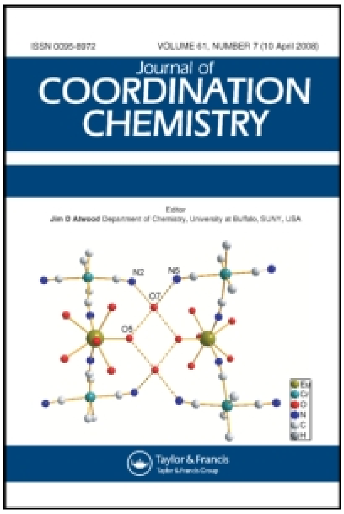

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MACROCYCLE COMPLEXATION CHEMISTRY. 29.†

SYNTHESIS AND CRYSTAL STRUCTURE OF [CuCl(18-thiacrown-6)]$_n$

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The room temperature single-crystal structure of [CuCl(18-thiacrown-6)]$_n$ is reported. The polymeric structure crystallizes in the triclinic space group $P\bar{1}$ with two formula units per unit cell. The cell dimensions are $a = 9.905(2)$, $b = 10.408(2)$, $c = 11.335(2)$ Å, $\alpha = 64.40(1)$, $\beta = 64.30(1)$, $\gamma = 82.47(1)°$ with a density of 1.61 g cm^{-3}. The structure was refined to conventional R values of 0.025 and, $R_w = 0.026$. The asymmetric unit contains one copper(I) ion, one chloride ion and two half molecules of two unique crown ether molecules, each of which resides around a crystallographic centre of inversion. The Cu(I) geometry is a distorted tetrahedron with three sulfur atoms (two from one thiacrown molecule and one from the other unique ether) and one chloride ion forming the vertices. As a result of the inversion symmetry one molecule bonds in a bidentate fashion to two Cu ions and the other bonds to two Cu ions in a unidentate fashion. The resulting complex is polymeric, propagating along a. The Cu–S distances average 2.33(3) Å with a 0.08 Å range and the Cu–Cl separation is 2.3017(8) Å.

Keywords: 18-thiacrown-6, copper(I), chloride, complex, X-ray structure

INTRODUCTION

Complexation of copper(I) with thiaethers has been studied extensively in recent years in order to determine the structural and electronic features that control coordination.[2–8] We have begun investigations oriented toward using this chemistry to selectively complex the Cu(I) and Cu(II) cations from solution mixtures containing various hard and soft metal ions. We have in this manner prepared and structurally characterized a Cu(I) chloride complex of 18-thiacrown-6 which exhibits unusual structural features for a complex of this type. This, our initial report in this particular use of macrocycle complexation chemistry, discusses the structure of [CuCl(18-thiacrown-6)]$_n$.

EXPERIMENTAL

Preparation and crystallization of [CuCl(18-thiacrown-6)]$_n$

$YCl_3 \cdot 6H_2O$ (1 mmol, 0.303 g) was mixed with $BaCl_2 \cdot 2H_2O$ (2 mmol, 0.134 g) and $Cu(C_2H_3O_2) \cdot 2H_2O$ (3 mmol, 0.264 g) in 15 cm^3 of a solution containing 18-thiacrown-6 (Aldrich Chemical Company, 1.25 mmol 0.451 g). The mixture was dissolved with 15 cm^3 of 3:1 acetonitrile/methanol solution. The volume of the solution was

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† For part 28 see reference 1.

reduced by slow evaporation. After several weeks crystals deposited along the walls of the flask. Two types of crystals were isolated—clear parallepipeds of [CuCl(18-thiacrown-6)]$_n$ and blue crystals of $Cu(C_2H_3O_2)\cdot 2H_2O$. The crystals of [CuCl(18-thiacrown-6)]$_n$ were separated, cleaned and mounted for the single-crystal X-ray diffraction experiment. Anal.: Calcd. for $C_{12}H_{24}ClCuS_6$: C, 31.35; H, 5.26%. Found: C, 32.12; H, 6.66%.

X-ray data collection, structure determination and refinement for [CuCl(18-thiacrown-6)]$_n$.

A transparent single crystal of the title compound was mounted on a pin and transferred to the goniometer. The space group was determined to be either $P\bar{1}$ or

TABLE I

Crystal data and summary of intensity data collection and structure refinement.

Cmpd.	[CuCl(18-thiacrown-6)]$_n$
Colour/Shape	Colourless/parallelepiped
M.W.	459.71
Space group	$P\bar{1}$
Temp., °C	20
Cell Constants[a]	
a, Å	9.905(2)
b, Å	10.408(2)
c, Å	11.335(2)
α, deg	64.40(1)
β, deg	64.30(1)
γ, deg	82.47(1)
Cell vol., Å^3	947.3
Formula units/unit cell	2
D_{calc}, g cm^{-3}	1.61
μ_{calc}, cm^{-1}	18.5
Diffractometer/Scan	Enraf-Nonius CAD-4/θ–2θ
Range of relative transm. factors, %	77/100
Radiation, graphite monochromator	MoKα (λ = 0.71073)
Max. crystal dimensions, mm	0.10 × 0.25 × 0.40
Scan width	0.80 + 0.35tanθ
Standard reflections	600; 080; 008
Decay of standards	±1%
Reflections measured	3436
2θ range, deg	$2 \leqslant 2\theta \leqslant 50$
Range of h, k, l	+11, ±12, ±13
Reflections observed [$F_o \geq 5\sigma(F_o)$][b]	2772
Computer programs[c]	SHELX[9]
Structure solution	MULTAN[10]
No. of parameters varied	181
Weights	$[\sigma(F_o)^2 + 0.00002\ F_o^2]^{-1}$
GOF	0.96
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma F_o\|$	0.025
R_w	0.026
Largest feature (final diff. map)	0.3e$^-$ Å^{-3}

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections θ > 20°.

[b] Corrections: Lorentz-polarization and absorption (empirical, psi scan).

[c] Neutral scattering factors and anomalous dispersion corrections from ref. 11.

$P1$. Subsequent solution and successful refinement of the structure were accomplished in the centric space group $P\bar{1}$. A summary of data collection parameters is given in Table I.

The geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded atom and allowed to ride on that atom with B fixed at 5.5 Å^2. Refinement of non-hydrogen atoms with anisotropic temperature factors led to the final values of $R = 0.025$ and $R_w = 0.026$. The final values of the positional parameters are given in Table II.

TABLE II
Final fractional coordinates for [CuCl(18-thiacrown-6)]$_n$.

Atom	x/a	y/b	z/c	B(eqv)[a]
Cu	0.33898(4)	0.25862(3)	0.45887(3)	2.29
Cl	0.25862(9)	0.46405(7)	0.49027(8)	2.85
S(1)	0.56150(8)	0.31090(7)	0.25017(7)	2.22
S(2)	0.46492(9)	0.12826(7)	0.60728(7)	2.40
S(3)	0.4007(1)	0.21971(8)	0.97429(7)	3.03
S(4)	0.14512(8)	0.12682(7)	0.49496(7)	2.02
S(5)	−0.15577(9)	0.09773(8)	0.92902(7)	2.82
S(6)	−0.06047(9)	0.53529(8)	0.86219(7)	2.86
C(1)	0.6879(3)	0.2190(3)	0.3336(3)	2.74
C(2)	0.6486(3)	0.2199(3)	0.4774(3)	2.70
C(3)	0.4037(3)	0.2087(3)	0.7345(3)	2.79
C(4)	0.4933(3)	0.1715(3)	0.8233(3)	2.85
C(5)	0.4599(4)	0.4058(3)	0.8954(3)	3.02
C(6)	0.3858(3)	0.5050(3)	0.8007(3)	2.26
C(7)	−0.0199(3)	0.1505(3)	0.6390(3)	2.34
C(8)	0.0040(3)	0.0875(3)	0.7758(3)	2.74
C(9)	−0.1621(3)	0.2872(3)	0.8823(3)	2.57
C(10)	−0.0294(3)	0.3552(3)	0.8744(3)	2.75
C(11)	−0.0808(4)	0.6222(3)	0.6940(3)	2.78
C(12)	−0.0983(3)	0.7783(3)	0.6584(3)	2.33

[a] $B(\text{eqv}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab\cos\gamma\beta_{12} + ac\cos\beta\beta_{13} + bc\cos\alpha\beta_{23}]$.

DISCUSSION

The selective complexation of Cu(I) from a solution also containing Y^{3+} and Ba^{2+} ions was expected. Cu(I) is a soft ion and S is a soft donor. Future investigations in our laboratories will make further use of size and electronic factors in preparing macrocycle complexes of mixed metal ions. Musker[2] has noted the influence of anion on the structure of Cu(I) complexes of thiaethers and we will continue our investigations with various anions.

This report will focus on the novel structure of the title complex presented in Figure 1. Two unique thiacrown ether molecules are observed, each residing around a crystallographic centre of inversion and each possessing different metal coordination and conformation. The crown molecule containing S(1)–S(3) coordinates two Cu$^+$ ions in a bidentate fashion (Figure 2). Only S(3) and its symmetry related position S(3)^a are not coordinated to metal ions. The two unique Cu–S distances

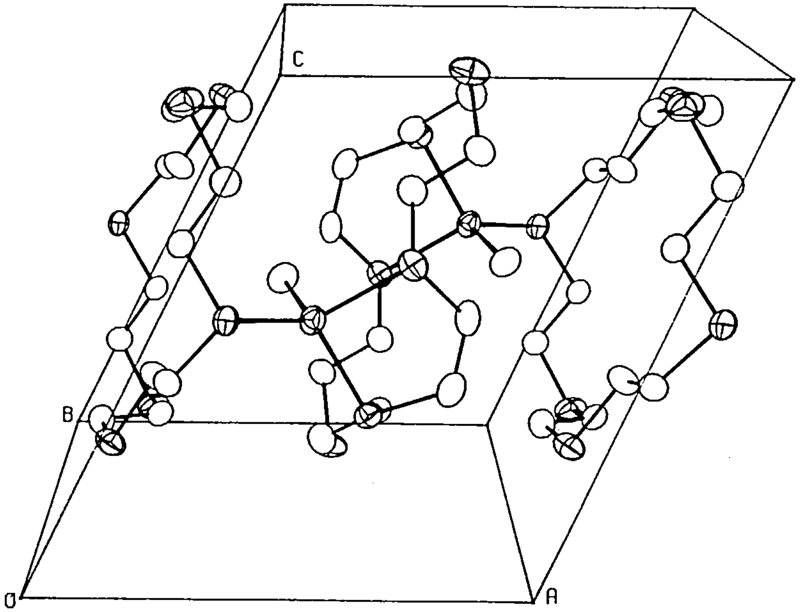

FIGURE 1 Cell packing diagram for the title complex depicting its polymeric nature.

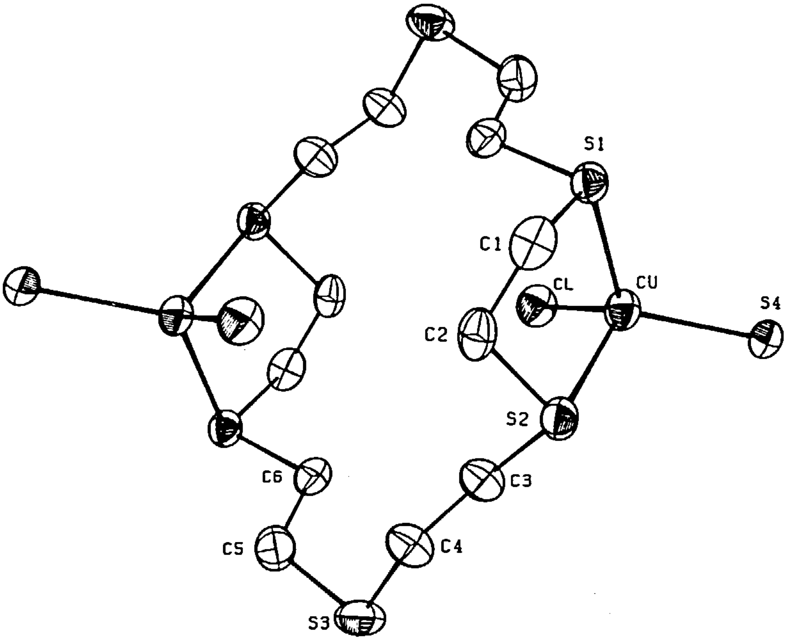

FIGURE 2 Thiacrown molecule bridging with bidentate interactions. Atoms are represented by their 50% probability ellipsoids for thermal motion. H atoms have been omitted.

(Table III) are quite different, Cu–S(1) = 2.3302(7) Å, Cu–S(2) = 2.3730(8) Å. The S(1)–Cu–S(2) bond angle of 91.66(3)° is compressed from a normal tetrahedral value of 109.5°. Most of the resulting distortion around the metal centre is observed in the S(1)–Cu–S(4) and S(2)–Cu–S(4) angles which have expanded to 119.36(3) and 113.21(3)°, respectively. All three S–Cu–Cl angles are more nearly tetrahedral, averaging 110.3(8)°.

TABLE III

Bond distances (Å) and angles (deg) for [CuCl(18-thiacrown-6)]$_n$.

Atoms	Distance	Atoms	Distance
Cu–Cl	2.3017(8)	Cu–S(1)	2.3302(7)
Cu–S(2)	2.3730(8)	Cu–S(4)	2.2935(7)
S(1)–C(1)	1.819(3)	S(1)–C(6)[a]	1.822(3)
S(2)–C(2)	1.818(3)	S(2)–C(3)	1.816(3)
S(3)–C(4)	1.811(3)	S(3)–C(5)	1.801(3)
S(4)–C(7)	1.824(3)	S(4)–C(12)[a]	1.819(3)
S(5)–C(8)	1.807(3)	S(5)–C(9)	1.807(3)
S(6)–C(10)	1.813(3)	S(6)–C(11)	1.813(3)
C(1)–C(2)	1.506(4)	C(3)–C(4)	1.517(4)
C(5)–C(6)	1.511(4)	C(7)–C(8)	1.513(3)
C(9)–C(10)	1.525(4)	C(11)–C(12)	1.502(4)

Atoms	Angle	Atoms	Angle
Cl–Cu–S(1)	109.80(3)	Cl–Cu–S(2)	109.76(3)
S(1)–Cu–S(2)	91.66(3)	Cl–Cu–S(4)	111.38(3)
S(1)–Cu–S(4)	119.36(3)	S(2)–Cu–S(4)	113.21(3)
Cu–S(1)–C(1)	98.61(9)	Cu–S(1)–C(6)[a]	103.16(9)
C(1)–S(1)–C(6)[a]	99.6(2)	Cu–S(2)–C(2)	95.57(9)
Cu–S(2)–C(3)	101.76(9)	C(2)–S(2)–C(3)	102.6(1)
C(4)–S(3)–C(5)	103.1(1)	Cu–S(4)–C(7)	105.6(1)
Cu–S(4)–C(12)[a]	107.2(1)	C(7)–S(4)–C(12)[a]	101.3(1)
C(8)–S(5)–C(9)	103.3(1)	C(10)–S(6)–C(11)	100.6(1)
S(1)–C(1)–C(2)	114.8(2)	S(2)–C(2)–C(1)	110.2(2)
S(2)–C(3)–C(4)	114.2(2)	S(3)–C(4)–C(3)	111.6(2)
S(3)–C(5)–C(6)	114.7(2)	S(1)[a]–C(6)–C(5)	109.0(3)
S(4)–C(7)–C(8)	109.1(2)	S(5)–C(8)–C(7)	113.3(2)
S(5)–C(9)–C(10)	114.8(2)	S(6)–C(10)–C(9)	112.3(2)
S(6)–C(11)–C(12)	109.1(2)	S(4)[a]–C(12)–C(11)	113.4(3)

[a] Atoms are related to those in Table II by the respective crystallographic centres of inversion.

The second thiacrown ether (S(4)–S(6)), depicted in Figure 3, also bridges two Cu$^+$ ions, however, in a unidentate fashion. Only two of the six sulfur atoms thus participate and the Cu–S(4) bond distance is the shortest of the three Cu–S interactions (2.2935(7) Å).

Each crown molecule adopts a different conformation, both of which are different from that observed in free 18-thiacrown-6.[12] In thiacrowns the C–S bonds prefer a *gauche* (*g*) geometry and the C–C bonds an *anti* (*a*) placement.[13] In free 18-thiacrown-6, all of the C–S bonds are *g* as are all but four of the C–S bonds in both unique crown molecules in the title complex (Table IV). In both molecules all but two

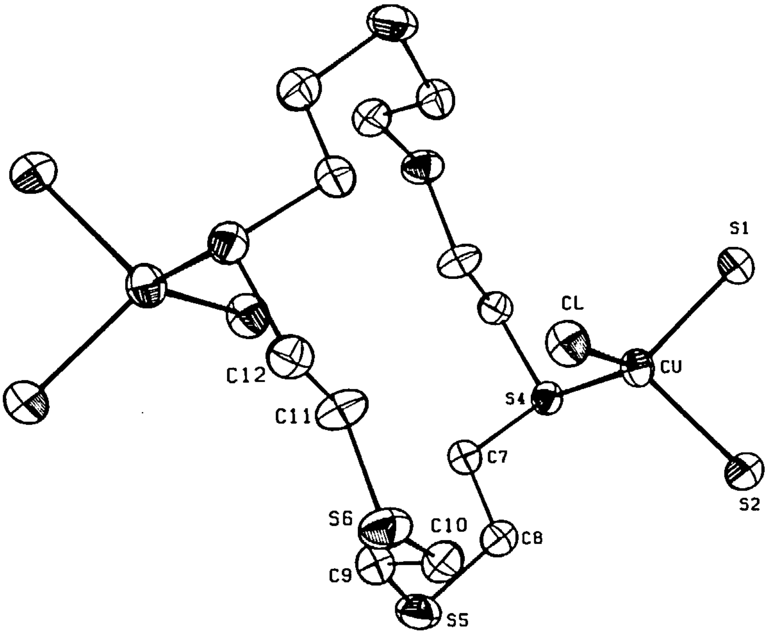

FIGURE 3 Thiacrown bridging with unidentate interactions.

TABLE IV
Torsion angles (deg) for [CuCl(18-thiacrown-6)]$_n$.

Atoms	Angle
S(1)-C(1)-C(2)-S(2)	61.9
C(1)-C(2)-S(2)-C(3)	−154.8
C(2)-S(2)-C(3)-C(4)	−68.0
S(2)-C(3)-C(4)-S(3)	−166.6
C(3)-C(4)-S(3)-C(5)	−84.1
C(4)-S(3)-C(5)-C(6)	74.1
S(3)-C(5)-C(6)-S(1)[a]	172.4
C(5)-C(6)-S(1)[a]-C(1)[a]	−170.7
C(6)-S(1)[a]-C(1)[a]-C(2)[a]	−71.4
S(4)-C(7)-C(8)-S(5)	−177.5
C(7)-C(8)-S(5)-C(9)	−67.5
C(8)-S(5)-C(9)-C(10)	−66.3
S(5)-C(9)-C(10)-S(6)	−168.7
C(9)-C(10)-S(6)-C(11)	−61.3
C(10)-S(6)-C(11)-C(12)	−176.4
S(6)-C(11)-C(12)-S(4)[a]	−172.1
C(11)-C(12)-S(4)[a]-C(7)[a]	−62.2
C(12)-S(4)[a]-C(7)[a]-C(8)[a]	175.5

[a] See footnote, Table III.

of the S–C–C–S torsion angles are *a* and these two both occur in the S(1)–S(3) molecule between the two coordinated sulfur atoms. (The symmetry-unique angle is S(1)–C(1)–C(2)–S(2) = 61.9°.) In addition, the four C–S–C–C angles which are *anti* in both molecules are in portions of the molecules leading to the coordinated sulfur atoms: C(1)–C(2)–S(2)–C(3) = −154.8°, C(5)–C(6)–S(1)^a–C(1)^a = −170.7° for the S(1)–S(3) ether and C(10)–S(6)–C(11)–C(12) = −176.4°, C(12)–S(4)^a–C(7)^a–C(8)^a = 175.5° for the S(4)–S(6) ether.

Another feature concerning the different conformations of the thiacrowns is worthy of note. In the S(1)–S(3) crown the six sulfur atoms are planar to 0.086 Å with each consecutive sulfur atom alternating up and down from the mean plane of all six. The sulfur atoms in the S(4)–S(6) molecule also alternate in sign of deviation from the mean plane. However, these six sulfur atoms are planar only to 0.77 Å.

The bonding within the macrocyclic rings is comparable to previous reports.[12,13] The average parameters are: (S(1)–S(3)) S–C = 1.814(7) Å, C–C = 1.511(4) Å, S–C–C = 112(2)°, C–S–C = 99(3)°; (S(4)–S(6)) S–C = 1.814(6) Å, C–C = 1.513(9) Å, S–C–C = 112(2)°; C–S–C = 102(1)°. Small differences in the averages of the C–S–C bond angles in the two unique crown molecules are noted. The major reason for these differences is compression of the C(1)–S(1)–C(6)^a bond angle to 99.6(2)°. S(1) and C(1) are involved in the only *gauche* S–C–C–S torsion angle in either macrocycle.

Two of the observed Cu–S distances fall within the range of 2.260(4) to 2.358(2) Å observed for other Cu(I)-thiacrown structural determinations.[6] The Cu–S(2) distance of 2.3730(8) Å, however, is quite long and may prove to be the current upper limit for Cu(I)–S interactions of this type.

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SUPPLEMENTARY MATERIAL

Tables of fractional coordinates for calculated H atoms, thermal parameters, least-squares planes results, and observed and calculated structure factors are available from R.D.R. upon request.

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