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Syntheses and Crystal Structures of Methyl 2-Pyridylmethylidenehydrazinecarbodithioate and of Its Copper(II) Complex: Supramolecular Arrays Exhibiting *pseudo*-Helical Arrangement Controlled by Hydrogen Bonding or S···S Contact

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A copper(II) complex of the Schiff base methyl 2-pyridylmethylidenehydrazinecarbodithioate (HNNS), derived from 2-pyridinecarbaldehyde and methyl hydrazinecarbodithioate, was synthesized and characterized by elemental analyses, IR, UV-vis spectra and cyclic voltammetric measurements, X-Ray diffraction studies showed that the ligand HNNS (**1**) crystallizes in the orthorhombic space group $Pna2_1$, with $a = 17.611(2)$, $b = 9.285(1)$, $c = 6.208(1)$ Å; $V = 1015.1(2)$ Å^3, $Z = 4$, final $R = 0.03$ for 1169 independent reflections. Complex [Cu(NNS)$_2$] (**2**) crystallizes in monoclinic space group $P2_1/c$, with $a = 11.898(2)$, $b = 9.798(2)$, $c = 18.091(4)$ Å; $\beta = 103.18(3)°$, $V = 2053.4(7)$ Å^3, $Z = 4$, final $R = 0.0505$ for 3460 observed reflections. Intermolecular interactions play important roles in the overall packing of the molecules in the crystal lattice. In **1**, an extended one-dimensional helical chain is formed via hydrogen bondings (N···N 2.971 Å), while S···S contacts (3.485 Å) assemble the helical chains in **2**. The assembly process of **2** is enantioselective, since the complex assumes either the Δ or Λ enantiomorph due to the *mer*-configuration of the unsymmetrical tridentate Schiff base, and the Δ isomer aggregates only with the Δ isomer and the Λ only with Λ to give helical structures described as $\Delta\Delta\Delta\Delta\cdots$ and $\Lambda\Lambda\Lambda\Lambda\cdots$, respectively.

The design and syntheses of molecules that can be organized into specific supramolecular assemblies in the solid state are areas of increasing interest over recent years,[1] since the incorporation of well-ordered structural components into a crystal lattice may lead to advanced new materials with designed physico-chemical properties. Such work will also provide a foundation for the understanding of how molecules can be organized and how functions can be revealed. Many efforts have been devoted to the use of supramolecular contacts, particularly hydrogen-bondings, between suitable organic molecules to generate one-, two- or three-dimensional arrays or networks.[2] However, the use of inorganic metal complexes for assembly or self-assembly by supramolecular forces is much less developed.

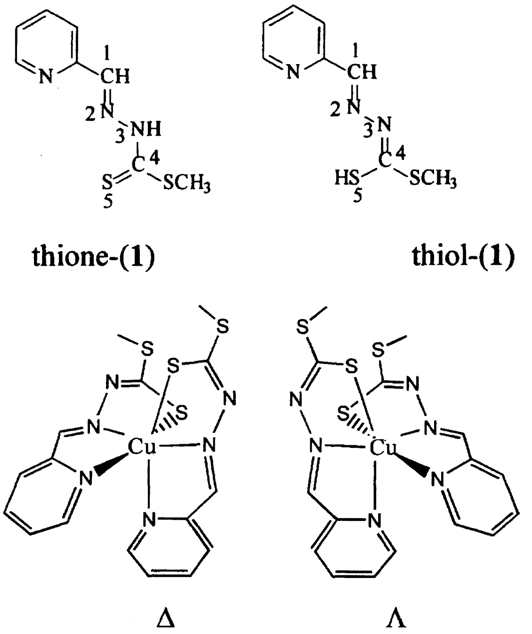
Some recent examples have helped to extend the understanding of this developing area.[3] One of the interests in the field of supramolecular chemistry is to assemble so-called helicate, double- and triple-helical metal complexes,[4] in which oligopyridines and related ligands are vigorously investigated for this purpose.

Schiff bases formed from α-*N*-heterocyclic carboxaldehydes, thiosemicarbazides and alkyl hydrazinecarbodithioates, as well as their transition metal complexes, have received intensive attention because of their potential biological activities.[5] Although there have been numerous studies on the preparation and spectral characterization of complexes, comparatively few crystal structures of these complexes have been reported.[6] We have been interested in the construction of low- and multi-dimensional architectures using metal complexes as building blocks.[7] In this paper we report on the crystal structures of the ligand methyl 2-pyridylmethylidenehydrazinecarbodithioate (HNNS, **1**) and its copper complex Cu(NNS)$_2$ (**2**), as depicted in Scheme 1. Different intermolecular interactions are found to play roles in their crystal packings.

Experimental

Synthesis. The ligand HNNS (**1**)[8] and the starting material Cu(oxen)·2H$_2$O (oxen = *N*,*N*′-bis(2-aminoethyl)oxamide)[9] were prepared according to literature methods.

Bis(methyl 2-pyridylmethylidenehydrazinecarbodithioato)copper(II) [Cu(NNS)$_2$] (2). To an aqueous solution (40 cm^3) of Cu(oxen)·2H$_2$O (0.136 g, 0.5 mmol) was added a methanol solution (10 cm^3) of Cu(ClO$_4$)$_2$·6H$_2$O (0.185 g, 0.5 mmol) with stirring at



Cu(NNS)₂ (2)

Scheme 1.

room temperature. Several minutes later, a methanol solution (50 cm^3) of HNNS (0.422 g, 2.0 mmol) was slowly added to give a dark-green solution. The mixture was kept at room temperature for several days to give dark-green prismatic crystal of **2** upon slow evaporation of the solvent. The crystals were filtered and dried in air. Yield: 0.416 g (86%). Found: C, 42.55; H, 3.42; N, 18.72%. Calcd for $C_{16}H_{16}N_6S_4Cu$: C, 42.51; H, 3.57; N, 18.59%.

Instrumentation. Infrared spectra were obtained from a Perkin–Elmer 1600 FTIR spectrometer as KBr pellets. UV-vis spectra were measured on a Shimadzu UV-240 spectrophotometer in an DMF solution at room temperature from 270 to 900 nm. Elemental analyses were performed on a Carlo-Erba 1106 element analyzer. Cyclic voltammetric measurements were performed on an HDV-7B potentiostat with an DCD-3 frequency generator, equipped with an LZ32-204 X–Y recorder in a three-electrode cell with platinum working and auxiliary electrodes and a saturated calomel electrode (SCE) as a reference. The supporting electrolyte was $Bu^n_4NClO_4$ (0.1 mol dm^{-3}) and the scan rate was 100 mV s^{-1}.

X-Ray Crystallographic Studies. Single crystals of suitable sizes were mounted on glass fibers with epoxy resin. The intensity data of **1** were collected on an R3M/E diffractometer by the ω–2θ scan technique using graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å). Three standard reflections monitored every 200 reflections showed a decay of 1.55%. LP corrections were applied, but no absorption corrections were carried out. The intensity data of **2** were collected on an MSC/Rigaku RAXIS IIC image-plate diffractometer at 293 K using graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å) from a rotating-anode X-ray generator operating at 50 kV and 90 mA. A self-consistent semiempirical absorption correction based on the Fourier-coefficient fitting of symmetry-equivalent reflections was applied using ABSCOR.[10] The structures were solved by direct methods and refined by full-matrix least-squares techniques using the SHELXLTL-PC program package.[11] Anisotropic thermal factors were assigned to all of the non-hydrogen atoms. The hydrogen atoms in **1**, except for those of C8, were located from Fourier syntheses. All of the other hydrogen atoms were fixed in idealized positions isotropically, and were only included during structure-factor calculations, but not refined. The structures were refined against F^2 using the weighting scheme $w = 1/[\sigma^2(F_o)^2 + AP^2 + BP]$, where $P = (F_o^2 + 2F_c^2)/3$. The atomic scattering factors were taken from Ref. 12. The crystal data and experimental details for **1** and **2** are given in Table 1. The selected atomic distances and bond angles are listed in Table 2. Tables of the atomic coordinates, thermal parameters, and complete atomic distances and bond angles are deposited as Document No. 72033 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Synthesis. The Schiff base HNNS is expected to exhibit thione-thiol tautomerism in solution, as shown in Scheme 1. In the thiol form, HNNS can act as a singly charged tridentate ligand by a loss of the thiol proton to coordinate to a metal ion via the mercapto sulfur, the central nitrogen N^2 (labeled as shown in the Scheme 1) and the pyridyl nitrogen atoms. This enthiolization seems to be markedly enhanced by the presence of metal ions, even under neutral conditions. The present case confirms such a behavior of HNNS, which replaces oxen to form a stable complex [Cu(NNS)$_2$], as shown in the following reaction:

$$\mathrm{Cu(oxen)\cdot 2H_2O + Cu(ClO_4)_2\cdot 6H_2O + 4HNNS} \xrightarrow{\mathrm{MeOH/H_2O}} \mathrm{2[Cu(NNS)_2] + (H_4oxen)(ClO_4)_2} \qquad (1)$$

Crystal Structures. The structure of **1** along with the atomic labeling scheme is shown in Fig. 1. The atomic distances of **1** indicate that the tautomeric thione form of the free ligand HNNS is dominant in the solid state. The N(2)–C(6) distance of 1.272(4) Å is typical of a C=N double bond, while the N(3)–C(7) bond of 1.344(4) Å is obviously longer, showing more of a single bond character. A distinct difference can also be found for the C–S bonds (S(1)–C(7) 1.659(3) and S(2)–C(7) 1.743(3) Å) in the free ligand. Upon coordination to the Cu(II) atom, the aforementioned bond distances show significant changes. The bond N(2)–C(6) (or N(5)–C-

Table 1. Crystallographic Data for HNNS (**1**) and Cu(NNS)$_2$ (**2**)

	1	**2**
Empirical formula	$C_8H_9N_3S_2$	$C_{16}H_{16}CuN_6S_2$
Formula weight	211.30	484.13
Temp/K	294	293
Crystal system	Orthorhombic	Monoclinic
Space group	$Pna2_1$	$P2_1/c$
a/Å	17.611(2)	11.898(2)
b/Å	9.285(1)	9.798(2)
c/Å	6.208(1)	18.091(4)
$\beta/^\circ$		103.18(3)
V/Å^3	1015.1(2)	2053.4(7)
Z	4	4
ρ_{calc}/g cm^{-3}	1.383	1.566
μ(Mo $K\alpha$)/mm^{-1}	0.481	1.484
$R(F_o)^{a)}$	0.0300	0.0505
$wR(F_o^2)^{b)}$	0.0642	0.1299

a) $R(F_o) = \sum(||F_o| - |F_c||)/\sum|F_o|$,
b) $wR(F_o^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[wF_o^4]\}^{1/2}$.

Table 2. Selected Bond Distances (Å) and Bond Angles (°) for HNNS (**1**) and Cu(NNS)$_2$ (**2**)

1			
S(2)–C(7)	1.743(3)	S(2)–C(8)	1.801(4)
S(1)–C(7)	1.659(3)	N(1)–C(4)	1.331(4)
N(1)–C(5)	1.342(4)	N(2)–C(6)	1.272(4)
N(2)–N(3)	1.373(3)	N(3)–C(7)	1.344(4)
C(6)–N(2)–N(3)	114.9(2)	C(7)–N(3)–N(2)	120.3(2)
N(2)–C(6)–C(5)	120.9(2)	N(3)–C(7)–S(1)	120.3(2)
N(3)–C(7)–S(2)	113.5(2)	S(1)–C(7)–S(2)	126.1(2)
2			
Cu(1)–N(5)	1.972(3)	Cu(1)–N(2)	2.031(3)
Cu(1)–N(4)	2.088(3)	Cu(1)–S(3)	2.3067(12)
Cu(1)–N(1)	2.449(3)	Cu(1)–S(1)	2.6323(13)
S(1)–C(7)	1.685(4)	S(2)–C(7)	1.776(4)
S(2)–C(8)	1.799(5)	S(3)–C(15)	1.719(4)
S(4)–C(15)	1.739(4)	S(4)–C(16)	1.789(5)
N(2)–C(6)	1.290(5)	N(2)–N(3)	1.381(4)
N(3)–C(7)	1.323(5)	N(4)–C(13)	1.327(5)
N(4)–C(9)	1.355(5)	N(5)–C(14)	1.287(4)
N(5)–N(6)	1.383(4)	N(6)–C(15)	1.307(5)
N(5)–Cu(1)–N(2)	172.29(13)	N(5)–Cu(1)–N(4)	79.78(13)
N(2)–Cu(1)–N(4)	103.68(12)	N(5)–Cu(1)–S(3)	82.93(9)
N(2)–Cu(1)–S(3)	93.14(9)	N(4)–Cu(1)–S(3)	162.47(9)
N(5)–Cu(1)–N(1)	99.44(12)	N(2)–Cu(1)–N(1)	74.51(12)
N(4)–Cu(1)–N(1)	81.56(12)	S(3)–Cu(1)–N(1)	98.50(9)
N(5)–Cu(1)–S(1)	109.38(9)	N(2)–Cu(1)–S(1)	77.69(10)
N(4)–Cu(1)–S(1)	90.30(9)	S(3)–Cu(1)–S(1)	98.22(4)
N(1)–Cu(1)–S(1)	148.15(9)	C(7)–S(1)–Cu(1)	89.18(14)
C(7)–S(2)–C(8)	104.2(2)	C(15)–S(3)–Cu(1)	94.55(14)
C(5)–N(1)–Cu(1)	135.4(3)	C(1)–N(1)–Cu(1)	106.8(3)
C(6)–N(2)–N(3)	115.4(3)	C(6)–N(2)–Cu(1)	120.7(3)
N(3)–N(2)–Cu(1)	123.2(2)	C(7)–N(3)–N(2)	113.8(3)
C(13)–N(4)–C(9)	118.8(3)	C(13)–N(4)–Cu(1)	129.7(3)
C(9)–N(4)–Cu(1)	111.5(2)	C(14)–N(5)–N(6)	118.9(3)
C(14)–N(5)–Cu(1)	116.8(3)	N(6)–N(5)–Cu(1)	124.2(2)
C(15)–N(6)–N(5)	110.8(3)	N(2)–C(6)–C(1)	120.9(4)
N(3)–C(7)–S(1)	129.9(3)	N(3)–C(7)–S(2)	107.6(3)
S(1)–C(7)–S(2)	122.5(2)	N(4)–C(9)–C(10)	121.7(4)
N(4)–C(9)–C(14)	114.8(3)	N(4)–C(13)–C(12)	122.0(4)
N(5)–C(14)–C(9)	117.0(3)	N(6)–C(15)–S(3)	127.5(3)
N(6)–C(15)–S(4)	120.1(3)	S(3)–C(15)–S(4)	112.4(2)

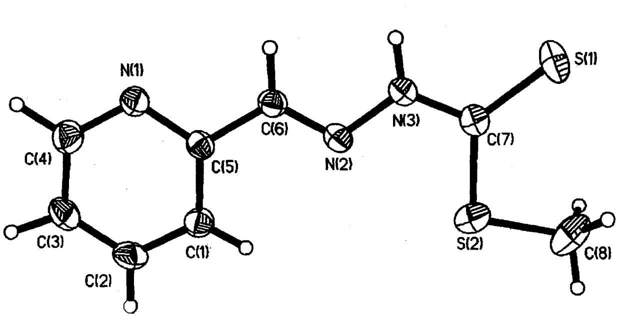


Fig. 1. ORTEP drawing of HNNS (**1**) showing atoms of thermal ellipsoids at the 30% probability level.

(14)) with 1.290(5) Å (or 1.287(4) Å) increased slightly as compared with the free ligand; N(3)–C(7) (or N(6)–C(15)), which was 1.323(5) Å (or 1.307(5) Å), decreased. In addition, the bond S(1)–C(7) (or S(3)–C(15)) of 1.685(4) Å (or 1.719(4) Å) increased by 0.026 Å (or 0.060 Å), suggesting a more single bond character. Thus, the Schiff base when coordinated in the complex is singly deprotonated and acts as a uni-charged ligand, adopting the tautomeric thiol form.

The molecule of complex [Cu(NNS)$_2$] (**2**) is neutral with the copper atom six-coordinated by the two tridentate NNS anions in an elongated octahedral geometry, as depicted in Fig. 2. The two approximately perpendicular ligands chelate the Cu(II) ion via the pyridyl nitrogen, the azomethine nitrogen, and the thiolato sulfur atoms in a *mer*-configuration with four 5-membered rings. The atoms N(4), N(5), S(3) of one ligand and the azomethine nitrogen atom N(2) of the other make up the equatorial plane with the central Cu(II) ion located essentially in the plane (deviating by 0.097 Å). The average Cu–N$_{\mathrm{eq}}$ distance of 2.030 Å with a quite small range is well within the distance of that found in the related copper(II) complex of an N-oxide derivative (HNOS).[7a] The axial bonds (Cu(1)–N(1) 2.449(3) Å and Cu(1)–S(1) 2.6323(13) Å) are longer than the equatorial ones, as commonly observed for octahedral copper(II) complexes due to the Jahn–Teller effect. Moreover, when comparing in detail the bond distances of the two ligands within a molecule, it is found that the longer Cu(1)–N(1) and Cu(1)–S(1) bonds correspond to a shorter C(7)–S(1) and a longer N(3)–C(7), while the shorter Cu(1)–N(4) and Cu(1)–S(3) bonds correspond to a longer C(15)–S(3) and a shorter C(15)–N(6). This finding may suggest such a result: the stronger binding of the ligand to the Cu(II) ion corresponds to a more complete enthiolization of the NNS ligand. In other words, the stronger is the binding of the ligand to metal, the more is their electron delocalization among the conjugated system of the Schiff base.

The intermolecular interactions play significant roles in the packing of both complexes. In **1**, the pyridyl nitrogen atom of one molecule acts as an acceptor to the hydrogen donating NH group of a nearby molecule. Repetition of this hydrogen bonding scheme (N···N 2.971 Å) assembles the

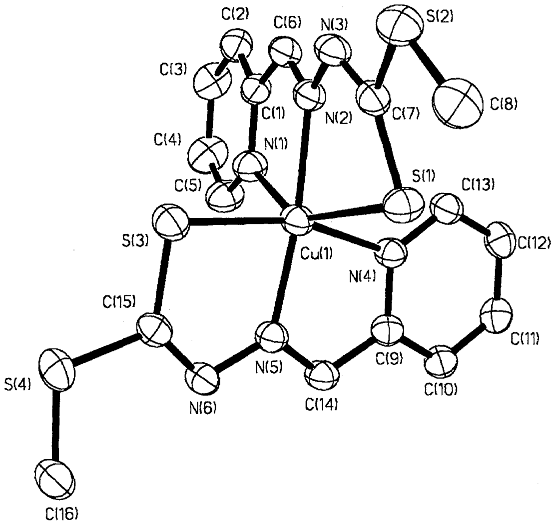


Fig. 2. ORTEP drawing of Cu(NNS)$_2$ (**2**) showing atoms of thermal ellipsoids at the 30% probability level.

molecules into one-dimensional helical chains, as shown in Fig. 3. In **2**, a similar one-dimensional helical chain can be formed, but controlled by S···S contacts (3.485 Å, Fig. 4). The short intermolecular contacts occurred from an interaction of the axially coordinated S(1) of one molecule and the free S(4) of the equatorially ligated NNS ligand of another molecule. The distance for such contact is less than the sum of the van der Waals radii of the two S atoms (3.60 Å), and compares well with those found in other sulfur-rich compounds.[13] Compounds **1** and **2** could provide convenient comparisons of the factors that control the supramolecular assembly of molecules. In the free Schiff base **1**, the presence of both a hydrogen bonding acceptor and donor atoms makes it possible to assemble the molecules by forming intermolecular N–H···N hydrogen bonds. Upon coordination to a copper atom, the Schiff base is singly deprotonated, thus precluding the formation of a hydrogen-bonded structure. However, the molecules here can be alternatively assembled by the relatively weak S···S contacts. Conversion of the factors that control the supramolecular structures with the same topology has previously been reported,[14] and is considered to be an important new strategy for crystal engineering.[15]

Another interesting phenomenon may be noted in which the two unsymmetrical tridentate ligands coordinated octahedrally to the Cu(II) ion are arranged in a *mer*-conformation, which is intrinsically chiral,[16] and result in either a Δ or a Λ enantiomorph, as shown in Scheme 1. When assembled by S···S contacts, the Δ isomer aggregates only with the Δ isomer and the Λ only with Λ to give extended *pseudo*-helical chains, described as $\Delta\Delta\Delta\Delta\cdots$ and $\Lambda\Lambda\Lambda\Lambda\cdots$, respectively.

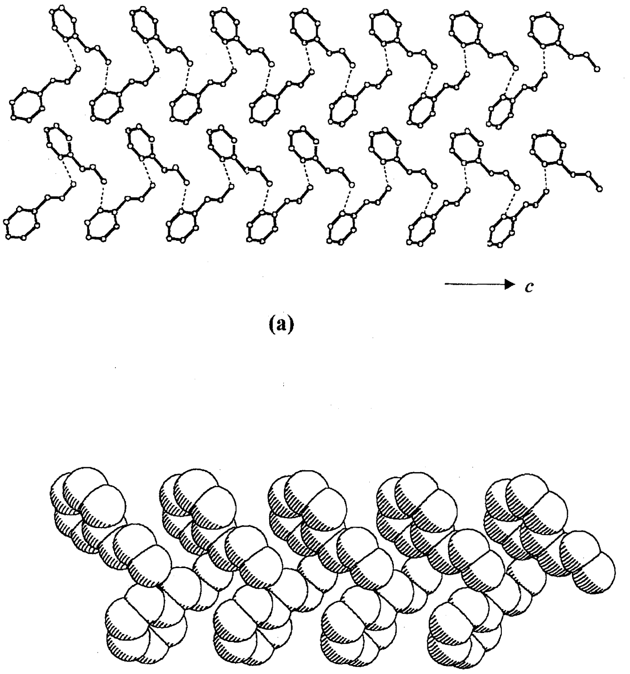


Fig. 3. Hydrogen-bonded *pseudo*-helical structure of HNNS (**1**) with the S=CSMe group omitted for clarity: (a) Two parallel helical chains running along the *c*-axis with the same helicity; (b) Space-filling representation of a helical chain.

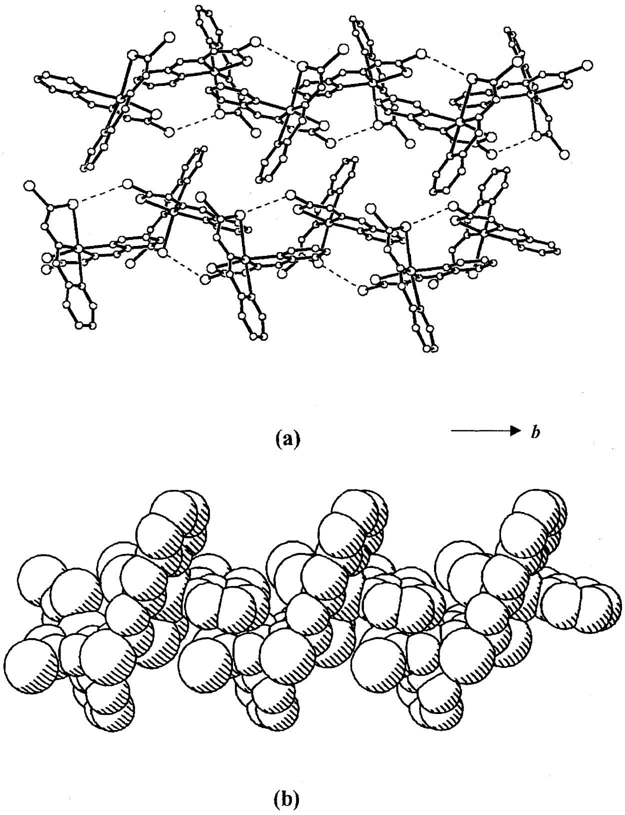


Fig. 4. The S···S contacted *pseudo*-helical structure of Cu(NNS)$_2$ (**2**) with the Me group omitted for clarity: (a) Parallel helical chains running along *b*-axis with right- or left-handed helicity; (b) Space-filling representation of one chain.

In the *bc*-plane of the crystal lattice of complex **2**, the Δ and Λ *pseudo*-helical chains running along the *b*-axis are alternatively arrayed, resulting in a racemic mixture of right- and left-handed *pseudo*-helices in the solid state (Fig. 5)

Spectroscopy. The IR spectrum of **1** displayed ν_{NH} at 3096 cm^{-1}, but no ν_{SH} at ca. 2570 cm^{-1}, indicating that **1** in the solid state is in the thione form.[8] After coordinating to Cu(II), the ν_{NH} band of the free ligand disappeared, thus confirming lose of the proton. Meanwhile, the ν_{CN} and ν_{CS} bands shift to lower energies (1471 and 1061 cm^{-1}, respectively) for complex **2**, as compared to those of the free ligand HNNS (1529 and 1109 cm^{-1}), indicating coordination of the azomethine nitrogen atom and the mercapto sulfur atom, which is consistent with the result obtained from X-ray diffraction analyses.

In the electronic spectra, the broad $\pi\rightarrow\pi^*$ absorption at 335 nm for HNNS shifts to 329 nm in the complex. The S→Cu charge transfer transition appears at 405 nm. The lowest energy band at around 640 nm in the complex is assigned to the d→d transition.[8]

Cyclic voltammetric measurements show that the free Schiff base has two irreversible reduction waves at −1.07 and −1.40 V, and an irreversible oxidation wave at 0.52 V, which are outside the range where the complex is reactive on the electrodes. The CV of the complex in DMF shows

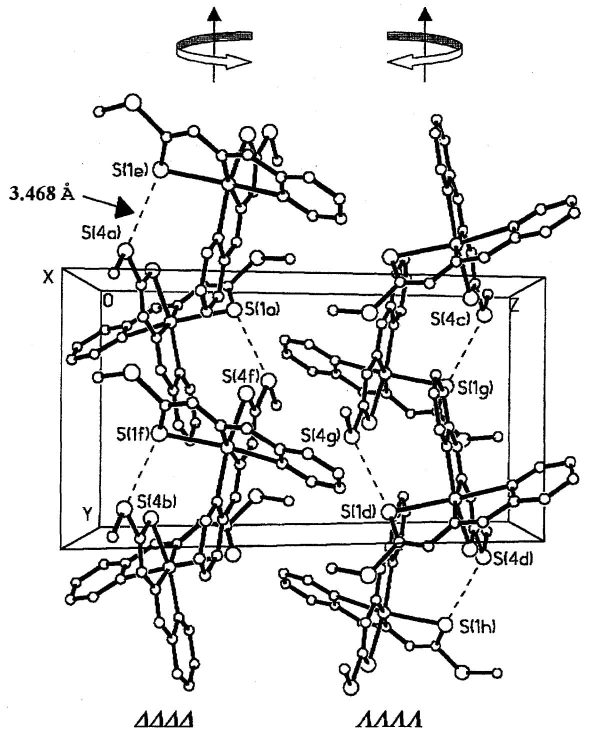


Fig. 5. View of the enantioselective assembly of the Δ isomers and Λ isomers by S···S contacts, showing alternatively arrayed $\Delta\Delta\Delta\Delta\cdots$ and $\Lambda\Lambda\Lambda\Lambda\cdots$*pseudo*-helical chains in the *bc*-plane resulting in a racemic mixture of right- and left-handed helices.

one quasi-reversible redox couple with $E_{1/2}$ at 0.37 V, corresponding to one-electron transfer as follows:

$$[\mathrm{Cu(II)(NNS)_2}] \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [\mathrm{Cu(I)(NNS)_2}]^- \qquad (2)$$

Summary

It has been noted that the achiral Schiff base HNNS is assembled by intermolecular hydrogen bonds to form one-dimensional *pseudo*-helical chains in the crystal lattice. While in the complex [Cu(NNS)$_2$], the enantiomers Δ and Λ are assembled by S···S contacts as a racemic mixture with right- and left-handed *pseudo*-helices coexisting in the crystal lattice. However, the self-assembly is found to be enantioselective, because the generated *pseudo*-helices consisting of $\Delta\Delta\Delta\Delta\cdots$ and $\Lambda\Lambda\Lambda\Lambda\cdots$ are obtained by the spontaneous selection of components of same chirality.[17] Compared to the helical structures of the double-stranded metal complexes formed by the arrangement of the oligopyridine ligands coordinated to the metal ions in a helical fashion,[4] the present *pseudo*-helical structures are formed by the hydrogen bond or S···S contacts. Most important, these results demonstrate how an one-dimensional *pseudo*-helical organic chain held together by N···HN hydrogen-binding is converted into a coordination polymer self-assembled instead of by S···S contacts. Such a transformation of the factors that control the self-assembly of the supramolecular arrays with a similar topology is considered to be an important strategy for crystal engineering;[14,15] also, the present self-assembly process may provide an alternative synthetic route of helical metal complexes.

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