Magnetic properties of intramolecularly hydrogen-bonded carboxylate copper(11) dimer complexes

Norikazu Ueyama,*a Yusuke Yamada,a Jiro Takeda,a Taka-aki Okamura,a Wasuke Morib and Akira Nakamura*a

^a Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

^b Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

Novel copper(II) dimer complexes,

 $[Cu_2\{OCOC_6H_3Me-2-(NHCOBu^t)-6\}_4(MeOH)(H_2O)]$ and $[Cu_2\{OCOC_6H_3(NHCOBu^t)_2-2,6\}_4(MeCN)_2]$, containing bulky, intramolecularly NH···O hydrogen-bonded carboxylate ligands, are synthesized; the former shows a distorted Cu–O–C–O–Cu structure with a magnetic exchange ($-2J = 302 \text{ cm}^{-1}$) between the two Cu^{II} ions while the latter has a twisted Cu–O–C–O–Cu structure with a relatively large exchange ($-2J = 460 \text{ cm}^{-1}$) through the NH···O hydrogen bonds.

The chemistry of dimeric copper(II) complexes with various carboxylates has been studied for 40 years, and is currently of interest in the area of magnetic materials. In these complexes, the *syn-syn* carboxylate ligands bridge between two Cu^{II} centres with Cu-Cu distances in the range 2.6–2.7 Å.¹⁻⁶ The copper ions exhibit antiferromagnetic interactions with -2J values in the range 250–325 cm⁻¹.³⁻⁶

Here we report the synthesis, structure and magnetic properties of the novel bulky carboxylate copper(II) dimer complexes [Cu₂{OCOC₆H₃Me-2-(NHCOBu^t)-6}₄(MeOH)-(H₂O)] **1** with a distorted Cu-O-C-O-Cu structure and [Cu₂{OCOC₆H₃(NHCOBu^t)₂-2,6}₄(MeCN)₂] **2**. These com-

plexes were synthesized by the reaction of CuSO₄·5H₂O and the appropriate carboxylic acid in water with recrystallization from methanol (1) or acetonitrile (2); both compounds were isolated as green plates. Elemental analysis confirmed the purity of these complexes and no paramagnetic impurities were present. Fig. 1 and 2 show the crystal structures of 1 and 2, respectively.[†] Each Cu^{II} is bonded to four carboxylate O atoms and a methanol or water O atom in 1 or one acetonitrile N atom in 2. The short distance between the carboxylate O and amide N indicates the presence of NH…O hydrogen bonds (mean 2.75 Å for 1, 2.67 Å for 2). The bridged carboxylate in 2 displays a twisted Cu-O-C-O-Cu structure due to the steric congestion of two bulky amide groups as shown in Fig. 2. The aromatic ring is rotated out of the carboxylate plane and the amide NH is hydrogenbonded to the carboxylate oxygen. Thus, the novel bulky carboxylate demonstrates both steric congestion and conformational restriction by NH...O hydrogen bonding.

The temperature dependence of the magnetic susceptibilities for 1 and 2 are illustrated in Fig. 3. The exchange-coupling constants (-2J) obtained from a least-squares fit of the data to



(1)

Fig. 1 Molecular structure of $[Cu_2\{OCOC_6H_3Me-2-(NHCOBu^1)-6\}(MeOH)(H_2O)]$ 1. Selected bond lengths (Å) and angles (°): Cu(1)–Cu(2) 2.634(4), Cu(1)–O(1) 1.93(2), Cu(1)–O(3) 1.97(2), Cu(1)–O(5) 1.96(2), Cu(1)–O(7) 1.99(2), Cu(2)–O(2) 1.97(1), Cu(2)–O(4) 1.97(2), Cu(2)–O(6) 2.01(2), Cu(2)–O(8) 1.97(2); O(1)–Cu(1)–Cu(2)–O(2) 4.2(6), O(3)–Cu(1)–Cu(2)–O(4) 2.9(6), O(5)–Cu(1)–Cu(2)–O(6) 0.9(6), O(7)–Cu(1)–Cu(2)–O(8) 5.5(6). Methyl groups of the Bu^t groups are omitted for clarity.

Fig. 2 Molecular structure of $[Cu_2 \{OCOC_6H_3(NHCOBu^1)_2-2,6\}_4(MeCN)_2]$ 2. Selected bond lengths (Å) and angles (°): Cu(1)–Cu(2) 2.624(3), Cu(1)–O(1) 2.00(1), Cu(1)–O(3) 1.98(1), Cu(1)–O(5) 1.92(1), Cu(1)–O(7) 1.97(1), Cu(2)–O(02) 1.95(1), Cu(2)–O(4) 1.96(1), Cu(2)–O(6) 2.00(1), Cu(2)–O(8) 1.97(1); O(1)–Cu(1)–Cu(2)–O(2) 13.6(4), O(3)–Cu(1)–Cu(2)–O(4) 13.9(5), O(5)–Cu(1)–Cu(2)–O(6) 14.2(5), O(7)–Cu(1)–Cu(2)–O(8) 13.2(5). Methyl groups of Bu^t groups are omitted for clarity.

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the Bleaney–Bowers equation are 302 and 462 cm⁻¹ for 1 and 2 respectively. The one NH···O hydrogen-bonded structure in 1 does not have a magnetic exchange through the hydrogen bond, but 2 has a conjugated pathway with two NH···O hydrogen bonds which contribute to the enhancement of the -2J value. A binuclear copper(II) complex [Cu(Heta)(eta)]₂[NO₃]₂ (Heta =



Fig. 3 Variable-temperature magnetic susceptibility data for (a) 1 and (b) 2. Solid lines were obtained from a least-squares fit of the data to the Bleaney–Bowers equation.

2-aminoethanol), in which the two Cu^{II} ions are square planar due to hydrogen bonding, has been reported to exhibit a relatively large interaction $(-2J 56-94 \text{ cm}^{-1})$ despite the large Cu…Cu separation (*ca*. 5 Å),⁸ since the d_{x2-y2} orbital associated with the magnetic interaction can symmetrically overlap with the p and s orbitals of the oxygen and hydrogen atoms. For the face-to-face copper(II) binuclear structures 1 and 2, it is interesting that the amide NH…O acts as a magnetic exchange pathway since many biologically important binuclear copper complexes with carboxylate bridges have been reported to have remarkable magnetic interactions.

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Footnote

† *Crystal data* for 1: orthorhombic, space group *Pbca*, *a* = 17.535(4), *b* = 38.781(7), *c* = 16.693(6) Å, *U* = 11352(4) Å³, *Z* = 8, *D_c* = 1.325 g cm⁻¹, μ (Mo-Kα) = 8.16 cm⁻¹, 1922 reflections with *I* > 3σ(*I*), final *R* and *R_w* values are 0.074 and 0.078 respectively. Hydrogen atoms were included in the refinement in idealized positions (C–H = 0.98 Å); max., min. peak, hole in the final difference map 0.55, -0.40 e Å⁻³.

For 2: orthorhombic, space group $P2_12_12_1$, a = 19.825(4), b = 20.489(3), c = 19.537(5) Å, U = 7935(2) Å³, Z = 4, $D_c = 1.244$ g cm⁻³, μ (Mo-K α) = 48 cm⁻¹, 3840 reflections with $I > 3\sigma(I)$. Final *R* and R_w values are 0.073 and 0.085 respectively. Hydrogen atoms were included in the refinement in idealized positions (C-H = 0.98 Å); max., min. peak, hole in the final difference map 0.57, -0.39 e Å⁻³. Both structures were solved using the Patterson method (DIRDIF92 PATTY in TEXSAN package software) and refined by full-matrix least squares. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/71.

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