



Two novel olefin-copper(I) coordination polymers with DHDAB as building blocks



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ABSTRACT

As stable organometallic moieties, olefin-copper(I) coordination polymers are of interesting properties. In this study, bioactive benzo[d]imidazol derivative 2,2'-(1,2-dihydroxyethane-1,2-diyl) bis(1,3-diallyl-3H-benzo[d]imidazol-1-ium) bromide (DHDAB) and CuCl reacted at different temperatures under hydrothermal reaction condition to afford two olefin-Cu(I) coordination polymers with novel structural features, a 3D [(DHDAB)Cu₆Br₄Cl₄]_n frame network and a 1D [(DHDAB)Cu₂Cl₄]_n infinite chain, respectively. The dielectric constants were measured at different frequencies with temperature variation.

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Introduction

Molecular architecture and self-assembly of coordination polymers have attracted much attention in coordination and organometallic chemistry in recent years [1–5], among which olefin-copper(I) complexes play important roles in biochemistry and modern organic chemistry and are employed as active species in copper catalysis [6]. In the past few years, synthesis of highly stable olefin-Cu(I) coordination polymers has been highlighted [7–11].

Benzo[d]imidazol and its analog, as active components *in vivo*, play crucial roles in biological metabolism [12]. Possessing two or more coordination sites, the above compounds are also popular among coordination chemists. Williams et al. [13] reported some polynuclear copper complexes with 1,2-bis(benzimidazol-2-yl)-1,2-ethanediol and its *N*-methylated analog as building blocks, all of which contained a planar Cu₂O₂ lozenge as a central element and in which the bridging oxygen belonged to an alkoxy group of the ligand. However, *N*-allylated compound of 1,2-bis(benzimidazol-2-yl)-1,2-ethanediol has never been employed for coordination hitherto. In order to investigate the bond formation between olefin and cuprous ion, a new ligand containing olefin functional group was designed and synthesized as a continuation of our project. The ligand 2,2'-(1,2-dihydroxyethane-1,2-diyl) bis(1,3-diallyl-3H-ben-

[d]imidazol-1-ium) bromide (DHDAB) was prepared by *Phillips condensation* of *L*-tartaric acid with 1,2-diaminobenzene in hydrochloric acid, followed by *N*-allylation with allyl bromide in the presence of sodium hydride. Under hydrothermal reaction conditions, DHDAB reacted with CuCl in methanol and water at different temperatures to afford two olefin-Cu(I) coordination polymers with novel structural features, a 3D complex (**1**) and a 1D complex (**2**), respectively, and the dielectric constants were measured at different frequencies with temperature variation.

Experimental section

Materials and physical measurement

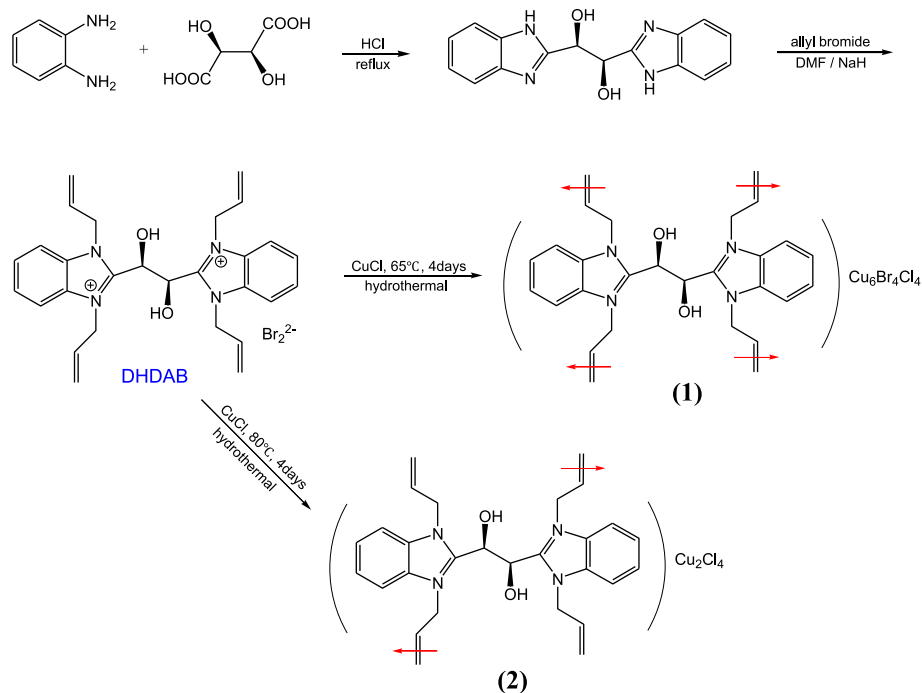
DHDAB was prepared as described in Scheme 1. Other reagents were obtained from commercial sources and used without further purification. Mass spectrum was measured on a Finnigan LCQTM spectrometer. FT-IR spectra were recorded on a Bruker VECTOR-22 spectrometer. Elemental analysis was determined by Elementar Vario EL III analyzer. Dielectric constant was measured using an automatic impedance Tonghui-2828 Analyzer with frequencies of 10 kHz, 90 kHz and 1 MHz, and pellet sample was made at 8 MPa.

Synthesis of DHDAB

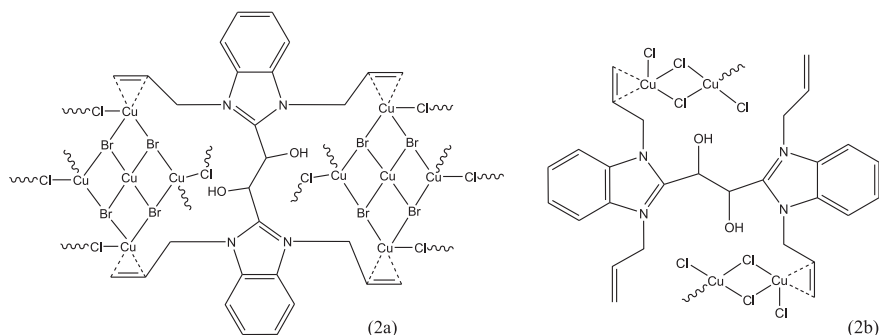
1,2-Di(1H-benzo[d]imidazol-2-yl) ethane-1,2-diol was prepared according to the literature [14] with modification. 2-aminoaniline

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Scheme 1. Synthesis of DHDAB and hydrothermal synthesis of complex **1** and **2**.



Scheme 2. The coordination details of complex **1** and **2** (2a and 2b).

(6.48 g, 60.0 mol) was dissolved in hydrochloric acid aqueous solution (30 mL, 4 mol/L) under stirring, and then *L*-tartaric acid (4.35 g, 29.0 mol) was added. The mixture was heated slowly to 120 °C and kept for 12 h. The reaction mixture was cooled to room temperature, and then poured into ice water (200 mL) under stirring. The resultant solution was adjusted to pH 10 with ammonia water (28%). The precipitate was collected by suction filtration, washed with water, and recrystallized from ethyl acetate, giving 5.65 g 1,2-di(1*H*-benzo[*d*]imidazol-2-yl)ethane-1,2-diol as pale pink crystalline powders in 66.2% yield. This product was sufficiently pure for further work.

1,2-Di(1*H*-benzo[*d*]imidazol-2-yl)ethane-1,2-diol (2.0 g, 6.7 mmol) was added to a 100 mL round bottom flask with dried DMF (50 mL). Sodium hydride (0.70 g, 29.1 mmol) was added in portion to the mixture under stirring. The above solution was stirred at 5 °C for 10 min, and then a solution of allyl bromide (3.4 g, 28.0 mmol) and dried DMF (10 mL) was added dropwise to the mixture. The reaction mixture was stirred at this temperature for 12 h, and then poured into ice-cold water (200 mL) with vigorous stirring for another 1 h. The precipitate was collected by suction filtration, washed with water adequately, and recrystallized from

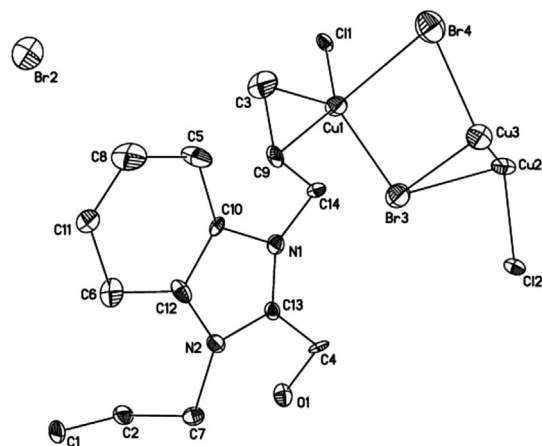


Fig. 1. ORTEP view of asymmetric unit in complex **1** showing 30% probability displacement ellipsoids. H atoms are omitted for clarity. The distances between coordinated C=C bond and Cu1, Cu2 are 1.9764 Å and 1.9735 Å, respectively.

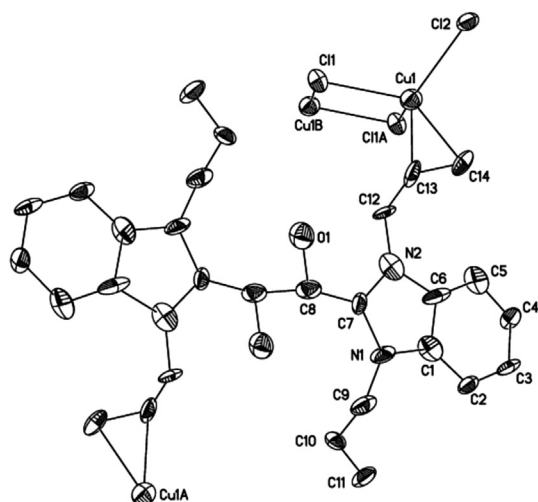


Fig. 2. ORTEP view of local coordination environment in complex **2** showing 30% probability displacement ellipsoids. H atoms are omitted for clarity. The distance between Cu and coordinated C=C bond is 2.0003 Å.

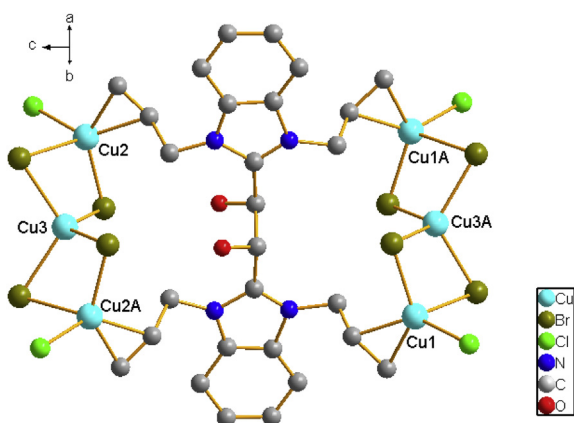


Fig. 3. A coordination environment perspective view of complex **1**. The two dissociative Br anions and H atoms have been omitted for clarity.

ethyl acetate, affording DHDAB (2.11 g) as yellowish crystalline powders in 51.3% yield.

Hydrothermal preparation of complex **1** and **2**

DHDAB (0.1 mmol) and CuCl (0.3 mmol) were placed in a thick-walled Pyrex tube. After addition of redistilled methanol (1.2 mL)

and water (0.2 mL), the tube was frozen with liquid N₂, then evacuated under vacuum and sealed with a torch. The tube was heated at 65 °C under hydrothermal reaction conditions for 4 days to furnish a pale yellow block crystal (**1**) with the yield of 35% based on DHDAB.

Using the same procedure with CuCl at 80 °C under hydrothermal reaction conditions for 4 days, a pale yellow block crystal (**2**) was produced with the yield of 30% based on DHDAB.

X-ray crystallography

The coordination details and molecular structures with atomic numbering schemes of complexes **1** and **2** are shown in Scheme 2, Figs. 1 and 2. A fine crystal was selected for structure determination on a Bruker SMART CCD diffractometer with graphite monochromatized MoK α ($\lambda = 0.71073$ Å) at 293(2) and 291(2) K, respectively. The crystal structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELXTL 97 program package.

Results and discussion

IR spectra

IR spectra of complexes **1** and **2** both show two weak peaks at 3005 cm⁻¹ (ν_{C-H}) and ca. 1610 cm⁻¹ ($\nu_{C=C}$). Compared with that of free ligand DHDAB (1642 cm⁻¹), the infrared absorption bathochromically shifts due to the formation of coordination bonds between olefin moieties and copper(I) ions, thus weakening C=C π -bond in olefin-Cu(I) complexes. This fact is consistent with the Dewar-Chatt-Duncanson structural motif [15].

Crystal structures

X-ray crystal analysis of complex **1** reveals that there are three different coordination environments for copper atoms in its crystal structure. Cu(1) and Cu(2) are coordinated in two distorted tetrahedral geometries, each of which is defined by two μ_3 -Br atoms, one μ_2 -Cl atom and the olefinic C=C group of DHDAB. The Cu(3) center is bound to four μ_3 -Br atoms with a tetrahedron coordination geometry, while each Br atom acts as a μ_3 -linker to bridge two Cu atoms [Cu(1), Cu(2)]. Thus, DHDAB acts as a four-dentate spacer, in which the four olefinic C=C moieties of the ligand molecule take part in the coordination with four Cu(I) atoms, while the Br atoms also bridge three Cu atoms. At the same time, μ_2 -Cl atoms play important roles in the structure which is completed by bridging of the olefinic C=C moieties with the adjacent Cu atom, forming a 3D coordination polymer (Fig. 3).

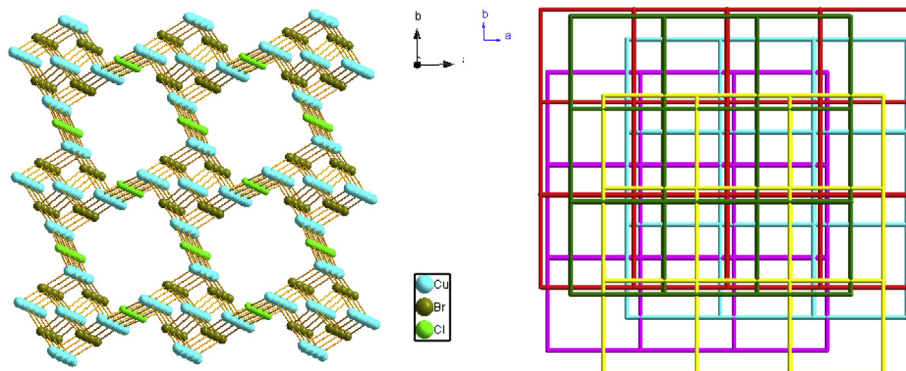


Fig. 4. Schematic view of the fivefold parallel interpenetrating [Cu₅Br₄]_n networks in **1**, each of which has the (6,4) topology. For clarity, the cluster Cu₂Br₄Cl bridging units are represented by a single line.

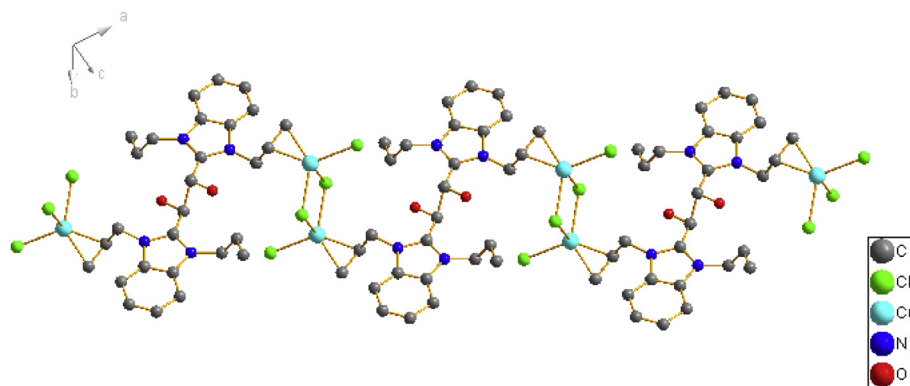


Fig. 5. An extending 1D infinite chain representation along certain direction of complex **2** through Cu_2Cl_4 cluster as connecting node between DHDAB molecules.

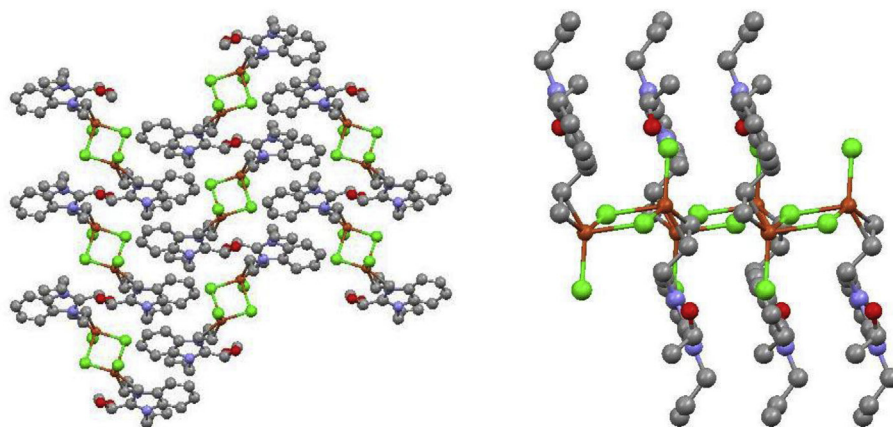


Fig. 6. π - π stacking plots along *a*- and *b*-axis for complex **2**, respectively.

Obviously, two dissociative bromide anions balance the charge of complex **1**.

Complex **1** crystallizes in space group $P4_2/m$. The lengths of two coordinated C=C bond [1.3996(56)Å] from four allyl groups in the ligand are equal. By representing the bridging units of $\text{Cu}_2\text{Br}_4\text{Cl}$ cluster with a single line and simplifying DHDAB as a rectangle geometry, a (6,4) topology for complex **1** is given in Fig. 4, which has the fivefold parallel interpenetrating $[\text{Cu}_5\text{Br}_4]_n$ frame networks.

Compared with olefin-Cu(I) complex **1**, only two olefinic C=C groups bind copper center in each side of DHDAB in complex **2**. The X-ray crystal structure determination result of complex **2** shows that each cuprous ion is coordinated in a distorted tetrahedral geometry, which is defined by two bridging μ_2 -Cl atoms, one terminal chloride atom and the olefinic C=C moiety. Thus, DHDAB acts as a bidentate spacer to link Cu_2Cl_4 units, forming a 1D infinite chain as shown in Fig. 5. Stable 3D networks form due to the π - π stacking interactions between neighboring strands (Figs. 6 and 7). Compared with the uncoordinated olefin moiety [1.3835(80) Å], the C-C bond distance between C13 and C14 [1.3329(85) Å] of the coordinated olefin moiety in **2** is slightly shorter than those found (1.374 Å) [16], and the distance between Cu and coordinated C=C bond in **2** is 2.0030 Å. Moreover, the bond lengths of Cu1-Cl1 [2.4532(26)] and Cu1-Cl1A [2.6143(29) Å] are comparable to those found in olefin-Cu(I) complexes (2.24–2.48 Å), whereas the Cu-Cl_{terminal} bond [2.4381(29)Å] is longer than that reported previously (2.2635 Å) [8,17].

The crystal data analysis of complex **2** indicates that four atoms [Cl(1), Cu(1), Cu(1B), Cl(1A)] fall in the same plane and form a parallelogram geometry. The angles of Cl1-Cu1-Cl1a and

Cu1-Cl1a-Cu1b are $82.508(56)^\circ$ and $97.492(59)^\circ$ respectively. Furthermore, the distances of Cu-C bond (2.077–2.144 Å) lie within normal ranges found in corresponding Cu-C (olefin) coordination polymers.

Dielectric constants

The permittivities ($\epsilon = \epsilon_1 - i\epsilon_2$, in which ϵ_1 and ϵ_2 are respectively the corresponding real and imaginary parts of dielectric constant [18], dielectric dissipation factor $D = \tan\delta = \epsilon_2/\epsilon_1$) of

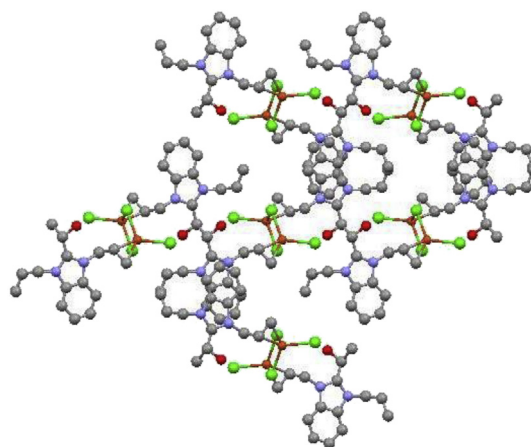


Fig. 7. π - π stacking plots along *c*-axis for complex **2**.

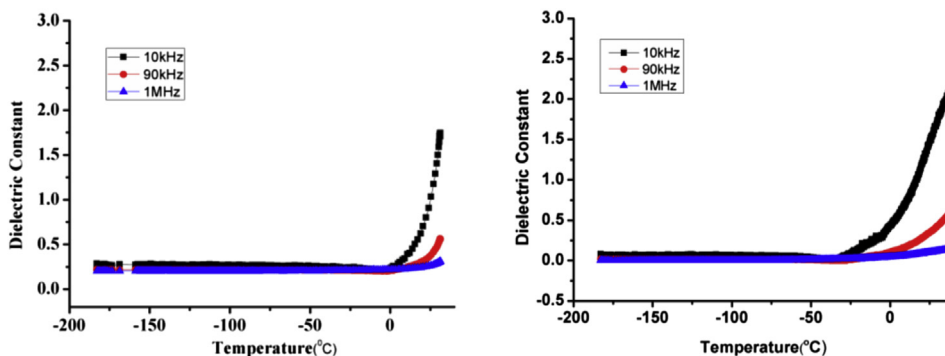


Fig. 8. Dielectric constants of complex **1** (left) and **2** (right).

powdered samples of **1** and **2** in the form of pellets were measured. As shown in Fig. 8, ϵ_1 gradually increases with rising temperature (-180 – 30 °C). In addition, as the frequency increases from $10^4 \rightarrow 9 \times 10^4 \rightarrow 10^6$ Hz, the dielectric constant gradually decreases. At 1 MHz, ϵ_1 changes less evidently than that at 10 kHz does in the measured temperature range, being consistent with the low dielectric dissipation (ϵ_2/ϵ_1) behavior at higher frequencies. However, at higher frequencies, the dipole reversal cannot keep up with the frequency change of alternating electric field, so the ϵ_1 gradually reduces with increasing frequency and remains unchanged at higher frequencies.

The density of complex **1** (2.353) is slightly larger than that of complex **2** (1.610). According to the *Clausius-Mossotti* equation [19], dielectric constant is proportional to the density of complex, to which the permittivity test results at different frequencies with temperature variation conform. The permittivity behaviors of complex **1** and **2** are normal and in terms of the overall structures.

Conclusion

In summary, the facile hydrothermal synthesis provides organometallic compounds with unique properties that are not readily accessible in solution. By introducing a flexible organic component, two stable coordination polymers, a three-dimension and a one-dimension olefin-Cu(I) complex based on DHDAB were synthesized under hydrothermal reaction condition and structurally characterized. The permittivity test results at different frequencies with temperature variation conform with the *Clausius-Mossotti* equation.

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Appendix A. Supplementary material

CCDC 1030004 and 1030005 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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