co–CN–Cu linkage. The resulting 1-D chains are further assembled along with $[Cu(L)]^{2-}$ ions, by the donation of the third cyanide nitrogen (N(14), N(20)) of $[Co(CN)_6]^{3-}$ to an axial site of $[Cu_2(L)]^{2+}$, to afford the 2-D grid structure.

Experimental

Physical Measurements. Elemental analyses of C, H, and N were obtained at the Elemental Analysis Service Center of Kyushu University. Metal analyses were made on a Shimadzu AA-660 atomic absorption/flame emission spectrometer. Infrared spectra were recorded on a Perkin Elmer BX FT-IR system using KBr disk.

Preparation. The synthesis of $[Cu_2(L)](ClO_4)_2$ were carried out by literature methods.[11]

$[Cu_2(L)]_3[Cr(ox)_3]_2\cdot 6MeOH$ (1). $[Cu_2(L)](ClO_4)_2$ (50 mg, 0.07 mmol) was dissolved in DMF (15 mL). To this solution was added a methanol solution (5 mL) of $(Et_4N)_3[Cr(ox)_3]$ (24 mg, 0.05 mmol). The mixture was allowed to stand for two weeks to give $[Cu_2(L)]_3[Cr(ox)_3]_2\cdot 6MeOH$ (**1**) as green plates. Drying **1** in vacuo and standing in open air afforded $[Cu_2(L)]_3[Cr(ox)_3]_2\cdot 10H_2O$ (**1′**). Analytical and IR data were obtained for **1′**. Anal. Found: C, 41.87; H, 3.89; N, 7.19; Cu, 15.3; Cr, 4.55%. Calcd for $C_{84}H_{98}N_{12}Cr_2Cu_6O_{40}$: C, 42.02; H, 4.11; N, 7.00; Cu, 15.9; Cr, 4.33%. IR (KBr disk): 1709, 1667, 1640, 1388 cm^{-1}.

$[Cu_2(L)]_3[Co(CN)_6]_2\cdot 6MeOH\cdot 2DMF$ (2). This compound was prepared as brown crystals in a way similar to that of **1**, using $(Et_4N)_3[Co(CN)_6]$ instead of $(Et_4N)_3[Cr(ox)_3]$. $[Cu_2(L)]_3[Co(CN)_6]_2\cdot 7H_2O$ (**2′**) was obtained on drying **2** in vacuo and on standing in open air. Analytical and IR data were obtained for **2′**. Anal. Found: C, 46.89; H, 4.17; N, 15.70; Cu, 17.12; Co, 5.13%. Calcd for $C_{84}H_{92}N_{24}Cu_6Co_2O_{13}$: C, 47.07; H, 4.32; N, 15.67; Cu, 17.78; Co, 5.50%. IR (KBr disk): 2129, 1640 cm^{-1}.

X-ray Crystallography. Each single crystal of **1** and **2** was coated with epoxy resin before efflorescence. All measurements were made on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo Kα ($\lambda = 0.71070$ Å) radiation. The data were collected at -90 ± 1 °C to a maximum 2θ value of 55.0°. The structures were solved by direct methods (SIR-92) and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included for structure analysis, but not refined. The final cycle of full-matrix least-squares refinement was based on all reflections ($2\theta < 54.97$).

The crystallographic parameters are as follows. **1**: $C_{90}H_{96}N_{12}O_{36}Cu_6Cr_2$, fw = 2407.08, triclinic, space group $P\bar{1}$, $a = 10.0500(1)$, $b = 11.3000(2)$, $c = 22.2500(4)$ Å, $\alpha = 75.890(1)$, $\beta = 77.670(8)$, $\gamma = 78.910(8)°$, $Z = 1$, $V = 2367.6694$ Å^3, $D_{calcd} = 1.688$ g cm^{-3}, 10452 reflections used, $R_1 = 0.051$ ($I > 2\sigma$), $R = 0.077$ (all data), $Rw = 0.163$ (all data), GOF = 1.29. **2**: $C_{96}H_{78}N_{26}O_{14}Cu_6Co_2$, fw = 2318.98, triclinic, space group $P\bar{1}$, $a = 9.963(2)$, $b = 21.623(5)$, $c = 23.290(5)$ Å, $\alpha = 90.025(4)$, $\beta = 90.011(4)$, $\gamma = 89.984(4)°$, $Z = 2$, $V = 5017.3677$ Å^3, $D_{calcd} = 1.535$ g cm^{-3}, 22336 reflections used, $R_1 = 0.073$ ($I > 2\sigma$), $R = 0.097$ (all data), $Rw = 0.197$ (all data), GOF = 1.72.

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk. Copies can be obtained on request, free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, by quoting the publication citation and the deposition numbers, CCDC-265536 and 265537, for compounds No. **1** and **2**, respectively.

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