Crystal Structure of an Ammonium Dithiocyanatocuprate(I) Complex
with 18-Crown-6, [NH₄(18-Crown-6){Cu(NCS)₂}]
Obtained from Zero Valent Metal

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The new macrocyclic dithiocyanatocuprate(I) complex [NH₄(18-crown-6){Cu(NCS)₂}] has been prepared using a direct method of interaction and characterized by X-ray crystallography (orthorhombic, space group Cmc₂1, with a = 12.453(2), b = 21.650(4), c = 8.151(2) Å, \( V = 2197.6(8) \text{ Å}^3 \), Z = 4, \( R_1(\text{F}) = 0.054; wR_2(\text{F}^2) = 0.141 \) for 972 unique reflections with \( I > 2\sigma(I) \) and \( R_1(\text{F}) = 0.082; wR_2(\text{F}^2) = 0.210 \) for all 1098 unique reflections). The lattice comprises complex cations [NH₄(18-crown-6)]⁺ and infinite polymeric anions [Cu(NCS)₂]⁻ of a one-dimensional zig-zag structure. The copper atoms adopt three-fold coordination [CuN₁S₂] (Cu-N 1.89(1), 1.90(1) Å; Cu-S 2.278(4) Å).

Introduction

The coordination chemistry of crown ethers is rich and versatile and led to useful approaches towards ligand design for selective complexation of a wide variety of metal ions, including alkali- and alkaline-earth-metal, lead(II), thallium(I) and ammonium cations [1–5]. Considerable attention has been paid to understanding the principles of anion–crown ether bonding through crystal structure studies of the complexes with 18-crown-6 (L), a readily available crown ether [2, 4]. It was found lately that the interaction in the M⁰⁺-18-crown-6 systems results in the formation of centrosymmetric encapsulates [M(L)]⁺⁺ or half-sandwiches [M(L)₂]⁺⁺, complex cations [M₂(L)₂]⁺⁺, sandwiches [M₃(L)₃]⁺⁺, and even triple decker club sandwiches [M₄(L)₄]⁺⁺[6], and the behaviour of practically every metal ion towards the crown ethers may be controlled by varying its counter anion [2, 7]. Evidently, any type of a strong moiety-moiety interaction in the anionic part of the structure may be considered to be important in crystal packing. Such interactions (cf. hydrogen bonding or coordination) lead to the closest disposition of anions in the lattice and, respectively, may promote compression of the macrocyclic cationic array as the fragments [M(L)]⁺⁺ are packed one on top of the other to form triple decker [6, 8] or higher club sandwiches [Mₙ(L)ₙ]⁺⁺[9]. The latter represent the most rarely encountered types of macrocyclic complexes [6].

Numerous species that can form a coordination polymeric structure may be suggested as suitable counter anions for the stabilization of the ‘compressed’ macrocyclic array, and different types of polymeric cyanato- and thiocyanatocuprates(I) [10, 11] are of special interest in this context. Recently we have found that the interaction of zero valent copper with ammonium thiocyanate (direct synthesis) allows to prepare a number of thiocyanatocuprates(I) of two- or three-dimensional structure [12, 13]. The Cu(I)-NCS⁻ array geometry, however, is often determined by the nature of the counter cation [11], and it appears that the structures of complex macrocyclic thiocyanatocuprates(I) have not yet been considered. In order to clarify the geometry of the [Cu(NCS)₂]ₙ⁻ moiety in the presence of macrocyclic cations, we have attempted to prepare compounds of composition [M(18-crown-6){Cu(NCS)₂}] and here we describe the synthesis and crystal structure of a [NH₄(18-crown-6){Cu(SCN)₂}] complex.

Experimental

All chemicals were commercial products of reagent grade, used without further purification. All experiments were carried out in air.

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Table I. Selected bond lengths (Å) and angles (°) for [NH$_4$(18-Crown-6){Cu(NCS)$_2$}]$^-$.

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-N(1)</td>
<td>1.90(1)</td>
</tr>
<tr>
<td>Cu-N(2)</td>
<td>1.89(1)</td>
</tr>
<tr>
<td>Cu-S(1a)</td>
<td>2.278(4)</td>
</tr>
<tr>
<td>S(1)-C(1)</td>
<td>1.66(1)</td>
</tr>
<tr>
<td>S(2)-C(2)</td>
<td>1.62(1)</td>
</tr>
<tr>
<td>N(1)-C(1)</td>
<td>1.12(1)</td>
</tr>
<tr>
<td>N(2)-C(2)</td>
<td>1.14(2)</td>
</tr>
<tr>
<td>O(1)-C(3)</td>
<td>1.40(1)</td>
</tr>
<tr>
<td>N(2)-Cu-N(1)</td>
<td>116(1)</td>
</tr>
<tr>
<td>N(2)-Cu-S(1a)</td>
<td>116(1)</td>
</tr>
<tr>
<td>S(1)-C(1)-N(1)</td>
<td>116(1)</td>
</tr>
<tr>
<td>S(2)-C(2)-N(2)</td>
<td>117(1)</td>
</tr>
<tr>
<td>C(3)-O(1)-C(3)</td>
<td>114(1)</td>
</tr>
<tr>
<td>C(4)-O(2)-C(5)</td>
<td>112(9)</td>
</tr>
<tr>
<td>C(7)-O(3)-C(6)</td>
<td>114.0(9)</td>
</tr>
</tbody>
</table>

aData Symmetry transformation used to generate equivalent atoms: a: -x, y, z; b: -x, -y, -0.5 + z.

For the preparation of the complex the following method was used:

Cu + 18-crown-6 + 2NH$_4$NCS + $\frac{1}{2}$O$_2$

$\rightarrow$ [NH$_4$(18-Crown-6){Cu(NCS)$_2$}]$^-$ + H$_2$O + NH$_3$

To a solution of 0.264 g (1 mmol) of 18-crown-6 and 0.228 g (3 mmol) of NH$_4$NCS in a mixture of 2-propanol / dimethylformamide (2:1 v/v) (10 ml) 0.0635 g (1 mmol) of copper powder was added. The mixture was heated to about 50-60 °C and stirred for 1 h until total dissolution of the copper was observed. The resulting slightly yellow solution was filtered and then cooled to room temperature. The colourless plate-like crystals of the complex deposited were filtered, washed with 2-propanol and dried in air. The yield was 0.314 g (70 %). The compound is soluble in hot 2-propanol, acetonitrile and DMF, and decomposes in water to precipitate CuNCS.

Analysis for C$_{14}$H$_{28}$CuN$_3$O$_6$S$_2$: Calcd C 36.39, H 6.11, N 9.10, Cu 13.75 %, Found C 35.76, H 5.98, N 8.41, Cu 13.70 %.

Preliminary unit cell parameters and intensities of 1098 unique reflections were recorded at 23 °C using an Enraf Nonius CAD-4 diffractometer operating in the $\omega$/2$\theta$ scan mode. The intensity data were collected within the range 1.88 ≤ $\theta$ ≤ 24.98° using graphite monochromated MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å). Corrections for Lorentz and polarization effects were applied. The structure was solved by direct methods and refined by full-matrix least squares techniques in the anisotropic approximation using SHELXS-86 and SHELXL-93 [14, 15]. The aliphatic CH$_2$ hydrogen atoms were placed at calculated positions with their isotropic U values set invariant at 0.08 Å$^2$. Attempts to locate the hydrogen atoms of NH$_4^+$ cation were not successful. Refinements were terminated with all non-hydrogen parameter shifts < 0.25 $\sigma$; the weighting schemes were $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $3P = (2F^2 + F_0^2)$ and $a$ and $b$ are constants adjusted by the program. Convergence was obtained at R1(F) = 0.054 and wR2(F$^2$) = 0.141; GOF(F$^2$) = 1.060; absolute structure parameter $x = -0.01(4)$ for 972 unique reflections with I > 2$\sigma$(I) and R1(F) = 0.082; wR2(F$^2$) = 0.210 for all 1098 unique data used (130 refined parameters; the largest peaks on a final difference synthesis were 1.19 and -0.39 e/Å$^3$).

Crystal data for C$_{14}$H$_{28}$CuN$_3$O$_6$S$_2$: FW = 462.05, orthorhombic, space group Cmc2$_1$, with a = 12.453(2), b = 21.650(4), c = 8.151(2) Å, V = 2197.6(8) Å$^3$, Z = 4, $\mu$ = 1.397 g·cm$^{-3}$, $\rho$ = 1.12 cm$^{-1}$, F(000) = 968.

Selected bond distances and angles are listed in Table I. Full crystallographic data have been deposited at the Cambridge Crystallographic Data Centre [16].

Fig. 1. The structure of the [NH$_4$(18-Crown-6)]$^+$ and {Cu(NCS)$_2$}$^{2-}$ moieties, showing the proposed hydrogen bonds as dashed lines and the atom labelling scheme.
Results and Discussion

The structure of \([\text{NH}_4(18\text{-crown-6})\{\text{Cu(NCS)}_2\}]\) is shown in Figures 1-2. The lattice comprises complex cations \([\text{NH}_4(18\text{-crown-6})]^+\) and infinite polymeric anions \([\text{Cu(NCS)}_2]^−\) of a one-dimensional zig-zag structure (Fig. 2). There are no significant interactions between the cations and the anionic part and the \(\text{N}(3)−\text{S}(2)\) separation of 3.303(5) Å may be attributed only to a very weak hydrogen bond \(\text{H}_3\text{N-H—SCN}\) (Fig. 1). Weak hydrogen bonds of a similar type are present also in the structure of \([(\text{CH}_3)_3\text{NH}]^+\{\text{Cu}_2(\text{NCS})_3\}^−\) (d(\(\text{N—S}\)) ca. 3.30 Å) [12].

The \([\text{NH}_4(18\text{-crown-6})]^+\) cation has a symmetric structure and the oxygen atoms \(\text{O}(1), \text{O}(4)\) and the ammonium nitrogen atom \(\text{N}(3)\) occupy special positions on an \(m\) plane at \(x = 0\). The short contacts \(\text{N}(3)−\text{O}(1)\) of 2.851(9) Å and \(\text{N}(3)−\text{O}(3)\) and \(\text{O}(3a) (−x, y, z)\) of 2.893(6) Å are consistent with the values reported for the hydrogen bonds \(+\text{N-H—O}\) in similar systems (cf. 2.84 Å for \([\text{H}_2\text{N-NH}_3]^+(18\text{-crown-6})\)\text{ClO}_4 [17]). The ammonium nitrogen atom \(\text{N}(3)\) deviates from the mean plane of six oxygen atoms by 0.961(5) Å. The macrocyclic molecule is structurally normal and has distorted \(D_{3d}\) geometry, the most stable conformation for this ligand in complexes with metal ions, ammonium and oxonium cations [18, 19]. The torsion angles of the C-C bonds correspond to a gauche conformation and those of C-O bonds to trans. Both the C-O (av. 1.42(1) Å) and C-C (av. 1.47(1) Å) distances (Table 1) are typical for macrocyclic polyethers (C-O 1.43±0.02, C-C 1.49±0.02 Å [19]). The maximum deviation of the 18-crown-6 oxygen atoms from their mean plane is 0.332(7) Å for \(\text{O}(4)\).

Atoms of the polymeric chains \([\text{Cu(NCS)}_2]^−\) occupy special positions and lie on a \(m\) plane at \(x = 0\). There are two types of thiocyanate groups in the structure; the \(\text{N}(2)\text{C}(2)\text{S}(2)\) group is coordinated monodentately via the nitrogen atom, while the \(\text{N}(1)\text{C}(1)\text{S}(1)\) group acts as a bridge between two copper atoms and adopts a Cu-NCS-Cu coordination mode (Fig. 2). These coordination modes are the most common for Cu\(^{1+}\)-NCS systems [11]. Both the unique thiocyanate groups are structurally normal. In general, the structure of the polymeric zig-zag anion \([\text{Cu(NCS)}_2]^−\) bears a close resemblance to the structures of the anionic moieties in \((\text{bedt-ttf})_2[\text{Cu(NCS)}_2]\) (bedttff: bis(ethylenedithio)tetrathiafulvalene) [20] and \(\text{K}[\text{Cu(CN)}_2]\) [10] (Fig. 2). The copper atoms adopt three-fold coordination \([\text{Cu}_2\text{S}]\) and the fragment \(\text{CuN}(1)\text{N}(2)\text{S}(1b)\) is planar (Fig. 2). The distances \(\text{Cu-N}(1), \text{Cu-N}(2)\) and \(\text{Cu-S}(1b)(−x, −y, 0.5+z)\) are found to be 1.90(1), 1.89(1) and 2.278(4) Å, respectively, and agree well with values reported for the \((\text{bedt-ttf})_2[\text{Cu(NCS)}_2]\) complex [11, 20].

Considering the possibility of using such polymeric dithiocyanatocuprate(I) anions for the stabilization of the ‘compressed’ macrocyclic array in the crystal structures, we note that in the infinite chains \([\text{Cu(NCS)}_2]^−\) running along 0z direction (Fig. 2) the period of translation refers to the \(c\) parameter of the unit cell of 8.151(2) Å.
Thus the distance between the two singly charged fragments [Cu(NCS)₂]⁻ along O₂ is twice less (e.g. 4.075(2) Å) in accord with the zig-zag structure of the polymeric anion (Fig. 2). The latter value lies within the range of typical separations Cs---Cs reported for systems [Cs(μ-18-crown-6)Cs] (3.923(4) to 4.335(1) Å [6]). It may be assumed, that in case of a 'side on' disposition of the polymeric dithiocyanatocuprate(I) anion to the cationic part in the structure of a complex with stoichiometry [Cs(18-crown-6){Cu(NCS)₂}⁺], the effective packing of the macrocyclic moieties [Cs(18-crown-6)]⁺ may result in the formation of polymeric linear cations [Cs(18-crown-6)]n⁺ in the form of an 'infinite sandwich'. As a close structural precedent for such a 'highly compressed' macrocyclic array we regard the unique crystal structure of [Cs(18-crown-6)]{TcNCU} [9], containing polymeric cations [Cs(18-crown-6)]n⁺ of an 'infinite sandwich' structure, accompanied in a 1:1 proportion by linear polymeric {TcNCU}n⁻ anions in 'side on' position to the cationic part (separations Cs---Cs in the cation and Tc≡N---Tc in the anion are 4.275(4) Å [9]). Such an effect of the packing forces, where the pressure of the crystal environment stabilizes one geometry over the other, was also discussed earlier [21, 22].

Studies of the Cs⁺-18-crown-6-[Cu(NCS)₂]n⁻ system are in progress.

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