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Color difference caused by chirality

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ABSTRACT

Synthesis, crystal structure and spectra properties of enantiopure and corresponding racemic Cu(II)-dipyridine amido complexes are reported. The different coordination styles result in the unexpected chiral-unrelated color changes between chiral and racemic complexes.

Enantiopure compounds are of central importance in many domains of chemistry. Compared with organic compounds, chirality in coordination compounds has received relatively fewer attention. [1] In recent times, interest in inorganic stereochemistry has rised rapidly partially due to the stereochemically well-defined building blocks for the assembly of supramolecular structures, a field that has found great interest in coordination chemistry. Many examples exist where molecular chirality is used to influence the supramolecular stereochemistry of containers, helical fibers, micelles, bilayers, and crystals. [2] For example, molecular chirality on the packing style of supramolecular systems affects the thermodynamic properties, and some chiral-related optical properties such as circular dichroism (CD), circularly polarised luminescence (CPL), optical rotation, chiroptical switching processes, and magneto-chiral effects. [3] However, the effects of molecular chirality on the chiral-unrelated properties of supramolecular systems, such as electronic absorption spectra, are rarely observed. [4] We report herein the synthesis, crystal structure and spectra properties of enantiopure and corresponding racemic Cu complexes, which shows quite different colors caused by different coordination styles.

Started from 2-methyl-pyridine and 1,2-diaminocyclohexane, the ligand 1,2-[bis(6′-pyridine-2′-carboxamido)-ethane]cyclohexane **2** was synthesized according to our previous studies as shown in Scheme 1. [5,6] The corresponding copper(II) complexes **1** were then obtained by the reaction of the ligand **2** and copper acetate in ethanol. [7] Dependent on different chirality of the starting materials, i.e. (*R*,*R*), (*S*,*S*), and *racemic*-1,2-diaminocyclohexane, the corresponding complexes **1** were obtained as red, red and purple crystals as shown in Fig. 1. Mixing the solution of (*R*,*R*) and (*S*,*S*)-**1** in the molar ratio of 1:1, and then crystallizing or simply removing the solvent, the purple solid appeared, showing the formation of the *racemic*-**1**.

The new complexes **1** are generally air- and moisture-stable. They are characterized by MS, IR, elemental analysis, UV–vis absorption spectra in solution and UV–vis solid reflection spectra. The single crystal structures of complexes **1** have been determined. The infrared spectra of the complexes display, in general, a large number of intense peaks in the range of 1600–600 $\mathrm{cm^{-1}}$. Disappearance of N–H stretching bands (3318 $\mathrm{cm^{-1}}$) in IR spectra supports the formation of Cu(II) complexes.

Enantiopure solid differs from racemic solid in the solid UV–vis reflection spectra mainly in the long-wavelength region (see supporting information, Fig. S3). (*R*,*R*)-1 and (*S*,*S*)-1 reflect much more ratio of visible light above 550 nm than *racemic*-**1**.

Spectroscopic and computational studies at the molecular level have been carried out to figure out the reason of the color difference. As expected, UV–vis absorption profiles of (*R*,*R*)**-1**, (*S*,*S*)**-1** and *racemic*-**1** solutions are not distinguishable from each other. Considerable broadening absorption bands at 400–600 nm are due to the excitation of metal and O=C–N to bipyridine group charge transfer (see supporting information, Fig. S5). In this region, the calculated spectrum of (*R*,*R*)**-1** shows two peaks at 532.8 and 530.8 nm with the oscillator strengths of 0.0002 and 0.0027, respectively (see supporting information, Fig. S4 and Table S1), which indicates strong $^{*}\rightarrow$ LUMO-1 character. An analysis of the relative orbitals (Fig. S5) clearly shows that those excitations correspond to an electron transfer from the metal and O=C–N to the bipyridine ligands.

The (*R*,*R*)**-1** and (*S*,*S*)**-1** exhibit converse CD signals in the UV/vis region as shown in Fig. 2. To investigate insightfully the relationship

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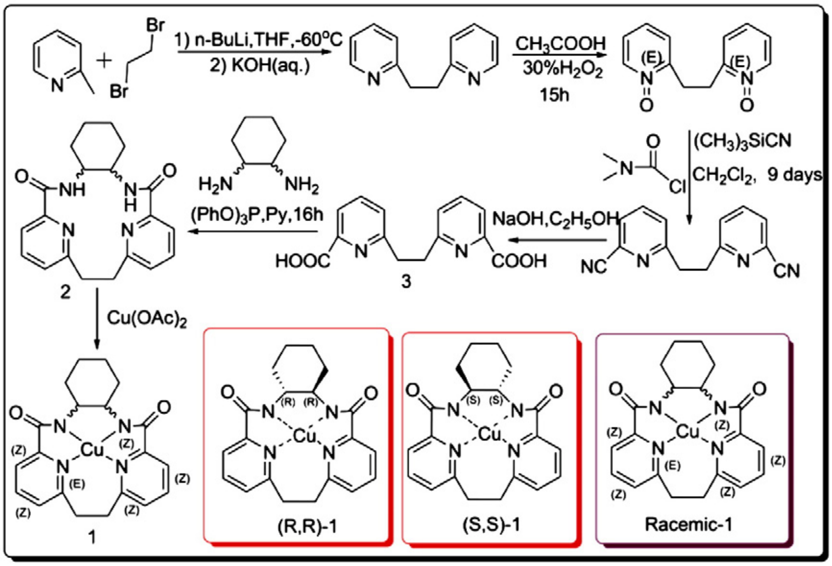

Scheme 1. Synthetic routine of ligand **2** and complexes **1**.

between observed CD spectrum and molecular geometry, rotatory strengths for the optimized structure of (*R,R*)**-1** are calculated at the B3LYP/6-31G(d) level. The results suggest the main features in the CD spectra observed are well matched by the computations for the (*R,R*)**-1**. For examples, positive and negative CD signals are predicted to be 531 and 352 nm respectively, which are in accordance with the observed positive and negative CD at 534 and 350 nm.

The reason of different color between homochiral and racemic solid complexes is assumed from the different crystal structures (Fig. 3). As shown in Fig. 4 and Table 1, apical Cu–O bonds are found only in the *racemic*-**1**. The Cu–N coordination bond lengths in the equatorial square plane are 1.917–2.033 Å for *racemic*-**1**, similar to the literature data, [8] but a little longer than that for optically active (*R,R*)-**1**(1.901–2.011 Å), manifesting a little looser of the coordination between Cu and the ligand in *racemic*-**1**. The difference also exists in the distortion angles of the equatorial square plane. N3 deviates off the N(1)–N(4)–Cu(1) plane about 164.2(5) ^{O} for *racemic*-**1**, significantly more than that for (*R,R*)-**1** (179.3(1)^{O}). Looser coordination of Cu-ligand and more distorted Cu centered plane are adopted for the *racemic*-**1** to make it possible to form an intermolecular apical coordination bond. The distance of Cu(1)–O(1) in *racemic*-**1** was elongated to 2.45(1) Å, as shown in Fig. 4, longer than the typical intramolecular Cu–O planar bond length around 1.95 Å, [8,9] but similar to Cu–O apical bond distances around 2.3 Å and some intermolecular Cu–O bond lengths around 2.373 and 2.858 Å. [10] Meanwhile, in the case of (*R,R*)-**1**, the distance of Cu–O atoms (3.19 (5) Å) seems to be too long to form effective bond. As a result, the copper ion adopts a square pyramidal 5-coordinated style in *racemic*-**1** while a square 4-coordinated style in the homochiral (*R,R*)-**1**. Different coordination environment in crystal results in a considerable difference in the energy levels of the electronic structure, and consequently the disparity in the energy absorption to lift the electrons through *d–d* transition.

On the crystallographic aspect, it is the steric hindrance of molecular structure that induces the different patterns of molecular packing between *racemic* and homochiral **1**. The molecules exist in a distorted plane, sharing nearly the same dihedral angles C(12)–C(13)–C(14)–C(15) around 110° both in the racemic and homochiral assemblies. The homochiral molecules distort unidirectionally and the repulsion in between each other set the Cu and O atoms apart from each other for at least 3.19(5) Å, much longer than the sum of their ionic radii. While in the case of racemic molecular packing, the (*R,R*) and (*S,S*)-molecules distort in the opposite direction, (dihedral angles C(12)–C(13)–C(14)–C(15) are 108.1(3)° for (*R,R*)-molecules and −108.1(3)° for (*S,S*)-molecules, respectively), which allows a couple of molecules with the mirror handness packing much closer than they could with the same chirality, thus make it possible for the Cu and O atoms to be close enough to form bonds.

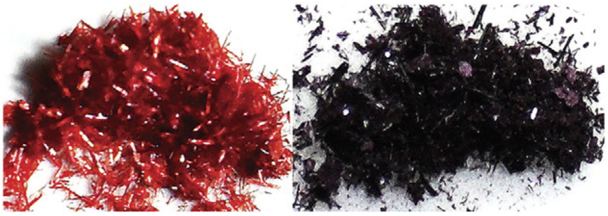

Fig. 1. The different crystal colors of (*R,R*)-**1,** (*S,S*)-**1**(red) and *racemic*-**1** (purple).

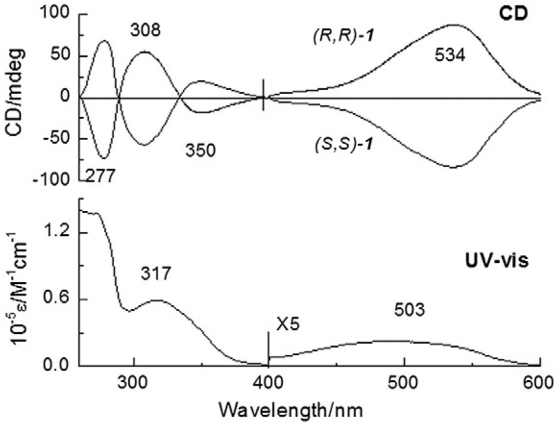

Fig. 2. CD spectra (up) and UV–vis absorption spectrum (bottom) of the (*R,R*)-**1** in CH_2Cl_2.

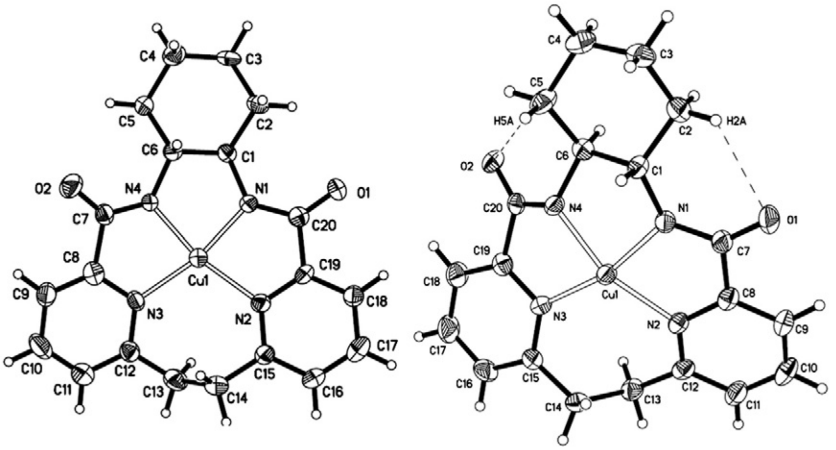

Fig. 3. Crystal structures of (*R,R*)-**1** (left) and the (*R,R*) part of *racemic*-**1**(right).

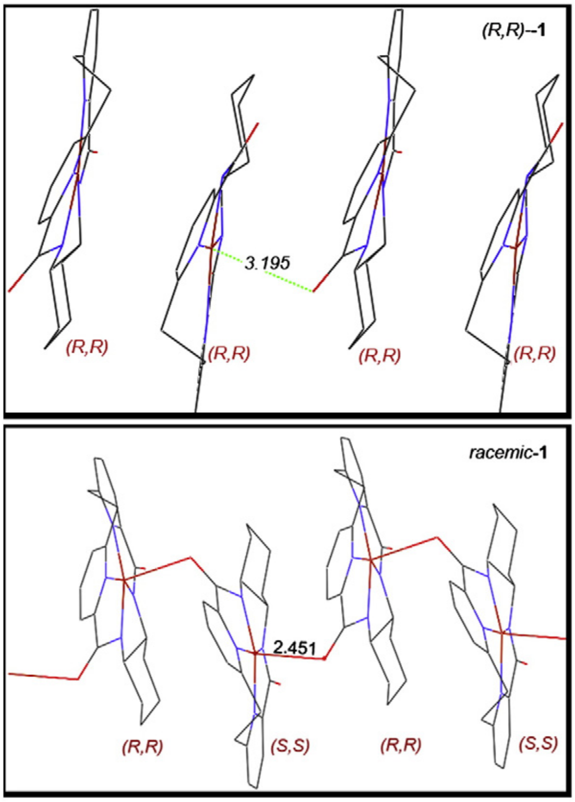

Fig. 4. Crystal packing drawing of (*R,R*)-**1** (up) and *racemic*-**1** (bottom).

Table 1
Selected bond lengths [Å] and torsion angles [°].

	R,R-**1**	*Racemic*-**1**
Cu(1)–N(1)	1.909(3)	1.917(2)
Cu(1)–N(4)	1.919(3)	1.941(2)
Cu(1)–N(3)	1.978(3)	1.991(2)
Cu(1)–N(2)	2.011(3)	2.033(2)
O(1)–C(20)	1.236(5)	1.235(4)
O(2)–C(7)	1.241(5)	1.261(3)
O(1)–Cu(1)[a]	3.19(5)	2.45(1)
N(1)–N(4)–Cu(1)–N(3)	179.3(1)	164.2(5)
N(1)–N(4)–Cu(1)–N(2)	31.8(6)	30.7(0)
C(12)–C(13)–C(14)–C(15)	−109.4(5)	108.1(3)

[a] Intermolecular O(1)–Cu(1).

Another evidence is the different color of chiral and racemic complexes in solvent. For example, both of *racemic*-**1** and homochiral **1** are red in CH_2Cl_2 and purple in methanol, which indicated the possibility of coordination of methanol with central metal. [11]

In conclusion, molecular chirality could not only influence the thermodynamic and chiral-related optical properties, but also influence chiral-unrelated optical properties. Circularly unpolarized visible light could interact in different way with chiral supramolecular system and corresponding racemic one, which caused the color changes between them.

Acknowledgements

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Appendix A. Supplementary material

CCDC 779242–779244 contains the supplementary crystallographic data for (*R,R*)-**1,** *racemic*-**1** and (*S,S*)-**1** respectively. The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax:(+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Additional structural figure, spectrum and computational detail are available as electronic supplementary information in the online version, at doi:10.1016/j.inoche.2010.09.016.

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[6] **Synthesis of 1,2-[bis(6′-pyridine-2′-carboxamido)-ethane]cyclohexane (2)** A solution of 0.114 g (1 mmol) 1,2-diaminocyclohexane in 60 mL dry pyridine was slowly added to a solution of the acid **3** 0.303 g (1 mmol) in 60 mL pyridine. After heating the solution to 50 °C, 0.62 g (2 mmol) triphenylphosphite was added

dropwise with continuous stirring. The temperature was then raised and kept at 100 °C for 9 h, the mixture was cooled down. After removal of pyridine under reduced pressure, the resulting brown oil was dissolved in dichloromethane, washed with water and sodium bicarbonate solution, and then dried over magnesium sulphate. After filtration and removal of solvent, The residue was finally purified by column chromatography on silica gel using hexane-ethyl acetate mixture as eluent(yield 12%). Selected IR data (KBr, cm^{-1}):$v = 3318$ (N-H), 1674 (C=O), 1656 (C–N), 1590, 1547, 1452, 1385. Elemental Anal. Calc. for $C_{20}H_{22}N_4O_2$: C, 68.49; H, 6.28; N, 15.98. Found: C, 68.17; H, 6.37; N, 15.79%. MS (EI): 350.4 (M+). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.52$(m, 2H, $H_{cylcohexane}$), 1.86(m, 4H, $H_{cylcohexane}$), 2.63(m, 2H, $H_{cylcohexane}$), 3.37(m, 4H, $-PyCH_2CH_2Py-$), 3.67(s, 2H, $H_{cylcohexane}$), 7.23(d, $J_1 = 7.6$ Hz, 2H, H_{Py}), 7.67(m, 2H, H_{Py}), 7.81 (d, $J_2 = 7.2$ Hz, 2H, H_{Py}), 8.45(s, 2H, H_{amide})ppm. ^{13}C NMR($CDCl_3$, 100 MHz) δ 166.9, 159.6, 150.1, 137.6, 125.3, 119.3, 56.5, 35.6, 32.3, 25.1 ppm.

[7] **General Synthesis of 1:** A batch of 0.105 g (0.30 mmol) ligand **2** was dissolved in 3 mL hot ethanol and a solution of 0.060 g (0.30 mmol) of $Cu(OAc)_2{\bullet}H_2O$ in 5 mL of ethanol was then added. The color of the mixture turned into purple immediately. After the mixture was refluxed for 3 h, the corresponding copper (II) complex **1** were collected by filtration, washed with ethanol, and dried under vacuum (99 mg, yield 80%). Crystals suitable for X-ray diffraction were grown via diffusion of Et_2O into a CH_3OH/CH_2Cl_2 solution of the complex. (*R,R*)-**1,** Color: red; Selected IR data (KBr, cm^{-1}):$v = 1623.82$ ((*R,R*)-**1**),C=O); Elemental Anal. Calc. for $C_{20}H_{20}N_4O_2Cu$: C, 58.27; H, 4.86; N, 13.60. Found: C, 58.25 ; H, 4.76 ; N, 13.62%. MS (ESI): 411.9 (M+). Crystal data for (*R,R*)-**1**, CCDC 779242, $C_{20}H_{20}N_4O_2Cu$: Orthorhombic, space group $P2_12_12_1$, $M_r = 411.94$, $a = 7.9450(3)$ Å, $b = 19.4403(6)$ Å, $c = 22.5762(7)$Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 3487.0(2)$Å^3, $Z = 8$, $\mu = 1.277\ mm^{-1}$, $D_c = 1.569\ Mg\ m^{-3}$, $F(0\,0\,0) = 1704$, 24700 reflections collected 7910 unique with $R_{int} = 0.1320$; final $R_1 = 0.0642$, $wR_2 = 0.1006$, GOF = 0.945 for all data. *Racemic*-**1,** Color: red; Selected IR data (KBr, cm^{-1}): $v = 1636.92$ (racemic-**1**, C=O); Elemental Anal. Calc. for $C_{20}H_{20}N_4O_2Cu$: C, 58.27; H, 4.86; N, 13.60. Found: C, 58.25 ; H, 4.76 ; N, 13.62 %. MS (ESI): 411.9 (M+). Crystal data for *racemic*-**1**, CCDC 779243, $C_{20}H_{20}N_4O_2Cu$: Orthorhombic, space group Pbca, $M_r = 411.94$, $a = 19.3385(14)$ Å, $b = 8.2962(6)$ Å, $c = 21.9447(17)$Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 3520.7(5)$Å^3, $Z = 8$, $\mu = 1.265\ mm^{-1}$, $D_c = 1.554\ Mg\ m^{-3}$, $F(0\,0\,0) = 1704$, 25327 reflections collected, 4020 unique with $R_{int} = 0.1691$; final $R_1 = 0.0576$, $wR_2 = 0.0993$, GOF = 1.000 for all data. (*S,S*)-**1,** Color: red; Selected IR data (KBr, cm^{-1}):$v = 1623.82$ ((*R,R*)-**1**),C=O); Elemental Anal. Calc. for $C_{20}H_{20}N_4O_2Cu$: C, 58.27; H, 4.86; N, 13.60. Found: C, 58.25 ; H, 4.76 ; N, 13.62 %. MS (ESI): 411.9 (M+). Crystal data for (*S,S*)-**1**, CCDC 779244, are almost the same with (*R,R*)-**1**, CCDC 779242. Data collection was performed on a Rigaku Mercury CCD X-ray diffractometer (Mo *K*a, $\lambda = 0.71073$ Å). The structure has been solved using direct methods using the SHELX97 program package. [12] All non-hydrogen atoms were refined anisotropically. The positions of metal atoms and their first coordination spheres were located from direct-methods E-maps; other non-hydrogen atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles and, during the final cycles, refined anisotropically. Hydrogen atoms were placed in calculated position and refined as riding atoms with a uniform value of U_{iso}.

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