Synthesis, X-Ray Structures, and Magnetic Properties of $[Cu_2(piv)_4(Et_3N)_2]$ and $[Cu_6(piv)_6(EtO)_6]$ (Hpiv = Pivalic Acid): Role of Base for Dinuclear Adduct and Oligonuclear Formation

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Copper(II) pivalate adduct with triethylamine, $[Cu_2(piv)_4(Et_3N)_2]$ (Hpiv = pivalic acid), and cyclic hexanuclear copper(II) complex, $[Cu_6(piv)_6(EtO)_6]$, have been synthesized and characterized by X-ray crystallography and magnetic susceptibility measurement.

Oligonuclear metal complexes have been the focus of active research because of their unique structures and magnetic properties.[1] We have been engaged in chemistry of copper(II) carboxylate dimers in order to examine the potential utility as "building blocks" in combination with linkage ligands for oligonuclear or polynuclear formation. One of our target compounds is chain complexes with an alternating di-μ-carboxylato- and di-μ-alkoxo-bridging mode for metal ions, in which a partial degradation of the dimer is necessary for the chain formation. In the previous study, we treated copper(II) trichloroacetate with pyrazine in methanolic solution to give a chain complex of μ-carboxylato- and μ-alkoxo-bridged tetranuclear copper(II) units linked by pyrazine, the tetranuclear formation being probably through the almost complete degradation of the dimer core due to the relatively strong acidic character of the trichloroacetate groups.[2] In this study, copper(II) pivalate was reacted with the base triethylamine or sodium methoxide because we expected that the decreased acidity by the introduction of the *t*-butyl groups on the carboxylates would lead to a moderate degradation suitable for the formation of our target chain complexes. The resultant complexes were an adduct complex with triethylamine, $[Cu_2(piv)_4(Et_3N)_2]$ (**1**), and a novel hexanuclear copper(II) complex with alternating di-μ-carboxylato- and di-μ-alkoxo-bridges, $[Cu_6(piv)_6(EtO)_6]$ (**2**), which are presented in this communication.

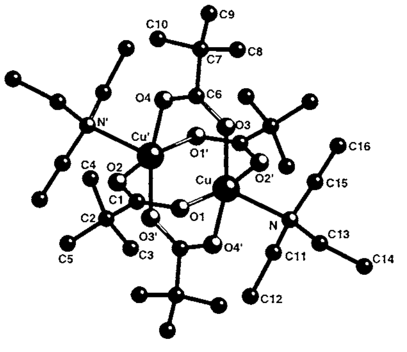

Figure 1. Perspective view of **1**. Selected bond distances (l/Å) and angles (ϕ/°): Cu-Cu' 2.681(1), Cu-O1 1.967(4), Cu-O2' 1.963(4), Cu-O3 1.967(4), Cu-O4' 1.966(4), Cu-N 2.300(4); O1-Cu-O3 90.1(2), O1-Cu-O4' 87.8(2), O3-Cu-O2' 88.6(2), O2'-Cu-O4' 90.4(2), O1-Cu-N 98.0(2), O3-Cu-N 97.7(2), O2'-Cu-N 95.7(2), O4'-Cu-N 95.6(2).

Triethylamine itself has a very poor coordinating ability and therefore is a useful base for deprotonating alcohol or phenol groups of organic ligands to cause their complexation.[3] However, when copper(II) pivalate[4] was treated with triethylamine in ethanol, dinuclear compound of **1** was isolated instead of μ-carboxylato- and μ-alkoxo-bridged species.[5] The X-ray crystallography of **1** reveals a dinuclear structure similar to those of ordinary adducts of copper(II) acetate (Figure 1).[6] The complex has the crystallographic inversion center at the center of the Cu_2 core. The Cu-Cu' distance (2.681(1) Å) is significantly longer than that of $Cu_2(piv)_4(pyz)$ (pyz = pyrazine, 2.584(2) Å).[2] It is to be noted that each triethylamine molecule is coordinated to the copper atom with the Cu-N distance of 2.300(4) Å. The copper atom is displaced towards the triethylamine molecule from the basal O1-O2'-O3-O4' plane by 0.23 Å, causing an elongation of the Cu-Cu' distance. The displacement of the copper atoms may be due to a steric hindrance between the ethyl groups of the trietylamine and the *t*-butyl groups of the pivalate ions. We are unaware of such an example of coordination of triethylamine, although many adducts have been found in copper(II) carboxylate chemistry.[7] The *syn-syn* bridging form of the carboxylate groups can be confirmed by the infrared spectrum of **1** [ν_{as}(COO) 1621, ν_s(COO) 1419 cm^{-1}] as in the case of $Cu_2(piv)_4(pyz)$.[2] The diffuse reflectance spectrum of **1** shows two absorption bands in the visible and near-UV region [716 and 375 nm]. The latter band is characteristic of copper(II) carboxylate dimers. The effective magnetic moment of **1** (1.93 B.M. per dinuclear molecule) is lower than the spin-only value at room temperature (2.45 B.M.). The magnetic moments measured down to 5 K (0.11 B.M.) indicate an appreciable antiferromagnetic interaction between the two copper atoms (Figure 2).[8]

In contrast, treatment of copper(II) pivalate with sodium methoxide in ethanol led to a dark green solution and subsequent isolation of a hexanuclear copper(II) complex **2** as dark green crystals.[9] The X-ray crystal structure of **2** shows that it is a rare

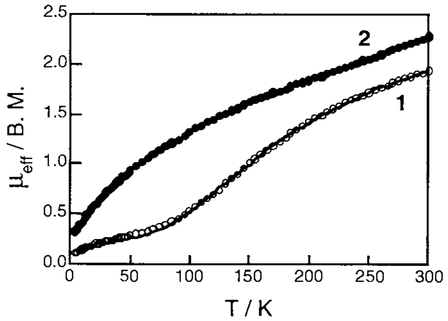

Figure 2. Temperature dependence of magnetic moments of **1** and **2**.

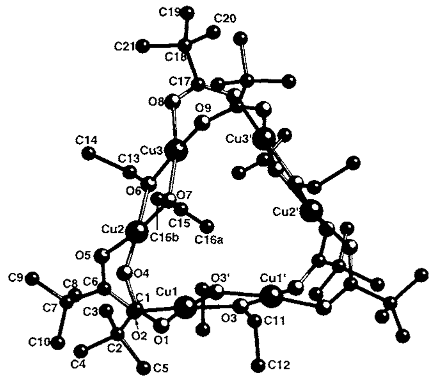

Figure 3. Perspective view of **2**. Disordered carbon atom C16 of ethoxide ion was refined with two sites C16a and C16b. Selected bond distances (*l*/Å) and angles (*ϕ*/°): Cu1-Cu1' 2.964(2), Cu1-Cu2 3.117(2), Cu2-Cu3 2.970(2), Cu3-Cu3' 3.068(2), Cu-O1 1.925(8), Cu1-O2 1.915(6), Cu1-O3 1.902(7), Cu1-O3' 1.881(8), Cu2-O4 1.907(8), Cu2-O5 1.935(7), Cu2-O6 1.903(7), Cu2-O7 1.889(7), Cu3-O6 1.907(6), Cu3-O7 1.907(8), Cu3-O8 1.915(7), Cu3-O9 1.929(6); Cu1'-Cu1-Cu2 118.75(7), Cu1-Cu2-Cu3 121.94(7), Cu2-Cu3-Cu3' 119.08(6), O1-Cu1-O2 92.1(3), O3-Cu1-O3' 76.6(3), O4-Cu2-O5 92.3(3), O6-Cu2-O7 77.3(3), O6-Cu3-O7 76.8(3), O8-Cu3-O9 93.0(3), Cu1-O3-Cu1' 103.2(2), Cu2-O6-Cu3 102.5(2), Cu2-O7-Cu3 103.0(3).

example of a cyclic hexanuclear structure (Figure 3).[6] The molecule lies on a crystallographic C_2 axis with three copper atoms, Cu1, Cu2, and Cu3, in the asymmetric unit, which are each bound to two oxygen atoms from pivalate ions and two ethoxo-oxygen atoms in a square plane. Cu1 is bridged to Cu2 in a *syn-syn* configuration by two pivalate ions and also bridged to Cu1' by two ethoxide ions which may be generated by a reaction of ethanol with sodium methoxide. Similarly Cu2 and Cu3 are also bridged alternately by two pivalate and two ethoxide ions. The six copper atoms are located at the corners of a hexagon such as a resonance form of benzene. The adjacent Cu-Cu distances alternate between short (2.964(2), 2.970(2) Å for ethoxo-bridges) and long (3.068(2), 3.117(2) Å for pivalato-bridges) contacts. The interior angles of the hexagon range between 118.75(7) and 121.94(7)°. This kind of cyclic hexanuclear species are still scarce, although few hexanuclear copper(II) complexes have been reported recently.[10-12] The ν_{as}(COO) and ν_{s}(COO) bands in the infrared spectrum of **2** appear at 1578 and 1424 cm^{-1}, respectively. The diffuse reflectance spectrum of **2** does not show the near-UV band, in contrast to that of **1**, but exhibits a broad band near 607 nm, characterisic of planar copper(II). As shown in Figure 2, the magnetic moment per hexanuclear molecule gradually decreases upon cooling from 2.27 B.M. at 300 K to 0.33 B.M. at 5 K, indicating a strong antiferromagnetism. The room-temperature values are considerably lower than those of Thompson's hexanuclear copper(II) complexes (3.06—3.58 B.M. per hexanuclear moplecule) which have alternating double (μ-phenoxo-μ-hydroxo) and single (μ-alkoxo) bridges.[11] The strong antiferromagnetism may be due to the different bridging mode, di-μ-alkoxo- and di-μ-pivalato-bridges. A magneto-structural relationship between Cu-O-Cu angles and magnetic coupling constants, *J*, is known to exist for di-μ-alkoxo-bridged complexes.[13] Considering the ethoxo-bridge angles (102.5(2)—103.2(2)°) observed for **2**, a strong antiferromagnetic interaction could be anticipated through the ethoxo-bridges, although the pivalato-bridges would be also responsible for the antiferromagnetism. Tokii *et al.* found that the strength of the antiferromagnetic interaction through di-μ-carboxylato-bridges is reduced to only one third of those of tetra-μ-carboxylato-bridges.[14]

In an effort to prepare complex **2** by using triethylamine, we could isolate this species in a different condition.[15] However, contamination of the triethylamine adduct sometimes occured in this case. Thus, the formation of dinuclear adduct or hexanuclear species seems to be depend on the basicity and coordinating ability of the base employed in the reaction. We consider the present method is promising to prepare chain compounds as well as oligonuclear metal species. Further studies are now in progress.

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5 Copper(II) pivalate[4] (402 mg, 0.756 mmol) was dissolved in 7 cm^3 of ethanol, and to this solution was added triethylamine (214 mg, 2.11 mmol). The resulting solution was allowed to stand at room temperature for one day. Green crystals were deposited.

6 Crystallographic data: for **1**; $C_{32}H_{66}Cu_2O_8N_2$, *F.W.* = 733.98, monoclinic, space group $P2_1/c$, a = 10.289(7), b = 17.570(2), c = 12.152(6) Å, β = 111.30(2)°, V = 2046(2) Å^3, Z = 2, D_c = 1.19 gcm^{-3}, μ(Mo Kα) = 10.82 cm^{-1}, crystal dimensions 0.10×0.13×0.15 mm^3, 3724 reflections measured ($2\theta_{max}$ = 50°), 2139 [$I \geq 3\sigma(I)$] used in the refinement, R = 0.046, R_w = 0.049. For **2**; $C_{42}H_{84}Cu_6O_{18}$, *F.W.* = 1258.39, monoclinic, space group $C2/c$, a = 25.743(10), b = 17.874(5), c = 16.211(6), β = 125.81(1)°, V = 6049(4) Å^3, Z = 4, D_m = 1.39, D_c = 1.38 gcm^{-3}, μ(Mo Kα) = 21.35 cm^{-1}, crystal dimensions 0.25×0.30×0.45 mm^3, 5520 reflections mesured ($2\theta_{max}$ = 50°), 2711 [$I \geq 3\sigma(I)$] used in the refinement, R = 0.061, R_w = 0.064. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation. All the structures were solved by the direct method and refined by the full-matrix least-squares method using a MolEN program package.

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8 The magnetic data were fitted to the Bleaney-Bowers equation with g = 2.22, J = -181 cm^{-1}, p (paramagnetic impurity fraction) = 0.0047, $N\alpha$ = 60 × 10^{-6} cgs emu.

9 An ethanol solution (4 cm^3) of NaOMe (16 mg, 0.30 mmol) was slowly diffused into an ethanol solution (4 cm^3) of copper(II) pivalate (105 mg, 0.197 mmol) by connecting these with 12 cm^3 of ethanol at room temperature. Dark green crystals of **2** were formed in several weeks.

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15 Reaction of copper(II) pivalate (108 mg, 0.203 mmol) and triethylamine (51 mg, 0.50 mmol) in ethanol (5 cm^3) over one month at room temperature gave dark green crystals.