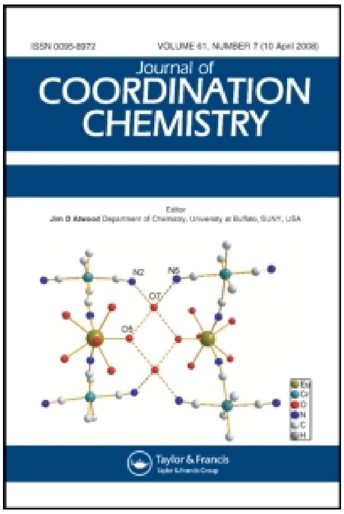

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Synthesis, crystal structure and spectroscopic properties of a chiral cyano-bridged heterobinuclear complex, (4*S*,11*S*)-[Cu(1,7-CT)(μ-CN)Fe(CN)$_4$NO]$\cdot$H$_2$O

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The chiral complex, (4*S*,11*S*)-[Cu(1,7-CT)(μ-CN)Fe(CN)$_4$NO]$\cdot$H$_2$O (1,7-CT = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,7-diene), and its enantiomer have been synthesized by reaction and conglomerate crystallization. They consist of heterobinuclear species in which the Cu and Fe centers are linked by a cyanide bridge and crystalline water. The Cu(II) is coordinated by five N atoms and exhibits a distorted square-pyramidal geometry, in which two hydrogen atoms on secondary amines lie in the inward side of the macrocyclic plane, while on the other moiety the Fe(II) is a slightly distorted octahedral structure. The binuclear molecules are linked through intermolecular O2–H2A···N1 and O2–H2B···N4 hydrogen bonds, forming two different waved chains that oriented the molecules for optical activity. IR spectrum shows the existence of bridging cyanide ligand. In methanol the specific rotations of enantiomers are $\pm 205\,\mathrm{deg}\cdot\mathrm{cm}^2\cdot(10\,\mathrm{g})^{-1}$, the peak positions of their circular dichroism spectra are close to that of their UV-Vis spectra and present up and down symmetric signals.

Keywords: Tetraazamacrocyclic copper(II) complex; Nitroprusside; Heterobinuclear; Racemic conglomerate; Circular dichroism spectra

1. Introduction

The Cu(II) tetraazamacrocyclic complex cation, [Cu(1,7-CT)]$^{2+}$ (1,7-CT = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,7-diene), has two chiral amine nitrogen centers at 4 and 11 positions, exhibiting two diastereoisomeric forms that can interconvert in solution, and can combine with different counterions to form new complexes with multiple ion-packing models [1, 2] and center-bridging structures [3, 4]. In the same complex cation, the change of anion leads to the change of structure and property. The reactions of [Cu(1,7-CT)]$^{2+}$ with CN$^-$ anion [5] and [Cu(CN)$_3$]$^{2-}$ anion [6] can constitute cyano-bridged homobinuclear structures. However, the heterobinuclear complex, especially the chiral heterobinuclear complex derived from [Cu(1,7-CT)]$^{2+}$ is not reported in the literature. Lu *et al.* [7] have obtained a chiral

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Co(III) complex that exhibits spontaneous resolution on crystallization by self-assembly of $[Co(1,7\text{-}CT)]^{3+}$ cation and SCN^- anions, which suggested that the introduction of special anions might provide an effective approach to design chiral complexes. The nitroprusside anion, $[Fe(CN)_5NO]^{2-}$, can serve as a useful counterion for designing heterobimetallic species [8, 9] and can take on various coordination modes [10, 11]. In current work, through the assembly of $[Cu(1,7\text{-}CT)]^{2+}$ cations and $[Fe(CN)_5NO]^{2-}$ anions, we have obtained a mixture of enantiomerically pure crystals of (4*S*,11*S*)-$[Cu(1,7\text{-}CT)\ (\mu\text{-}CN)Fe(CN)_4NO]\cdot H_2O$ (**1**) and its opposite as a racemic conglomerate, and determined the single crystal structure of **1**. The IR spectrum, specific rotations, UV-Vis spectrum and circular dichroism spectra of the title complex and its enantiomer have also been determined and discussed.

2. Experimental

2.1. *Reagents and instruments*

All chemicals obtained commercially were of reagent grade and used without further purification. Elemental analyses for C, H and N were carried out using a VarioEL III analyzer. The crystal structure was determined by a Bruker Smart APEX II CCD X-ray diffractometer. The IR spectra were recorded on a PE FT–IR spectrometer as KBr pellets in the 4000–400 cm^{-1} region. The specific rotation measurement was carried out with a Perkin-Elmer Model 341 Polarimeter at 20°C, $\lambda_D = 589$ nm. The UV-Vis measurements were performed on a PE Lambda 25 UV/Vis spectrometer, using methanol as solvent. The circular dichroism measurements were performed on a JASCO J-810 Circular Dichroism Chiroptical Spectrometer.

2.2. *Synthesis of (4S,11S)-[Cu(1,7-CT)(μ-CN)Fe(CN)$_4$NO]·H$_2$O*

The mononuclear complex $[Cu(1,7\text{-}CT)]I_2\cdot 2.5H_2O$ was prepared as described previously [12]. A solution of $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ (2 mmol, 0.5958 g) in water (10 mL) was added dropwise to a deep purple solution of $[Cu(1,7\text{-}CT)]I_2\cdot 2.5H_2O$ (2 mmol, 1.2864 g) in methanol/water mixture (v/v = 1:1, 40 mL) with continuous stirring at room temperature. The resulting purple solution was filtered, the filtrate was allowed to stand in air for five days, and purple-black crystals were isolated. These crystals were again dissolved in methanol, and water was diffused slowly into the solution. A week later, well-developed blocky single crystals suitable for X-ray diffraction were obtained. Yield: 0.7630 g, 66%. Anal. Calcd for $C_{21}H_{34}CuFeN_{10}O_2$ (%): C, 43.64; H, 5.93; N, 24.24. Found: C, 43.73; H, 5.90; N, 24.08.

2.3. *Crystal structure determination and refinement*

A blocky single crystal with dimensions $0.50 \times 0.30 \times 0.20\ mm^3$ was mounted on the diffractometer equipped with a graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) by using the ϕ–ω scan technique at 273(2) K. A total of 12623 reflections were collected, of which 5154 were independent with $R_{int} = 0.0681$.

Multi-scan absorption correction was applied using SADABS [13]. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 using the SHELXTL-97 program [14, 15]. All of the non-hydrogen atoms were refined anisotropically; all the hydrogen atoms attached to carbon atoms were placed in calculated positions and the water hydrogen atoms and amine hydrogen atoms were determined from a difference Fourier map. The final refinement converged to $R_1 = 0.0289$, $wR_2 = 0.0617$ $[I > 2\sigma(I)]$. A summary of the crystallographic data is provided in table 1. The selected bond lengths and angles are listed in table 2. Hydrogen-bonding interactions are given in table 3.

Table 1. Crystallographic data for **1**.

Empirical formula	$C_{21}H_{34}CuFeN_{10}O_2$
Formula weight	577.97
Temperature (K)	273(2)
Wavelength (Å)	0.71073
Crystal system, space group	Orthorhombic, $P2(1)2(1)2(1)$
Unit cell dimensions (Å, °)	
a	11.4724(3)
b	11.6564(3)
c	19.9381(4)
α	90
β	90
γ	90
Volume (Å^3)	2666.26(11)
Absorption coefficient (mm^{-1})	1.379
θ range (°)	2.02–26.01
Z, calculated density (mg m^{-3})	4, 1.440
$F(000)$	1204
Crystal shape/crystal colour	Block/purple-black
Crystal size (mm^3)	0.50 × 0.30 × 0.20
Reflections collected/unique	12623/5154 [$R_{\text{int}} = 0.0681$]
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	0.964
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0289$, $wR_2 = 0.0617$
R indices (all data)	$R_1 = 0.0335$, $wR_2 = 0.0633$
Absolute structure parameter	0.014(11)
Largest diff. Peak and hole (e Å^{-3})	0.394 and −0.264

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Cu(1)–N(6)	2.305(2)	Fe(1)–C(1)	1.928(3)	C(1)–N(1)	1.143(4)
Cu(1)–N(7)	2.035(2)	Fe(1)–C(2)	1.940(3)	C(2)–N(2)	1.138(4)
Cu(1)–N(8)	1.9876(19)	Fe(1)–C(3)	1.937(3)	C(3)–N(4)	1.142(4)
Cu(1)–N(9)	2.013(2)	Fe(1)–C(4)	1.930(3)	C(4)–N(5)	1.147(4)
Cu(1)–N(10)	1.988(2)	Fe(1)–C(5)	1.949(3)	C(5)–N(6)	1.139(3)
Fe(1)–N(3)	1.644(3)	N(3)–O(1)	1.126(3)		
N(6)–Cu(1)–N(7)	89.82(9)	N(8)–Cu(1)–N(10)	174.19(9)	C(2)–Fe(1)–C(4)	173.40(13)
N(6)–Cu(1)–N(8)	92.98(9)	N(9)–Cu(1)–N(10)	93.87(9)	C(5)–N(6)–Cu(1)	141.3(2)
N(6)–Cu(1)–N(9)	104.71(8)	C(1)–Fe(1)–N(3)	95.97(12)	Fe(1)–C(1)–N(1)	176.9(3)
N(6)–Cu(1)–N(10)	92.77(8)	C(2)–Fe(1)–N(3)	94.12(13)	Fe(1)–C(2)–N(2)	178.2(3)
N(7)–Cu(1)–N(8)	94.08(9)	C(3)–Fe(1)–N(3)	95.56(12)	Fe(1)–C(3)–N(4)	179.2(3)
N(7)–Cu(1)–N(9)	165.48(9)	C(4)–Fe(1)–N(3)	92.41(13)	Fe(1)–C(4)–N(5)	177.3(3)
N(7)–Cu(1)–N(10)	85.17(10)	C(5)–Fe(1)–N(3)	178.58(12)	Fe(1)–C(5)–N(6)	176.9(2)
N(8)–Cu(1)–N(9)	85.41(9)	C(1)–Fe(1)–C(3)	168.37(12)	Fe(1)–N(3)–O(1)	177.0(3)

Table 3. Hydrogen bond lengths (Å) and angles (°) for **1**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
N(9)–H(9)···O(2)^{i}	0.80(2)	2.15(2)	2.937(3)	168(3)
O(2)–H(2B)···N(1)^{ii}	0.82(2)	2.05(2)	2.861(4)	174(3)
O(2)–H(2A)···N(4)^{iii}	0.75(2)	2.16(2)	2.901(4)	172(4)

Symmetry codes: (i) = $-x+1$, $y-1/2$, $-z+1/2$; (ii) = $x-1$, y, z; (iii) = $-x+3/2$, $-y$, $z+1/2$.

3. Results and discussion

3.1. *Crystal structure*

X-ray structure analysis shows that **1** and its enantiomer are chiral and crystallize in space group $P2_12_12_1$ as a racemic conglomerate, consisting of heterobinuclear species in which two secondary amine hydrogens are on the inward side of the macrocycle and uncoordinated water molecules, as shown in figure 1. The Cu(II) is five-coordinate in a distorted square-pyramidal geometry with the four donor N atoms of macrocyclic ligand in the basal plane and one bridging cyanide N atom in the apical position. The in-plane Cu–N distances are not identical, ranging from 1.9876(19) to 2.035(2) Å, revealing a small tetragonal distortion of the CuN_4 plane and exhibiting that the Cu–N bonds to imines are slightly shorter than Cu–N bonds to secondary amines due to the different hybridization of the N atoms. The axial Cu1–N6 bond is elongated, just as in $[Cu(C_{10}H_{24}N_6)Fe(CN)_5NO]\cdot H_2O$ [16], which is 0.299 Å longer than the average in-plane Cu–N distance. The N7–Cu1–N9 and N8–Cu1–N10 angles are 165.48(9)° and 174.19(9)°, respectively. The two five-membered chelate CuN_2C_2 rings are in *gauche* conformations and the two six-membered rings are in twist conformations, the dihedral angle between two mean CuN_2C_2 planes is 23.5°. The $[Fe(CN)_5NO]^{2-}$ anion has a distorted octahedral structure and coordinates to Cu(II) ion through an axial cyanide; the other four radial cyanides constitute the octahedral equatorial plane. The Fe–C bond to the bridging cyanide is longer than Fe–C bonds to the terminal cyanides, and the mean Fe–C distance of 1.937 Å is longer than the Fe–N distance by 0.293 Å. The N=O distance of **1** [1.126(3) Å] and its Fe–N distance [1.644(3) Å] are still close to those of $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ [17] after forming the cyanide bridge. The Fe–N–O and Fe–C–N angles are nearly linear, but all the N–Fe–C angles are larger than 90° and the four equatorial cyanides are bent away from the axial nitrosyl. The bridging cyanide links the Cu(II)-Fe(II) centers in a bent fashion with the C5–N6–Cu1 bond angle of 141.3(2)° that is about 15.72° smaller than the value reported for $[Cu(C_8H_{21}N_5O_2)Fe(CN)_5NO]\cdot 2H_2O$ [18]. The $[Fe(CN)_5NO]^{2-}$ moiety lies obliquely on one side of the CuN_4 coordination plane with the N6–Cu1–N9 angle of 104.71° and the N6–Cu1–N7 angle of 89°.

The packing diagram of **1** reveals that the O2^{i} [symmetry code: (i) $-x+1$, $y-1/2$, $-z+1/2$] atom belonging to water acts as a hydrogen-bond donor to N1^{ii} and N4^{iii} [symmetry codes: (ii) $x-1$, y, z; (iii) $-x+3/2$, $-y$, $z+1/2$] as well as a hydrogen-bond acceptor from N9. The binuclear units of **1** exhibit four kinds of arrangements in crystal structure, which distribute separately in two layers (A) and (B), as shown in figure 2. The layers (A) and (B) are each made up of one-dimensional chains that are constructed by cyanide N atoms and water molecules through O2–H2A···N1 and O2–H2B···N4 hydrogen bonds. These waved chains are held together further through interlayer

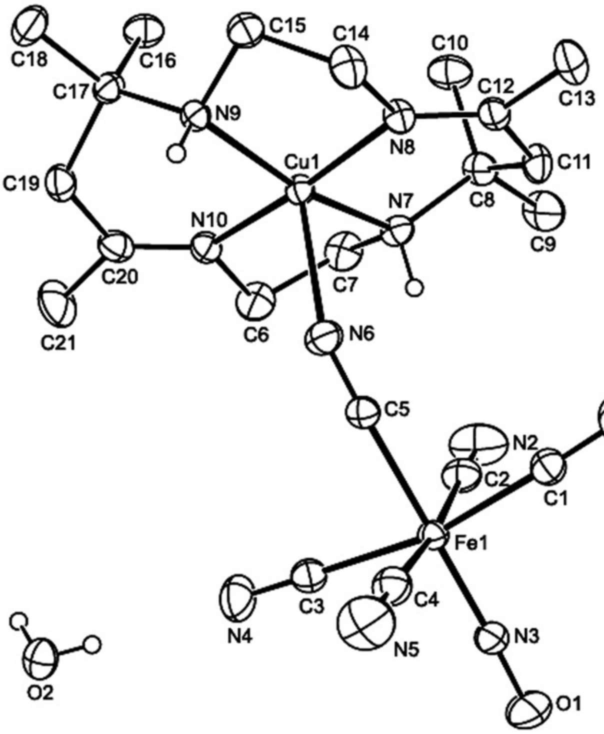

Figure 1. Geometric structure of **1** showing the atom labels. Displacement ellipsoids are drawn at the 30% probability level. H atoms on C atoms are omitted for clarity.

N9–H9 ··· O2 hydrogen bonds and van der Waals forces, forming a three-dimensional framework with optical activity by the stacking sequence of ABAB ··· .

The intrinsic molecular structures of **1** and its enantiomer should be responsible for their chirality because their chirality persists in solution. In **1**, the formation of cyano-bridge and coordination of $[Fe(CN)_5NO]^{2-}$ anion to Cu(II) in a bent and oblique fashion induce the twist of the macrocycle and loss of symmetry of the whole binuclear molecule, and become the origin of molecular chirality. Thus the two chiral amine nitrogen atoms have the same optical configuration, either both *S* for **1** or both *R* for its enantiomer. However, the pair molecules do not favor the arrangement of racemic crystal structure and spontaneous resolution occurs on crystallization.

3.2. *IR spectrum*

The informative aspect of the IR spectra of cyanide-bridged complexes is their cyanide stretching frequencies. As shown in figure 3(a), **1** and its enantiomer show two medium C≡N stretching bands at 2133 and 2149 cm^{-1}, indicating that there are two kinds of C≡N vibrations. Bridging cyanide frequencies in cyanide-bridged complexes are generally observed at higher frequency than those of terminal cyanides [19, 20], and the band at 2149 cm^{-1} is reasonably assigned to the bridging cyanide, which shifts to lower frequency compared to the 2174 cm^{-1} of axial cyanide in $Na_2[Fe(CN)_5NO] \cdot 2H_2O$ [21].

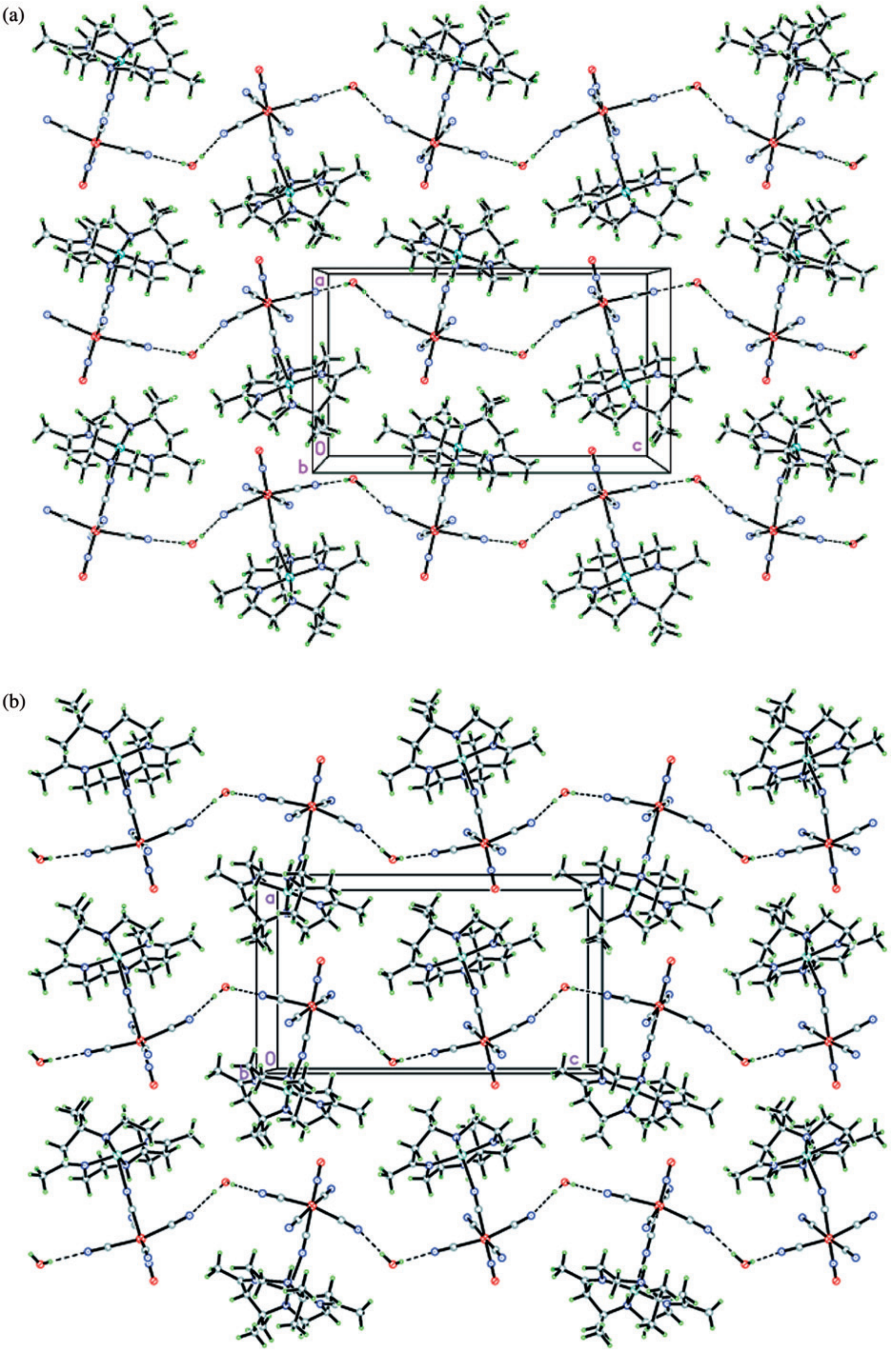

Figure 2. Molecular packing diagram along the *ac* plane for **1** showing two alternating layers (a) and (b) that consist of one-dimensional waved chains. The O–H···N hydrogen bonds are illustrated as dashed lines.

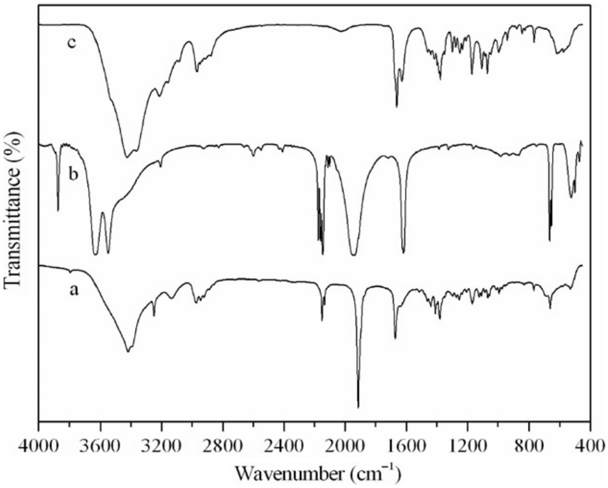

Figure 3. The infrared spectra of: (a) $[Cu(1,7\text{-}CT)(\mu\text{-}CN)Fe(CN)_4NO]\cdot H_2O$; (b) $Na_2[Fe(CN)_5NO]\cdot 2H_2O$; (c) $[Cu(1,7\text{-}CT)]I_2\cdot 2.5H_2O$.

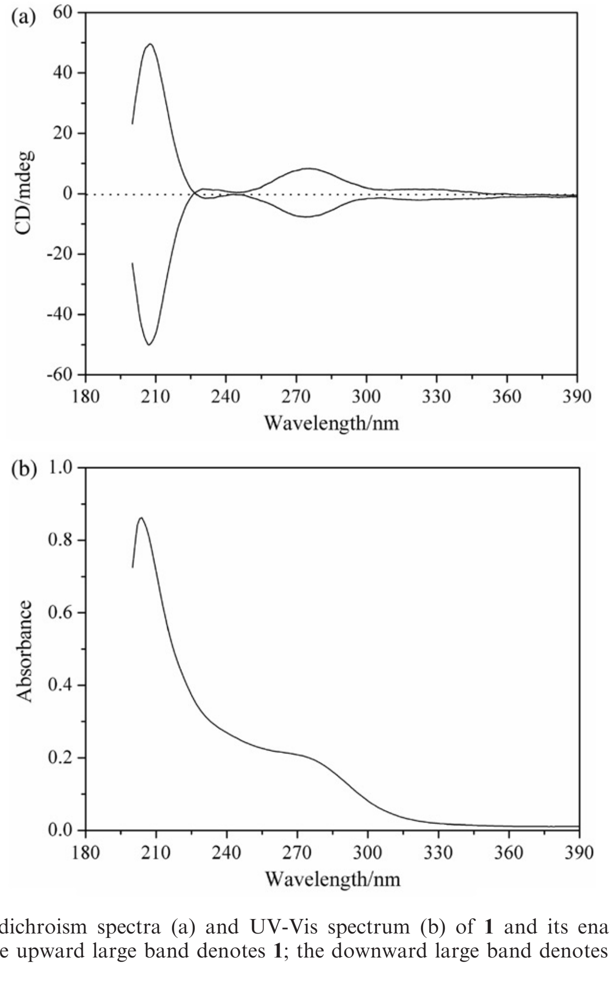

Figure 4. Circular dichroism spectra (a) and UV-Vis spectrum (b) of **1** and its enantiomer. In circular dichroism spectra, the upward large band denotes **1**; the downward large band denotes its enantiomer.

This demonstrates weakening of the C≡N bond upon formation of a cyanide bridge [22] and proves that the $[Fe(CN)_5NO]^{2-}$ anion is coordinated to Cu(II) center through an axial cyanide. The band at $2133\,cm^{-1}$ is ascribed to the stretching vibration of terminal C≡N, which is slightly shifted to lower frequency relative to the 2157 and $2144\,cm^{-1}$ of radial C≡N stretching in sodium nitroprusside. The strong single absorption band at $1913\,cm^{-1}$ is assigned to the N=O stretching vibration, which is obviously lower than $1946\,cm^{-1}$ of $Na_2[Fe(CN)_5NO]\cdot 2H_2O$. The strong C=N stretching bands at $1671\,cm^{-1}$ and the C–N stretching bands at 1123 and $1168\,cm^{-1}$ can be clearly observed, proving that there are two different bonding N atoms. The absorption at $661\,cm^{-1}$ is attributed to the Fe–N stretching vibration, and the Fe–C–N bending vibration is found at $521\,cm^{-1}$ for nitroprusside and $529\,cm^{-1}$ for **1** and its enantiomer. The bands at 2943, 2971 and $3133\,cm^{-1}$ belong to the N–H stretching vibration, and the band at $3417\,cm^{-1}$ belongs to O–H stretching vibration of water. In figures 3(b) and 3(c), the infrared spectra of $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ and $[Cu(1,7\text{-}CT)]I_2\cdot 2.5H_2O$ are listed at the same time too, in which the absorption at $3873\,cm^{-1}$ being the double-frequency of the N=O stretching vibration.

3.3. *Specific rotations, UV-Vis spectrum and circular dichroism spectra*

Several blocky crystals (about 1 mg/granule) are sorted out with tweezers in the product and are dissolved into methanol (2 mL) giving peach solutions, and then their optical rotations, UV-Vis spectrum and circular dichroism spectra are determined. The specific rotatory power of two enantiomerically pure crystals may take on positive and negative values, respectively, in methanol $[\alpha]_D^{20} = \pm 205\,deg\,cm^2\cdot(10\,g)^{-1}$. The UV-Vis spectrum of **1** and its enantiomer reveal a band at 278 nm corresponding to the π–π^* electronic transition of the imine groups, and an intense absorption at about 204 nm associated with the charge transfer ($L \rightarrow Cu^{2+}$). Correspondingly, their circular dichroism spectra show a negative Cotton effect for **1** and a positive Cotton effect for **1**'s enantiomer at 275 nm corresponding to the π–π^* electronic transition of imine chromophore; a positive Cotton effect for **1** and a negative Cotton effect for its enantiomer at 207 nm associated with charge transfer of CuN_5 chromophore. The band positions of circular dichroism spectra of two enantiomerically pure crystals are close to that of their UV-Vis spectrum, and the circular dichroism spectra take on two opposite and antisymmetric absorption signals, which give direct evidence for the formation of racemic conglomerate, as shown in figure 4. It has been shown that the rotary direction of **1** is clockwise by simulation of the optical rotation using the Gaussian 03 program [23] and has been proven that the upward large band of the circular dichroism spectra corresponds to the positive optical rotation by using the same sample solution to determine synchronously optical rotation and circular dichroism spectrum.

Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC 610095 for **1**. The copy of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge

CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc. cam.ac.uk or http://www.ccdc.cam.ac.uk).

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References

[1] H.-Y. Shen, B.-W. Sun, D.-Z. Liao, Z.-H. Jiang, S.-P. Yan, G.-L. Wang, K.-B. Yu. *Chem. J. Chin. Univ.*, **19**, 1533 (1998).
[2] L. Ballester, A.M. Gil, A. Gutiérrez, M.F. Perpiñán, M.T. Azcondo, A.E. Sánchez, E. Coronado, C.J. Gómez-García. *Inorg. Chem.*, **39**, 2837 (2000).
[3] H.-Y. Shen, W.-M. Bu, D.-Z. Liao, Z.-H. Jiang, S.-P. Yan, G.-L. Wang. *Inorg. Chem.*, **39**, 2239 (2000).
[4] A. Tomkiewicz, J. Mroziński, I. Brüdgam, H. Hartl. *Eur. J. Inorg. Chem.*, 1787 (2005).
[5] R. Jungst, G. Stucky. *Inorg. Chem.*, **13**, 2404 (1974).
[6] H. Yuge, T. Soma, T.K. Miyamoto. *Collect. Czech. Chem. Commun.*, **63**, 622 (1998).
[7] T.-H. Lu, T.H. Tahirov, B.-H. Chen, C.-Y. Lai, C.-S. Chung. *Acta Cryst.*, **C52**, 2684 (1996).
[8] M. Clemente-León, E. Coronado, J.R. Galán-Mascarós, C.J. Gómez-García, T. Woike, J.M. Clemente-Juan. *Inorg. Chem.*, **40**, 87 (2001).
[9] H.L. Shyu, H.-H. Wei. *J. Coord. Chem.*, **47**, 319 (1999).
[10] M. Belicchi-Ferrari, F. Bisceglie, C. Casoli, S. Durot, I. Morgenstern-Badarau, G. Pelosi, E. Pilotti, S. Pinelli, P. Tarasconi. *J. Med. Chem.*, **48**, 1671 (2005).
[11] W. Dong, S.-F. Si, D.-Z. Liao, Z.-H. Jiang, S.-P. Yan. *J. Coord. Chem.*, **56**, 531 (2003).
[12] N.V. Podberezskaya, N.V. Pervukhina, L.I. Myachina. *J. Struc. Chem.*, **27**, 268 (1986).
[13] G.M. Sheldrick, *SADABS. Program for Multi-scan Absorption Correction of Area Detector Data*, V2.10, University of Göttingen, Göttingen, Germany (2003).
[14] G.M. Sheldrick. *SHELXS97*: *Program for Solution of Crystal Structures*, University of Göttingen, Göttingen, Germany (1997).
[15] G.M. Sheldrick. *SHELXL97*: *Program for Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany (1997).
[16] X. Peng, H.-Z. Kou, M. Xiong, R.-J. Wang. *Acta Cryst.*, **E59**, m252 (2003).
[17] P.T. Manoharan, W.C. Hamilton. *Inorg. Chem.*, **2**, 1043 (1963).
[18] L. Shen, Y.-J. Zhang, G.-D. Sheng, H.-T. Wang. *Acta Cryst.*, **C58**, m382 (2002).
[19] C.A. Bignozzi, F. Scandola. *Inorg. Chem.*, **23**, 1540 (1984).
[20] D.F. Shriver, J. Posner. *J. Am. Chem. Soc.*, **88**, 1672 (1966).
[21] R.K. Khanna, C.W. Brown, L.H. Jones. *Inorg. Chem.*, **8**, 2195 (1969).
[22] C.A. Bignozzi, R. Argazzi, J.R. Schoonover, K.C. Gordon, R.B. Dyer, F. Scandola. *Inorg. Chem.*, **31**, 5260 (1992).
[23] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr, T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople. *Gaussian 03 Program (Version 6.0)*, Gaussian, Inc., Pittsburgh, PA, USA (2004).