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The first crystal structure of a bis(crown ether) compound that forms an intramolecular sandwich complex with rubidium picrate

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3-Nitro-2,6-bis(4′-benzo-15-crown-5)aminopyridine and its rubidium picrate complex were synthesized, and the first known example of a bis(crown ether) rubidium picrate intramolecular sandwich complex was obtained. The structure is confirmed by solid state studies: $C_{39}H_{44}N_7O_{19}Rb \cdot CH_3OH \cdot H_2O$, triclinic, $P\bar{1}$. $a = 11.481(4)$, $b = 14.519(4)$, $c = 15.960(6)$ Å, $\alpha = 63.28(3)$, $\beta = 73.75(3)$, $\gamma = 80.66(3)°$, $D_c = 1.53$ g/cm^3, $Z = 2$, and $R = 0.091$ for the 2350 observed reflections. The rubidium cation is intramolecularly sandwiched by ten oxygen atoms. The Rb—O bond lengths range from 2.849(12) Å to 3.02(2) Å. The picrate anion is linked by ionic interactions to the large cation.

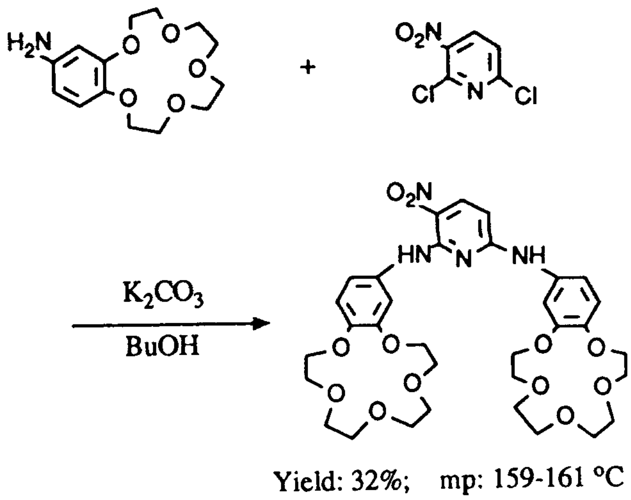
INTRODUCTION

Pedersen and Frensdorff[1] suggested that the stability of a cation crown either complex depends on the relationship between cation diameter and the ligand hole size. To a limited degree, this is true.[2] However, when the cation is too large to fit well into the ligand, the cation and the crown ether can form a sandwich complex.[3] Bis(crown ether) connected by a short aliphatic chain were first prepared in 1975 by Burgoin *et al.*[4] The macrorings of the bis(crown ether) solvate the cation by forming complexes in which the cation is sandwiched between the two adjacent cyclic donor group arrays. Sandwich complexes may be more stable and exhibit different selectivities from their monocyclic analogs.[5−8] We report here the synthesis and crystal structure of the intramolecular sandwich complex of 3-nitro-2,6-bis(4′-benzo-15-crown-5)-aminopyridine with rubidium picrate, a novel example of such sandwich structures.

RESULTS AND DISCUSSION

Ligand synthesis

The bis(crown) ligand was prepared by a single pot procedure involving hydrogenation and subsequent nucleophilic aromatic substitution on 3-nitro-2,6-dichloropyridine. 4′-Nitrobenzo-15-crown-5 was hydrogenated (H_2, Pd/C) in *n*-butanol solution. After reduction, the catalyst was removed by filtration and the alcoholic solution of aminocrown was added to 3-nitro-2,6-dichloropyridine and K_2CO_3, also in *n*-BuOH. The product was isolated (32%) as red needles and used directly in the complexation experiments. The synthetic scheme is illustrated in Scheme 1.



Scheme 1

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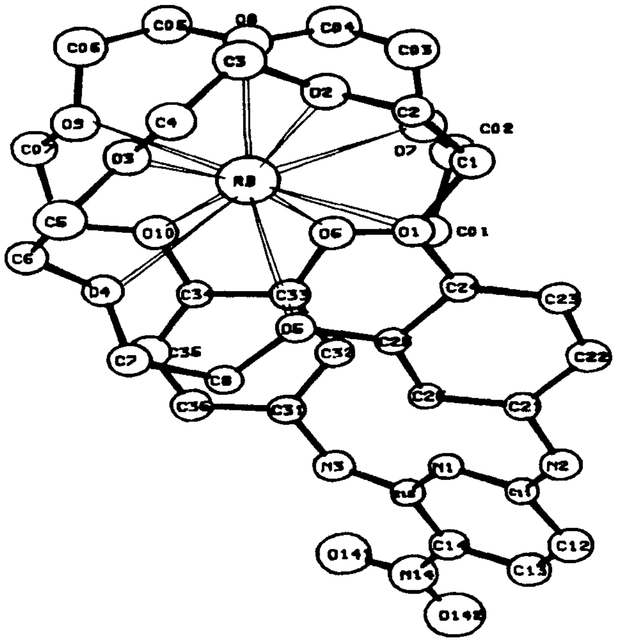

Figure 1 ORTEP plot of the rubidium picrate complex of 3-nitro-2.6-bis(4′-benzo-15-crown-5)aminopyridine.

Complexation and solid state structure

Crystals of the sandwich complex were obtained from a mixture of methanol and chloroform. The yellow crystals thus obtained (mp: 249 °C) had a stoichiometry ligand·Rb·CH_3OH·H_2O. Solution of the structure revealed one bis(crown) Rb complex, one methanol molecule and one water molecule in the asymmetric unit. The Rb cation is stabilized by ion-dipole interactions with the ten oxygen atoms of the two crown ether rings forming an intramolecular sandwich structure in which the Rb—O bond distances range from 2.849(12) Å to 3.02(2) Å. The picrate anion is not involved in the coordination sphere of the cation. The methanol and water molecules arise from the solvent. The molecular configuration of the complex cation is shown in Fig. 1.

A bond lengths and angles of greatest interest are recorded in Tables 1 and 2. The dihedral angles between the pyridine ring and the two benzene rings are 44.1° and 38.5°, respectively. One of the dihedral angles between the crown ether ring and the attached benzene ring is 15° and the other is 7.5°. The dihedral angle between the two benzene rings is 15° and the dihedral angle between the two crown ether rings is 5.0°. Thus the two crown ether rings are almost parallel. This configuration is advantageous for chelating Rb as it places the macrorings in nearly parallel planes above and below (on either side) of the cation providing a symmetrical coordination sphere. It appears that rotation about the C—N singles bonds provide whatever conformational adjustment is required to obtain the most stable structure.

Although 1:1 crown·cation complexes are more widely known than are single or multilayer sandwich complexes, the latter are very well established. When the diameter of the cation is larger than the hole size of the crown, the cation may reside slightly above the mean plane of the macroring in which the O donors on the crown ether ring are arranged, or a 2:1 or 3:2 complex with a sandwich structure may be formed. The diameter of Rb^+ (2.96 Å)[9] is larger than benzo-15-crown-5 hole size (1.7–2.2 Å)[9], then a bis(crown ether) can coordinate with it to form a stable intramolecular sandwich complex between the two adjacent crown rings. In the structure presented here, Rb—O bond lengths range from 2.849(12) Å to 3.02(2) Å, the average length (2.93 Å) is shorter (3.02 Å) than those previously reported.[10,11] Thus, this sandwich complex involves stronger per unit oxygen coordination than previously observed.

Table 1 Selected bond lengths (Å)

Rb	O1	3.02(2)	Rb	O2	2.849(12)
Rb	O3	2.857(14)	Rb	O4	2.915(15)
Rb	O5	2.92(2)	Rb	O6	2.947(14)
Rb	O7	2.945(15)	Rb	O8	2.90(2)
Rb	O9	2.88(2)	Rb	O10	3.001(13)
O	C41	1.27(3)	O1	C24	1.34(2)
O01	C	1.45(3)	O2	C2	1.42(3)
O2	C3	1.43(2)	O3	C4	1.39(2)
O3	C5	1.44(3)	O4	C6	1.42(2)
O4	C7	1.39(3)	O5	C8	1.45(2)
O5	C25	1.35(2)	C1	C2	1.44(2)
C3	C4	1.51(3)	C5	C6	1.45(2)
C7	C8	1.49(2)	N1	C11	1.29(3)
C11	C12	1.41(3)	C24	C25	1.44(2)
O	C41	1.27(3)	C41	C42	1.40(3)
C41	C46	1.39(4)	C14	N14	1.42(2)
N14	O141	1.25(3)	N14	O142	1.22(2)
N2	C11	1.34(2)	N2	C21	1.42(2)
N3	C15	1.31(3)	N3	C31	1.43(2)

Table 2 Selected bond angles (°)

C1	O1	C24	118(1)
C2	O2	C3	116(2)
C4	O3	C5	114(2)
C6	O4	C7	113(2)
C8	O5	C25	119(1)
O1	C1	C2	108(2)
O2	C2	C1	107(2)
C11	N1	C15	122(2)
C11	N2	C21	124(2)
C15	N3	C31	126(1)
O141	N14	O142	120(2)
N14	C14	C13	119(2)
N14	C14	C15	125(2)
O	C41	C42	120(3)
O	C41	C46	127(2)

Table 3 Atomic coordinates and thermal parameters

Atom	*x/a*	*y/b*	*z/c*	*Beq.*
Rb	0.4128(3)	0.3497(3)	0.3509(2)	6.19(9)
O	1.066(2)	0.812(1)	−0.230(1)	6.1(6)
O1	0.284(1)	0.438(1)	0.493(1)	2.4(4)
O01	1.127(2)	0.924(1)	−0.419(1)	5.0(5)
O2	0.307(1)	0.228(1)	0.549(1)	3.0(4)
O02	0.924(1)	1.067(1)	−0.412(1)	4.8(5)
O3	0.567(1)	0.234(1)	0.4803(9)	3.0(4)
O4	0.655(1)	0.421(1)	0.3045(9)	2.4(4)
O5	0.459(1)	0.536(1)	0.3609(9)	2.1(4)
O6	0.308(1)	0.500(1)	0.189(1)	3.1(4)
O7	0.155(1)	0.368(1)	0.347(1)	3.3(4)
O8	0.309(1)	0.191(1)	0.335(1)	3.5(4)
O9	0.566(1)	0.228(1)	0.258(1)	3.6(4)
O10	0.521(1)	0.428(1)	0.138(1)	3.1(4)
O141	0.462(2)	1.031(1)	−0.167(1)	5.5(6)
O142	0.362(2)	1.164(1)	−0.156(1)	6.8(7)
O421	1.069(2)	0.600(1)	−0.147(1)	6.1(5)
O422	0.898(2)	0.576(2)	−0.051(1)	7.7(7)
O441	1.006(2)	0.806(2)	0.172(1)	8.5(7)
O442	0.929(2)	0.664(2)	0.213(1)	5.6(6)
O461	1.087(2)	1.015(2)	−0.260(1)	7.6(7)
O462	1.193(2)	1.012(2)	−0.168(2)	11.0(7)
N1	0.323(1)	0.859(1)	0.1264(9)	1.9(4)
N2	0.213(1)	0.857(1)	0.271(1)	2.7(4)
N3	0.438(1)	0.855(1)	−0.011(1)	2.9(4)
N14	0.394(2)	1.071(1)	−0.118(1)	4.4(5)
N42	0.990(2)	0.625(2)	−0.092(1)	5.0(6)
N44	0.980(2)	0.740(2)	0.152(1)	5.2(6)
N46	1.125(2)	0.970(2)	−0.185(2)	6.3(7)
C	1.242(2)	0.972(2)	−0.445(2)	5.2(8)
C01	0.190(2)	0.535(1)	0.220(1)	3.0(6)
C1	0.184(2)	0.368(1)	0.557(1)	2.6(6)
C02	0.114(2)	0.438(2)	0.269(2)	3.6(6)
C2	0.236(2)	0.270(1)	0.614(1)	2.2(5)
C03	0.122(2)	0.263(2)	0.381(2)	4.4(7)
C3	0.394(2)	0.147(2)	0.586(1)	3.7(6)
C04	0.186(2)	0.214(2)	0.322(2)	4.7(7)
C4	0.511(2)	0.188(2)	0.578(1)	3.2(6)
C05	0.385(2)	0.144(2)	0.280(2)	3.9(7)
C5	0.680(2)	0.280(2)	0.459(1)	3.7(6)
C06	0.512(2)	0.130(2)	0.295(1)	4.4(7)
C6	0.729(2)	0.335(1)	0.356(1)	2.5(5)
C07	0.618(2)	0.264(2)	0.159(1)	3.4(6)
C7	0.671(2)	0.510(1)	0.316(1)	2.7(6)
C08	0.636(2)	0.377(2)	0.120(1)	3.7(6)
C8	0.568(1)	0.586(1)	0.292(1)	2.1(4)
C11	0.256(1)	0.907(1)	0.175(1)	1.7(4)
C12	0.223(2)	1.014(2)	0.135(1)	3.3(6)
C13	0.270(1)	1.064(1)	0.036(1)	3.2(4)
C14	0.345(2)	1.015(1)	−0.018(1)	2.6(5)
C15	0.372(2)	0.908(1)	0.034(1)	1.9(5)
C21	0.232(2)	0.749(1)	0.324(1)	2.0(5)
C22	0.134(2)	0.695(1)	0.397(1)	2.8(5)
C23	0.145(2)	0.594(1)	0.454(1)	2.4(5)
C24	0.255(1)	0.538(1)	0.4438(9)	2.1(4)
C25	0.356(2)	0.594(1)	0.369(1)	1.7(5)
C26	0.340(2)	0.694(1)	0.312(1)	1.7(5)
C31	0.465(2)	0.746(1)	0.031(1)	2.3(5)
C32	0.372(2)	0.678(2)	0.093(1)	2.4(5)
C33	0.393(2)	0.573(1)	0.126(1)	2.6(5)
C34	0.509(2)	0.534(1)	0.098(1)	2.0(5)
C35	0.599(2)	0.602(2)	0.038(1)	3.2(6)
C36	0.580(2)	0.700(2)	0.007(1)	2.9(5)
C41	1.049(2)	0.800(2)	−0.144(1)	3.6(6)
C42	1.004(2)	0.708(2)	−0.067(1)	3.0(6)
C43	0.982(2)	0.688(2)	0.026(1)	3.7(6)
C44	1.004(2)	0.763(2)	0.051(1)	3.5(6)
C45	1.054(2)	0.854(2)	−0.021(1)	3.3(6)
C46	1.073(2)	0.869(2)	−0.113(1)	3.4(6)

A number of interesting characteristics were observed in the crown ether skeleton of the Rb^+ complex. For example, all crown ether ring carbon atoms are on the same side of the least-square planes defined by the five oxygen atoms of each crown ether except for C1. The distances between Rb and the two planes are 1.749 Å and 1.785 Å, respectively.

We have prepared a novel bis(crown ether) using a direct, double nucleophilic aromatic substitution reaction. Although each ring is individually too small to effectively complex and stabilize Rb^+, the pyridine bridge provides appropriate spacing for the formation of the first Rb^+ bis(crown) sandwich complex.

EXPERIMENTAL SECTION

Synthesis of 3-nitro-2,6-bis(4′-benzo-15-crown-5)-aminopyridine

20% $Pd(OH)_2/C$ (0.30 g) and 4′-nitrobenzo-15-crown-5 (3.13 g, 10 mmol) were mixed in *n*-butanol (40 mL) and hydrogenated under 3 Kg/cm^2 H_2 at 55–60 °C for 4 h. The catalyst was filtered under nitrogen, and the solution was added to the mixture of 3-nitro-2,6-dichloropyridine (0.97 g, 5.0 mmol) and potassium carbonate (3.0 g) in *n*-butanol (50 mL), the solution was then refluxed for 12 h. The mixture was filtered and washed with anhydrous ethanol (2 × 10 mL), the solvent was removed *in vacuo*. The residue was mixed with aluminum oxide (20 g) and continuously extracted with petroleum ether (60–90 °C) for 16 h. The solvent was evaporated, and the residue was crystallized from ethanol two times to afford red needle crystals (1.58 g, 32%, mp: 159–161 °C). IR (KBr disc): 3298, 1621, 1599, 1447, 1258, 1136, 1051 cm^{-1}; ^1H-NMR ($CDCl_3$, TMS): 2.29 (s, 2H), 3.65–4.15 (m, 32H), 6.14 (d, 1H, J = 3 Hz), 7.10 (m, 6H), 8.19 (d, 1H, J = 3 Hz) ppm; MS (FAB method): 687 (M + 1). *Anal.* Calcd. for $C_{33}H_{42}N_4O_{12}$: C, 57.72, H, 6.17, N, 8.16%; Found: C, 57.57, H, 6.06, N, 7.90%.

Preparation of 3-nitro-2,6-bis(4′-benzo-15-crown-5)-aminopyridine rubidium picrate

3-Nitro-2,6-bis(4′-benzo-15-crown-5)aminopyridine (2 mmol) in chloroform (10 mL), was added to the solution of rubidium picrate (2 mmol) in methanol (40 mL). The mixture was refluxed for 3 h, then concentrated to about 15 mL and cooled. Yellow crystals were obtained. mp: 249 °C. IR (KBr discs): 3263, 2905, 2869, 1564, 1510, 1259, 1183, 1047 cm^{-1}. *Anal.* Calcd. for $C_{39}H_{44}N_7O_{19}Rb$: C, 46.82, H, 4.43, N, 9.80, Rb, 8.54%; Found: C, 46.70, H, 4.31, N, 9.80, Rb, 8.67%.

Data collection

$C_{39}H_{44}N_7O_{19}Rb \cdot CH_3OH \cdot H_2O$, Mr = 1050.33, recrystallized from methanol as yellow, regular bricks. Crystal dimensions: 0.4 × 0.3 × 0.18 mm. Intensity data were collected on Enraf-Nonius CAD4-diffractometer with MoK$_\alpha$ ($\lambda = 0.71069$ Å) radiation, using the $\Theta/2\Theta$ scan technique in the θ range 2°–25°.8304 unique reflections were measured. The corrections for absorption were applied. Crystal data: triclinic, P$\bar{1}$, a = 11.481(4), b = 14.519(4), c = 15.960(6) Å, $\alpha = 63.28(3)$, $\beta = 73.75(3)$, $\gamma = 80.66(3)$°, V = 2279.4(7) Å^3, D$_c$ = 1.53 g/cm^3, Z = 2.

Structure determination

The structure was determined by MULTAN82 program and Fourier techniques. Hydrogen atoms were located from ideal positions. The non-H-atom coordinates and thermal parameters were refined by blocked-diagonal and full matrix least-squares methods with $I > 3\sigma(I)$ for the 2350 observed reflections. The final R = 0.091. The hydrogen atom parameters were not refined. Final fractional coordinates are given in Table 3.

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