

The First Example of a Discrete Thiocyanatocuprate(I) Anion. Crystal Structure of Bis[6-amino-1,3-dimethyl-5-(2'-ethyl)phenylazonium Uracil] Tris(thiocyanato-S)-cuprate(I)

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The crystal structure of the title compound $[H_2L]_2[Cu(SCN)_3]$ [where H_2L^+ is the 6-amino-1,3-dimethyl-5-(2'-ethyl)phenylazonium uracil cation] was determined by X-ray crystallography. The compound crystallizes in the monoclinic system, space group $P2_1$, with $a = 7.740(3)$, $b = 40.09(3)$, $c = 11.950(7)$ Å, $\beta = 97.11(4)^\circ$, $Z = 4$, $R = 0.125$, $wR = 0.108$. The structure consists of discrete $[Cu(SCN)_3]^{2-}$ anions and H_2L^+ cations joined together by hydrogen bonds. There are two non-equivalent tris(thiocyanato-S)cuprate(I) anions in the structure. In each anion the copper(I) atom is coordinated to the sulfur atoms of the three thiocyanate anions in a distorted trigonal planar configuration.

The available structural information on copper(I)-thiocyanate systems is limited to copper thiocyanate itself^{1,2} and a few salts of the polynuclear anions $[Cu(SCN)_2]_x^-$,³ $[Cu(SCN)_3]_x^-$ ⁴ and $[Cu_2(SCN)_3]_x^-$.⁵ The lack of structural information on any discrete thiocyanate cuprate(I) anions prompted us to investigate such systems. Large 6-amino-5-phenylazonium uracil cations were used in these studies because of their ability to stabilize AuX_2^- ($X = Cl^-$ and Br^-)⁶ and $CuBr_3^-$ anions.⁷ Here we report the preparation and crystal structure of bis[6-amino-1,3-dimethyl-5-(2'-ethyl)phenylazonium uracil] tris(thiocyanato-S)cuprate(I), the first example of a stable $[Cu(SCN)_3]^{2-}$ anion.

Experimental

6-Amino-1,3-dimethyl-5-(2'-ethyl)phenylazouracil (HL) was synthesized by coupling 2-ethylaniline and 6-amino-1,3-dimethyl uracil as described previously.⁶ The compound was recrystallized from hot ethanol in 75% yield (m.p. 264–265 °C).

Infrared spectra were recorded in the 4000–180 cm^{-1} range with a Perkin-Elmer 983G spectrometer using KBr pellets.

Preparation of $[H_2L]_2[Cu(SCN)_3]$. The compound was prepared by adding 0.24 g (1 mmol) of $Cu(NO_3)_2 \cdot 3H_2O$ and 0.97 g (10 mmol) KSCN to a boiling solution of 0.58 g (2 mmol) HL in 50 cm^3 ethanol/water (20:1), and the mixture was boiled for an additional 10 min. After filtration of the hot reaction mixture, the resulting solution was allowed to stand at room temperature. Orange analytically pure needle-like crystals formed within one week. The yield was 30% (m.p. 204–205 °C).

X-Ray experimental. Crystal data, the details of data collection and the structure refinement are summarized in Table 1. Numerous attempts to crystallize a specimen suitable for X-ray data collection yielded apparently well formed needle-like crystals, but careful inspection using a polarizing microscope showed the specimen to be opaque and to be formed of numerous thin mosaic sheets. Several crystals were examined, but the peak profiles were always highly broadened and the diffraction power was modest even at low reflection angles. The crystal chosen for data collection was covered with two-component epoxy glue. The check reflections measured periodically during the data collection showed only statistical variation. ψ -Scans for several intense reflections verified the absence of noteworthy variable absorption. The data were corrected for Lorentz and polarization effects and for dispersion. In view of the poor crystal quality and poor statistics of the weak reflections, we focused our

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Table 1. Crystal data, data collection and structure refinement.

Crystal data	
[C ₁₄ H ₁₈ N ₆ O ₂] ₂ [Cu(SCN) ₃]	$\theta = 4-7^\circ$
$M_r = 814.44$	$V = 3680(4) \text{ \AA}^3$
Monoclinic	$Z = 4$
$P2_1$	$D_x = 1.470 \text{ Mg m}^{-3}$
$a = 7.740(3) \text{ \AA}$	MoK α
$b = 40.09(3) \text{ \AA}$	$\lambda = 0.71069 \text{ \AA}$
$c = 11.950(7) \text{ \AA}$	$\mu = 0.81 \text{ mm}^{-1}$
$\beta = 97.11(4)^\circ$	$T = 296 \text{ K}$
Lattice parameters from 15 reflections	Orange needle $0.12 \times 0.16 \times 0.28 \text{ mm}$
Data collection	
Nicolet P3F four-circle diffractometer	ω scan, scan speed $1.5-15^\circ \text{ min}^{-1}$, scan width 1.5° for reflections
Absorption correction: none	$R_{\text{int}} = 0.077$
5311 measured reflections	$\theta_{\text{max}} = 22.5^\circ$
4884 independent reflections	3 standard reflections, frequency 100 reflections, variation 1.5%
1335 observed reflections, criterion $ F > 6\sigma(F)$	
$h_{\text{min}} = 0$	$h_{\text{max}} = 8$
$k_{\text{min}} = 0$	$k_{\text{max}} = 43$
$l_{\text{min}} = -12$	$l_{\text{max}} = 12$
Refinement	
Partial rigid group refinement	Refinement on F
$R = 0.125$	152 parameters
$wR = 0.108$	1335 reflections in refinements
$S = 3.62$	$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\text{max}} = 0.054$	$\Delta\rho_{\text{min}} = -0.8 \text{ e \AA}^{-3}$
Extinction correction: none	$\Delta\rho_{\text{max}} = 1.0 \text{ e \AA}^{-3}$
	Atomic scattering factors included in the XTAL2.6 system ^a

^aHall and Stewart.⁹

main interest on the general structure of the compound. Accordingly two criteria were used to limit the data. 1820 reflections with $|F| > 4\sigma(F)$ and 1335 reflections with $|F| > 6\sigma(F)$ were considered in refinements of individual non-hydrogen atoms and a final rigid group refinement, respectively.

The structure was partly solved by heavy-atom methods using the SHELXS-86 program.⁸ A series of subsequent Fourier maps and refinements by the XTAL program system⁹ revealed all the non-hydrogen atoms. Owing to the lack of significant reflections, attempts were made to refine all non-hydrogen atoms with a reduced number of parameters. However, the refinements with anisotropic thermal parameters for the copper atoms and isotropic thermal parameters for the other non-hydrogen atoms resulted in high R -values (> 0.14 for 1820 reflections) and several abnormal temperature and/or bond parameters for the cations. To obtain more realistic bond parameters for the cations, the rigid group method was employed by using the program XTAL.

The two following atom groups of [H₂L]Br·2H₂O¹⁰ were assumed to be 'ideal' groups and included in the final rigid-group refinement: the phenyl group, including the non-hydrogen atoms directly bonded to the phenyl group [N(8) and C(15)], and the substituted pyrimidine moiety, including all non-hydrogen atoms directly bonded to the ring.

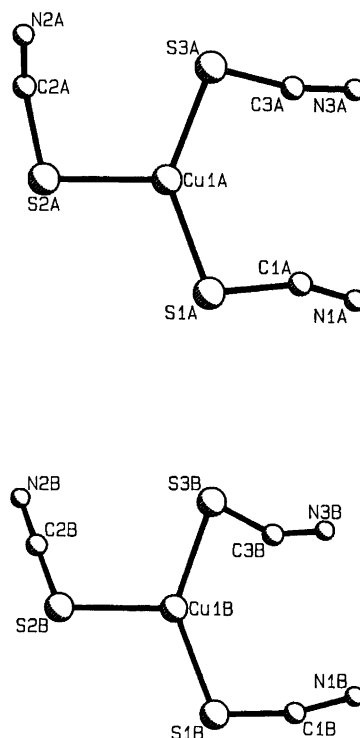


Fig. 1. Perspective view of the two independent [Cu(SCN)₃]²⁻ anions.

Positional and thermal parameters of the atoms of $[\text{Cu}(\text{SCN})_3]^{2-}$ and the ethyl carbons C(16) of cations **2** and **4** were refined like those of individual atoms. The parameters of ethyl carbons C(16) of cations **1** and **3** were not refined. The positions, orientations and group isotropic thermal parameters of the rigid groups were refined. Anisotropic thermal parameters were applied only in refining the positions of the copper atoms. The hydro-

gen atoms were not included in the calculations. Scattering factors for neutral atoms were those included in the programs. The refinements of this atomic arrangement resulted in the final R -value of 0.126 ($wR = 0.108$). Refinement of the enantiomeric model did not decrease the R -value. Clearly, the main reason for the modest R -value was the poor crystal quality. A second reason was that the assumed rigid groups were not exactly rigid.

Table 2. Positional and isotropic displacement parameters for non-hydrogen atoms.

Atom	x/a	y/b	z/c	$U/\text{Å}^2$
Anions				
Cu(1A)	0.038(1)	0.0000 ^a	0.0489(9)	0.045(5)
S(1A)	-0.095(3)	0.0367(6)	-0.073(2)	0.051(8)
S(2A)	-0.002(3)	-0.0534(6)	-0.018(2)	0.045(8)
S(3A)	0.218(3)	0.0009(8)	0.211(2)	0.088(9)
N(1A)	-0.094(8)	0.100(2)	0.013(5)	0.05(2)
N(2A)	0.295(8)	-0.084(2)	0.110(5)	0.06(2)
N(3A)	0.208(9)	0.066(2)	0.272(6)	0.07(3)
C(1A)	-0.071(8)	0.074(2)	-0.004(6)	0.02(2)
C(2A)	0.17(1)	-0.076(2)	0.067(6)	0.04(3)
C(3A)	0.19(1)	0.039(3)	0.240(8)	0.088(9)
Cu(1B)	0.577(1)	0.2381(3)	0.294(1)	0.068(6)
S(1B)	0.712(3)	0.2021(6)	0.426(2)	0.044(8)
S(2B)	0.622(4)	0.2937(8)	0.349(3)	0.12(1)
S(3B)	0.397(4)	0.2366(9)	0.127(3)	0.12(1)
N(1B)	0.701(8)	0.138(2)	0.303(6)	0.07(3)
N(2B)	0.321(9)	0.329(2)	0.274(6)	0.08(3)
N(3B)	0.44(1)	0.178(2)	0.094(9)	0.18(5)
C(1B)	0.713(9)	0.164(2)	0.370(6)	0.04(3)
C(2B)	0.45(1)	0.314(2)	0.307(6)	0.04(3)
C(3B)	0.44(1)	0.202(3)	0.136(9)	0.12(1)
Cation 1				
O(102)	-0.057(4)	0.2449(7)	0.208(2)	0.039(6)
O(104)	0.285(4)	0.2087(9)	0.513(2)	0.039(6)
N(101)	0.022(3)	0.1907(6)	0.210(2)	0.039(6)
N(103)	0.122(3)	0.2277(5)	0.359(2)	0.039(6)
N(106)	0.108(5)	0.1358(6)	0.213(3)	0.039(6)
N(107)	0.281(5)	0.1432(8)	0.417(3)	0.039(6)
N(108)	0.393(7)	0.146(1)	0.510(4)	0.031(9)
C(101)	-0.076(4)	0.1868(9)	0.098(2)	0.039(6)
C(102)	0.022(3)	0.2225(6)	0.257(2)	0.039(6)
C(103)	0.124(5)	0.2615(6)	0.405(2)	0.039(6)
C(104)	0.208(3)	0.2025(7)	0.419(2)	0.039(6)
C(105)	0.204(3)	0.1703(6)	0.369(2)	0.039(6)
C(106)	0.110(3)	0.1646(5)	0.260(2)	0.039(6)
C(109)	0.468(4)	0.1173(9)	0.564(2)	0.031(9)
C(110)	0.558(4)	0.1221(7)	0.672(2)	0.031(9)
C(111)	0.627(4)	0.0939(9)	0.724(2)	0.031(9)
C(112)	0.610(5)	0.0630(8)	0.675(3)	0.031(9)
C(113)	0.522(6)	0.0591(8)	0.570(3)	0.031(9)
C(114)	0.451(5)	0.086(1)	0.514(2)	0.031(9)
C(115)	0.574(8)	0.1564(9)	0.724(4)	0.031(9)
C(116)	0.6560	0.1670	0.8480	0.040
Cation 2				
O(202)	-0.136(3)	0.405(1)	0.553(2)	0.050(6)
O(204)	0.251(8)	0.3221(7)	0.571(3)	0.050(6)
N(201)	0.122(5)	0.4138(5)	0.660(2)	0.050(6)
N(203)	0.052(4)	0.3626(7)	0.566(2)	0.050(6)
N(206)	0.384(6)	0.422(1)	0.770(2)	0.050(6)

Continued.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U/Å²</i>
N(207)	0.492(3)	0.362(2)	0.714(3)	0.050(6)
N(208)	0.557(9)	0.332(4)	0.688(5)	0.06(1)
C(201)	0.062(8)	0.4468(6)	0.689(3)	0.050(6)
C(202)	0.004(3)	0.3945(8)	0.589(2)	0.050(6)
C(203)	-0.075(6)	0.343(1)	0.494(2)	0.050(6)
C(204)	0.214(5)	0.3500(6)	0.601(2)	0.050(6)
C(205)	0.331(3)	0.370(1)	0.673(2)	0.050(6)
C(206)	0.281(4)	0.4031(9)	0.704(2)	0.050(6)
C(209)	0.723(7)	0.322(2)	0.734(3)	0.06(1)
C(210)	0.765(7)	0.289(1)	0.718(2)	0.06(1)
C(211)	0.930(9)	0.279(1)	0.763(3)	0.06(1)
C(212)	1.046(4)	0.301(3)	0.819(3)	0.06(1)
C(213)	1.00(1)	0.334(2)	0.833(3)	0.06(1)
C(214)	0.84(1)	0.3441(7)	0.791(4)	0.06(1)
C(215)	0.64(1)	0.265(3)	0.656(4)	0.06(1)
C(216)	0.51(1)	0.254(2)	0.733(6)	0.06(3)
Cation 3				
O(302)	0.674(4)	-0.0057(7)	0.156(2)	0.035(6)
O(304)	0.333(3)	0.030(1)	-0.149(2)	0.035(6)
N(301)	0.600(3)	0.0487(6)	0.152(2)	0.035(6)
N(303)	0.511(3)	0.0123(5)	-0.000(2)	0.035(6)
N(306)	0.526(5)	0.1043(6)	0.145(3)	0.035(6)
N(307)	0.336(4)	0.0958(8)	-0.053(3)	0.035(6)
N(308)	0.246(7)	0.093(1)	-0.152(4)	0.036(9)
C(301)	0.704(4)	0.0529(9)	0.262(2)	0.035(6)
C(302)	0.598(2)	0.0167(6)	0.106(2)	0.035(6)
C(303)	0.514(5)	-0.0214(6)	-0.048(2)	0.035(6)
C(304)	0.416(2)	0.0369(7)	-0.057(2)	0.035(6)
C(305)	0.421(3)	0.0692(6)	-0.008(2)	0.035(6)
C(306)	0.518(3)	0.0751(5)	0.100(2)	0.035(6)
C(309)	0.172(4)	0.1215(9)	-0.207(3)	0.036(9)
C(310)	0.076(4)	0.1165(8)	-0.312(3)	0.036(9)
C(311)	0.002(4)	0.145(1)	-0.363(2)	0.036(9)
C(312)	0.021(5)	0.1755(8)	-0.315(3)	0.036(9)
C(313)	0.115(6)	0.1797(8)	-0.212(3)	0.036(9)
C(314)	0.191(5)	0.153(1)	-0.158(3)	0.036(9)
C(315)	0.057(8)	0.0821(9)	-0.364(4)	0.036(9)
C(316)	-0.0586	0.0814	-0.4808	0.040
Cation 4				
O(402)	-0.584(4)	0.330(1)	-0.018(2)	0.047(6)
O(404)	-0.356(8)	0.4147(5)	0.193(3)	0.047(6)
N(401)	-0.305(4)	0.3244(5)	0.061(2)	0.047(6)
N(403)	-0.469(3)	0.3734(7)	0.082(2)	0.047(6)
N(406)	-0.020(5)	0.320(2)	0.139(3)	0.047(6)
N(407)	-0.035(5)	0.379(2)	0.238(2)	0.047(6)
N(408)	-0.01(1)	0.412(3)	0.271(4)	0.05(1)
C(401)	-0.299(8)	0.2918(5)	0.007(3)	0.047(6)
C(402)	-0.462(3)	0.3417(7)	0.039(2)	0.047(6)
C(403)	-0.634(5)	0.392(1)	0.056(3)	0.047(6)
C(404)	-0.335(5)	0.3873(5)	0.152(2)	0.047(6)
C(405)	-0.177(3)	0.369(1)	0.172(2)	0.047(6)
C(406)	-0.163(3)	0.337(1)	0.123(2)	0.047(6)
C(409)	0.135(7)	0.424(1)	0.338(3)	0.05(1)
C(410)	0.129(6)	0.458(1)	0.367(3)	0.05(1)
C(411)	0.272(9)	0.4698(9)	0.434(3)	0.05(1)
C(412)	0.412(5)	0.450(2)	0.470(3)	0.05(1)
C(413)	0.415(8)	0.417(2)	0.441(4)	0.05(1)
C(414)	0.28(1)	0.4045(8)	0.374(4)	0.05(1)
C(415)	-0.03(1)	0.479(3)	0.326(5)	0.05(1)
C(416)	-0.183(7)	0.484(1)	0.405(5)	0.02(2)

^aFixed in order to fix the origin.

Table 3. Selected bond lengths (in Å) and angles (in °) for $[\text{Cu}(\text{SCN})_3]^{2-}$ anions.

Cu(1A)–S(1A)	2.24(2)	Cu(1B)–S(1B)	2.29(2)
Cu(1A)–S(2A)	2.29(2)	Cu(1B)–S(2B)	2.34(3)
Cu(1A)–S(3A)	2.24(3)	Cu(1B)–S(3B)	2.29(3)
S(1A)–Cu(1A)–S(2A)	110.8(9)	S(1B)–Cu(1B)–S(2B)	112(1)
S(1A)–Cu(1A)–S(3A)	138(1)	S(1B)–Cu(1B)–S(3B)	139(1)
S(2A)–Cu(1A)–S(3A)	111(1)	S(2B)–Cu(1B)–S(3B)	109(1)

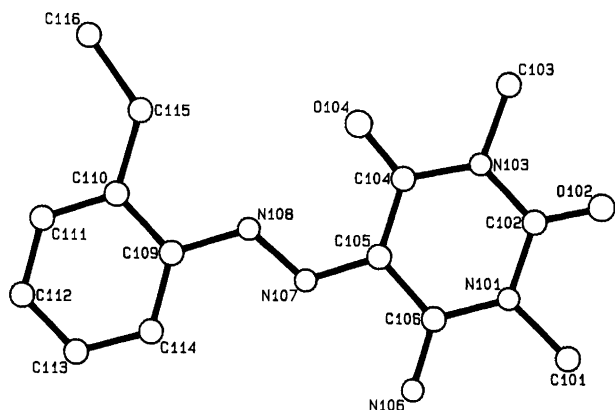


Fig. 2. Perspective view of cation 1.

Results and discussion

In the presence of excess KSCN, Cu(II) is reduced to Cu(I); the $[\text{Cu}(\text{SCN})_3]^{2-}$ complex anion forms and can be isolated as orange crystals of $[\text{H}_2\text{L}]_2[\text{Cu}(\text{SCN})_3]$. The silent ESR spectrum of the compound confirms the oxidation state +1 of the copper atoms.

The asymmetric unit of the structure contains two discrete $[\text{Cu}(\text{SCN})_3]^{2-}$ anions surrounded by four large H_2L^+ cations. The anions are approximately mirror images of each other. Positional parameters, selected bond lengths and angles for the anions, and hydrogen-bond

distances are listed in Tables 2, 3 and 4, respectively. Perspective views of the anions, and cation 1, are presented in Figs. 1 and 2, respectively, and the packing diagram is shown in Fig. 3.

The thiocyanate ion can coordinate to metal ions through either S or N atoms. Among the factors influencing the relative stabilities of these two bonding modes, the most important one is the nature of the central metal ion, in accordance with the HSAB principle.¹¹ The $[\text{Cu}(\text{SCN})_3]^{2-}$ anion must contain S-bonded thiocyanato ions, since a soft (class b) polarizable metal ion such as Cu(I) shows preference for the softer S donor over the less polarizable nitrogen donor atom. Furthermore, the hydrogen bonding ability of the H_2L^+ counterion and the polar nature of the mixture of solvents used in the preparation of the complex also favour the S-coordination of the thiocyanate ligand, since the nitrogen end of the NCS^- ion forms stronger hydrogen bonds than the S atom with the solvent molecules and/or the amino group of the H_2L^+ counter-ion. The crystal structure analysis confirms this bonding mode. The copper(I) atoms are clearly coordinated, in a distorted trigonal planar configuration, to three sulfur atoms from three thiocyanate anions (cf. Fig. 1). The shortest intermolecular distances involving copper atoms are 3.24(3) and 3.15(3) Å for $\text{Cu}(1\text{A})\cdots\text{O}(302)$ and $\text{Cu}(1\text{B})\cdots\text{O}(102)$, respectively. It must be pointed out that structural studies on mononuclear three-coordinated Cu(I)–sulfur

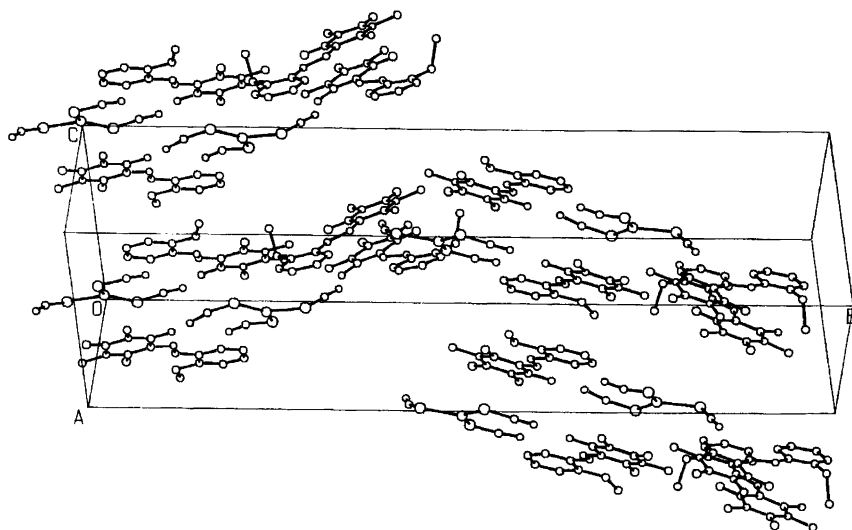


Fig. 3. The packing in the crystal.

Table 4. Hydrogen-bond contact distances (in Å).

Intramolecular			
N(108)···O(104)	2.66(6)	N(308)···O(304)	2.60(6)
N(208)···O(204)	2.63(9)	N(408)···O(404)	2.71(10)
Intermolecular			
N(1A)···N(106)	3.03(7)	N(1B)···N(306)	2.56(7)
N(2A)···N(206) ⁱⁱ	2.71(7)	N(2B)···N(406)	2.94(7)
N(3A)···N(106)	2.97(7)	N(3B)···N(306)	3.06(10)

ⁱⁱEquivalent position $1-x, -\frac{1}{2}+y, 1-z$.

complexes, such as [Cu(SCN)₃]²⁻, are scarce,¹² probably owing to the pronounced tendency of Cu⁺ ions to form polynuclear complexes with sulfur ligands. Pronounced deviations from exact trigonal planar symmetry are evident in the S–Cu–S angles (cf. Table 3). One of the S–Cu–S angles [S(1A)–Cu(1A)–S(2A) = 138(1)° and S(1B)–Cu(1B)–S(2B) = 139(1)°] is greater than the other two angles [109(1)–112(1)°]. Such a distortion is evident in the structure of the tris(thiophenolato)cuprate(I) anion.¹³

The clear non-equivalence of the S–Cu–S angles and the thiocyanate anions might be due to hydrogen bonds involving all the nitrogen atoms of the thiocyanate anions and the amino groups of each H₂L⁺ cation (cf. Table 4).

Characteristic features are observed for the cations in [H₂L]₂[Cu(SCN)₃].^{6,7,10} Protonation at the N(8) nitrogen atom of the azo group, a strong intermolecular hydrogen bond between N(8) and the carbonyl oxygen atom O(4) [the mean value of the N(8)···O(4) distances is 2.65(2) Å] and approximate coplanarity of the molecules [the dihedral angle between the mean plane through the pyrimidine moiety and the phenyl group ranges from 4.7(7) to 11(2)°]. Each ethyl group is situated at the same side of the molecule as the N(8)–H(8) bond. Moreover, there is an important difference between the pairs of similar cations **1**, **3** and **2**, **4**: whereas for the cations **1**, **3** the C(15)–C(16) bond of the ethyl group is approximately in the plane of the benzene ring [C(16) is displaced from this plane by –0.12 Å for cation **1** and –0.04 Å for cation **3**], for the cations **2**, **4** the bond is directed away from this plane [C(16) is displaced by 1.40(11) and –1.40(10) Å from this plane for cations **2** and **4**, respectively]. The first mentioned orientation of the C(15)–C(16) bond has also been observed in the compound [H₂L]Br·2H₂O.¹⁰

Work is in progress to prepare further compounds containing discrete thiocyanate cuprate(I) anions.

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