

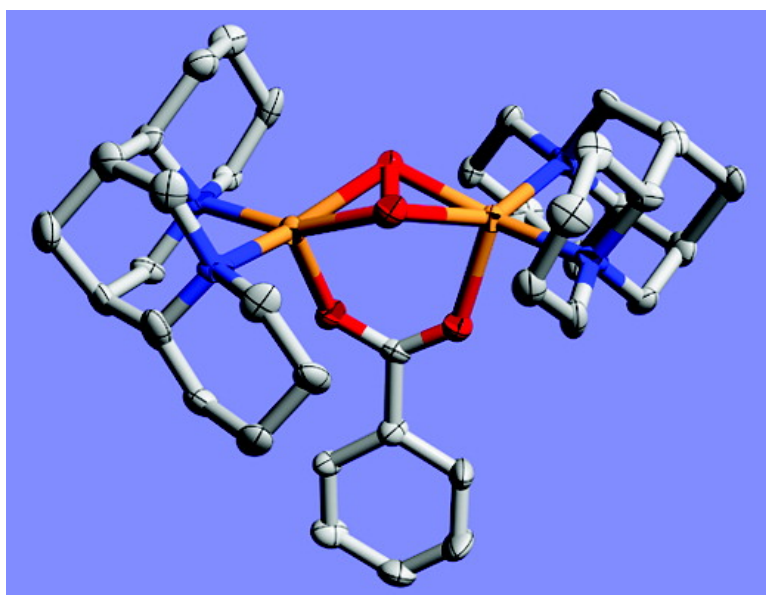
Communication

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 Dicopper Core Structure with a Carboxylate Group**

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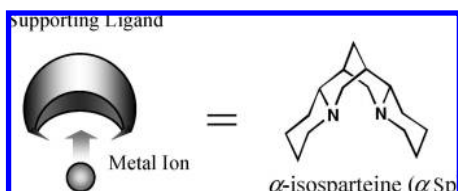
## Formation of a Bridged Butterfly-Type $\mu$ - $\eta^2$ : $\eta^2$ -Peroxo Dicopper Core Structure with a Carboxylate Group

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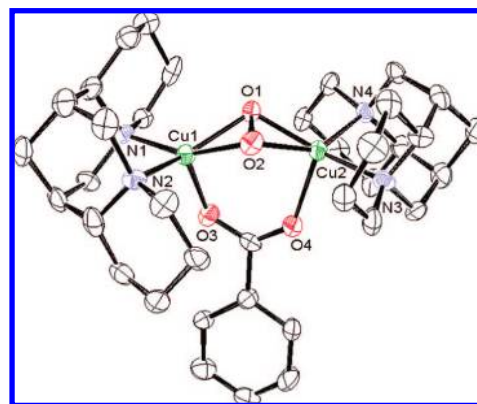
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The  $\mu$ - $\eta^2$ : $\eta^2$ -peroxodicopper(II) ( $\text{Cu}_2(\mu\text{-}\eta^2$ : $\eta^2\text{-O}_2)$ ) and bis( $\mu$ -oxo)dicopper(III) ( $\text{Cu}_2(\mu\text{-O})_2$ ) species have been investigated in the model studies of type III copper proteins, and these structures are also considered as important motifs for  $\text{O}_2$ -activating metalloproteins in biological systems.<sup>1,2</sup> The interconversion between these species in solution was found to depend on organic solvents and counteranions.<sup>2,3</sup> Recent studies of the interconversion equilibrium in copper-aliphatic diamine complex systems strongly suggested that coordination of counteranions promotes the conversion of  $\text{Cu}_2(\mu\text{-O})_2$  to  $\text{Cu}_2(\mu\text{-}\eta^2$ : $\eta^2\text{-O}_2)$  species.<sup>2b,3b,c</sup> However, direct evidence for formation of the anion-coordinating structure is yet to be presented. Here, we report the formation and crystal structure of a new  $\text{Cu}_2(\mu\text{-}\eta^2$ : $\eta^2\text{-O}_2)$  complex with a bridging carboxylate ligand.<sup>4a</sup> Structural studies and density functional theory (DFT) calculations suggested factors regulating stepwise-activation of dioxygen by bridging-carboxylate ligation to the dicopper core.



We reported earlier that an alkaloid, (–)-sparteine (Sp), forms a distorted bis( $\mu$ -hydroxo)dicopper(II) ( $\text{Cu}_2(\mu\text{-OH})_2$ ) complex because of its preorganized structure and that a copper(I) complex of Sp is oxygenated to form a  $\text{Cu}_2(\mu\text{-O})_2$  species.<sup>4b</sup> We now synthesized the copper complexes of  $\alpha$ -isosparteine ( $\alpha\text{Sp}$ ), which is one of the stereoisomers of Sp and, with its structural constraint, enforces tetrahedral distortion around the transition metal(II) ions.<sup>4,5</sup> The Cu(I) complex of  $\alpha\text{Sp}$ ,  $[\text{Cu}^{\text{I}}(\alpha\text{Sp})(\text{CH}_3\text{CN})]\text{SbF}_6$  (**1**· $\text{SbF}_6$ ), reacted with dioxygen to generate a  $\text{Cu}_2(\mu\text{-O})_2$  species,  $[\text{Cu}_2(\alpha\text{Sp})_2(\mu\text{-O})_2]^{2+}$  (**2**),<sup>4a</sup> in organic solvents ( $\text{CH}_2\text{Cl}_2$ , THF, and acetone) at  $-80^\circ\text{C}$ . The brown-colored solution in  $\text{CH}_2\text{Cl}_2$  exhibited two intense absorption bands centered at  $\lambda_{\text{max}}$  ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ ) = 321 nm (10600) and 433 nm (22000) and resonance Raman (rR) bands at  $\nu = 631$  and  $602\text{ cm}^{-1}$  for the adducts with  $^{16}\text{O}_2$  and  $^{18}\text{O}_2$ , respectively ( $\Delta\nu[^{16}\text{O}_2\text{-}^{18}\text{O}_2] = 29\text{ cm}^{-1}$ ) (Supporting Information, Figures S1, S2). These spectral features are characteristic of the reported  $\text{Cu}_2(\mu\text{-O})_2$  species ( $\text{Cu}\leftarrow\text{O}$  LMCT bands,  $\lambda_{\text{max}} \approx 300$  and  $400\text{ nm}$ ; rR frequencies and their isotope shifts of the  $\text{Cu}_2(\mu\text{-O})_2$  core stretching mode,  $\nu \approx 600\text{ cm}^{-1}$  and  $\Delta\nu[^{16}\text{O}_2\text{-}^{18}\text{O}_2] \approx 25\text{ cm}^{-1}$ ).<sup>2c</sup> When a



**Figure 1.** ORTEP view of  $[\text{Cu}^{\text{II}}_2(\alpha\text{Sp})_2(\mu\text{-}\eta^2$ : $\eta^2\text{-O}_2)(\text{Bz}^-)]^+$  (**3**) with thermal ellipsoids drawn at the 30% probability. The hydrogen atoms and a  $\text{SbF}_6^-$  molecule are omitted for clarity. Selected bond distances ( $\text{\AA}$ ) and angles (deg): O1–O2, 1.498(15); Cu1–N1, 1.981(12); Cu1–N2, 1.977(14); Cu2–N3, 1.983(13); Cu2–N4, 1.998(13); Cu1–O1, 1.976(11); Cu1–O2, 1.873(11); Cu2–O1, 1.912(10); Cu2–O2, 1.977(11); Cu1–O3, 2.124(11); Cu2–O4, 2.111(12); N1–Cu1–N2, 90.8(5); N3–Cu2–N4, 90.6(5); O1–Cu1–O2, 45.7(4); O1–Cu2–O2, 45.3(4).

colorless acetone solution containing **1**· $\text{SbF}_6$  and benzoate ( $\text{Bz}^-$ ) in the molar ratio of 1/0.5 was bubbled with  $\text{O}_2$  at  $-80^\circ\text{C}$ , the solution turned dark blue, giving two intense absorption bands centered at  $\lambda_{\text{max}}$  ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ ) = 372 nm (19500) and 745 nm (1300) (Figure S3). The rR spectrum of the dark-blue oxygenated acetone solution by using  $^{16}\text{O}_2$  at  $-80^\circ\text{C}$  exhibited an intense peak at  $\nu = 756\text{ cm}^{-1}$ , which shifted to  $715\text{ cm}^{-1}$  upon using  $^{18}\text{O}_2$  ( $\Delta\nu[^{16}\text{O}_2\text{-}^{18}\text{O}_2] = 41\text{ cm}^{-1}$ ) (Figure S4). These spectral features were analogous to those of the previously reported  $\text{Cu}^{\text{II}}_2(\mu\text{-}\eta^2$ : $\eta^2\text{-O}_2)$  species ( $\text{Cu}\leftarrow\text{O}$  LMCT bands,  $\lambda_{\text{max}}$  ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ ) = 340–380 nm (18000–25000) and 510–550 nm (ca. 1000); rR frequencies and its isotope shifts of O–O,  $\nu = 730\text{--}760\text{ cm}^{-1}$  and  $\Delta\nu[^{16}\text{O}_2\text{-}^{18}\text{O}_2] \approx 40\text{ cm}^{-1}$ ),<sup>2c</sup> although the CT band observed at 745 nm is in the lower energy region than that reported for usual out-of-plane  $\pi_{\text{v}}^* \rightarrow d_{x^2-y^2}$  peroxo to Cu(II) CT (510–550 nm). To structurally define the dark-blue dioxygen adduct, we isolated the dark-blue crystals of the adduct suitable for X-ray measurements from the acetone solution at  $-85^\circ\text{C}$ . The crystallographic analysis revealed that the dioxygen adduct,  $[\text{Cu}^{\text{II}}_2(\alpha\text{Sp})_2(\mu\text{-}\eta^2$ : $\eta^2\text{-O}_2)(\text{Bz}^-)]\text{-SbF}_6$  (**3**· $\text{SbF}_6$ ), has a dicopper core bridged by a side-on peroxide ion and a  $\text{Bz}^-$  ligand, as shown in Figure 1. The atomic distance between two copper centers in **3** ( $\text{Cu1}\cdots\text{Cu2} = 3.265(2)\text{ \AA}$ ) lies in between the values reported for  $\text{Cu}^{\text{II}}_2(\mu\text{-}\eta^2$ : $\eta^2\text{-O}_2)$  cores (3.48–3.56  $\text{\AA}$ )<sup>6</sup> and  $\text{Cu}^{\text{III}}_2(\mu\text{-O})_2$  cores (2.74–2.91  $\text{\AA}$ )<sup>2a,c</sup> structurally defined

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by X-ray crystallography, and it is consistent with the values for the butterfly-shaped  $\text{Cu}^{\text{II}}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-O}_2)$  core structures estimated by EXAFS studies (3.22–3.37 Å).<sup>7</sup> Interestingly, the  $\text{Cu}_2\text{O}_2$  core of **3** is extremely bent with a hinge angle  $\delta = 132^\circ$  along the O1–O2 axis, which is much smaller than the angles of structurally determined  $\text{Cu}^{\text{II}}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-O}_2)$  complexes ( $\delta = \text{ca. } 163^\circ$ )<sup>6</sup> and the calculated one ( $\delta = \text{ca. } 150^\circ$ ).<sup>3c,8</sup> The asymmetric coordination bond distances of the side-on peroxide oxygen atoms in the equatorial positions,  $\text{Cu}\text{--O}_{\text{peroxo}} = 1.873(11)\text{--}1.977(11)$  Å, and the O–O bond distance of side-on peroxide, 1.498(15) Å, are in agreement with the reported values of  $\text{Cu}^{\text{II}}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-O}_2)$  complexes ( $\text{Cu}\text{--O}_{\text{peroxo}} = 1.89\text{--}1.95$  Å and  $\text{O}\text{--O} = 1.41\text{--}1.49$  Å).<sup>6</sup> The axial coordination of the bridging carboxylate group of  $\text{Bz}^-$  should be important for forming such an extremely bent  $\text{Cu}_2\text{O}_2$  core in **3**. Surprisingly, the bond distances between the copper ions and the carboxylate oxygen atoms of  $\text{Bz}^-$  in the axial positions,  $\text{Cu}\text{--O}_{\text{Bz}} = 2.124(11)$  and  $2.111(12)$  Å, are longer than the equatorial  $\text{Cu}\text{--O}_{\text{peroxo}}$  bonds but are shorter than the typical values for the axial nitrogen coordination to Cu(II) in  $\text{N}_2\text{O}_2$  planes in dicopper(II)  $\mu\text{-}\eta^2\text{:}\eta^2\text{-peroxo}$  complexes with tridentate ligands ( $\text{Cu}\text{--N}_{\text{ax}} = 2.14\text{--}2.27$  Å).<sup>6</sup> The deviations of the copper atoms from least-squares planes of the equatorial  $\text{N}_2\text{O}_2$  coordination in **3**, are 0.36 and 0.35 Å for Cu1 and Cu2, respectively, which are larger than the typical values reported for  $\text{Cu}^{\text{II}}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-O}_2)$  structures (0.21–0.29 Å).<sup>6</sup> This is probably due to the strong axial coordination of the bridging  $\text{Bz}^-$  ligand. To check the coordination properties around the copper ions, we performed theoretical calculations of the electronic structure of **3** by spin unrestricted broken-symmetry ( $M_s = 0$ ) DFT using atomic coordinates fixed to the crystal structure (Table S1). The results supported that the side-on peroxo O atoms of **3** occupy the equatorial positions, the atomic spin densities being ca.  $-0.57$  and  $0.57$  for Cu1 and Cu2 atoms, and ca.  $0.04$  and  $-0.03$  for O1 and O2 atoms, respectively. The bond order parameters of the Cu–O bonds in **3** were calculated to be ca.  $0.11\text{--}0.17$  for  $\text{Cu}\text{--O}_{\text{peroxo}}$  and ca.  $0.07$  for  $\text{Cu}\text{--O}_{\text{Bz}}$ , indicating that the equatorial  $\text{Cu}\text{--O}_{\text{peroxo}}$  bonds are more covalent than the axial  $\text{Cu}\text{--O}_{\text{Bz}}$  bonds and that the latter are more ionic/electrostatic. Indeed, the atomic charge values were ca.  $+1.42$  to  $+1.43$  for Cu1 and Cu2 atoms, and those for O3 and O4 atoms of  $\text{Bz}^-$  were more negative (ca.  $-0.85$  to  $-0.88$ ) than those of peroxo O1 and O2 atoms (ca.  $-0.68$ ). On the basis of these results, a reasonable interpretation of the strong axial coordination is that the ionic and polarized axial Cu–O bonds of  $\text{Bz}^-$  are strengthened by electrostatic interaction with their local atomic charges. Relevant to this, the rR study indicated that the core stretching mode frequencies of the  $\text{Cu}_2(\mu\text{-O})_2$  species, **2**, is ca.  $30\text{ cm}^{-1}$  higher ( $\nu = 631\text{ cm}^{-1}$ ) than those of the other  $\text{Cu}_2(\mu\text{-O})_2$  species ( $580\text{--}616\text{ cm}^{-1}$ ),<sup>2,3</sup> suggesting that  $\alpha\text{Sp}$  is a weaker  $\sigma$ -electron-donating ligand than the others.<sup>9</sup> In this case,  $\alpha\text{Sp}$  does not destabilize  $d_{x^2-y^2}$  orbital efficiently, and the energy gaps of the two Cu–O LMCT transitions of **2** ( $\lambda_{\text{max}} = 321, 433\text{ nm}$ ) are smaller than those of the typical coplanar  $\text{Cu}_2(\mu\text{-O})_2$  complexes with  $N,N'$ -peralkylated aliphatic diamine ligands (297–319 and 397–407 nm).<sup>2,3</sup> On the basis of the above considerations, we may conclude that because of the less effective  $\sigma$ -donating property of  $\alpha\text{Sp}$  the remaining positive charge on the Cu centers is favorable for coordination of an exogenous anionic ligand such as  $\text{Bz}^-$  in the axial position. In fact, addition of an equimolar amount of  $\text{Bz}^-$  to the yellow-brown solution of **2** in acetone at  $-80^\circ\text{C}$  readily gave the dark-blue solution of **3** (Figure S5).

In summary, we succeeded in synthesizing  $[\text{Cu}^{\text{II}}_2(\alpha\text{Sp})_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-O}_2)(\text{Bz}^-)]\text{SbF}_6$  (**3**· $\text{SbF}_6$ ) and determining the novel coordination structure of a carboxylate-bridged butterfly type  $\mu\text{-}\eta^2\text{:}\eta^2\text{-peroxide}$

dicopper(II) core. The “bridged butterfly core” was supported by an exogenous ligand,  $\text{Bz}^-$ , in the axial position, losing its strong planarity regardless of the Jahn–Teller effect<sup>10</sup> on the  $d_{x^2-y^2}$  ground-state of Cu(II)  $d^9$ -configuration. We consider that weaker  $\sigma$ -donation of  $\alpha\text{Sp}$  to the copper centers promotes the more electrostatic/ionic axial coordination of  $\text{Bz}^-$  in **3**. Axial coordination of negative  $\text{Bz}^-$  to **2** elongates the equatorial Cu–O bonds to destabilize the bis( $\mu\text{-oxo}$ ) state, converting it to the corresponding  $\mu\text{-}\eta^2\text{:}\eta^2\text{-peroxo}$  state of **3**. The preorganized, constrained, and sterically hindered ligand,  $\alpha\text{Sp}$ , forms a distorted coordination environment with less effective  $d\sigma\text{--}p\sigma$  orbital overlaps, decreasing the stabilization effect on 3d orbitals and enhancing electrostatic/ionic coordination properties in the metal-dioxygen intermediate. Thus, in distorted and less covalent coordination geometries, a carboxylate group should have an influence on the reactivity of a transition metal ion through the more electrostatic/ionic binding, which may be related to the controlled stepwise reduction of dioxygen at carboxylate-bridged dimetal active centers as seen in nonheme diiron proteins.<sup>11</sup>

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**Supporting Information Available:** Synthesis, and absorption and rR spectral characterization of **2**· $(\text{SbF}_6)_2$  and **3**· $\text{SbF}_6$ , theoretical calculation and X-ray crystallographic data of **3**· $\text{SbF}_6$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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