

a single bond.¹ The $\nu(\text{Pt}^{\text{I}}-\text{Pt}^{\text{I}})$ Raman frequency found in **2**, 149 cm^{-1} , is in good agreement with other complexes containing a Pt_2^{I} system.⁴ The oxygen atoms in the coordination sphere of the Pt^{I} atoms deviate by about 0.5 Å from the planes defined by the central metal atom and the four surrounding atoms, i.e., Pt_2OCl_2 .

The interplanar angle about the Pt-Pt bonds is 52.0°, 45.1°, and 54.9° in **1**, **2**, and **3**, respectively. These values are similar to those found in other diplatinum(I) systems and close to the optimal value of 45°.^{1c,d,f} The dimensions of the $\text{Pt}_2^{\text{I}}\text{O}_2(\text{DMSO})_4$ fragment in **1** are very similar to those reported for $[\text{Pt}^{\text{II}}_2(\text{OH})_2(\text{DMSO})_4]^{2+}$, **II**.⁵ The main difference is in the dihedral angle between the two PtO_2 planes which is about 35° in **1** compared with the planar Pt_2O_2 system in the di- μ -hydroxo compound. The formation of **1** from K_2PtCl_4 is obviously a multistage process. The first stage is the formation of *cis*- $\text{PtCl}_2(\text{DMSO})_2$.⁶ Colorless crystals of this compound are precipitated and are redissolved when DMF is added to the reaction mixture. When K_2PtCl_4 was replaced by *cis*- $\text{PtCl}_2(\text{DMSO})_2$ as a starting material, the same product, **1**, was obtained. Scheme I is proposed for the formation of **1** from *cis*- $\text{PtCl}_2(\text{DMSO})_2$. The formation of **II** from *cis*- $\text{PtCl}_2(\text{DMSO})_2$ in the presence of water was previously reported,⁵ and the postulated Pt_2^{I} species, **III**, may be formed by the reduction of Pt^{II} by the $\text{CH}_3\text{O}^-/\text{CH}_3\text{OH}$ mixture as found in other systems.^{1a,f} The attraction of the dinegative intermediate **II** to the dipositive intermediate **III** may promote their fusion into the product **1**.

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Supplementary Material Available: Tables of atomic positional parameters for **1**, **2**, and **3** (3 pages). Ordering information is given on any current masthead page.

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The First X-ray Crystalline Structure of the Bis(monoazacrown ether) Complex.

A Bis(crown ether) or a Lariat Ether?

Gong-Xin He,[†] Kiyoshi Kikukawa,^{†,§} Hiroshi Ohe,[‡] Mitsuo Machida,[‡] and Tsutomu Matsuda*[†]

Department of Organic Synthesis, Faculty of Engineering and Department of Physics, Faculty of Science, Kyushu University, Hakozaki Higashi-ku, Fukuoka 812, Japan

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The bis(crown ether) is one of the macrocyclic polyethers which has been designed to improve the cation-binding properties.¹ Extraction behaviors and homogeneous stability constants have provided conclusive demonstrations for the cooperation of the two crown units in many bis(crown ether)s in the complexation with the cations being larger than their hole size.² To date, however, there is no unequivocal evidence on how the two crown rings

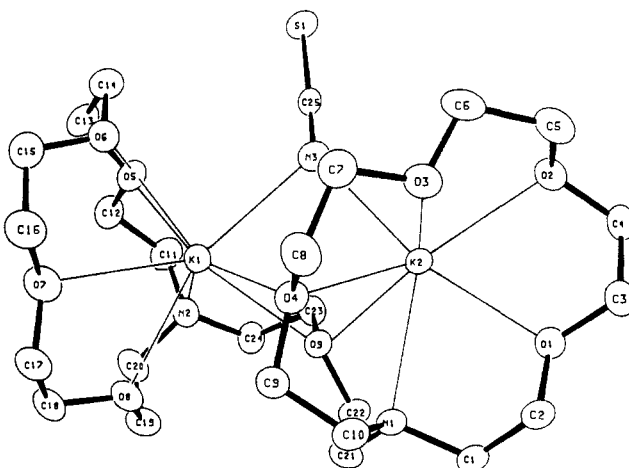
[†] Department of Organic Synthesis.

[‡] Department of Physics.

[§] Present address: Department of Industrial Chemistry, Faculty of Engineering (Kyushu Campus), Kinki University, Iizuka 820, Japan.

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K1-O5	2.731(4)	K2-O1	2.718(4)	K1-N2	2.951(4)
K1-O6	2.840(5)	K2-O2	2.758(3)	K1-N3	2.820(5)
K1-O7	2.874(5)	K2-O3	2.819(4)	K2-N1	2.939(4)
K1-O8	2.837(4)	K2-O4	2.985(4)	K2-N3	2.742(6)
K1-O9	2.967(5)	K2-O9	2.827(3)	K1-O4	2.916(4)

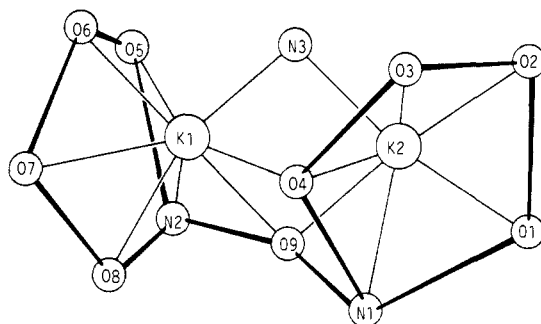


Figure 1. Perspective (top) and skeletal (bottom) drawings of $\text{BOA15C5}\cdot 2\text{KSCN}\cdot \text{H}_2\text{O}$, along with the coordination bond distances (Å).

cooperate in the complexation, although many X-ray analytical results on mono(crown ether) complexes have been reported³ and Gokel et al. gave the evidence for the side-arm participation in the crystalline lariat ether complexes.⁴ X-ray analyses of the bis(monoaza-15-crown-5)potassium thiocyanate complex presented here show that the bis(crown ether) can bind two K^+ cations and that the oxygen atom in the bridging chain interacts directly with both ring-bound cations.

The structure of the KSCN complex of 1,5-bis(*N*-monoaza-15-crown-5)-3-oxapentane (BOA15C5) is shown in Figure 1 along with a skeletal drawing of the donor atoms and metal ions in which their relative arrangements were depicted.⁵ The whole molecule

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(5) $\text{C}_{22}\text{H}_{48}\text{N}_2\text{O}_9\cdot 2\text{KSCN}\cdot \text{H}_2\text{O}$, a white crystalline solid, mp 132-133 °C; IR (Nujol) 3490, 3390, 2060, 2040, 1120, 1080, 940, 850 cm^{-1} ; Crystal data: triclinic $P1$, $a = 12.071$ (5) Å, $b = 16.619$ (4) Å, $c = 9.817$ (2) Å, $\alpha = 106.67$ (5)°, $\beta = 99.80$ (9)°, $\gamma = 72.03$ (9)°, $V = 1787$ Å³, $Z = 2$, $d_c = 1.341$ g cm^{-3} , $R = 0.074$ for 6690 data. Anal. Calcd for $\text{C}_{22}\text{H}_{50}\text{N}_4\text{O}_{10}\text{K}_2\text{S}_2$: C, 43.31; H, 6.99; N, 7.77. Found: C, 43.35; H, 6.93; N, 7.93. No effort has been made to locate the hydrogen atoms.

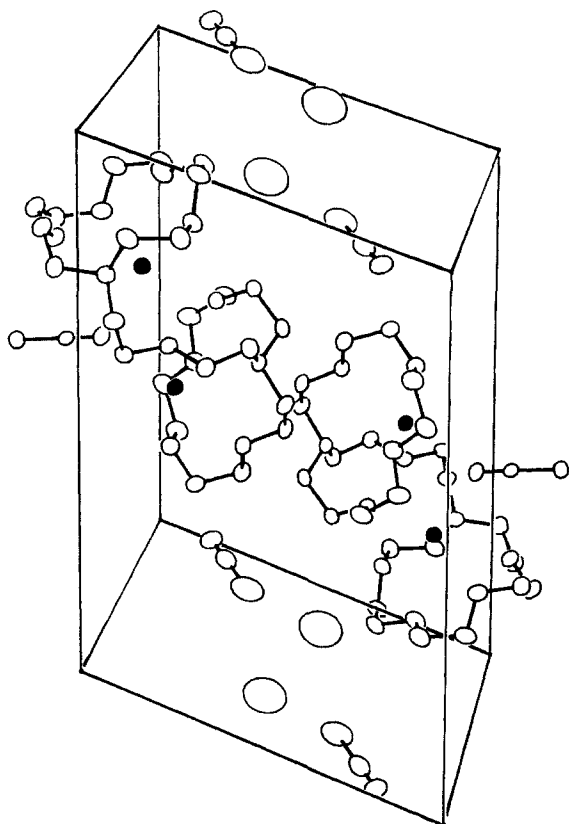


Figure 2. Unit-cell packing diagram for BOA15C5·2KSCN·H₂O (●, potassium cations).

of BOA15C5 encapsulates two K⁺ cations instead of one. The two cations are mainly bound by each crown ring, respectively, and are bridged by two oxygens (O4 and O9) and one anionic nitrogen (N3). Another SCN⁻ anion forms only a hydrogen bond with a water molecule present in the crystal. The anion is not in the coordination sphere of the cations and therefore is not pictured in Figure 1 but can be found in the unit-cell packing diagram (Figure 2). A similar bridge-binding was reported by Truter et al. in the KSCN complex of dibenzo-24-crown-8 (DB24C8-2KSCN),⁶ in which two K⁺ cations are held in the large crown ring and bridged by two ring oxygens and two anionic nitrogens. However, the complex is much more symmetric than our complex here, and the distance between the two K⁺ in DB24C8-2KSCN (3.41 (1) Å) is shorter than that in BOA15C5-2KSCN (3.925 (2) Å).

The arrangement of donor atoms in each crown ring around one K⁺ cation is very similar to that in the K⁺ complex of N-pivot lariat monoaza-15-crown-5.^{4c} The five donor atoms of the macrocyclic ring are disposed in a half-chair-like arrangement, and each cation resides significantly out of the average plane. The oxygen atom in the bridging chain (O9) coordinates to both cations like a lariat donor atom. However, the coordination sphere for the two cations is not identical. One of the right ring oxygen atoms, O4 in Figure 1, interacts with both cations (K1 and K2), and the donation of the right ring to K1 does not occur with the whole ring but with only one of the ring oxygens. Interestingly the oxygen atom, O4, is even closer to K1 than to K2, and K1-O4 is slightly shorter than K1-O9 although O9 is the first lariat donor atom for K1. Thus, K1 is octacoordinated while K2 is still heptacoordinated. In the complexes of N-pivot lariat monoaza-15-crown-5, it has been reported that the potassium cation can be heptacoordinated or octacoordinated according to the number of the donor atoms in the sidearm.^{4c}

The crystallographic result here is in line with the observations in the study of the stability constants and ¹³C NMR in homo-

geneous solutions,^{2c} i.e., under the conditions of high [K⁺]/[crown unit] most of the complexes may exist as a 2:2 crown unit-cation complex, and the oxygen atom in the bridging chain interacts specifically with the cation held in the cavity. A similar lariat-ether effect was also observed in other bis(crown ether) systems which contain a monoazacrown unit.⁷ The structure of the complex also gives the explanation why BOA15C5 can extract most of alkali-metal cations efficiently without the selectivity expected from its ring size.^{2c} As pointed out by Gokel et al. for the flexible ligands the guest cation organizes the host's donor group array.^{4c}

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Supplementary Material Available: Details of X-ray analyses and tables of distances and angles, positional parameters, and thermal parameters (7 pages). Ordering information is given on any current masthead page.

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Enantioselective Enzymatic Sterol Synthesis by Ultrasonically Stimulated Bakers' Yeast

Jorge Bujons, Richard Guajardo, and Keith S. Kyler*

Department of Chemistry, University of Miami
Coral Gables, Florida 33124

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Studies on the in vitro enzymatic formation of lanosterol from 2,3-oxidosqualene (1 → 2) have utilized the sedimented microsomes from various mammalian (e.g., rat and hog) liver cells as the typical source of the cyclizing enzyme 2,3-oxidosqualene lanosterol-cyclase.¹⁻⁵ However, the use of the microsomal cyclase has severely limited the enzymatic process to only small scale (1-3 mg or less) substrate conversions. Consequently, this enzymatic process has not been used previously for preparative purposes. We now wish to report that an "ultrasonically stimulated" suspension of bakers' yeast (*Saccharomyces cerevisiae*) is an *inexpensive, convenient, and direct* source of a sterol cyclase⁶ which can be

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