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Studies on Crystal Structure and Electrical Conductivity for $Cu_4I_4(CH_3NHCS)_2$ and $CuI(CH_3NHCS)_2$ Polymer Complexes

T. Fukami*, H. Ishida, I. Kiyuna, N. Matayoshi and C. Fukuhara

Faculty of Science, University of the Ryukyus, Okinawa 903-0213, Japan

Abstract: Single crystals of $Cu_4I_4(CH_3NHCS)_2$ and $CuI(CH_3NHCS)_2$ polymer complexes have been crystallized. Electrical conductivity and X-ray diffraction measurements have been performed on these compounds. The space group symmetries (monoclinic C2/m and triclinic P-1) and the crystal structures are determined at room temperature. It is suggested from the temperature dependence of the conductivity that these complexes become a proton superionic conductor gradually as the temperature is raised. The difference in the conductivity at high temperature between these compounds is discussed with the refined structures.

INTRODUCTION

Solid state ionic is a new research field attraction of much current attention. Many research groups in the world have investigated for the development of hydrogen fuel cells [1]. Proton conduction plays an important role in the solid electrolytes of the fuel cells. A commercially available fuel cell is well known to be sulfonic-acid-based perfluorinated organic polymers such as the so-called "Nafion". The protonic and electronic conducting systems provide a unique opportunity for exploring novel physical and chemical properties.

Recently, many kinds of metal-complex-based conductors with dithiooxamide ligands have been synthesized as a novel proton conductive system [2-8]. The ligand in the compounds has an S-cis or S-trans conformation. Some complexes in these conductors are a proton conductive two-dimensional coordination polymer. They show the electrical conductivities of about 10^{-3} - 10^{-6} S/cm under relative humidity, and are established to be a proton superionic conductor [2-7,9,10]. The conductivity depends on the quantity of water molecules contained in the polymer complexes. Thus, the water uptake in the complexes is important for the achievement of the high conductivity.

Rousseau *et al.* have performed structural and vibrational studies of a $Cu_4I_4(CH_3NHCS)_2$ polymer complex, and reported the bands and assignments proposed for the different isotopes [8]. Moreover, the atomic coordinates, and the bond distances and angles of the complex have been presented in the paper, but the space group and the lattice parameters have not been presented. Those are used as basic data and important for the physical properties, and moreover, are also necessary for comparing the crystal structure in the same type of complex.

The $Cu_4I_4(CH_3NHCS)_2$ and $CuI(CH_3NHCS)_2$ complexes have been synthesized from acetonitrile solutions containing CuI and dithiooxamide ligands. The electrical conductivity of these complexes and the crystal structure of the $CuI(CH_3NHCS)_2$ complex have not been reported yet. The purpose of this paper is to report the crystal structures of the $Cu_4I_4(CH_3NHCS)_2$ and $CuI(CH_3NHCS)_2$ polymer complexes at room temperature and to discuss the temperature dependence of the electrical conductivity due to proton conduction with the refined structures.

EXPERIMENTAL

Single crystals of $Cu_4I_4(CH_3NHCS)_2$ and $CuI(CH_3NHCS)_2$ polymer complexes were grown by slow evaporation from acetonitrile solutions containing molar ratios 4:1 and 1:1 of CuI and N, N'-dimethyl-dithiooxamide at room temperature, respectively. The color and morphology of the obtained crystals were reddish brown and thin plates, respectively.

The electrical conductivity measurements were carried out using an LCR-meter (NF2330A) at a frequency of 100 kHz in an atmosphere of dried helium gas. Fine powders of the two complexes were compressed into disks (13 mm in diameter and about 0.40 mm in thick) under a pressure about 0.30 GPa. A carbon-paste was used as electrodes for the conductivity measurements. The X-ray measurements were carried out by using an Enraf-Nonius CAD-4 four-circle automatic diffractometer with graphite monochromated Mo Kα radiation (λ=0.71073Å) [11]. Data were collected at room temperature by θ/2θ scan technique in the ranges $3.17 \le \theta \le 34.94$ and $2.81 \le \theta \le 29.97$ for the $Cu_4I_4(CH_3NHCS)_2$ and $CuI(CH_3NHCS)_2$ complexes, respectively. The intensity data were corrected for Lorentz-polarization and absorption effects. The structures were solved with the direct method using the SHELXS program in a SDP crystallographic software package, and refined on F by the full-matrix least-squares method [12,13]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located by difference Fourier syntheses and refined isotropically. Crystal data and the experimental conditions are listed in Table **1**.

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*Address correspondence to this author at the Faculty of Science, University of the Ryukyus, Okinawa 903-0213, Japan;
E-mail: fukami@sci.u-ryukyu.ac.jp

Table 1. Basic Crystallographic Data, Data Collection, and Structure Refinement Parameters

Crystal Data and Experimental Conditions		
Empirical Formula	$Cu_4I_4(CH_3NHCS)_2$	$CuI(CH_3NHCS)_2$
Mr	910.04	338.69
Crystal color	Reddish brown	Reddish brown
Morphology	Plate	Plate
Crystal system	Monoclinic	Triclinic
Space group	C2/m	P-1
Unit cell dimensions a /Å	8.0393(6)	7.6639(9)
b /Å	12.5606(10)	9.5616(6)
c /Å	8.3679(6)	13.9723(10)
α /°		78.458(7)
β /°	111.519(6)	76.748(8)
γ /°		74.062(8)
V /Å^3	786.1(1)	948.0(2)
Z	2	4
D(cal.) /Mg m^{-3}	3.845	2.373
μ(Mo Kα) /mm^{-1}	13.43	5.935
Temperature /K	297 (1)	297(1)
Sample size /mm	0.34×0.32×0.06	0.30×0.22×0.10
θ range for data collection /°	3.17-34.94	2.81-29.97
Index ranges	$-12 \leq h \leq 0$ $-20 \leq k \leq 0$ $-12 \leq l \leq 13$	$0 \leq h \leq 10$ $-12 \leq k \leq 13$ $-19 \leq l \leq 19$
Reflections collected/unique	1871/1695	5892/5512
Number of standard reflections	3	3
Interval time /min.	120	120
Intensity decay /%	-0.56	-2.21
Number of reflections used	1476 [$I > 2\sigma(I)$]	4785 [$I > 2\sigma(I)$]
Number of parameters	54	246
Goodness-of-fit on F	1.247	0.960
Maximum of shift/esd	0.048	0.093
Final R indices (refinement on F)	R1=0.053 WR2=0.064	R1=0.033 wR2=0.042
R indices (all data)	R1=0.060 WR2=0.068	R1=0.044 wR2=0.052
Largest difference peak and hole /eÅ^3	1.950, -2.032	1.994, -1.124
Extinction coefficient	$2.20(5)\times10^{-6}$	$1.91(2)\times10^{-6}$

Weighting scheme $w = 1/[\sigma^2(F) + (0.02F)^2 + 1.0]$.

RESULTS AND DISCUSSION

Fig. (**1**) shows the temperature dependence of the electrical conductivity σ of the (a) $Cu_4I_4(CH_3NHCS)_2$ and (b) $CuI(CH_3NHCS)_2$ polymer complexes on heating. It is clearly seen in the conductivity curves of $Cu_4I_4(CH_3NHCS)_2$ and $CuI(CH_3NHCS)_2$ to bend upward at about 435 and 425 K, respectively. The conductivities increase almost monotonously linear with increasing temperature above the bending temperatures. These increases of the conductivity for the $Cu_4I_4(CH_3NHCS)_2$ and $CuI(CH_3NHCS)_2$ complexes, respectively, are observed to be about 2 and 4 orders of magnitude, and the conductivities at high temperature (463 K) for the both compounds are estimated to be 5.2×10^{-4} and 2.0×10^{-3} S/cm. These results indicate that these complexes are identified as a proton superionic conductor due to proton conduction actively at above the bending temperatures, as similar to other complexes containing the dithiooxamide ligand [2-7,9,10]. That is, they become an ionic conductor with fast proton diffusions gradually as the temperature is raised.

On the other hand, the increase of about 1 order of magnitude is detected in the conductivity curve of $Cu_4I_4(CH_3NHCS)_2$ in the temperature range from room temperature to the bending temperature (435 K), but no temperature dependence of the conductivity for the $CuI(CH_3NHCS)_2$ complex is observed in the range from room temperature to 425 K. Thus, it is considered that a part of the protons in the $Cu_4I_4(CH_3NHCS)_2$ complex begins to transfer gradually with increasing temperature in the temperature range, and the proton migration in the $CuI(CH_3NHCS)_2$ complex does not exist at all in the temperature rage.

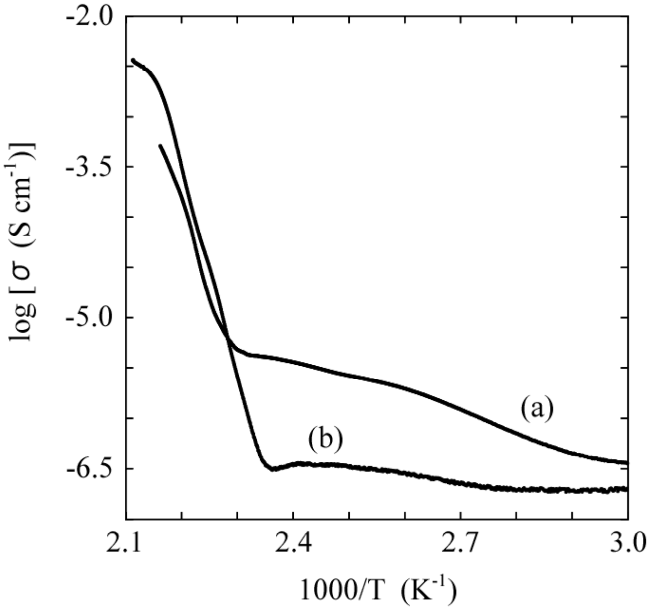

Fig. (1). Temperature dependences of electrical conductivity σ for (a) $Cu_4I_4(CH_3NHCS)_2$ and (b) $CuI(CH_3NHCS)_2$ polymer complexes at 100 kHz on heating.

From the studies of the X-ray diffraction measurements, the observed lattice parameters at room temperature indicated monoclinic and triclinic systems for the $Cu_4I_4(CH_3NHCS)_2$ and $CuI(CH_3NHCS)_2$ complexes, respectively. Furthermore, by the observed systematic extinction conditions the space group of $Cu_4I_4(CH_3NHCS)_2$ was proposed to be monoclinic Cm, C2 or C2/m, and that of $CuI(CH_3NHCS)_2$ was proposed to be triclinic P1 or P-1. The crystal structures of the complexes were refined with the space groups C2/m and P-1, which have higher symmetry than the other groups, respectively. The numbers of the parameters refined are one-half of that of the other groups. Therefore, this is the proper choice for the structural determination. The positional parameters in fractions of a unit cell and the thermal parameters of the atoms are listed in Table **2**. The selected interatomic distances and angles, and hydrogen bond geometry are given in Tables **3** and **4**, respectively. Figs. (**2**,**3**) show the projections of the crystal structures of the $Cu_4I_4(CH_3NHCS)_2$ and $CuI(CH_3NHCS)_2$ complexes at room temperature.

The refined C2/m structure of $Cu_4I_4(CH_3NHCS)_2$ is not directly compared with the previously reported one [8]. Because of the lattice parameters and the space group have not been presented in the previous paper. However, the obtained bond distances and angles about the dithiooxamide ligand are very similar to those previous reported. Thus, it is probably that the obtained C2/m structure is equal to the previously reported one. It is confirmed that there are the dithiooxamide ligands of the S-trans form in the refined structure. Moreover, the obtained structure of the ligand is similar to that in $CuCl(C_2N_2S_2H_4)_{1.5}(H_2O)_{0.45}$ and $CuCl(C_2N_2S_2H_4)$ complexes [14,15]. In the complex of $Cu_4I_4(CH_3NHCS)_2$, the lengths of the C(1)-C(1), S-C(1), N-C(1) and N-C(2) bonds in the dithiooxamide ligand are 1.53(1), 1.71(1), 1.30(1) and 1.47(2) Å, respectively. Moreover, the lengths of the N-H and C(2)-H bonds are around 1 Å, as shown in Tables **3** and **4**. It is seen in Fig. (**2**) that the Cu and I atoms are located between the dithiooxamide ligands in the ac-plane and in the range 2.20-4.08 Å along the b-direction. There are three equivalent Cu atoms around the I atom, and the distances between these atoms are about 2.7 Å. There exist six C(2)-H· · ·C(2) and two N-H· · ·S hydrogen bonds between the neighboring dithiooxamide ligands on the ac-plane, and the lengths of the C-H· · ·C bonds are 4.00(2) or 4.65(2), and of the N-H· · ·S bonds are 3.00(1) Å, as shown in Table **4**. Furthermore, there are weak N-H· · ·I and N-H· · ·Cu hydrogen bonds in the structure. Thus, these results indicate the existence of the proton conductive two-dimensional coordination layer consisting of the dithiooxamide ligands in the $Cu_4I_4(CH_3NHCS)_2$ complex.

On the other hand, the obtained P-1 structure of $CuI(CH_3NHCS)_2$ is a little similar to the C2/m structure of $Cu_4I_4(CH_3NHCS)_2$. It is also confirmed that there are the dithiooxamide ligands of the S-trans form in this structure. Moreover, the Cu and I atoms are located between the dithiooxamide ligands, but the configuration around the I atom is different from that in the C2/m structure. There are two equivalent Cu atoms around the I atom, and the distances between these atoms are about 2.7 Å. In the complex of $CuI(CH_3NHCS)_2$, there are many bonds in the dithiooxamide ligand, as shown in Tables **3** and **4**. The lengths of the C-C bonds, the S-C bonds and the two types of the N-C bonds are in the ranges of 1.512(6)-1.509(5), 1.675(4)-1.681(4), 1.306(5)-1.313(5) and 1.446(7)-1.459(6) Å, respectively. The lengths of the N-H and C-H bonds are around 1 Å. There exist ten C-H· · ·C and two N-H· · ·S hydrogen bonds between the neighboring dithiooxamide ligands, and the bond lengths are in the ranges of 3.675(8)-4.311(8) and 3.037(5)-3.097(4) Å, respectively. Moreover, there are weak N-H· · ·I and N-H· · ·Cu hydrogen bonds, and in addition, many very weak hydrogen bonds (N-H· · ·N, N-H· · ·C, C-H· · ·I, C-H· · ·Cu, C-H· · ·S and C-H· · ·N bonds). Thus, these results indicate that the structure of the dithiooxamide ligands is very similar to that in $Cu_4I_4(CH_3NHCS)_2$ and there are a lot of hydrogen-bonded chains in the $CuI(CH_3NHCS)_2$ complex. That is, the number of the chain is very different from that in the $Cu_4I_4(CH_3NHCS)_2$ complex. This complex does not have the two-dimensional coordination layer for the proton conduction but a three-dimensional conduction channel.

It has been reported that the protons in the dithiooxamide ligand are transferred by the derivation from the dibasic acid character and the proton coupled redox property [6,16]. Generally, it is believed that the proton conduction in hydrogen-bonded crystals is caused by the proton hopping between stable positions on the bonds in the hydrogen-bonded chains.

Table 2. Atomic Coordinates and Thermal Parameters ($Å^2$) with Standard Deviations in Brackets for (a) $Cu_4I_4(CH_3NHCS)_2$ and (b) $CuI(CH_3NHCS)_2$ Polymer Complexes. The Anisotropic Thermal Parameters are Defined as Exp [$-2\pi^2$ (U11$a^{*2}h^2$ + U22$b^{*2}k^2$ + U33$c^{*2}l^2$ + 2U12a*b*hk + 2U13a*c*hl + 2U23b*c*kl)]. Isotropic Thermal Parameters for H Atoms are Listed Under U11

(a)

Atom	X	Y	Z	U11	U22	U33	U12	U13	U23
I	0.01793(6)	0.20381(4)	0.24914(6)	0.0201(1)	0.0269(2)	0.0195(1)	-0.0022(1)	0.0061(1)	-0.0015(2)
Cu	0.8034(1)	0.1755(1)	0.4175(1)	0.0305(4)	0.0276(5)	0.0305(4)	-0.0011(4)	0.0138(3)	-0.0014(4)
S	0.6946(3)	0	0.3690(3)	0.0215(8)	0.0171(9)	0.0292(9)	0	0.0136(6)	0
N	0.3429(11)	0	0.2869(11)	0.019(3)	0.023(4)	0.016(3)	0	0.000(2)	0
C(1)	0.5007(11)	0	0.4088(12)	0.016(3)	0.011(3)	0.019(3)	0	0.004(2)	0
C(2)	0.3109(18)	0	0.1028(15)	0.033(5)	0.039(6)	0.019(4)	0	0.002(4)	0
H(1)	0.17(3)	0	0.03(3)	0.03(6)					
H(2)	0.37(2)	0.06(1)	0.07(2)	0.03(4)					
H(3)	0.23(3)	0	0.31(3)	0.03(6)					

(b)

Atom	X	Y	Z	U11	U22	U33	U12	U13	U23
I(1)	0.08689(3)	0.18987(3)	0.01667(2)	0.0404(1)	0.02875(9)	0.0363(1)	-0.00994(7)	-0.01422(8)	-0.00183(8)
I(2)	0.29483(4)	0.65057(3)	0.59982(2)	0.0442(1)	0.0458(1)	0.0300(1)	0.0048(1)	-0.0074(1)	-0.0037(1)
Cu(1)	0.91127(7)	0.08873(6)	0.91013(4)	0.0398(2)	0.0347(2)	0.0395(2)	-0.0091(2)	-0.0070(2)	-0.0040(2)
Cu(2)	0.59431(8)	0.42498(6)	0.57945(4)	0.0435(2)	0.0395(2)	0.0341(2)	-0.0104(2)	-0.0096(2)	-0.0029(2)
S(1)	0.6151(1)	0.2361(1)	0.94732(7)	0.0365(4)	0.0455(5)	0.0346(4)	0.0020(4)	-0.0140(3)	-0.0156(3)
S(2)	0.5323(2)	0.2020(1)	0.65969(7)	0.0708(5)	0.0355(4)	0.0267(4)	-0.0219(3)	-0.0141(3)	-0.0018(3)
S(3)	0.2071(1)	0.4839(1)	0.36026(8)	0.0389(4)	0.0280(4)	0.0456(4)	-0.0060(3)	-0.0178(3)	-0.0013(3)
S(4)	-0.0513(2)	0.9251(1)	0.25328(8)	0.0521(5)	0.0263(4)	0.0333(4)	-0.0039(4)	-0.0023(4)	-0.0018(3)
N(1)	0.4133(4)	0.4050(4)	0.8191(2)	0.034(1)	0.031(1)	0.031(1)	-0.004(1)	-0.004(1)	-0.007(1)
N(2)	0.5516(5)	0.0265(4)	0.8288(3)	0.057(2)	0.030(1)	0.032(1)	-0.009(1)	-0.012(1)	-0.003(1)
N(3)	0.0135(5)	0.6034(3)	0.2186(2)	0.039(1)	0.027(1)	0.036(1)	-0.008(1)	-0.010(1)	-0.005(1)
N(4)	-0.0754(6)	0.7614(4)	0.4290(3)	0.058(2)	0.038(2)	0.029(1)	-0.005(2)	-0.003(1)	-0.006(1)
C(1)	0.5162(5)	0.2753(4)	0.8464(3)	0.025(1)	0.032(1)	0.027(1)	-0.007(1)	-0.002(1)	-0.007(1)
C(2)	0.3752(7)	0.5309(5)	0.8715(3)	0.050(2)	0.036(2)	0.047(2)	0.003(2)	-0.009(2)	-0.019(1)
C(3)	0.5359(5)	0.1606(4)	0.7817(3)	0.029(1)	0.032(1)	0.028(1)	-0.008(1)	-0.005(1)	-0.006(1)
C(4)	0.5743(9)	-0.1009(5)	0.7821(4)	0.091(3)	0.030(2)	0.052(2)	-0.012(2)	-0.024(2)	-0.006(2)
C(5)	0.0640(5)	0.6191(4)	0.2986(3)	0.029(1)	0.027(1)	0.030(1)	-0.008(1)	-0.004(1)	-0.002(1)
C(6)	0.0797(7)	0.4721(4)	0.1708(3)	0.053(2)	0.033(2)	0.043(2)	-0.010(1)	-0.009(2)	-0.013(1)
C(7)	-0.0213(5)	0.7674(4)	0.3323(3)	0.028(1)	0.030(1)	0.031(1)	-0.007(1)	-0.004(1)	-0.004(1)
C(8)	-0.1742(10)	0.8861(6)	0.4797(4)	0.094(4)	0.051(3)	0.042(2)	0.007(3)	-0.001(3)	-0.020(2)
H(1)	0.385(7)	0.435(6)	0.751(4)	0.02(1)					
H(2)	0.556(8)	0.003(6)	0.885(4)	0.03(2)					
H(3)	-0.052(7)	0.675(6)	0.181(4)	0.02(1)					
H(4)	-0.036(8)	0.681(6)	0.466(4)	0.03(2)					
H(5)	0.285(8)	0.527(6)	0.924(4)	0.03(2)					
H(6)	0.354(9)	0.598(7)	0.823(5)	0.05(2)					
H(7)	0.477(8)	0.539(6)	0.888(4)	0.03(2)					
H(8)	0.607(9)	-0.185(7)	0.820(5)	0.04(2)					
H(9)	0.462(12)	-0.108(10)	0.781(7)	0.09(3)					
H(10)	0.667(9)	-0.101(7)	0.736(5)	0.05(2)					
H(11)	0.009(8)	0.502(7)	0.104(4)	0.03(2)					
H(12)	0.011(9)	0.413(7)	0.190(5)	0.05(2)					
H(13)	0.183(8)	0.423(7)	0.178(5)	0.04(2)					
H(14)	-0.167(8)	0.862(7)	0.548(5)	0.04(2)					
H(15)	-0.275(9)	0.956(7)	0.446(5)	0.05(2)					
H(16)	-0.136(9)	0.949(7)	0.452(5)	0.04(2)					

Table 3. Selected Interatomic Distances (in Å) and Angles (in Degrees) of (a) $Cu_4I_4(CH_3NHCS)_2$ and (b) $CuI(CH_3NHCS)_2$ Polymer Complexes at 297 K

(a)

S-C(1)	1.709(11)	C(1)-C(1)^{a}	1.530(15)
N-C(1)	1.304(11)	N-C(2)	1.466(16)
I···Cu^{b}	2.620(1)	I···Cu^{c}	2.652(1)
I···Cu^{d}	2.679(1)	Cu···Cu^{e}	2.649(2)
Cu···Cu^{f}	2.949(1)	Cu···S	2.351(1)
S···N	2.654(9)	N···C(1)^{a}	2.391(12)
S···C(1)^{a}	2.839(12)	S···C(2)	3.072(12)
C(1)···C(2)	2.453(14)	S···H(2)	2.98(11)
N···H(1)^{c}	2.08(18)	N···H(2)	2.06(16)
C(1)···H(3)	2.02(19)	C(1)···H(2)	2.76(13)
C(2)···H(3)	2.03(25)	C(1)···H(3)^{a}	2.56(17)
S-C(1)-N	122.9(8)	S-C(1)-C(1)^{a}	122.4(6)
N-C(1)-C(1)^{a}	114.8(9)	C(1)-N-C(2)	124.5(11)

(b)

S(1)-C(1)	1.681(4)	S(2)-C(3)	1.676(4)
N(1)-C(1)	1.310(4)	N(1)-C(2)	1.459(6)
N(2)-C(3)	1.306(5)	N(2)-C(4)	1.446(7)
C(1)-C(3)	1.512(6)	S(3)-C(5)	1.681(3)
S(4)-C(7)	1.675(4)	N(3)-C(5)	1.311(6)
N(3)-C(6)	1.453(6)	N(4)-C(7)	1.313(5)
N(4)-C(8)	1.447(7)	C(5)-C(7)	1.509(5)
C(2)-H(6)	0.84(6)	C(4)-H(9)	0.88(10)
C(6)-H(11)	1.14(7)	C(6)-H(13)	0.82(6)
C(8)-H(15)	1.01(6)	I(1)···Cu(1)^{g}	2.6781(8)
I(1)···Cu(1)^{h}	2.6530(6)	I(2)···Cu(2)	2.6886(6)
I(2)···Cu(2)^{i}	2.6323(6)	Cu(1)···Cu(1)^{j}	3.1031(8)
Cu(1)···S(1)	2.324(1)	Cu(1)···S(4)^{i}	2.303(1)
Cu(2)···Cu(2)^{i}	2.8522(8)	Cu(2)···S(2)	2.321(1)
Cu(2)···S(3)^{i}	2.323(2)	S(1)···N(1)	2.636(3)
S(1)···C(2)	3.049(4)	S(1)···C(3)	2.792(4)
S(2)···N(2)	2.619(3)	S(2)···C(1)	2.802(4)
S(3)···N(3)	2.636(4)	S(3)···C(6)	3.056(5)
S(3)···C(7)	2.802(3)	S(4)···N(4)	2.632(4)
S(4)···C(5)	2.799(4)	S(4)···C(8)	3.064(5)
N(1)···C(3)	2.382(5)	N(2)···C(1)	2.376(5)
N(3)···C(7)	2.373(6)	N(4)···C(5)	2.369(5)
C(1)···C(2)	2.445(6)	C(3)···C(4)	2.435(6)
C(5)···C(6)	2.448(7)	C(6)···C(7)	3.771(6)
C(7)···C(8)	2.449(7)	C(1)-N(1)-C(2)	123.9(4)
C(3)-N(2)-C(4)	124.4(4)	C(5)-N(3)-C(6)	124.6(3)
C(7)-N(4)-C(8)	125.0(4)	S(1)-C(1)-N(1)	123.1(3)
S(1)-C(1)-C(3)	121.9(2)	N(1)-C(1)-C(3)	115.0(3)
S(2)-C(3)-N(2)	122.4(3)	S(2)-C(3)-C(1)	122.9(3)
N(2)-C(3)-C(1)	114.7(3)	S(3)-C(5)-N(3)	122.9(3)
S(3)-C(5)-C(7)	122.8(3)	N(3)-C(5)-C(7)	114.4(3)
S(4)-C(7)-N(4)	123.0(3)	S(4)-C(7)-C(5)	123.0(3)
N(4)-C(7)-C(5)	114.0(3)		

Symmetry codes: (a), 1-x, -y, 1-z; (b), x-1, y, z; (c), 1-x, y, 1-z; (d), x-1/2, 1/2-y, z; (e), 3/2-x, 1/2-y, 1-z; (f), 2-x, y, 1-z; (g), x-1, y, z-1; (h), 1-x, -y, 1-z; (i), 1-x, 1-y, 1-z; (j), 2-x, -y, 2-z.

Table 4. Hydrogen Bond Geometry (in Å and Degrees) of (a) $Cu_4I_4(CH_3NHCS)_2$ and (b) $CuI(CH_3NHCS)_2$ Polymer Complexes

(a)

D-H···A	D-H	H···A	D···A	D-H···A
C(2)-H(1)···C(2)^{a}	1.05(19)	3.64(20)	4.653(19)	164(6)
C(2)-H(2)···C(2)^{b}	0.97(15)	3.43(16)	4.004(22)	118(3)
N-H(3)···I	0.97(24)	3.02(11)	3.588(7)	119(6)
N-H(3)···Cu^{c}		3.28(18)	3.807(9)	116(8)
N-H(3)···S^{c}		2.57(22)	3.003(10)	107(2)

(b)

D-H···A	D-H	H···A	D···A	D-H···A
C(2)-H(5)···C(6)^{d}	0.88(5)	3.35(7)	3.675(8)	104(5)
C(2)-H(5)···C(6)^{e}		3.45(6)	4.284(6)	158(5)
C(2)-H(7)···C(2)^{f}	0.88(7)	3.68(6)	4.311(8)	132(4)
C(2)-H(7)···C(6)^{g}		3.29(6)	4.076(7)	150(5)
C(4)-H(8)···C(6)^{c}	0.88(6)	3.11(6)	3.841(6)	142(5)
C(4)-H(10)···C(8)^{h}	0.85(6)	3.52(7)	4.234(7)	144(7)
C(6)-H(12)···C(2)^{d}	0.84(7)	3.15(7)	3.675(8)	123(5)
C(6)-H(13)···C(2)^{g}	0.82(6)	3.43(7)	4.076(7)	138(6)
C(6)-H(13)···C(4)^{c}		3.15(6)	3.841(6)	145(6)
C(8)-H(14)···C(4)^{i}	0.95(6)	3.44(6)	4.234(7)	143(4)
C(8)-H(16)···C(8)^{j}	0.74(7)	3.57(8)	4.071(12)	128(6)
N(1)-H(1)···I(2)	1.00(5)	2.71(5)	3.599(3)	149(4)
N(1)-H(1)···Cu(2)		2.56(5)	3.307(3)	132(4)
N(1)-H(1)···S(2)		2.64(5)	3.064(4)	106(3)
N(2)-H(2)···I(1)^{k}	0.77(6)	3.78(5)	4.039(3)	104(4)
N(2)-H(2)···Cu(1)		3.16(7)	3.442(5)	105(5)
N(2)-H(2)···S(1)		2.73(7)	3.037(5)	106(5)
N(3)-H(3)···I(1)^{l}	0.88(5)	2.85(5)	3.610(3)	145(4)
N(3)-H(3)···Cu(1)^{g}		2.73(6)	3.251(3)	119(5)
N(3)-H(3)···S(4)		2.78(6)	3.097(4)	103(5)
N(4)-H(4)···I(2)	0.85(5)	3.40(7)	3.913(5)	121(6)
N(4)-H(4)···Cu(2)^{g}		3.21(6)	3.614(4)	112(4)
N(4)-H(4)···S(3)		2.67(6)	3.092(4)	112(4)

Symmetry codes: (a), -x,-y,-z; (b), 1-x,-y,-z; (c), 1-x,-y,1-z; (d), -x,1-y,1-z; (e), x,y,1+z; (f), 1-x,1-y,2-z; (g), 1-x,1-y,1-z; (h), 1+x,-1+y,z; (i), -1+x,1+y,z; (j), -x,2-y,1-z; (k), x,y,1+z; (l), -x,1-y,-z.

There is no large difference in the structure of the ligands between the $Cu_4I_4(CH_3NHCS)_2$ and $CuI(CH_3NHCS)_2$ complexes. Therefore, it is necessary for the interpretation of the difference in the conductivity to establish the proton transfer

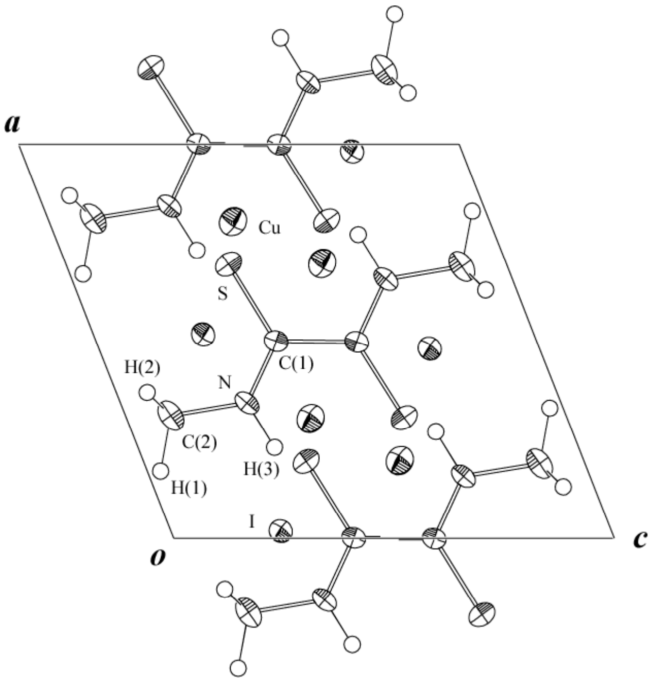

Fig. (2). Projection on the ac-plane of the crystal structure of $Cu_4I_4(CH_3NHCS)_2$ at 297 K with 50% probability-displacement ellipsoids.

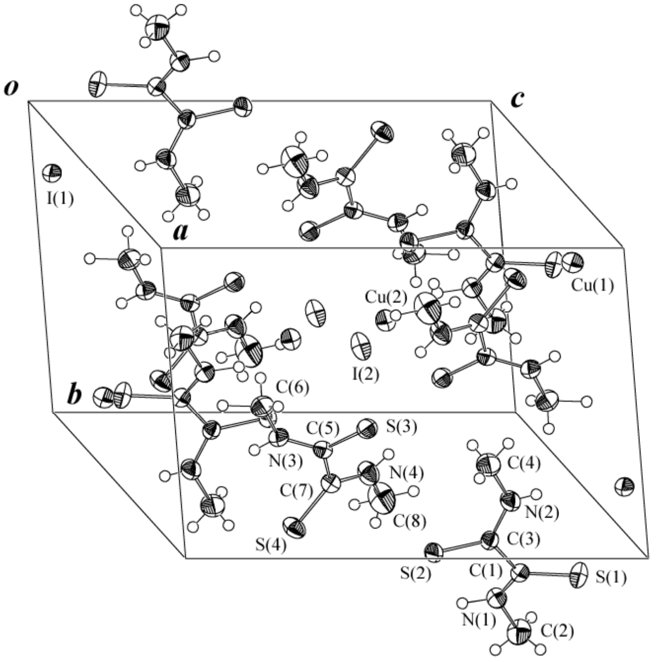

Fig. (3). Perspective view of the crystal structure of $CuI(CH_3NHCS)_2$ at 297 K with 50% probability-displacement ellipsoids.

on the hydrogen bond. As mentioned above, there are the six and ten C-H· · ·C hydrogen bonds between the neighboring ligands in the $Cu_4I_4(CH_3NHCS)_2$ and $CuI(CH_3NHCS)_2$ complexes, respectively. The hydrogen-bonded chains for the proton conduction channel are produced by the hydrogen bonds between the ligands. The conductivity at high temperature of $CuI(CH_3NHCS)_2$ is almost four times larger than that of $Cu_4I_4(CH_3NHCS)_2$. Thus, it is probable that this difference in the conductivity is caused by the difference in the number of the C-H· · ·C hydrogen bonds between the dithiooxamide ligands.

In summary, the single crystals of the $Cu_4I_4(CH_3NHCS)_2$ and $CuI(CH_3NHCS)_2$ polymer complexes have been crystallized from the acetonitrile solutions. The electrical conductivity and X-ray diffraction measurements have been performed on these complexes. The space group symmetries (monoclinic C2/m and triclinic P-1) and the structures of $Cu_4I_4(CH_3NHCS)_2$ and $CuI(CH_3NHCS)_2$ are determined at room temperature. It is suggested from the temperature dependence of the conductivity that these complexes become the proton superionic conductor gradually as the temperature is raised above the bending temperatures. The difference in the conductivity at high temperature of these complexes is suggested to be caused by the difference in the number of the hydrogen bonds between the dithiooxamide ligands.

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