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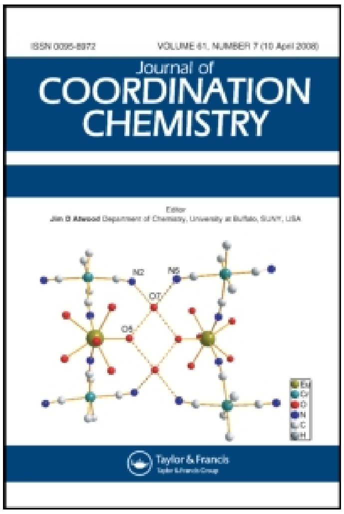

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UTILIZATION OF CROWN ETHER CHEMISTRY TO PREPARE BIMETALLIC COMPOUNDS: PREPARATION AND STRUCTURAL CHARACTERIZATION OF [Ba(15-CROWN-5)$_2$][CuCl$_4$]

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UTILIZATION OF CROWN ETHER CHEMISTRY TO PREPARE BIMETALLIC COMPOUNDS: PREPARATION AND STRUCTURAL CHARACTERIZATION OF [Ba(15-CROWN-5)$_2$][CuCl$_4$]

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A solid hetero-bimetallic complex of Ba^{+2} and Cu^{+2} was prepared by slow evaporation of a 3/1 CH_3CN/CH_3OH mixture containing 15-crown-5 and the chloride salts of Ba^{+2}, Cu^{+2}, and Y^{+3}. The resulting complex was studied using single crystal X-ray diffraction. [Ba(15-crown-5)$_2$][CuCl$_4$] crystallizes in the monoclinic space group *Pn* with cell parameters (20°C), $a = 12.119(2)$, $b = 9.386(2)$, $c = 13.475(3)$Å, $\beta = 93.81(2)$°, and $D_{calc} = 1.70$ g cm^{-3} for $Z = 2$. Ba^{+2} is coordinated to all 10 oxygen atoms of two 15-crown-5 molecules in a sandwich geometry. Cu^{+2} is coordinated to the four chloride anions and exhibits a distorted tetrahedral geometry. The two shortest Cu···Ba separations are 6.855(2) and 6.902(2)Å.

KEY WORDS: 15-crown-5, barium, copper, chloride, bimetallic complex, X-ray structure.

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INTRODUCTION

The preparation of novel hetero-bimetallic complexes is of increasing relevance to several interdisciplinary fields including catalysis,[2] biological science,[3] and material science (e.g., as precursors for high temperature superconductors[4] or organic conductors[5]). We have been interested in these compounds as precursors for high temperature superconductors. The current synthesis routes which are based on high temperature reactions have several disadvantages for practical use. While various groups are focussing on preparing materials with low sintering temperatures using alkoxides[6,7] and other nonselective complexing agents,[8,9] we have begun an investigation of relatively straightforward coordination chemistry with readily available crown ether ligands to produce precursor materials. A recent communication has appeared by Norman and Peg[10] in which volatile crown ether complexes of barium hexafluoroacetylacetone were prepared.

Our initial investigations have centred on the cations in the widely studied 1-2-3 superconductor, $YBa_2Cu_3O_{7-\delta}$. A few groups have been able to prepare bimetallic complexes of Ba^{+2} and Cu^{+2} by incorporating hard and soft cavities in Schiff base compounds,[11] porphyrins,[12] or crown ether-substituted phthalocyanines.[13] While successful, these routes require complicated synthetic schemes to obtain the ligands before any complexation can be contemplated.

It was our hope that by utilizing the differences in the cationic nature of Ba^{+2}, Cu^{+2}, and Y^{+3} and our knowledge of crown ether chemistry, that the desired compounds could be prepared without complicated syntheses.

For our initial investigation, we chose a mixture of the halide salts of the three cations of interest and 15-crown-5 in a nonaqueous solvent (3/1 CH_3CN/CH_3OH). The reaction of 15-crown-5 with each of the metals under similar conditions produced very different types of complexes. The ligand 15-crown-5 can take up all primary coordination sites for Ba^{+2} by forming a sandwich complex as in $[Ba(15\text{-crown-}5)_2]Br_2 \cdot 2H_2O$.[14] The softer Cu^{+2} ion, on the other hand, prefers the halide ions in the primary coordination sphere with two water molecules; thus, the crown ether is hydrogen bonded in the second coordination environment as in $[CuBr_2(OH_2)_2] \cdot 15$-crown-5[15] (crown ether complexed directly to Cu^{+2} can be obtained under anhydrous conditions[16]). Yet a third complex type is observed for the hard Y^{+3} ion where coordination of water molecules is prefered over either halide ions or the crown ether. The structure of $[Y(OH_2)_8]Cl_3 \cdot 15$-crown-5 has been reported.[17] Our results are consistent with the reactions of 15-crown-5 and each metal individually.

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EXPERIMENTAL

Preparation and Crystallization of $[Ba(15\text{-crown-}5)_2][CuCl_4]$

The reaction of $YCl_3 \cdot 6H_2O$ (1 mmol, 0.303 g), $BaCl_2 \cdot 2H_2O$ (2 mmol, 0.134 g), and $CuCl_2 \cdot 2H_2O$ (3 mmol, 0.165 g) in 15 cm^3 of a 3/1 CH_3CN/CH_3OH solution containing 15-crown-5 (1.25 mmol) produced the crystalline complex $[Ba(15\text{-crown-}5)_2][CuCl_4]$. The mixture was stirred at 60°C for 24 hours, cooled to 22°C, and concentrated to 1–5 cm^3. The remaining mixture was evaporated over a period of several weeks. During this time, crystals formed along the walls of the flask. Formula weight = 783.22; anal. calcd. for $BaC_{20}H_{40}O_{10}CuCl_4$: C, 30.67; H, 5.14%. Found: C, 30.23%; H, 5.03%.

X-ray Data Collection, Structure Determination and Refinement of $[Ba(15\text{-Crown-}5)_2][CuCl_4]$

A yellow, single crystal of the complex was used in the structural characterization. The space group was determined to be either *P2/n* or *Pn* from systematic absences. The subsequent solution and successful refinement of the structure was carried out in the acentric space group *Pn*. Crystal data collection and refinement parameters are summarized in Table 1.

Least-squares refinement with isotropic thermal parameters led to $R = 0.068$. The hydrogen atoms were placed in calculated positions 0.95Å from the bonded carbon atoms and allowed to ride on that atom with B fixed at 5.5Å^2. An investigation of inverse configurations led to the current enantiomer. Refinement of the nonhydrogen atoms with anisotropic temperature factors led to final values of $R = 0.040$ and $R_w = 0.045$. A final difference Fourier map showed no feature greater than 0.8e$^-$/Å^3. Final positional parameters are given in Table 2.

Table 1 Crystal data and summary of intensity data collection and structure refinement

	$[Ba(15\text{-crown-}5)_2][CuCl_4]$
colour/shape	yellow/parallelepiped
formula weight	783.22
space group	*Pn*
temperature, °C	20
cell constants[a]	
a, Å	12.119(2)
b, Å	9.386(2)
c, Å	13.475(3)
β, deg	93.81(2)
cell volume, $Å^3$	1529
formula units/unit cell	2
D_{calcd}, $g\,cm^{-3}$	1.70
μ_{calcd}, cm^{-1}	24.3
diffractometer/scan	Enraf-Nonius CAD-4/ω-2θ
range of relative transmission factors, %	77/100
radiation, graphite monochromator	$MoK\alpha(\lambda=0.71073Å)$
maximum crystal dimensions, mm	$0.08\times0.18\times0.25$
scan width	$0.80+0.35\tan\theta$
standard reflections	(0,0,6), (0,4,0), (6,0,0)
decay of standards	±1%
reflections measured	2994
2θ range, deg	$2\leqslant2\theta\leqslant50$
range of h, k, l	+13, +11, ±16
reflections observed $[F_o\geqslant5\sigma(F_o)]$[b]	2415
computer programs[c]	SHELX
structure solution	SHELXS
No. of parameters varied	323
weights	$[\sigma(F_o)^2+0.001F_o^2]^{-1}$
GOF	1.62
$R=\sum\Vert F_o\vert-\vert F_c\Vert/\sum\vert F_o\vert$	0.040
R_w	0.045
R (inverse cofiguration)	0.042
largest feature in final difference map	$0.8e^-Å^{-3}$

[a]Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 24 reflections $\theta>20°$. [b]Corrections: Lorentz-polarization and absorption (empirical, psi scan). [c]Neutral scattering factors and anomalous dispersion corrections.

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DISCUSSION

An ORTEP illustration of the ionic pair is presented in Figure 1. The $[Ba(15\text{-crown-}5)_2]^{+2}$ sandwich cation is nearly identical to that observed in $[Ba(15\text{-crown-}5)_2]Br_2{\cdot}2H_2O$. The ten Ba-O separations range from 2.80(1) to 2.907(9)Å (Table 3) and average 2.86(4)Å (*versus* 2.82(4)Å in the bromide complex). Even the crown ether conformations where each crown has a different conformation are the same as observed for the bromide complex.

Ba^{+2} has approximately pentagonal antiprismatic geometry although the five oxygen atoms deviate significantly from planarity (0.45Å maximum deviation for O(1)-O(5), 0.13Å for O(6)-O(10)). The more planar O(6)-O(10) fragment has a less frequently observed conformation characterized by all O-C-C-O torsion angles of $-60°$ and one of each pair of C-O-C-C angles forced toward a *gauche* position (104° average).

Table 2 Final fractional coordinates for $[Ba(15\text{-crown-}5)_2][CuCl_4]$

Atom	x/a	y/b	z/c	B(eqv)[a]
Cu	−0.7146(2)	−0.4618(2)	−0.6985(1)	3.18
Ba	−0.2500	0.12576(6)	−0.7500	2.00
Cl(1)	−0.5903(3)	−0.3567(3)	−0.5871(3)	3.15
Cl(2)	−0.6940(4)	−0.5876(4)	−0.8405(3)	4.02
Cl(3)	−0.7697(4)	−0.6406(4)	−0.5999(3)	4.20
Cl(4)	−0.8043(5)	−0.2623(5)	−0.7558(3)	5.58
O(1)	−0.4412(7)	−0.0533(8)	−0.7719(6)	2.40
O(2)	−0.4397(7)	0.1812(8)	−0.6465(7)	2.83
O(3)	−0.2457(7)	0.3172(9)	−0.5864(6)	2.78
O(4)	−0.1554(8)	0.042(1)	−0.5567(6)	3.20
O(5)	−0.2405(7)	−0.1705(9)	−0.6900(7)	2.99
O(6)	−0.2896(8)	0.4152(9)	−0.8205(7)	3.28
O(7)	−0.0763(9)	0.321(1)	−0.7577(9)	4.36
O(8)	−0.0356(9)	0.037(1)	−0.7954(8)	4.52
O(9)	−0.2168(8)	−0.035(1)	−0.9232(7)	3.31
O(10)	−0.3782(8)	0.182(1)	−0.9347(7)	3.16
C(1)	−0.534(1)	−0.019(1)	−0.7175(9)	2.51
C(2)	−0.540(1)	0.141(1)	−0.707(1)	2.32
C(3)	−0.441(1)	0.331(1)	−0.615(1)	2.72
C(4)	−0.346(1)	0.348(1)	−0.5398(9)	3.11
C(5)	−0.155(1)	0.289(2)	−0.519(1)	3.48
C(6)	−0.158(1)	0.140(2)	−0.475(1)	4.00
C(7)	−0.173(1)	−0.102(2)	−0.522(1)	3.95
C(8)	−0.157(1)	−0.199(1)	−0.608(1)	3.62
C(9)	−0.342(1)	−0.247(1)	−0.684(1)	3.10
C(10)	−0.417(1)	−0.205(1)	−0.771(1)	2.68
C(11)	−0.196(1)	0.490(2)	−0.848(1)	4.31
C(12)	−0.105(1)	0.467(2)	−0.772(1)	4.93
C(13)	0.017(1)	0.287(2)	−0.804(1)	4.97
C(14)	0.048(2)	0.139(2)	−0.769(2)	5.41
C(15)	−0.024(1)	−0.023(3)	−0.890(2)	8.30
C(16)	−0.110(1)	−0.102(2)	−0.923(1)	5.06
C(17)	−0.257(1)	0.022(2)	−1.014(1)	3.55
C(18)	−0.370(1)	0.071(2)	−1.004(1)	3.11
C(19)	−0.375(1)	0.321(1)	−0.978(1)	3.39
C(20)	−0.382(1)	0.426(1)	−0.896(1)	3.30

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

The $[CuCl_4]^{-2}$ anion has the flattened tetrahedral geometry commonly observed for this anion.[18−21] The two widest angles (Cl(1)-Cu-Cl(2) and Cl(3)-Cu-Cl(4)) average 131.6(7)°, while the remaining angles range from 98.2(1) to 102.6(2)° and average 100(2)°. The Cu-Cl bond lengths range from 2.268(4) to 2.279(4)Å and average 2.274(4)Å.

Recent developments in oxidation/reduction-metal complexations for superconducting precursor material has produced a $[Ba(18\text{-crown-}6)]_2[CuCl_4]_2\cdot 2H_2O$ complex[21] where the $[CuCl_4]^{-2}$ anion has a flattened tetrahedral geometry with Cu-Cl-Ba interactions. The reported structure differs substantially from the 18-crown-6 complex; there are no bridged interactions between the Cu···Ba due to the insulation of the Ba^{+2} metal by complete coordination with the two 15-crown-5 ligands.

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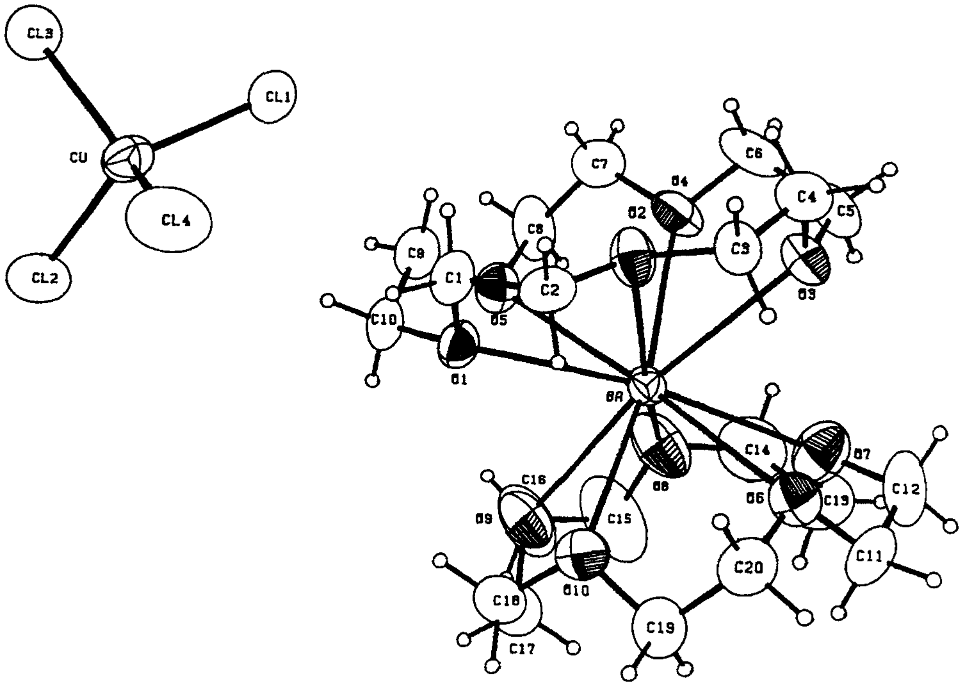

Figure 1 ORTEP illustration of [Ba(15-crown-5)$_2$][CuCl$_4$]. The atoms are illustrated with 50% probability thermal ellipsoids. The hydrogen atoms have been arbitrarily reduced.

Table 3 Bond distances (Å) and angles (deg) for [Ba(15-crown-5)$_2$][CuCl$_4$]

Atoms	Distance	Atoms	Distance
Cu-Cl(1)	2.279(4)	Cu-Cl(2)	2.277(5)
Cu-Cl(3)	2.268(4)	Cu-Cl(4)	2.274(5)
Ba-O(1)	2.862(8)	Ba-O(2)	2.816(8)
Ba-O(3)	2.842(8)	Ba-O(4)	2.884(9)
Ba-O(5)	2.896(8)	Ba-O(6)	2.907(9)
Ba-O(7)	2.80(1)	Ba-O(8)	2.83(1)
Ba-O(9)	2.828(9)	Ba-O(10)	2.893(9)
O(1)-C(1)	1.42(1)	O(1)-C(10)	1.45(1)
O(2)-C(2)	1.46(2)	O(2)-C(3)	1.47(1)
O(3)-C(4)	1.43(1)	O(3)-C(5)	1.41(2)
O(4)-C(6)	1.43(2)	O(4)-C(7)	1.45(2)
O(5)-C(8)	1.47(1)	O(5)-C(9)	1.43(1)
O(6)-C(11)	1.40(2)	O(6)-C(20)	1.47(2)
O(7)-C(12)	1.43(2)	O(7)-C(13)	1.37(2)
O(8)-C(14)	1.42(2)	O(8)-C(15)	1.41(2)
O(9)-C(16)	1.44(2)	O(9)-C(17)	1.40(2)
O(10)-C(18)	1.42(2)	O(10)-C(19)	1.43(2)
C(1)-C(2)	1.50(1)	C(3)-C(4)	1.49(2)
C(5)-C(6)	1.52(2)	C(7)-C(8)	1.50(2)
C(9)-C(10)	1.49(2)	C(11)-C(12)	1.48(2)
C(13)-C(14)	1.51(2)	C(15)-C(16)	1.33(2)
C(17)-C(18)	1.45(2)	C(19)-C(20)	1.49(2)

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Table 3 *Continued*

Atoms	Angle	Atoms	Angle
Cl(1)-Cu-Cl(2)	132.3(2)	Cl(1)-Cu-Cl(3)	98.2(1)
Cl(2)-Cu-Cl(3)	99.3(2)	Cl(1)-Cu-Cl(4)	98.5(2)
Cl(2)-Cu-Cl(4)	102.6(2)	Cl(3)-Cu-Cl(4)	130.9(2)
O(1)-Ba-O(2)	58.5(2)	O(1)-Ba-O(3)	115.1(2)
O(2)-Ba-O(3)	58.2(2)	O(1)-Ba-O(4)	101.7(3)
O(2)-Ba-O(4)	83.8(3)	O(3)-Ba-O(4)	59.1(2)
O(1)-Ba-O(5)	58.8(2)	O(2)-Ba-O(5)	93.3(2)
O(3)-Ba-O(5)	113.1(3)	O(4)-Ba-O(5)	58.7(3)
O(1)-Ba-O(6)	113.6(3)	O(2)-Ba-O(6)	82.3(3)
O(3)-Ba-O(6)	69.9(3)	O(4)-Ba-O(6)	126.6(3)
O(5)-Ba-O(6)	172.3(3)	O(1)-Ba-O(7)	170.7(3)
O(2)-Ba-O(7)	122.6(3)	O(3)-Ba-O(7)	68.9(3)
O(4)-Ba-O(7)	87.5(3)	O(5)-Ba-O(7)	128.5(3)
O(6)-Ba-O(7)	59.0(3)	O(1)-Ba-O(8)	123.6(3)
O(2)-Ba-O(8)	162.1(3)	O(3)-Ba-O(8)	112.5(3)
O(4)-Ba-O(8)	78.5(3)	O(5)-Ba-O(8)	76.0(3)
O(6)-Ba-O(8)	109.7(3)	O(7)-Ba-O(8)	58.7(3)
O(1)-Ba-O(9)	76.2(3)	O(2)-Ba-O(9)	132.3(3)
O(3)-Ba-O(9)	168.6(3)	O(4)-Ba-O(9)	122.0(3)
O(5)-Ba-O(9)	73.4(3)	O(6)-Ba-O(9)	104.9(3)
O(7)-Ba-O(9)	99.7(3)	O(8)-Ba-O(9)	58.9(3)
O(1)-Ba-O(10)	68.5(2)	O(2)-Ba-O(10)	89.0(3)
O(3)-Ba-O(10)	122.3(2)	O(4)-Ba-O(10)	170.0(3)
O(5)-Ba-O(10)	115.0(3)	O(6)-Ba-O(10)	58.8(3)
O(7)-Ba-O(10)	102.3(3)	O(8)-Ba-O(10)	108.4(3)
O(9)-Ba-O(10)	58.9(3)	Ba-O(1)-C(1)	118.3(6)
Ba-O(1)-C(10)	114.6(7)	C(1)-O(1)-C(10)	112.8(9)
Ba-O(2)-C(2)	110.6(7)	Ba-O(2)-C(3)	110.1(7)
C(2)-O(2)-C(3)	112.6(9)	Ba-O(3)-C(4)	119.8(7)
Ba-O(3)-C(5)	110.9(8)	C(4)-O(3)-C(5)	114(1)
Ba-O(4)-C(6)	119.4(8)	Ba-O(4)-C(7)	119.1(8)
C(6)-O(4)-C(7)	110(1)	Ba-O(5)-C(8)	113.2(7)
Ba-O(5)-C(9)	118.5(7)	C(8)-O(5)-C(9)	115(1)
Ba-O(6)-C(11)	115.8(8)	Ba-O(6)-C(20)	113.1(7)
C(11)-O(6)-C(20)	112(1)	Ba-O(7)-C(12)	117.5(9)
Ba-O(7)-C(13)	121(1)	C(12)-O(7)-C(13)	111(1)
Ba-O(8)-C(14)	113(1)	Ba-O(8)-C(15)	117.3(9)
C(14)-O(8)-C(15)	113(2)	Ba-O(9)-C(16)	114.2(8)
Ba-O(9)-C(17)	117.6(8)	C(16)-O(9)-C(17)	116(1)
Ba-O(10)-C(18)	112.7(8)	Ba-O(10)-C(19)	119.3(8)
C(18)-O(10)-C(19)	113(1)	O(1)-C(1)-C(2)	109(1)
O(2)-C(2)-C(1)	106(1)	O(2)-C(3)-C(4)	106(1)
O(3)-C(4)-C(3)	109(1)	O(3)-C(5)-C(6)	113(1)
O(4)-C(6)-C(5)	107(1)	O(4)-C(7)-C(8)	107(1)
O(5)-C(8)-C(7)	111(1)	O(5)-C(9)-C(10)	108(1)
O(1)-C(10)-C(9)	112(1)	O(6)-C(11)-C(12)	109(1)
O(7)-C(12)-C(11)	113(1)	O(7)-C(13)-C(14)	105(2)
O(8)-C(14)-C(13)	112(2)	O(8)-C(15)-C(16)	113(2)
O(9)-C(16)-C(15)	116(1)	O(9)-C(17)-C(18)	109(1)
O(10)-C(18)-C(17)	113(1)	O(10)-C(19)-C(20)	107(1)
O(6)-C(20)-C(19)	113(1)		

The packing of the molecular ions is depicted in Figure 2. The two closest Cu···Ba separations of 6.855(2) and 6.906(2)Å are longer than those typically found for bimetallic complexes of ligands incorporating both hard and soft cavities.[11]

The synthesis and structural characterization of the title complex has demonstrated

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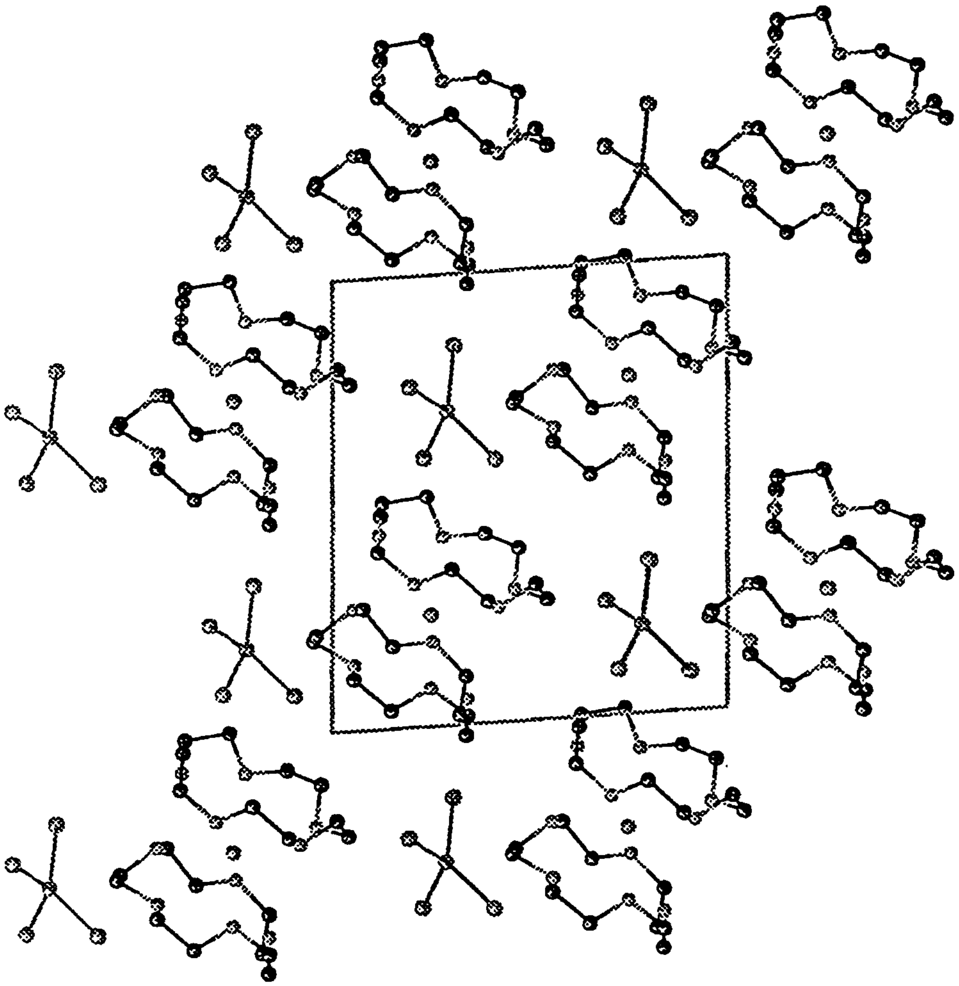

Figure 2 SYBYL (Tripos Associates, St. Louis, MO) representation of the ionic packing in the xy plane.

the ability to form bimetallic complexes using the highly selective and specific nature of crown ethers. Metal-crown ether complexation chemistry may be used to design specific and selective multimetal complexes with crown ethers and can be tailored for the preparation of new materials.

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Supplementary Material

Full lists of hydrogen atom coordinates, anisotropic thermal parameters and observed and calculated structure factors are available from the authors upon request.

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