Three Olefin Copper(I) Dimeric Complexes with 2-, 3-, and 4-Pyridylacrylic Acid and Their Electrochemical Properties

Yong-Hua Li,† Xi-Sen Wang,† Hong Zhao,† Rong-Xin Yuan,∗† Jing Zhang,† Ren-Gen Xiong,∗† Xiao-Zeng You,† Huang-Xian Ju,† and Zi-Ling Xue‡

Coordination Chemistry Institute, The State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, 210093, P. R. China, and Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996

Received April 11, 2003

UV irradiation of 2-, 3-, or 4-pyridylacrylic acid (2-, 3-, and 4-HPYA) with CuI at 230 nm in 4 N HCl for 1 week and subsequent hydrothermal reactions yielded three novel highly stable 3-D copper(I)−olefin dimers, [2-H2PYA]Cu2n−Cl4{(1), [3-H2PYA]Cu2n−Cl4{(2), and [4-H2PYA]Cu2n−Cl4{(3), respectively, in which H-bonds play a key role in the stabilization of supramolecular Cu(I)−olefin system and thus the formation of the 3-D networks. The electrochemical properties of 1−3 are also reported.

Introduction

Copper(I)−olefin complexes are used extensively in light-olefin/paraffin separation and enantio separation as the coordination of Cu(I) to ω−olefin is labile. These complexes also take part in a variety of stress responses and developmental processes, as shown in the smallest plant hormone.1,2 Recently, supramolecular motifs based on olefin−Cu(I) are a topic of intense interest,3 particularly for their luminescent mental processes, as shown in the smallest plant hormone.1,2

It is worthy noting that, in the formation of many remarkably stable olefin−Cu(I) coordination polymers, bridging spacers by carboxylate and pyridyl groups often play a key role in stabilizing the supramolecular systems.3 Stable discrete molecular Cu(I) complexes of bidentate olefin−carboxylate or pyridyl ligands such as 2-, 3-, and 4-pyridylacrylic acid with uncoordinated carboxylate or pyridyl groups are virtually unknown. It is difficult to avoid the binding of these carboxylate or pyridyl groups to Cu(I) ion to give polymeric structures.

Halides are known good bridging spacers in Cu(I)−olefin systems to give stable Cu(I)−olefin polymer with a prismane Cu6X6 cluster as connection corner unit.4 We found that the UV irradiation at ca. 230 nm of a mixture of CuCl, 2-, 3-, and 4-pyridylacrylic acids (2-, 3-, and 4-HPYA), and HCl, followed by hydrothermal reactions, afforded three stable dimeric Cu(I)−olefin complexes, [Cu+nCl2(2-HPYCH=CHCOOH)2], or [2-H2PYA]Cu2n−Cl4{(1), [Cu2nCl2(3-HPYCH=CHCOOH)] or [3-H2PYA]Cu2n−Cl4{(2), and [Cu2nCl2(4-HPYCH=CHCOOH)] or [4-H2PYA]Cu2n−Cl4{(3). In these complexes, the pyridyl group is protonated to lose its coordination ability, and the carboxylate group is not bonded to Cu(I) either (Scheme 1). H-bonds among carboxyl groups as well as between the H−N atoms of the pyridyl ring and terminal Cl−ligands gave 3-D networks of these stable Cu(I)−olefin complexes 1−3. Herein we report


the synthesis, solid-state structures, and electrochemical properties of 1−3.

Results and Discussion

Compounds 1−3 were prepared respectively by hydrothermal reactions of CuCl with 2-, 3-, and 4-HPYA in the presence of 1 N HCl after the mixtures were irradiated by UV at 230 nm for 1 week. The olefinic \( \pi-\pi \) double bond may be activated under UV irradiation so that the reaction of olefin with Cu(I) easily took place because without UV irradiation; the same reaction under hydrothermal reaction conditions was not observed. Probably the hydrothermal reactions can also lead to good crystallization. In comparison to the IR spectra of free ligands, 1−3 show a peak at 1720−1690 cm\(^{-1} \), and the carboxyl groups of 2−3, and 4-HPYA in 1−3 are uncoordinated \(-\text{COOH} \) groups. 1−3 were found highly thermally stable, as the TGA of the polycrystalline 1−3 showed no weight loss before ca. 232, 183, and 168 °C, respectively. EPR spectra of single-crystal samples of 1−3 are silent, indicating that the oxidation state of the Cu atoms in 1−3 is +1.

The X-ray crystal analysis of compound 1 (Figure 1a) revealed that the Cu(I) ion in 1 is coordinated in a distorted tetrahedral geometry defined by two bridging \( \mu_2-\text{Cl} \) ligands, one terminal \( \text{Cl}^- \) ligand, and the \( \text{C}==\text{C} \) moiety in 2-HPYA. Interestingly, the pyridyl group is protonated to lose its coordinating ability, and the carboxylate groups are uncoordinated as well. The carboxylate groups are H-bonded (O−H•••Cl, 3.107 Å) as well as between the protonated N atom and terminal Cl\(^-\) ligand (N−H•••Cl, 3.361 Å), as shown in Figure 2b, to give a 3-D network in 2 (Figure S2; see Supporting Information).

Similar to the structures of 1 and 2, the local geometry of the Cu atom in 3 can be best described as a distorted tetrahedron with two \( \mu_2\) bridging Cl\(^-\) ligands, one terminal Cl\(^-\) ligand, and one olefin moiety. The H-bonds in 3 are similar to those in 1. Strong H-bonds (O−H•••O, 2.639 Å) between carboxylate groups (Figure 3b) as well as between the protonated N atom and terminal Cl\(^-\) ligand (N−H•••Cl, 3.405 Å) give a 3-D network in 3 (Figure S3; see Supporting Information).

The coordination mode of the carboxylate group in 1−3 is quite different from those of the Cu(I)−olefin coordination polymers found in [(3-PYA)Cu_2(N)]_n (4), [(2-PYA)Cu]_nH_2O)]_n (5), and [Cu_2(O_2CCCH=CHCO_2)]_n (6)\(^{[3]} \) in which the carboxylate groups of 4 and 5, in a syn−syn bidentate bridging mode, link two Cu atoms to form a chair-like eight-membered ring while the carboxylate groups of fumaric acid act as tridentate ligands to link three Cu(I) atoms. The coordination mode of the carboxylate group in 1−3 is however similar to those found in [(2,2′-bpy)(4-HPYA)-
or 2-D coordination polymers. It is noteworthy that the stable and 
4 
(Ł[1.359(7) Å], 6,7
interactions of adjacent two pyridyl rings are normal and lie within the 
carbonylic acid dimer was created via H-bonds. The Cu
(2.092 Å) in
three pyridyl groups in 1–3 are protonated and are not coordinated to Cu(I), while these pyridyl groups in 4, 5, 
and 7–9 coordinated to Cu(I), resulting in the formation 1-D or 2-D coordination polymers. It is noteworthy that the stable Cu(I)–olefin coordination polymers 1–9 form similar 3-D networks through H-bonds except that there are weak stabilizing \( \pi-\pi \) interactions of adjacent pyridyl rings in 4 and 5.3b

The C–C bond distances (1.372–1.375 Å) of the coordinated olefin moiety in 1–3 are slightly longer than those found in 
[Cu(2,2'-bipy)(C\(_2\)H\(_4\))]ClO\(_4\) [1.360(13)–1.346(18) Å],3c [Cu(phen)(C\(_2\)H\(_4\))]ClO\(_4\) [1.361(22) Å],3c [Cu\(_2\)(HB(3,5-Me\(_2\)PZ\(_2\))\(_2\))(C\(_2\)H\(_4\))]Cl [1.347(5) Å],6,7 [Cu\(_3\)(C\(_2\)H\(_4\))\(_2\)(dipyrindylamine) [1.359(7) Å],6,7 [Cu\(_4\)(C\(_2\)H\(_4\))\(_2\)(dipyrindylamine) [1.362(6) Å],8 [Cu(HB(3,5-Me\(_2\)PZ\(_2\))\(_2\))(C\(_2\)H\(_4\)])

\[1.329(9)\ Å]6,8 [Cu\(_2\)(COT)\(_2\)(hfacac)\(_2\)] [1.31(1)–1.33(1) Å],9

7 [1.361(6) Å],9b 8 [1.359(12) Å],9b and [Cu(S,S)-L(1-butene-3-ol)][L=(1,5,25)-N, N′-bis(mesitylmethyl)-1,2-diphenyl-1,2-ethanediamine, 1.36(1) Å]b but are comparable to that in 9 [1.375(5) Å]9b and 4 [1.367(7) Å].9b The lengthening of the C–C double bond may be typical of ethylene ligands that are \( \eta^2 \)-bonded to low-valent electron-rich transition metals. Moreover, the Cu–Cl
terminal and Cu–Cl\(_b\) (2.272–2.572 and 2.236–2.320 Å) bond lengths in 1–3 are normal and lie within the distances expected for Cu(I) complexes. The Cu–C bond distances (2.059–2.092 Å) in 1–3 are comparable to those found in other reported Cu(I) organometallic compounds.

As seen from Figure 4, the cyclic voltammograms of CuCl, 

\([2(\text{H}_{3}PYA)_{2}]\text{Cu}_{3}\text{Cl}_{6}(\text{I})\) \((1)\), [(3-H\(_2\)PYA)\(_2\)Cu\(_2\)Cl\(_4\)] \((2)\), and 

\(4(3)-\text{H}_{3}PYA)_{2}\text{Cu}_{2}\text{Cl}_{4}\) \((3)\) complexes displayed one oxidation peak and a similar cathodic wave in the sweep range of +300 mV to –1100 mV. Their anodic peak potentials were –308, –300, –290, and –278 mV at 100 mVs, respectively. No peak was observable in the solution of ligand, suggesting
that the anodic peaks were attributed to the oxidation of metal centers in complexes. The single oxidation peak indicated that two metal centers in complexes were in the same local coordination geometry. The cathodic peaks came from the reduction of Cu(I) centers to Cu. There are two metal centers in one complex molecule of 1–3; the peak current of CuCl was larger than those of 1–3 at the same Cu mole number. More positive anodic peak potentials and lower peak currents of 1–3 than those of CuCl are a result of the Cu(I) centers by the H2PYA+ ligands. The decrease in anodic peak current was due to the smaller diffusion coefficient of these complexes. The resulting difference between the peak potentials of the three complexes may be due to different steady constants which is similar to that found in [CuBr3(TTT)2]n and [CuBr6(TTT)2]n [TTT = triallyl-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione].

Experimental Section

Preparation of 1. CuCl (1 mmol) and 2-HPYA (1 mmol) were placed in a thick Pyrex tube (ca. 20 cm in length). After addition of 0.3 mL of 4 N HCl, the tube was frozen with liquid N2, evacuated under vacuum, and sealed with a torch. The tube was irradiated at 200 °C for 15 min. The electrodes were used for electrochemical experiments in the deaerated acetonitrile solutions by purging with pure nitrogen for 10 min. The working electrodes were comprising a saturated calomel electrode (SCE) as reference, a platinum disk working electrode. The working electrodes were pre-cycling 494.48(11) Å3, 995.86(16) Å3, Z = 2, T = 293(2) K, ρcalc = 1.896 g cm−3, Mo Kα radiation (λ = 0.71073 Å), μ = 2.695 mm−1, Rf = 0.0345, wR2 = 0.0812 for 2563 observed reflections from 3485 independent reflections, GOF = 1.278.

Crystal data for 2: C13H16Cl2CuNO2, Mw = 284.59, monoclinic, space group P21/n, a = 9.8845(9) Å, b = 9.6189(9) Å, c = 10.9299(10) Å, β = 106.604(2)°, V = 995.86(16) Å3, Z = 4, T = 293(2) K, ρcalc = 1.898 g cm−3, Mo Kα radiation (λ = 0.71073 Å), μ = 2.698 mm−1, Rf = 0.0334, wR2 = 0.0812 for 1468 observed reflections from 1758 independent reflections, GOF = 1.024.

Crystal data for 3: C13H16Cl2CuNO2, Mw = 284.59, triclinic, space group P1 (No. 2), a = 7.21079(11) Å, b = 8.5682(11) Å, c = 8.7294(11) Å, α = 76.57(3)°, β = 79.859(3)°, γ = 71.527(2)°, V = 494.48(11) Å3, Z = 2, T = 293(2) K, ρcalc = 1.911 g cm−3, Mo Kα radiation (λ = 0.71073 Å), μ = 2.711 mm−1, Rf = 0.0375, wR2 = 0.0676 for 2159 observed reflections from 3476 independent reflections, GOF = 0.730.

Electrochemical Properties of 1–3. Electrochemical studies were performed with a BAS 100 B electrochemical analyzer (Bioanalytical Systems Inc.) using a standard three-electrode system comprising a saturated calomel electrode (SCE) as reference, a platinum wire as auxiliary electrode, and a platinum disk (1.0 mm diameter) as working electrode. The working electrodes were polished to a mirrorlike surface with 0.3 and 0.05 µm alumina slurry on microcloth pads (Buehler), rinsed with water and ethanol, and sonicated in twice-distilled water. After being dried in heated air, the electrodes were used for electrochemical experiments in the deaerated acetonitrile solutions by purging with pure nitrogen for 15 min.

Acknowledgment. This work was supported by The Mayor State Basic Research Development Program (Grant No. G2000077500), the Distinguished Young Scholar Fund from NSFC (Nos. 20025103 and No. 20028101), the National Natural Science Foundation of China, EYPF of MOE, P.R.C. BK2003204 (Jiangsu, P. R. China), and the National Science Foundation of the U.S.

Supporting Information Available: Crystallographic CIF files (excluding structure factors) for 1–3 and an additional figure. This material is available free of charge via the Internet at http://pubs.acs.org.