Copper(II) carboxylate dimers prepared from ligands designed to form a robust π···π stacking synthon: supramolecular structures and molecular properties.

Autorzy

Daniel L. Reger

A. Debreczeni

Mark D. Smith

Julia Jezierska

Andrew Ozarowski

Rok wydania

2012

Czasopismo

Inorganic Chemistry

Numer woluminu

51

Strony

1068-1083

DOI

10.1021/ic202198k

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

The reactions of bifunctional carboxylate ligands (1,8-naphthalimido)propanoate, ($\mathbf{L_{C2}}^-$), (1,8-naphthalimido)ethanoate, ($\mathbf{L_{C1}}^-$), and (1,8-naphthalimido)benzoate, ($\mathbf{L_{C4}}^-$) with $Cu_2(O_2CCH_3)_4(H_2O)_2$ in methanol or ethanol at room temperature lead to the formation of novel dimeric $[Cu_2(\mathbf{L_{C2}})_4(MeOH)_2]$ (**1**), $[Cu_2(\mathbf{L_{C1}})_4(MeOH)_2]\cdot 2(CH_2Cl_2)$ (**2**), $[Cu_2(\mathbf{L_{C4}})_4(EtOH)_2]\cdot 2(CH_2Cl_2)$ (**3**) complexes. When the reaction of $\mathbf{L_{C1}}^-$ with $Cu_2(O_2CCH_3)_4(H_2O)_2$ was carried out at −20 °C in the presence of pyridine, $[Cu_2(\mathbf{L_{C1}})_4(py)_4]\cdot 2(CH_2Cl_2)$ (**4**) was produced. At the core of complexes **1**–**3** lies the square $Cu_2(O_2CR)_4$ “paddlewheel” secondary building unit, where the two copper centers have a nearly square pyramidal geometry with methanol or ethanol occupying the axial coordination sites. Complex **4** contains a different type of dimeric core generated by two κ^1-bridging carboxylate ligands. Additionally, two terminal carboxylates and four trans situated pyridine molecules complete the coordination environment of the five-coordinate copper(II) centers. In all four compounds, robust $\pi\cdots\pi$ stacking interactions of the naphthalimide rings organize the dimeric units into two-dimensional sheets. These two-dimensional networks are organized into a three-dimensional architecture by two different noncovalent interactions: strong $\pi\cdots\pi$ stacking of the naphthalimide rings (also the pyridine rings for **4**) in **1**, **3**, and **4**, and intermolecular hydrogen bonding of the coordinated methanol or ethanol molecules in **1**–**3**. Magnetic measurements show that the copper ions in the paddlewheel complexes **1**–**3** are strongly antiferromagnetically coupled with –*J* values ranging from 255 to 325 cm^{-1}, whereas the copper ions in **4** are only weakly antiferromagnetically coupled. Typical values of the zero-field splitting parameter *D* were found from EPR studies of **1**–**3**and the related known complexes $[Cu_2(\mathbf{L_{C2}})_4(py)_2]\cdot 2(CH_2Cl_2)\cdot(CH_3OH)$, $[Cu_2(\mathbf{L_{C3}})_4(py)_2]\cdot 2(CH_2Cl_2)$ and $[Cu_2(\mathbf{L_{C3}})_4(bipy)]\cdot(CH_3OH)_2\cdot(CH_2Cl_2)_{3.37}$ ($\mathbf{L_{C3}}^-$ = (1,8-naphthalimido)butanoate)), while its abnormal magnitude in $[Cu_2(\mathbf{L_{C2}})_4(bipy)]$ was qualitatively rationalized by structural analysis and DFT calculations.

Adres publiczny

https://doi.org/10.1021/ic202198k

Strona internetowa wydawcy

https://www.acs.org/content/acs/en.html