

Short Communication

Crystal Structure of Bis[6-amino-1,3-dimethyl-5-(2'-ethyl)phenylazonium Uracil] Tris(thiocyanato-*S*)cuprate(I). Redetermination at 193 K

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Our investigations of discrete thiocyanate cuprate(I) anions have been prompted by the lack of structural information on these systems. In a previous paper¹ we reported the 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 $[\text{Cu}(\text{SCN})_3]^{2-}$ anion. The accuracy of the data, which were collected at ambient room temperature, was low owing to the poor crystal quality and limited amount of data. The structure had to be refined mainly as consisting of rigid groups, and the refinements resulted in a high *R*-value of 0.125 ($wR = 0.108$). In view of the novel $[\text{Cu}(\text{SCN})_3]^{2-}$ anions in the structure, we continued our efforts to obtain better crystals and more accurate bond parameters for the anions. Recently we prepared new crystals of the title compound, and collected data at 193 K. All non-hydrogen atoms have now been refined as individual atoms.

Experimental

6-Amino-1,3-dimethyl-5-(2'-ethyl)phenylazouracil (HL) and $[\text{H}_2\text{L}]_2[\text{Cu}(\text{SCN})_3]$ were synthesized as described earlier.¹

Crystal data. $[\text{C}_{14}\text{H}_{18}\text{N}_5\text{O}_2]_2[\text{Cu}(\text{SCN})_3]$, $M_r = 814.44$, monoclinic, $P2_1$, $a = 7.725(9)$, $b = 40.125(8)$, $c = 11.842(7)$ Å, $\beta = 96.19(7)^\circ$, $V = 3649(5)$ Å³, $Z = 4$, $D_x = 1.484$ Mg m⁻³, $\lambda(\text{MoK}\alpha) = 0.71069$ Å, $\mu = 0.81$ mm⁻¹, $T = 193$ K, final $R(F) = 0.079$ and $wR = 0.082$ for 2510 unique reflections and 456 variables.

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The unit cell parameters were determined and the data were collected at 193 K on a Rigaku AFC-7S diffractometer. The data were corrected for Lorentz and polarization factors and for absorption (empirical correction). A total of 7037 reflections were collected ($2\Theta_{\text{max}} = 50^\circ$), giving 6532 unique reflections ($R_{\text{int}} = 0.070$), of which 2510 were considered as observed. Coordinates of the earlier data¹ were used as starting parameters and the structure was refined by the Xtal program system.² Cu and S atoms were refined with anisotropic and C, N and O atoms with isotropic displacement parameters. Hydrogen atoms, except those of the amino groups, were placed in calculated positions with $X-H = 0.96$ Å. Hydrogen atoms were not refined. Further details of the X-ray experiment are included in the supplementary material.

Infrared spectra were recorded in the 4000–180 cm⁻¹ range, with a Perkin-Elmer 983G spectrometer, from KBr pellets.

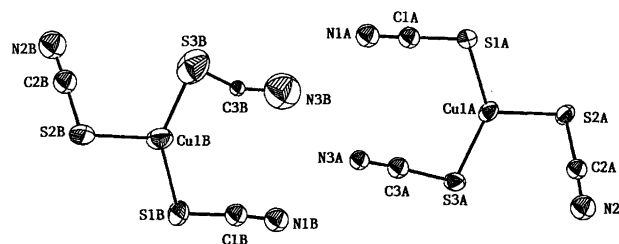


Fig. 1. Perspective view of the two independent $[\text{Cu}(\text{SCN})_3]^{2-}$ anions. Thermal ellipsoids are shown at 50% probability levels.

Table 1. Bond lengths (in Å) and angles (in °) for $[\text{Cu}(\text{SCN})_3]^{2-}$ anions.

Cu(1A)—S(1A)	2.227(8)	Cu(1B)—S(1B)	2.253(9)
Cu(1A)—S(2A)	2.264(8)	Cu(1B)—S(2B)	2.316(11)
Cu(1A)—S(3A)	2.228(8)	Cu(1B)—S(3B)	2.271(12)
S(1A)—C(1A)	1.65(3)	S(1B)—C(1B)	1.64(3)
S(2A)—C(2A)	1.62(3)	S(2B)—C(2B)	1.63(3)
S(3A)—C(3A)	1.69(3)	S(3B)—C(3B)	1.41(3)
N(1A)—C(1A)	1.18(4)	N(1B)—C(1B)	1.15(4)
N(2A)—C(2A)	1.12(4)	N(2B)—C(2B)	1.16(4)
N(3A)—C(3A)	1.16(4)	N(3B)—C(3B)	1.30(4)
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S(1A)—Cu(1A)—S(2A)	111.1(3)	S(1B)—Cu(1B)—S(2B)	109.9(3)
S(1A)—Cu(1A)—S(3A)	135.7(3)	S(1B)—Cu(1B)—S(3B)	139.0(4)
S(2A)—Cu(1A)—S(3A)	113.1(3)	S(2B)—Cu(1B)—S(3B)	111.0(4)
Cu(1A)—S(1A)—C(1A)	108(1)	Cu(1B)—S(1B)—C(1B)	107(1)
Cu(1A)—S(2A)—C(2A)	100(1)	Cu(1B)—S(2B)—C(2B)	104(1)
Cu(1A)—S(3A)—C(3A)	102(1)	Cu(1B)—S(3B)—C(3B)	89(1)
S(1A)—C(1A)—N(1A)	178(3)	S(1B)—C(1B)—N(1B)	175(3)
S(2A)—C(2A)—N(2A)	177(3)	S(2B)—C(2B)—N(2B)	176(3)
S(3A)—C(3A)—N(3A)	175(3)	S(3B)—C(3B)—N(3B)	158(2)

Results and discussion

The asymmetric unit of the structure contains two $[\text{Cu}(\text{SCN})_3]^{2-}$ anions, labelled **A** and **B**, and four large, approximately coplanar $[\text{H}_2\text{L}]^+$ cations joined together by hydrogen bonds. Atomic coordinates and thermal parameters, full listing of bond lengths and angles, hydrogen bond contact distances and least-squares planes are presented as supplementary material, and are available from the authors on request. Bond lengths and angles for the $[\text{Cu}(\text{SCN})_3]^{2-}$ anions are listed in Table 1.

The present data allow us to compare the two independent $[\text{Cu}(\text{SCN})_3]^{2-}$ anions. The copper atoms have distorted trigonal planar coordination, and the copper atoms are removed from the S_3 coordination plane by 0.052(4) and $-0.040(5)$ Å for anions **A** and **B**, respectively. Even though the anions are almost mirror images of each other, some significant differences between them can be observed. There seems to be a tendency for the Cu—S bonds to be longer in anion **B** than in **A**. Although not all the differences are significant, the trend is observable even in the former inaccurate data.¹ Thus, the Cu—S distances vary from 2.227(8) to 2.316(11) Å, and the Cu—S(2) and Cu—S(3) distances are significantly longer in **B** than in **A**.

In each of the non-equivalent $[\text{Cu}(\text{SCN})_3]^{2-}$ ions the three angles around copper are different, and one of the angles is much greater than the other two. Similar distortion has been reported for the tris(thiophenolato)cuprate(I) anion.³ Dissimilarity was also found between the two $[\text{Cu}(\text{SCN})_3]^{2-}$ anions. The S(1)—Cu(1)—S(3) angle is more open in anion **B** than anion **A**.

Differences also exist in the orientation of the coordinated SCN^- ions with respect to the coordination planes and in the geometry of the ions. Five of the six SCN^- ions are linear within experimental error, but, in the SCN^- ion labelled 3B the S—C—N angle of $158(2)^\circ$ deviates significantly from linearity. Likewise, the S—C bond is much shorter in ion 3B than in the other SCN^- ions [1.41(3) vs. 1.62(3)–1.69(3) Å], and the Cu(1B)···C(3B) distance is much shorter than the other Cu···C distances [2.65(2) vs. 3.01(3)–3.16(3) Å]. In good accord with this, the infrared spectrum obtained in the solid state shows thiocyanate vibrations at 2107 and 2093 cm^{-1} , indicating that two different SCN^- species are present. An explanation for the observed differences could be a weak interaction between Cu(1B) and C(3B). The observed differences of the Cu—S bond lengths between anions **A** and **B** support this explanation. Moreover, the thermal motions of S(3B) and N(3B) indicate some disorder.

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References

1. Kivekäs, R., Ruiz, J. and Colacio, E. *Acta Chem. Scand.* 48 (1994) 382.
2. Hall, S. R. and Stewart, J. M., Eds. *XTAL3.0 Reference Manual*. Universities of Western Australia, Australia, and Maryland, USA 1990.
3. Cingi, M. B., Manotti Langredi, A. M., Tiripicchio, A. and Tiripicchio Camellini, M. *Acta Crystallogr., Sect. B* 33 (1977) 3772.

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