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Synthesis and Crystal Structure of Polymeric Thiocyanato-Bridged Copper(II) Complex with 4-Nitro-2-[(2-piperidin-1-ylethylimino)methyl] Phenolate[1]

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Abstract—A polymeric thiocyanato-bridged Schiff base copper(II) complex $[Cu(L)(NCS)]_n$, where L is 4-nitro-2-[(2-piperidin-1-ylethylimino)methyl]phenolate, has been synthesized and structurally characterized by elemental analysis, infrared spectra, and single crystal X-ray diffraction. The complex crystallizes in the monoclinic space group $P2_1$ with a = 8.527(5), b = 10.296(6), c = 9.697(6) Å, β = 103.77(2)°, V = 826.8(8) Å^3, Z = 2. In the complex, the Cu atom is in a square pyramidal coordination with one O and two N donor atoms of the Schiff base ligand and with one thiocyanate N atom, defining the basal plane, and with one symmetry related thiocyanate S atom occupying the apical position. The thiocyanate ligand links the Cu atoms through the end-to-end bridging mode.

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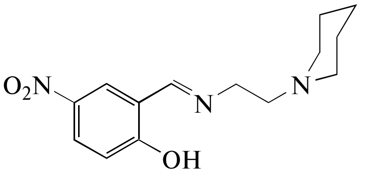
INTRODUCTION

Metal complexes with Schiff base ligands composed of salicylaldehyde and its derivatives with primary amines have received much attention for many years [1–4]. Schiff base copper(II) complexes have been extensively investigated for their magnetic and biological properties [5–8]. Thiocyanate anions are widely used as bridging groups for the preparation of polynuclear copper(II) complexes with Schiff bases [9–11]. In this paper, a novel end-to-end thiocyanato-bridged polymeric copper(II) complex $[Cu(L)(NCS)]_n$ (**I**) derived from the Schiff base ligand 4-nitro-2-[(2-piperidin-1-ylethylimino)methyl]phenol (**HL**) has been synthesized and structurally characterized.



(HL)

EXPERIMENTAL

Materials and measurements. All chemicals were available commercially as AR grade and were used without further purification. C, H, and N elemental analyses were performed on a Vario-EL-III analyzer. Copper was determined by titration with EDTA. The infrared spectra were recorded on a PerkinElmer 2000 spectrophotometer with KBr pellets in the region 4000–400 cm^{-1}.

Synthesis of $[Cu(L)(NCS)]_n$. 5-Nitrosalicylaldehyde (0.167 g, 1 mmol) and 1-(2-aminoethyl)piperidine (0.128 g, 1 mmol) were mixed and stirred in methanol (50 ml) at room temperature for 30 min to give an orange solution. To the solution was added with stirring a methanol solution (30 ml) of ammonium thiocyanate (0.076 g, 1 mmol) and copper acetate monohydrate (0.199 g, 1 mmol). The final mixture was further stirred at room temperature for 30 min to give a deep blue solution. The resulting solution was allowed to stand at room temperature without further disturbing for a week to give blue block-shaped single crystals. The crystals were isolated by filtration, washed three times with methanol, and dried in air. The yield was 82%.

For $C_{15}H_{18}CuN_4O_3S$

anal. calcd., %:	C, 45.3;	H, 4.6;	N, 14.1;	Cu, 16.0.
Found, %:	C, 45.1;	H, 4.7;	N, 14.1;	Cu, 16.2.

Crystal structure determination. The suitable single crystal of the complex was mounted on a glass fiber for data collection performed on a Bruker SMART

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Table 1. Crystallographic data and structure refinement parameters of **I**

Parameter	Value
Fw	397.93
Crystal shape/color	Block/blue
Crystal siz, mm	0.32 × 0.27 × 0.27
Crystal system	Monoclinic
Space group	$P2_1$
a, Å	8.527(5)
b, Å	10.296(6)
c, Å	9.697(6)
β, deg	103.77(2)
V, Å^3	826.8(8)
Z	2
$\mu(\text{Mo}K_\alpha)$, cm^{-1}	1.469
$T_{\min}/T_{\max}$	0.6508/0.6925
Measured reflections	3921
Unique reflections	2683
Observed reflections	1910
Parameters/restraints	217/1
Goodness of fit on F^2	0.977
R_1, wR_2 ($I \geq 2\sigma(I)$)*	0.0705, 0.1630
R_1, wR_2 (all data)*	0.0939, 0.1791

* $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table 2. Selected bond lengths (Å) and bond angles (deg)*

Bond	d, Å	Bond	d, Å
Cu(1)–N(1)	1.937(8)	Cu(1)–N(2)	2.111(8)
Cu(1)–N(3)	1.932(10)	Cu(1)–O(3)	1.956(7)
Cu(1)–S(1*A*)	2.806(3)		
Angle	**ω, deg**	**Angle**	**ω, deg**
N(3)Cu(1)N(1)	164.9(3)	N(3)Cu(1)O(3)	90.4(3)
N(1)Cu(1)O(3)	91.3(3)	N(3)Cu(1)N(2)	93.6(3)
N(1)Cu(1)N(2)	84.4(3)	O(3)Cu(1)N(2)	175.7(3)
N(3)Cu(1)S(1*A*)	95.1(3)	N(1)Cu(1)S(1*A*)	100.0(2)
O(3)Cu(1)S(1*A*)	84.0(2)	N(2)Cu(1)S(1*A*)	97.2(2)

* Symmetry code for (*A*): $2 - x$, $-1/2 + y$, $2 - z$.

1000 CCD area diffractometer equipped with a graphite-monochromatic $\text{Mo}K_\alpha$ radiation ($\lambda = 0.71073$ Å) at 298 K. The unit cell dimensions were obtained with the least-squares refinements, and the structures were solved by direct methods using the SHELXTL-97 program [12]. The final refinement was performed by full-matrix least-squares methods with anisotropic thermal parameters for the non-hydrogen atoms on F^2. Hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms. Multiscan absorption correction was applied by using the SADABS program [13]. The crystallographic data and experimental details for structural analysis of the complex are

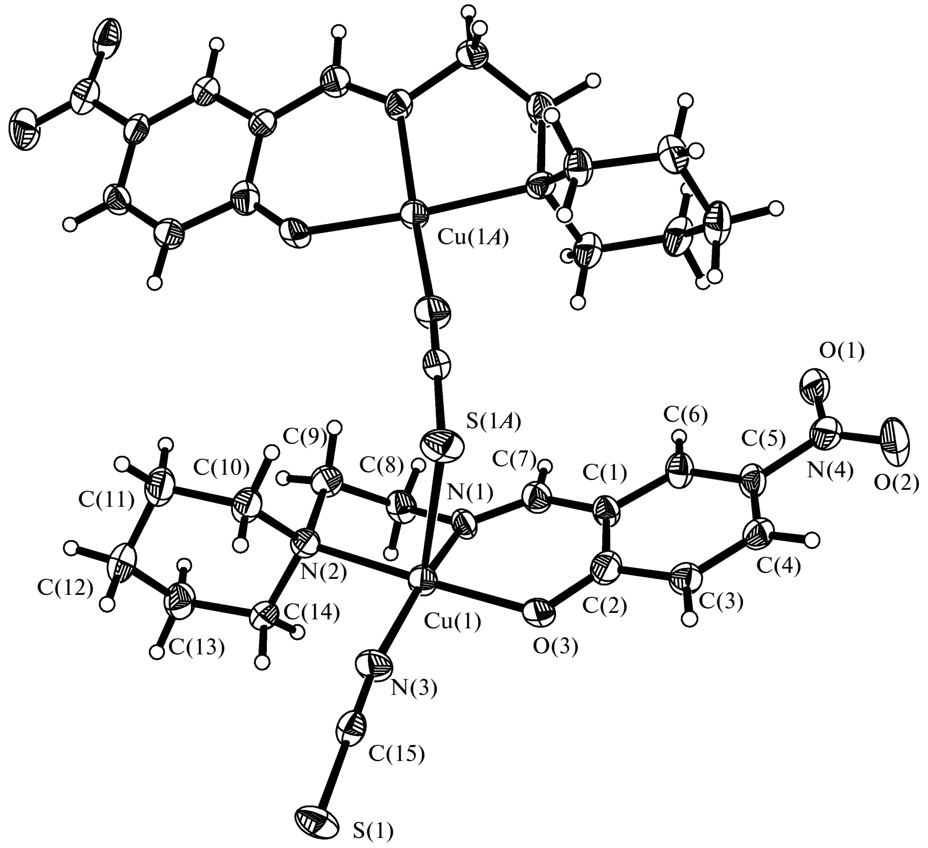

Fig. 1. Molecule of complex **I**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Atoms labeled with the suffix (*A*) or unlabeled are at the symmetry position $2 - x$, $-1/2 + y$, $2 - z$.

summarized in Table 1. Selected bond lengths and angles are given in Table 2.

Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (no. 794038; deposit@ccdc.cam.ac.uk or http://www.ccdc. cam.ac.uk).

RESULTS AND DISCUSSION

The reaction of HL, ammonium thiocyanate, and copper acetate in methanol gave a novel end-to-end thiocyanato-bridged polymeric copper(II) complex. The elemental analyses are in accordance with the formula proposed by the X-ray single-crystal structure determination.

The Schiff base HL shows a weak and broad band at 3413 cm^{-1} corresponding to ν(OH) of the phenolic group, which is absent in the copper(II) complex. The strong and sharp band at 1643 cm^{-1} for HL is assigned to ν(C=N), which is shifted to lower frequencies (1621 cm^{-1}) in the spectrum of the complex. The intense band indicative of the thiocyanate group is at 2108 cm^{-1}. The spectrum of the complex also shows some new bands in the 470–430 cm^{-1} regions, which reflect the formation of Cu–O and Cu–N bonds [14, 15].

The asymmetric unit of the complex is shown in Fig. 1. The complex is an end-to-end thiocyanato-bridged polymeric copper(II) complex. The Cu atom is in a square pyramidal coordination with one O and two N donor atoms of the Schiff base ligand and with one thiocyanate N atom, defining the basal plane, and with one symmetry related thiocyanate S atom, occupying the apical position. The deviation of the Cu atom from the least-squares plane defined by the four basal donor atoms is 0.135(2) Å. The Cu–N and Cu–O bond lengths are within normal values and are comparable to those observed in other copper(II) complexes with Schiff bases [16–18]. The bond length of Cu–S is much longer than those of the Cu–O and Cu–N, yet it is also comparable with the values in the end-to-end thiocyanato-bridged copper(II) complexes [9, 11, 19]. The significant distortion of the square pyramid is revealed by the bond angles between the apical and basal donor atoms, ranging from 84.0(2)° to 100.0(2)°. The bridging NCS groups in the complex are nearly linear and show bent coordination modes with the copper atoms (N(3)–C(15)–S(1)/Cu(1)–N(3)–C(15)/Cu(1)–S(1)^{i}–C(15)^{i} = 178.3(10)°/167.9(9)°/99.3(3)°).

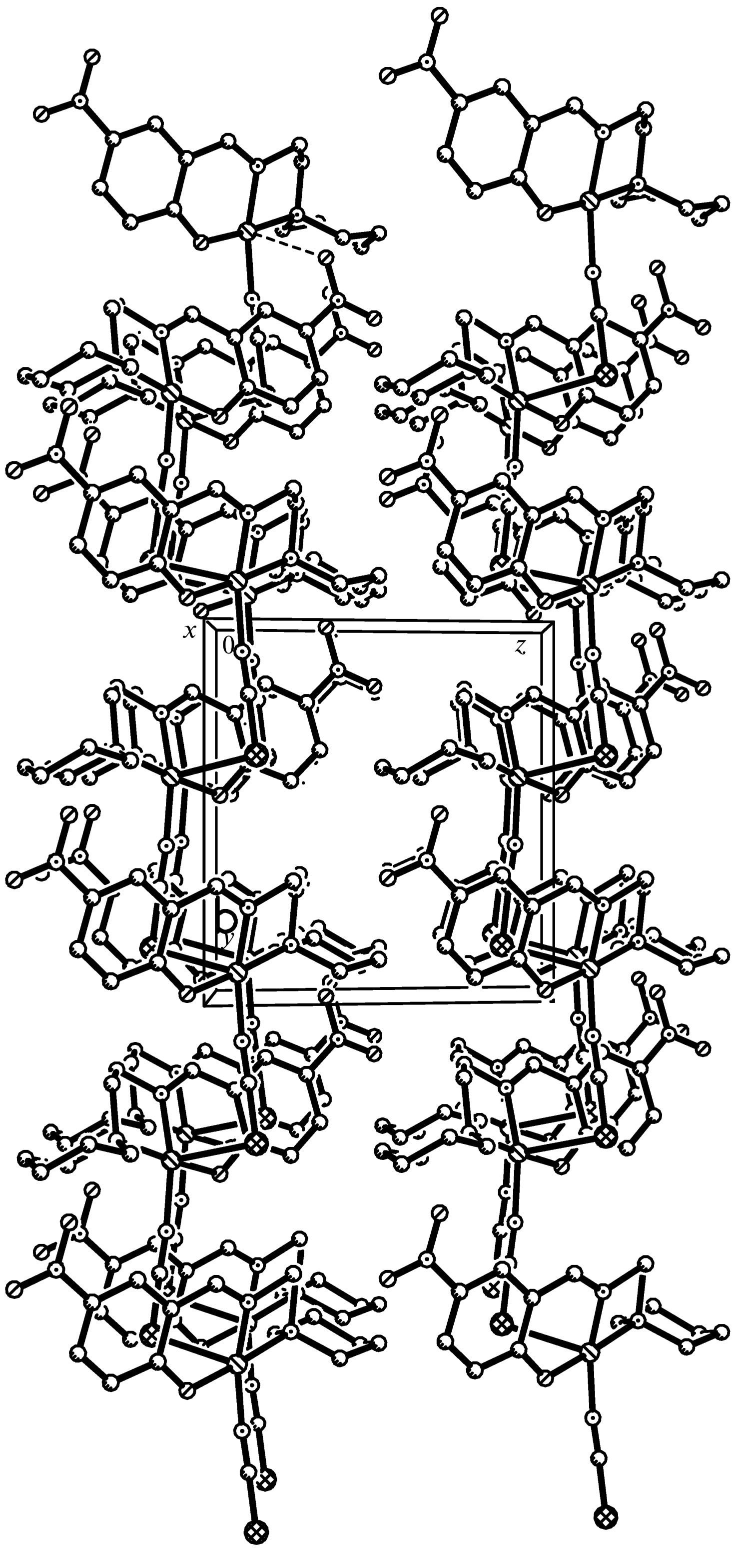

Fig. 2. Molecular packing of complex **I** viewed along the *x* axis.

In the crystal structure, the [CuL] units are linked by the end-to-end thiocyanate ligands, forming polymeric chains running along the *y* axis, as shown in Fig. 2.

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