IR Spectroscopy of Two Polymorphs of Copper(I) Thiocyanate and of Complexes of Copper(I) Thiocyanate with Thiourea and Ethylenethiourea

Graham A. Bowmaker[a] and John V. Hanna[b]

[a] Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand
[b] Department of Physics, University of Warwick, Gibbet Hill Rd., Coventry CV4 7AL, U. K.

Reprint requests to Prof. G. A. Bowmaker. Fax: +64 9 373 7422.
E-mail: ga.bowmaker@auckland.ac.nz

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

Syntheses and infrared spectroscopic studies are reported for two different polymorphs of copper(I) thiocyanate and for adducts of copper(I) thiocyanate with thiourea ('tu') and ethylenethiourea ('etu' = imidazolidine-2-thione; $(CH_2NH)_2CS$)). These include the previously reported complex CuSCN/etu (1 : 2), which has a trigonal monomeric structure, and CuSCN/etu (1 : 1), which has a three-dimensional polymeric structure. A mechanochemical/infrared study of the CuSCN : tu (1 : 2) system showed that no 1 : 2 complex exists in this case, the product being a mixture of a 1 : 3 complex and a novel 1 : 0.5 complex. The latter complex was prepared both mechanochemically and from solution, and characterized by infrared and solid-state ^{65}Cu broadline NMR spectroscopy. Diagnostic ligand and metal-ligand bands in the IR and far-IR spectra are assigned for both polymorphs of CuSCN and for all of the complexes studied and are discussed in relation to the structures of the complexes.

Key words: Copper(I), Thiourea, Infrared Spectroscopy

Introduction

Numerous adducts of copper(I) salts with thiourea ligands (RNH)(R′NH)CS (≡ 'xtu') have been structurally defined, in a variety of mono-, oligo- and polynuclear forms, and recent developments in the synthesis of such complexes have resulted in the identification of further novel forms [1]. Adducts of copper(I) halides feature strongly among the reported structures, but there are surprisingly few reports of products of reactions of copper(I) thiocyanate with thiourea or related ligands. We have recently reported a study of the products of reaction of AgSCN with such ligands, and have shown that polymeric 1 : 1 adducts with unusual structures can be prepared in addition to the previously known 1 : 2 complexes [2]. In contrast to this, until very recently, there have been no reports of corresponding 1 : 2 complexes of CuSCN. A recent study of the CuSCN/etu system (etu = imidazolidine-2-thione, 'ethylenethiourea'; $(CH_2NH)_2CS$) by conventional solution synthesis in acetonitrile resulted in the identification of a 1 : 1 adduct, which has a three-dimensional polymeric structure; this product was obtained when either 1 : 1 or 1 : 2 CuSCN/etu ratios were used in the reaction mixture [3]. In view of the existence of CuX/etu (1 : 2) for X = Cl, Br, I [1], the existence of a corresponding X = SCN complex would be expected. In a preliminary communication we recently reported the preparation of a 1 : 2 complex, prepared by solvent-assisted solid-state synthesis as well as by a more conventional aqueous solution method, which showed that the product is the three-coordinate mononuclear complex [SCNCu(etu)$_2$] [4]. In the present paper we report the detailed infrared spectroscopic characterization of this compound and a comparison with the previously reported 1 : 1 complex, together with the results of a corresponding study of the CuSCN/tu system (tu = thiourea, $(NH_2)_2CS$).

Solid CuSCN can exist in several polymorphic forms [5, 6], and in order to compare the infrared spectra of the CuSCN complexes with those of uncomplexed CuSCN, it was necessary to obtain bulk samples of the pure polymorphs. Solution and mechanochemical methods are described here for the preparation of pure, homogeneous samples of the α- and β-phases of CuSCN, and these were used to record the complete

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infrared spectra of the two phases for the first time. This aspect of the study is of potential interest in materials chemistry, as CuSCN has recently found application as a semiconductor for charge transport in cells for solar energy conversion [7].

Experimental Section

Copper(I) thiocyanate (Strem), thiourea (BDH) and ethylenethiourea (Aldrich) were used as received.

Synthesis

α-CuSCN

CuSCN (2.00 g, 16.4 mmol) was added to a solution of KSCN (27.0 g, 278 mmol) in water (58 mL), and the mixture was stirred and heated to boiling until all of the CuSCN had dissolved to form a pale yellow solution. After cooling to r. t. the resulting solution was slowly poured into water (800 mL) with stirring. The product formed as a fine white precipitate, which was collected by filtration and washed with water. Yield 1.91 g (95.5 %).

β-CuSCN

CuSCN (2.00 g, 16.4 mmol) in an agate mortar and pestle was treated with pyridine (1.60 g, 20.2 mmol), and the mixture was ground to form a yellow powder. This was allowed to stand for 3 h in a fume cupboard to allow removal of excess pyridine by evaporation. The yield of product (3.24 g, 98.2 %) indicates that this is a 1 : 1 CuSCN : pyridine adduct. A portion of this product (1.53 g) in an open container was heated in a 120 °C oven overnight to produce pure β-CuSCN as a colorless powder. Yield 0.95 g (102 %).

CuSCN : etu (1 : 2)

Method 1. Ethylenethiourea (0.205 g, 2.00 mmol) was pulverized by grinding for about 1 min in an agate mortar and pestle. This was then mixed with CuSCN powder (0.122 g, 1.00 mmol) without grinding, and the mixture was placed in a 5 mL glass sample vial that could be sealed with a plastic cap. To this mixture a few drops of water (just sufficient to form a non-fluid paste) were added using a small pipette. The sealed tube was placed in an oven at 70 °C for 2 h and then removed and allowed to cool to r. t. The water was removed following the reaction by allowing the mixture to stand for a few minutes in air at ambient temperature.

Method 2. CuSCN (0.122 g, 1.00 mmol) was dissolved in a solution of KSCN (1.70 g, 17.5 mmol) in water (3.5 mL) by boiling. The resulting boiling solution was added to a boiling solution of etu (0.306 g, 3.00 mmol) in water (4 mL). The mixture turned milky white and then clarified as an oil separated. The oil solidified, and crystals of product formed upon cooling the mixture to r. t. The product was collected and washed with water. Yield 0.31 g (95 %). Examination of the product under a microscope showed that it consisted of a mixture of crystals and lumps of solidified oil that could be physically separated. The yield of crystalline product was about 30 %. The elemental analysis was carried out on the crystalline product. Anal. for $C_7H_{12}CuN_5S_3$: calcd. C 25.79, H 3.71, N 21.49; found C 25.6, H 3.9, N 21.6.

CuSCN : etu (1 : 1)

Method 1. Ethylenethiourea (0.153 g, 1.50 mmol) was ground to a powder by grinding for about 1 min in an agate mortar and pestle. This was then mixed with CuSCN powder (0.182 g, 1.50 mmol) without grinding, and the mixture was placed in a 5 mL glass sample vial that could be sealed with a plastic cap. To this mixture a few drops of water (just sufficient to form a non-fluid paste) were added using a small pipette. The sealed tube was placed in an oven at 70 °C for 19 h and then removed and allowed to cool to r. t. The water was removed following the reaction by allowing the mixture to stand for a few minutes in air at ambient temperature.

Method 2. CuSCN (0.182 g, 1.50 mmol) was dissolved in a solution of KSCN (2.60 g, 26.8 mmol) in water (5 mL) by boiling. To the resulting boiling solution was added a boiling solution of etu (0.153 g, 1.50 mmol) in water (4 mL). The mixture turned white, and an off-white microcrystalline solid separated upon cooling the mixture to r. t. The product was collected and washed with water. Yield 0.32 g (95 %). Anal. for $C_4H_6CuN_3S_2$: calcd. C 21.47, H 2.70, N 18.78; found C 21.7, H 2.8, N 19.0.

CuSCN : tu (1 : 0.5)

Method 1. Thiourea (0.076 g, 1.00 mmol) was ground to a powder by grinding for about 1 min in an agate mortar and pestle. This was then ground for about 1 min with CuSCN powder (0.243 g, 2.00 mmol), and the mixture was placed in a 5 mL glass sample vial that could be sealed with a plastic cap. To this mixture a few drops of water (just sufficient to form a non-fluid paste) were added using a small pipette. The sealed tube was placed in an oven at 60 °C for 17 h, and the resulting off-white product was dried by heating in the unsealed sample tube at 60 °C for 5 h followed by cooling to r. t.

Method 2. A mixture of CuSCN (0.730 g, 6.00 mmol) and thiourea (0.457 g, 6.00 mmol) in water (20 mL) was heated to boiling with stirring and grinding the solids. Some of the CuSCN dissolved, while the remainder changed to a finely divided pale-yellow solid. The mixture was allowed to cool to r. t., and the pale-yellow solid product was collected and washed with water. Yield 0.86 g (90 %). Anal. for $C_{1.5}H_2CuN_2S_{1.5}$: calcd. C 11.28, H 1.26, N 17.54; found C 11.4, H 1.4, N 17.1.

Table 1. Wavenumbers (cm^{-1}) of selected bands in the IR spectra of CuSCN and some of its complexes with thiourea (tu) and ethylenethiourea (etu).

	(x)tu vibrations		SCN vibrations				Metal-ligand vibrations	
Compound	ν(CS)	ν(NH)	ν(CN)	ν(CS)	δ(SCN)	$2 \times \delta$(SCN)	ν(CuS), ν(CuN)	π(CuSCN)
α-CuSCN			2150	742, 739	427	880, 870, 860	210, 250	120
β-CuSCN			2172	747	431	876, 866	203, 242	107
CuSCN : tu (1 : 0.5)	714	3203, 3296, 3416	2126, 2116(sh)	755	447, 455	885, 894	231, 258	123
CuSCN : tu (1 : 3)	710	3171, 3277, 3370(sh)	2052					
CuSCN : etu (1 : 1)	491	3340	2103		454, 460		204, 231	147
CuSCN : etu (1 : 2)	492	3323	2026				251	175, 199

Method 3. CuSCN (0.730 g, 6.00 mmol) was dissolved in a solution of KSCN (10.5 g, 108 mmol) in water (18 mL) by boiling. To the resulting slightly yellow boiling solution was added a boiling solution of tu (0.228 g, 3.00 mmol) in water (15 mL). The solution became slightly darker in color (yellow-orange), and a pale-yellow microcrystalline solid separated upon cooling the mixture to r. t. The product was collected and washed with water. Yield 0.75 g (78 %). Anal. for $C_{1.5}H_2CuN_2S_{1.5}$: calcd. C 11.28, H 1.26, N 17.54; found C 11.5, H 1.2, N 17.6.

Mechanochemical experiments

The solvent-assisted mechanochemical/FTIR method [8, 9] was used to study CuSCN : n xtu reactions for various values of n in water. CuSCN (0.4 – 2.0 mmol) and the appropriate amount of xtu ligand were lightly ground to form a homogeneous mixture using a mortar and pestle of the type normally used to prepare IR samples. Water (1 – 8 drops, just sufficient to form a paste upon grinding) was added, and the mixture was ground for a few minutes and allowed to dry in the fume cupboard before recording the IR spectrum of a sample of the product. The systems studied were as follows:

$$\text{CuSCN} : n\ \text{tu}; \quad n = 2, 3$$

$$\text{CuSCN} : n\ \text{etu}; \quad n = 1, 2$$

The reactions with tu were complete after one mechanochemical treatment, producing viscous liquid products even in the absence of added solvent. In the case of the CuSCN : etu reactions, the IR spectra of the white powder products showed that complete reaction was only achieved after several cycles of the mechanochemical treatment described above, particularly when using this method to produce larger quantities (2 mmol) of product. This need for multiple treatments of the reaction mixture was overcome by using the solvent-assisted solid-state synthesis method [4], as described above in the syntheses of the individual compounds.

Solvent-assisted mechanochemistry was also used to prepare a bulk sample of the pure β-phase of CuSCN (see above). The product was identified as β-CuSCN by IR spectroscopy (see Results and Discussion). No change in the IR spectrum was observed upon grinding the commercial sample of CuSCN with acetonitrile or dimethylformamide.

Spectroscopy

IR spectroscopy

IR spectra were recorded at 4 cm^{-1} resolution on dry powders using a Perkin Elmer Spectrum 400 FT-IR spectrometer equipped with a Universal ATR sampling accessory. The IR spectra of the polymorphs of CuSCN were recorded at 2 cm^{-1} resolution. Far-infrared spectra were recorded at 4 cm^{-1} resolution using a Perkin-Elmer Spectrum 400 FTIR or a Nicolet 8700 FTIR spectrometer on samples suspended in Polythene disks.

^{65}Cu broadline NMR spectroscopy

Static broadline ^{65}Cu NMR data were acquired at ambient temperature on 14.1 T and 18.8 T systems using Bruker Avance II+-600 and Varian CMX Infinity-800 spectrometers operating at ^{65}Cu Larmor frequencies of 170.39 MHz and 227.08 MHz, respectively. These measurements were performed using Bruker 5/7.5 mm static horizontal solenoid design probes. All static ^{65}Cu data were acquired with the solid echo $\theta - \tau - \theta - \tau -$(acquire) experiment with an extended phase cycle to capture undistorted echoes with minimal influence from residual echo tails [10, 11]. 'Non-selective' (solution) $\pi/2$ pulse times of 2 μs were calibrated on a solid Cu(I)Cl sample from which a 'selective' (solid) θ pulse of 0.6 μs was employed in all solid echo measurements. The τ delay was 20 μs, and the relaxation delay between transients was 0.5 s. All ^{65}Cu isotropic chemical shifts δ_{iso} are referenced directly to a secondary reference of Cu(I)Cl which was assigned to δ = 0.0 ppm, and this resonance was measured at $\delta = -337.0$ ppm relative to the primary standard saturated $[Cu(CH_3CN)_4]ClO_4$ in dry CH_3CN at 20 °C.

Results and Discussion

Synthesis

A recent study of the CuSCN/etu system by conventional solution synthesis in acetonitrile resulted in the formation of a 1 : 1 adduct, which was shown to have a three-dimensional polymeric structure; this product was obtained for both 1 : 1 and 1 : 2 CuSCN/etu ratios in the reaction mixture [3]. In the present study we initially attempted to obtain a 1 : 2 complex in a similar manner by changing the solvent from acetonitrile to water, and by increasing the etu/CuSCN ratio in the reaction mixture. The identity and purity of the products was monitored by IR spectroscopy; assignments for the main diagnostic bands are given in Table 1. Heating aqueous 1 : 2 or 1 : 3 CuSCN/etu mixtures to boiling did not result in complete dissolution of the solid materials, and the products obtained upon cooling the reaction mixture contained both the 1 : 2 and 1 : 1 complexes (ν(CN) = 2026, 2103 cm^{-1} respectively; Table 1). Solvent-assisted mechanochemical synthesis using a 1 : 2 CuSCN/etu mixture was more successful, but the pure 1 : 2 complex was only obtained after several cycles of mechanochemical treatment, particularly when using this method to produce larger quantities (2 mmol) of product. The need for multiple treatments of the reaction mixture was overcome by using a solvent-assisted solid-state synthesis method, and the same method was used to prepare a bulk sample of the 1 : 1 complex (see Experimental Section). Crystalline samples of both complexes were prepared by an aqueous solution method that involved dissolution of CuSCN in a solution containing excess KSCN prior to reaction with etu. The 1 : 1 complex was obtained using a 1 : 1 CuSCN/etu ratio, but the 1 : 2 complex required excess etu with a CuSCN/etu ratio of 1 : 3 (see Experimental Section). The IR spectra of these compounds were identical to those of the products of the solid-state syntheses, and are listed in Table 1.

Heating an aqueous 1 : 2 CuSCN/tu mixture to boiling resulted in dissolution of a substantial proportion of the CuSCN and the formation of an insoluble complex of 1 : 0.5 stoichiometry (ν(CN) = 2126, 2116(sh) cm^{-1}; Table 1). Corresponding treatment of a 1 : 3 mixture resulted in complete dissolution of the CuSCN, implying the existence of a 1 : 3 complex. This was confirmed by mechanochemical treatment of a 1 : 3 mixture, which resulted in the formation of a clear, viscous liquid product that did not solidify upon standing (ν(CN) = 2052 cm^{-1}; Table 1). Mechanochemical treatment of a 1 : 2 mixture produced a suspension of the solid 1 : 0.5 complex in the liquid 1 : 3 complex.

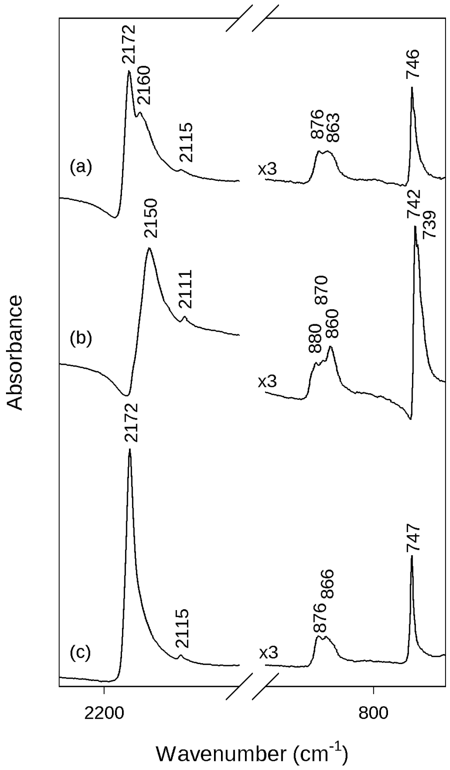
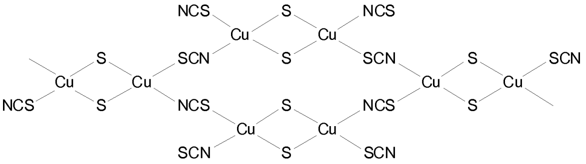


Fig. 1. IR spectra of (a) a commercial sample of CuSCN, (b) α-CuSCN, (c) β-CuSCN.

Copper(I) thiocyanate forms a number of different polymorphs [5, 6]. A commercial sample of CuSCN (Strem) was shown by IR spectroscopy to consist of both α and β polymorphs, with ν(CN) bands at 2160 and 2172 cm^{-1}, respectively (Fig. 1(a)) [5]. In order to compare the vibrational spectra of the CuSCN complexes with those of uncomplexed CuSCN, it was necessary to obtain bulk samples of the pure polymorphs. The pure α-phase was obtained by dissolving the CuSCN in concentrated aqueous KSCN solution and re-precipitation by dilution of the solution with water (Fig. 1(b)). The pure β-phase was obtained by mechanochemical treatment with pyridine followed by removal of the pyridine by heating (Fig. 1(c)). The IR spectrum of material similarly treated but dried under ambient conditions showed that this reaction proceeds *via* the formation of an intermediate CuSCN/pyridine complex, which was shown by gravimetric analysis to be the 1 : 1 CuSCN : py complex that has been identified previously [12]. In the mechanochemical reaction it was noted that addition of an excess of pyridine, sufficient to form a mobile fluid, resulted in a substantial degree of aerial oxidation of copper(I) to copper(II), as evidenced by the rapid development of a prominent green coloration in the reaction mixture. However, when the CuSCN is ground with the minimum amount of pyridine necessary to form the complex, no visible aerial oxidation is apparent. Presumably the 1 : 1 CuSCN : pyridine complex that results from this mechanochemical synthesis could also be prepared by dissolution of CuSCN in bulk pyridine solvent, but this reaction would have to be carried out under an inert atmosphere in order to avoid oxidation. Hence, it appears that the mechanochemical method can eliminate the need for inert atmosphere methods (Schlenk techniques, *etc.*) in some cases. We have encountered another example of this behavior in the solvent-assisted mechanochemical synthesis of a 1 : 2 CuI : etu complex using dimethylformamide as a solvent [1]. This emphasises the fundamental difference between solvent-assisted mechanochemical and conventional bulk solution synthesis. The pyridine-assisted transformation of α- to β-CuSCN also demonstrates the existence of a mechanism of solvent-assisted mechanochemical synthesis in which the solvent is itself a reactant that can be removed after completion of the initial reaction. These new aspects further augment the previously discussed features of the nature and mechanism of solvent-assisted mechanochemical synthesis [8, 9].

Crystal structures

The crystal structures of the α- and β-phases of CuSCN have been reported previously [5, 6]. They are both three-dimensional infinite polymeric structures in which the copper atom is tetrahedrally coordinated to three S atoms and one N atom of the bridging SCN groups. The high symmetry of the β-phase results in the equivalence of all three Cu–S bonds, the linearity of N–C–S and Cu–N–C, and almost ideal tetrahedral values for the other angles [Cu–S, N are 2.343(1), 1.923(11) Å; S–Cu–S 110.78(5), N–Cu–S 108.13(5), Cu–S–Cu 110.78(5), Cu–S–C 108.13(5)°] [5]. By contrast, the structure of the α-phase is not symmetry-constrained, and the bond lengths and angles show wide divergence from equivalence and ideal values [Cu–S, N 2.319(3), 2.354(2), 2.367(2), 1.927(6) Å; N–C–S 178.7(7), Cu–N–C 166.70, S–Cu–S 103.01(7), 107.28(7), 110.15(7), N–Cu–S 115.0(2), 114.4(2), 106.3(2), Cu–S–Cu 129.9, 111.4, 99.8, Cu–S–C 104.9, 104.7, 103.4°] [5].



Scheme 1.

The crystal structures of CuSCN/etu (1 : 1) and (1 : 2) have been reported previously [3, 4]. The 1 : 2 complex is trigonal monomeric [SCNCu(etu)$_2$], in which the thiocyanate is N-bonded and Cu, and S, C, N lie in the mirror plane of space group $P2_1/m$, which relates the two etu ligands; Cu–S, N are 2.2243(4), 1.963(2) Å; S–Cu–N, Cu–N–C, N–C–S 119.357(12), 149.97(19), 177.5(2)°; the S_2N(core)/SC_3N_2(etu) dihedral angle is 7.48(5)° [4]. The 1 : 1 adduct, has a three-dimensional polymeric structure in which two etu ligands and two CuSCN moieties combined *via* etu S to form a dimeric repeat unit, $\{Cu_2(\mu_2\text{-}S\text{-etu})_2(SCN)_2\}$, with S-bonded SCN ligands. The unequal Cu–S distances [2.3851(16) and 2.4061(15) Å] form a parallelogram with a Cu_2S_2 central core, and the angles within the $Cu(\mu_2\text{-}S)_2Cu$ core are 71.53(5) and 108.47(5)° at S and Cu atoms, respectively. The dimeric repeat units are linked with other such units *via* the free N donor atoms of SCN to form the three-dimensional polymeric structure (Scheme 1) [Cu–S(SCN) distance, 2.3701(16) Å; Cu–N(SCN), 1.982(4) Å]. The Cu···Cu distance at 2. 8002(15) Å is equal to the sum of the van der Waals radii of Cu atoms, at 2.80 Å. The angles at Cu vary over a wide range, *ca.* 71.53(5) – 114.02(6)°, as a result of an distorted tetrahedral geometry around each Cu atom [3].

Infrared spectroscopy

Selected bands in the IR spectra of the complexes studied in this work are listed in Table 1. The ν(CN) band of the thiocyanate group, which occurs at about 2170 cm^{-1} in CuSCN, shows a decrease in frequency upon complexation with the thiourea ligand. In both polymorphs of CuSCN, the SCN group is bridging [5, 6], and ν(CN) occurs above 2100 cm^{-1}. The 1 : 2 etu complex contains terminal N-bonded thiocyanate (see above), and ν(CN) occurs below 2100 cm^{-1}, at 2026 cm^{-1}. The 1 : 1 complex contains bridging thiocyanate [3], and ν(CN) occurs at 2103 cm^{-1}. An empirical correlation between the thiocyanate bonding mode and the ν(CN) wavenumber asserts that "ν(CN) is generally lower in N-bonded complexes (near and below 2050 cm^{-1}) than in S-bonded complexes (near 2100 cm^{-1})" and that "bridging complexes exhibit ν(CN) well above 2100 cm^{-1}" [13]. The results for the above two complexes are in good agreement with these rules, particularly in relation to the 2100 cm^{-1} boundary that distinguishes bridging from terminal bonding. In the original report of the 1 : 1 complex [3], the ν(CN) frequency was reported as 2060 cm^{-1}, but this is not in agreement with the results of the present work or with the expectation that the bridging SCN group should give rise to a ν(CN) frequency above 2100 cm^{-1}. The reason for these discrepancies is not known at present, but a unit cell determination confirmed that the complex prepared in the present study is the same as that previously reported.

The structures of CuSCN : tu 1 : 0.5 and 1 : 3 are currently not known, but the ν(CN) frequencies (Table 1) are consistent with bridging and terminal SCN bonding modes respectively, according to the criteria discussed above.

The far-IR spectra of α- and β-CuSCN are shown in Fig. 2. The band at about 430 cm^{-1} is assigned to the δ(SCN) mode of the thiocyanate group. For the SCN$^-$ ion in KSCN, this mode occurs at 471, 486 cm^{-1}, and in AgSCN it occurs at 423, 446 cm^{-1} [2], the splitting being due to lifting of the double degeneracy of this mode by the low site symmetry of the ion in the solid. This mode generally shows a shift to lower wavenumber upon coordination of SCN$^-$ to metal ions [13], and this is the case for both CuSCN and AgSCN. In both polymorphs of CuSCN this band shows no splitting, reflecting the higher symmetry of the SCN bonding environment in these cases [5, 6]. The first overtone of this mode, 2 × δ(SCN), is clearly visible in the mid-IR spectrum at about 870 cm^{-1} (Table 1). The bands below 250 cm^{-1} are due to metal-ligand vibrations ν(CuS), ν(CuN), and lattice modes. By analogy with the assignments made previously for AgSCN [2], the two bands between 200 and 250 cm^{-1} are assigned to the ν(CuS), ν(CuN) modes. These bands are better resolved in the spectrum of β-CuSCN, which has the more symmetrical crystal structure of the two polymorphs, with only one Cu–S and one Cu–N bond length [5]. In previous studies of coinage metal halide complexes we have shown that the primary factor that determines the number of metal-halogen vibrational bands is the number of distinct metal-halogen bond lengths [14]. As thiocyanate is a pseudohalide, a similar principle should apply to the ν(CuS), ν(CuN) modes in β-CuSCN. This results in prediction of one ν(CuS) and one ν(CuN) band, and the two bands at 204, 242 cm^{-1} are assigned accordingly (Table 1, Fig. 2(c)). Assignment in this order would be consistent with the assignments for AgSCN, for which it was shown that $\nu(\mathrm{AgS}) < \nu(\mathrm{AgN})$ [2]. The results for α-CuSCN are consistent with this. In this polymorph the band corresponding to ν(CuS) = 203 cm^{-1} occurs at 210 cm^{-1}, but shows some evidence of splitting into more than one component (Fig. 2(b)). This is consistent with the crystal structure of the α-phase, which has three different Cu–S bond lengths, but only one Cu–N bond length [5]. A similar situation occurs for AgSCN, but in this case the Ag–S bond lengths are more dissimilar, and three separate ν(AgS) bands are resolved [2]. This is a clear indication of the higher effective symmetry of the metal and thiocyanate coordination environments in CuSCN compared to AgSCN, even in the case of α-CuSCN, where such symmetry is not enforced crystallographically. This is consistent with the lack of splitting of the δ(SCN) band in CuSCN, as discussed above.

The far-IR spectra of α- and β-CuSCN also show a strong band at 120 and 107 cm^{-1}, respectively (Fig. 2). By analogy with a similar assignment for CuCN [15],

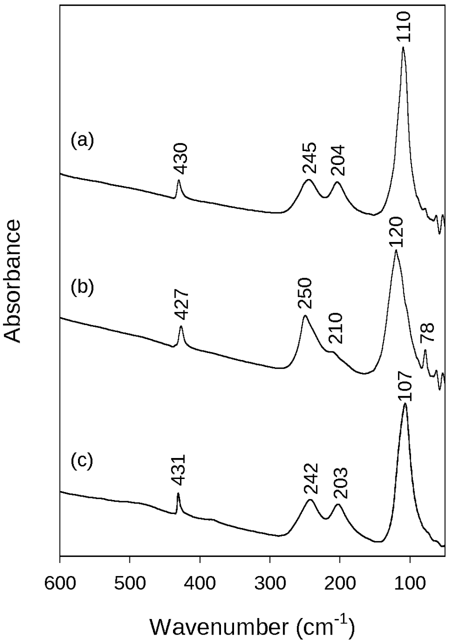


Fig. 2. Far-IR spectra of (a) a commercial sample of CuSCN, (b) α-CuSCN, (c) β-CuSCN.

this is attributed to a lattice vibration π(CuSCN) involving vibration of the Cu sub-lattice against the SCN sub-lattice in a direction perpendicular to the SCN groups (Table 1).

The above results for CuSCN provide a basis for the assignment of bands in the far-IR spectra of the CuSCN : (x)tu complexes. The far-IR spectra of uncomplexed etu and of CuSCN : etu 1 : 1 and 1 : 2 are shown in Fig. 3, and assignments of selected bands are given in Table 1. The assignment of the δ(SCN) bands is complicated by their overlap with the strong etu bands that cover the region 400 – 600 cm^{-1}, but in the 1 : 1 complex a weak doublet at 454, 460 cm^{-1} is thus assigned (Fig. 3(b); Table 1). There are several bands below 260 cm^{-1} which are assigned to the metal-ligand vibrations ν(CuS), ν(CuN) (Table 1). In the 1 : 1 complex the bands at 204, 231 cm^{-1} are assigned to ν(CuS), ν(CuN) respectively, by analogy with the corresponding assignments for CuSCN (see above). The stronger band at 147 cm^{-1} is possibly due to the π(CuSCN) mode (see previous paragraph), and is tentatively assigned thus. The 1 : 2 complex only shows a band at 251 cm^{-1} that is assigned to ν(AgN); in contrast to the case of the 1 : 1 complex, which shows both ν(CuS) and ν(CuN) due to the presence of bridging SCN, there is only a single band due to ν(CuN) of the terminally bonded thiocyanate. The exact origin of the strong doublet at 175, 199 cm^{-1} is not clear at present, although similar bands in the far-IR spectra of complexes containing terminally bonded thiocyanate have been reported previously [16].

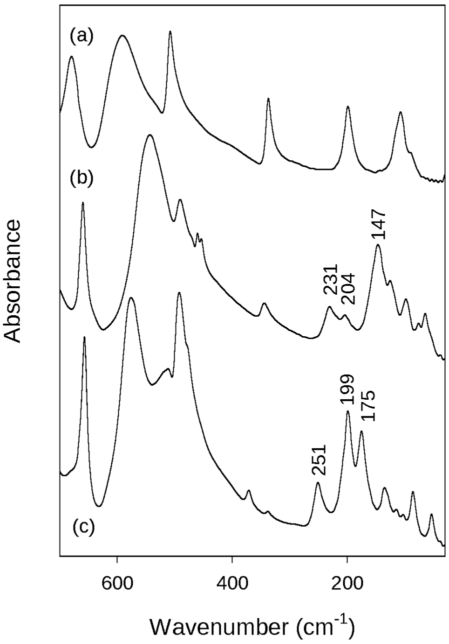


Fig. 3. Far-IR spectra of (a) uncomplexed etu, (b) CuSCN : etu (1 : 1), (c) CuSCN : etu (1 : 2).

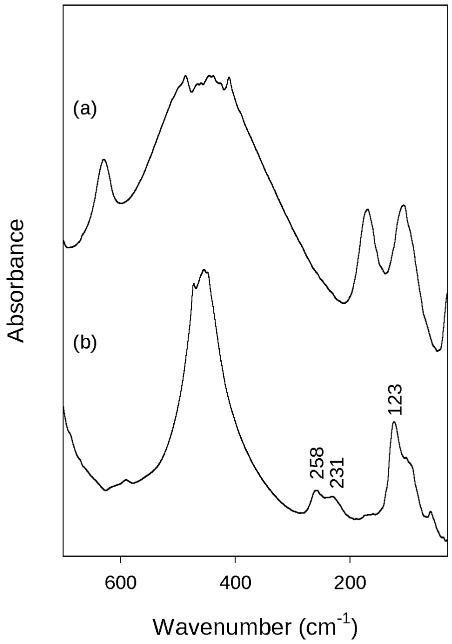


Fig. 4. Far-IR spectra of (a) uncomplexed tu, (b) CuSCN : tu (1 : 0.5).

The far-IR spectra of uncomplexed tu and of CuSCN : tu 1 : 0.5 are shown in Fig. 4, and assignments of selected bands are given in Table 1. The assignment of the δ(SCN) bands in the 1 : 0.5 complex is complicated by their overlap with the strong tu bands that cover the region 400 – 600 cm^{-1}, but a weak doublet at 447, 455 cm^{-1} is evident on top of the strong tu band in this region, and is thus assigned (Fig. 4(b); Table 1). The bands at 231, 258 cm^{-1} are assigned to ν(CuS), ν(CuN) respectively, by analogy with the corresponding assignments for CuSCN (see above). The stronger band at 123 cm^{-1} is possibly due to the π(CuSCN) mode (see above), and is tentatively thus assigned. These results indicate that the structure is a polymeric one that involves bridging thiocyanate, in agreement with the conclusion based on the ν(CuN) frequency (see above).

NMR spectroscopy

As the structure of CuSCN : tu 1 : 0.5 is not known at present, further information about the Cu(I) coor-

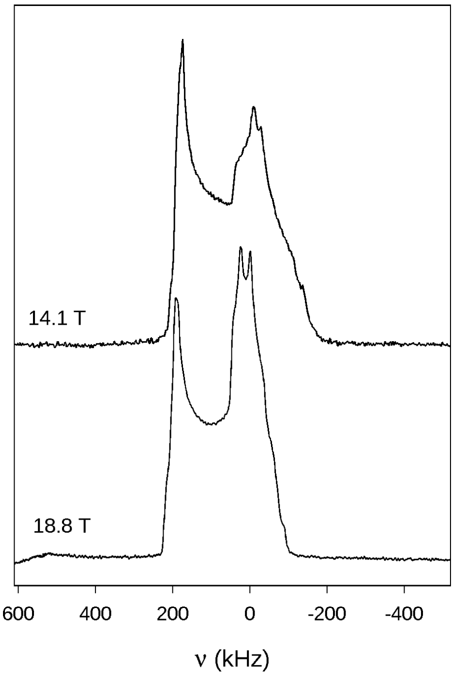


Fig. 5. Broadline static ^{65}Cu NMR spectra at 14.1 and 18.8 T of CuSCN : tu (1 : 0.5).

dination environment was sought through the acquisition of ^{65}Cu broadline NMR spectra at magnetic field strengths of 14.1 and 18.8 T (^{1}H 600 and 800 MHz spectrometers), and the results are shown in Fig. 5. Because of its lower nuclear quadrupole moment, ^{65}Cu is the preferred copper nuclide for NMR studies due to its intrinsically narrower linewidth, despite its lower natural abundance. In compounds where the Cu atom lies on a site of nearly exact tetrahedral symmetry, the ^{65}Cu quadrupole coupling constant (C_Q) is very small, and the ^{65}Cu NMR static powder spectrum is that of a first-order broadened system that exhibits a relatively sharp ($-1/2 \leftrightarrow +1/2$) central transition and broader ($\pm 1/2 \leftrightarrow \pm 3/2$) satellite transitions. This has recently been demonstrated for the tetrahedrally coordinated [Cu(t-BuNC)$_4$]X (X = Cl, Br, I) complexes [17]. For systems with larger distortions from tetrahedral coordination of the Cu(I) environment and concomitant larger ^{65}Cu quadrupole coupling constants, the ($\pm 1/2 \leftrightarrow \pm 3/2$) satellites become too broad to detect, and the ($-1/2 \leftrightarrow +1/2$) central transition spectrum shows a line shape with characteristic singularities due to second-order quadrupole broadening. A further complication in the analysis of ^{65}Cu static lineshapes is caused by the influence of ^{65}Cu chemical shift anisotropy (CSA), which introduces additional distortion and singularities in the ^{65}Cu central transition spectrum [17 – 21]. The second-order quadrupole broadened spectra of Fig. 5 also display some CSA contribution to the central transition spectra, as evidenced by the presence of such additional singularities, however, the significant $1/B_0$ field dependence (indicated by the fact that the spectrum measured at 18.8 T is narrower than that at 14.1 T) suggests that these high-field spectra are still dominated by a quadrupole interaction [18]. This situation is similar to that reported recently for the binuclear 1 : 2 complexes of copper(I) halides with diphenylthiourea (dptu), [(dptu)XCu(μ-S-dptu)$_2$CuX(dptu)] (X = Cl, Br, I), which exhibit distorted tetrahedral coordination about the Cu atom, and where ^{65}Cu C_Q values of *ca.* 15 MHz were measured [19]. The corresponding linewidths in the spectra of CuSCN : tu 1 : 0.5 (Fig. 5) indicate a ^{65}Cu quadrupole coupling constant of *ca.* 15 – 20 MHz for this system. This is consistent with the presence of copper atoms with distorted tetrahedral coordination in this compound, and suggests a three-dimensional polymeric structure for this complex, similar to that of the 1 : 1 CuSCN/etu complex, but with two different kinds of bridging thiocyanate ligand, as indicated by the IR spectrum.

Conclusions

Methods for the bulk synthesis of the α- and β-polymorphs of copper(I) thiocyanate are reported. The pyridine-assisted transformation of α- to β-CuSCN demonstrates the existence of a mechanism of solvent-assisted mechanochemical synthesis in which the solvent is itself a reactant that can be removed after completion of the initial reaction. Thiourea and ethylenethiourea show distinctly different complexation behavior towards copper(I) thiocyanate, with the latter forming 1 : 1 and 1 : 2 complexes and the former forming only 1 : 0.5 and 1 : 3 complexes. This is rather surprising, given the similarity in the S-donor ligand properties for the two ligands involved, and is possibly the result of the rather different H-bonding properties of the two ligands. H-bonding has been shown to play an important role in determining the nature and structure of coinage metal(I) complexes with thiourea ligands [20].

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