

This article was downloaded by:

On: 29 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713649759>

Molecular Structure of RbSCN Complex with N-(4'-hydroxy-3',5'-diisopropylbenzyl)-monoaza-15-crown-5 Ether: Two Structures in a Unit Cell

Yoichi Habata^a; Atsushi Watanabe^a; Sadatoshi Akabori^a

^a Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba, Japan

To cite this Article Habata, Yoichi , Watanabe, Atsushi and Akabori, Sadatoshi(2011) 'Molecular Structure of RbSCN Complex with N-(4'-hydroxy-3',5'-diisopropylbenzyl)-monoaza-15-crown-5 Ether: Two Structures in a Unit Cell', *Supramolecular Chemistry*, 18: 4, 539 – 543

To link to this Article: DOI: 10.1080/10610270108028300

URL: <http://dx.doi.org/10.1080/10610270108028300>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Communication

Molecular Structure of RbSCN Complex with N-(4'-hydroxy-3',5'-diisopropylbenzyl)-monoaza-15-crown-5 Ether: Two Structures in a Unit Cell

YOICHI HABATA*, ATSUSHI WATANABE and SADATOSHI AKABORI

Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba 274-8510, Japan

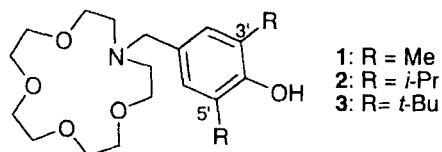
Molecular structures of the RbSCN complexes with N-(4'-hydroxy-3',5'-diisopropylbenzyl)-monoaza-15-crown-5 ether (2-RbSCN) and N-(4'-hydroxy-3',5'-di-*tert*-butylbenzyl)-monoaza-15-crown-5 ether (3-RbSCN) are reported. Crystal data (2-RbSCN) $C_{24}H_{39}N_2O_5SRb$, $M = 553.11$, monoclinic, space group $P2_1$, $a = 9.835(4)$, $b = 15.44(3)$, $c = 18.563(6)$ Å, $\beta = 99.58(4)$, $U = 2779(4)$ Å³, $Z = 4$, $D_c = 1.322$ g cm⁻³, $v = 18.87$ cm⁻¹, $R = 0.047$, $R_w = 0.049$ for the 5339 independent reflections (of 5712 measured reflections) and 590 parameters. (3-RbSCN) $C_{52}H_{86}N_4O_{10}S_2Rb_2$, $M = 1162.32$, triclinic, space group $P\bar{1}$, $a = 9.917(2)$, $b = 24.644(6)$, $c = 12.572(3)$, $\alpha = 89.38(2)$, $\gamma = 96.13(2)$, $\gamma = 89.34(2)$ Å, $U = 3054(1)$ Å³, $Z = 2$, $D_c = 1.264$ g cm⁻³, $\mu = 17.20$ cm⁻¹, $R = 0.051$, $R = 0.053$ for the 6864 independent reflections (of 7201 measured reflections) and 316 parameters. The molecular structures of the RbSCN complexes with a series of N-(4-hydroxy-3',5'-dialkylbenzyl)-monoaza-15-crown-5 ethers (1, 2 and 3) were systematically changed depending upon the size of the R groups at positions 3' and 5' in the side arm; 1 (R=Me), a polymer-like (1:1)_n complex; 2 (R = *i*-Pr), a mixture of 1:1 complex and polymer-like (1:1)_n complex; 3 (R = *t*-Bu), a dimeric 1:1 complex.

Keywords: Crown ether; Alkali metal; Crystal structure; Polymer-like; Complex

Increasing attention has been focused on the polymer-like complexes of armed macrocycles [1]. The side arms in the armed macrocycles are used for intermolecular interaction and the unit structures are repeated in polymers of those complexes. Recently, we reported that armed-monoaza-15-crown-5 ether (1), having a 4'-hydroxy-3',5'-dimethylbenzyl group as a side arm, forms polymer-like complexes with sodium, potassium, rubidium and cesium thiocyanates [2]. We are interested in structural changes in the metal complexes of the armed-monoaza crown ethers when size of the R groups at positions 3' and 5' in the phenol moiety are changed. To see how the size of the R groups influences the structure of the complexes, new

*Corresponding author.

armed-monoaza crown ethers (**2** and **3**) having isopropyl- and *tert*-butyl groups at positions 3' and 5' and their RbSCN complexes were prepared. Here, we report a unique complex system of RbSCN with the new armed-monoaza crown ethers.



New armed-monoaza crown ethers (**2** and **3**) were prepared using Mannich reactions [3, 4] of *N*-methoxymethyl-monoaza-15-crown-5 ether

with 2,6-diisopropyl- or 2,6-di-*tert*-butylphenol in ca. 70% yields [5]. The RbSCN complexes with **2** and **3** were quantitatively obtained [5].

Figure 1 shows the molecular structure of the RbSCN complex with **3** having bulky *tert*-butyl groups at positions 3' and 5' [6]. The Rb(1)⁺ ion is seven-co-ordinated by the four ring O(1–4) atoms, the ring N(1) atoms and two N(2 and 2*) atoms of SCN[−] ions. The SCN[−] ions bridge between two incorporated Rb(1 and 1*)⁺ ions, thus resulting in the formation of a dimeric 2:2 complex. The Rb–O (ring), Rb–N(ring) and Rb–N (two SCN) bond lengths are comparable with that of 1-RbSCN (see caption of Fig. 1) [2]. In the 3-RbSCN complex, the O(5) atom of the phenolic OH group in the side arm can not

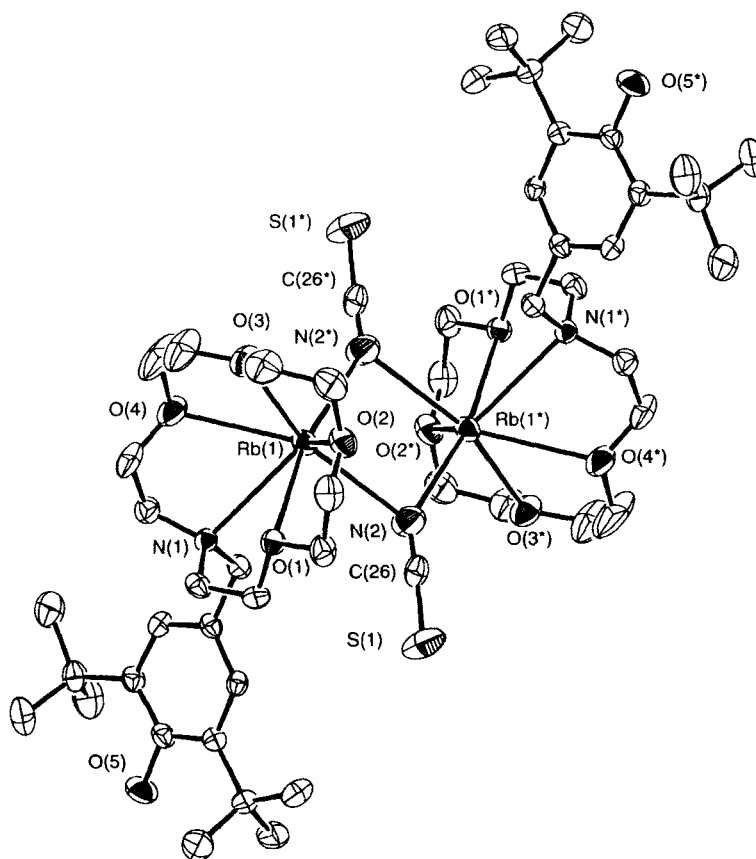


FIGURE 1 Molecular structure (non-hydrogen atoms) of 3-RbSCN. Thermal ellipsoids are drawn at the 30% probability level. Important bond lengths, Rb(1)–O(1) 2.949(4), Rb(1)–O(2) 2.897(5), Rb(1)–O(3) 2.937(5), Rb(1)–O(4) 2.951(5), Rb(1)–N(1) 3.076(4), Rb(1)–N(2) 2.984(4), Rb(1)–N(2*) 2.939(7) Å.

co-ordinate to the $\text{Rb}(1)^+$ ion owing to the bulk of the *tert*-butyl groups.

The RbSCN complex of **2** having isopropyl groups (medium size between *tert*-butyl and methyl groups) at positions 3' and 5' in the side arm forms a unique complex system (Fig. 2 and 3) [6]. The X-ray study shows that the complex consists of a polymer-like $(1:1)_n$ complex and a 1:1 complex. The $\text{Rb}(1)^+$ ion is six-co-ordinated by the four ring O(1–4) atoms, the ring N(1) atoms and the N(2) atom of SCN- ion, while the $\text{Rb}(2)^+$ ion is seven-co-ordinated by the four ring O(6–9) atoms, the ring N(3) atom, the N(4) atom of SCN- ion and the O(10*) atom of the phenolic OH group in the side arm of the nearest-neighbor molecule (Fig. 3). The

polymer-like and 1:1 complexes are aligned alternately (Fig. 3). An important difference in both of the polymer-like and 1:1 complexes is dihedral angles N(ring)-Rb-N(SCN)-C(SCN). Figure 4 shows schematic drawings of the polymer-like and 1:1 complexes of **2**-RbSCN. In the polymer-like complex (Fig. 4(a)), the dihedral angle N(3)–Rb(2)–N(4)–C(48) is 171° , while the dihedral angle N(1)–Rb(1)–N(2)–C(24) in the 1:1 complex (Fig. 4(b)) is -70° . The O(10*) atom of the phenolic OH group in the side arm of the nearest-neighbor molecule binds to the $\text{Rb}(2)^+$ ion to form the polymer-like complex. On the other hand, the phenol moiety of the nearest-neighbor molecule covers the open space around the $\text{Rb}(1)^+$ ion (the distances

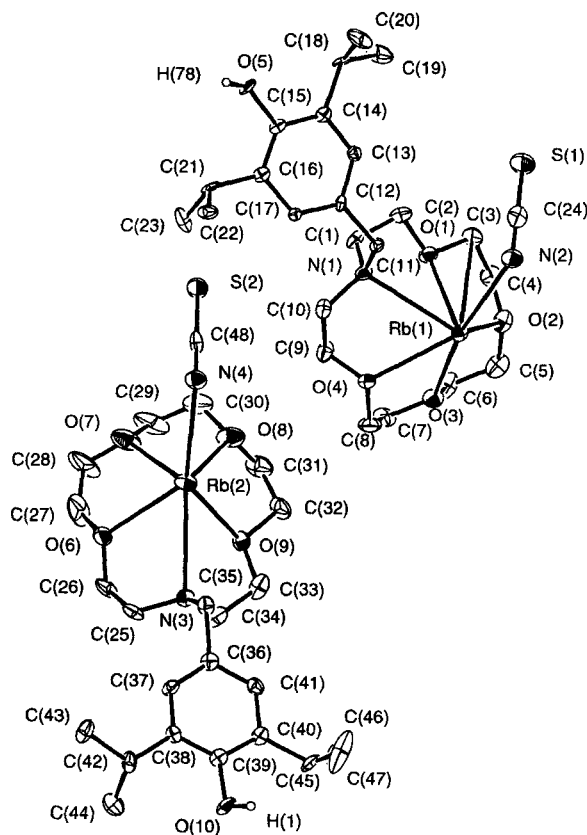


FIGURE 2 Molecular structure (non hydrogen atoms) of **2**-RbSCN. Thermal ellipsoids are drawn at the 30% probability level. Important bond lengths Rb(1)–O(1) 2.885(1), Rb(1)–O(2) 2.92(1), Rb(1)–O(3) 2.93(1), Rb(1)–O(4) 2.84(1), Rb(1)–N(1) 3.10(1), Rb(1)–N(2) 3.16(1), Rb(2)–O(6) 2.87(1), Rb(2)–O(7) 2.88(1), Rb(2)–O(8) 2.89(1), Rb(2)–O(9) 2.95(1), Rb(2)–O(10*) 2.928(10), Rb(2)–N(3) 3.05(1), Rb(2)–N(4) 3.05(2) Å.

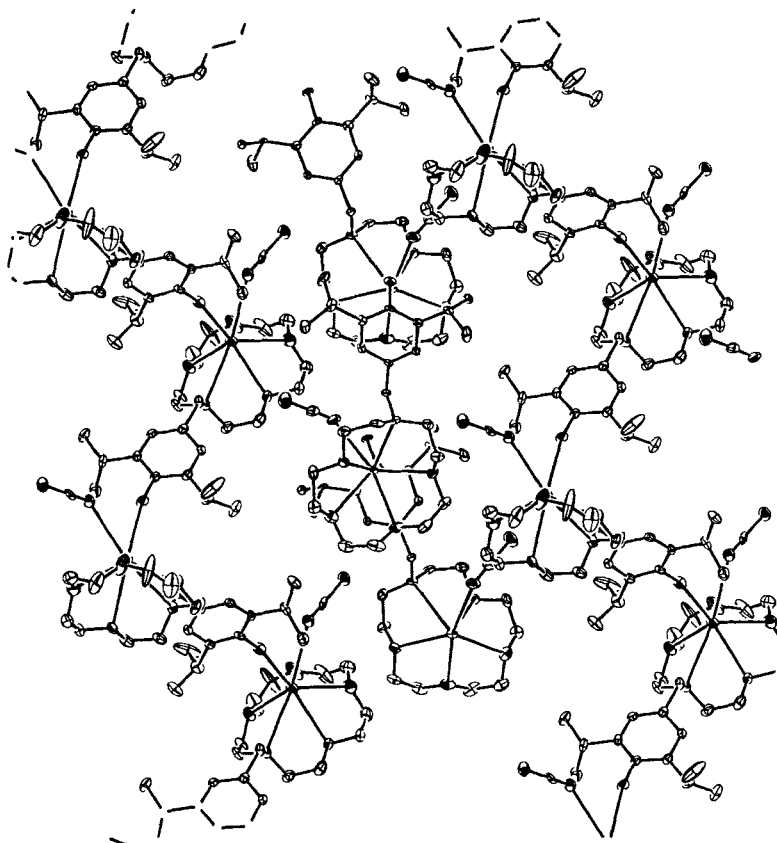


FIGURE 3 The ORTEP packing diagram (non-hydrogen atoms) of 2-RbSCN. Thermal ellipsoids are drawn at the 30% probability level.

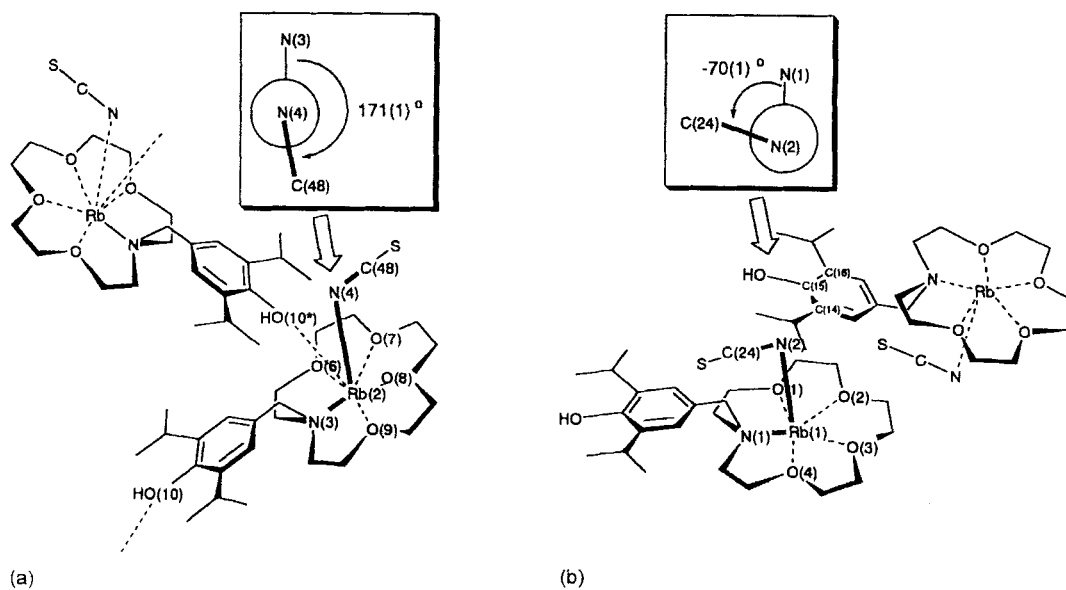


FIGURE 4 Schematic drawings of (a) polymer-like (1:1)_n complex part and (b) 1:1 complex part in 2-RbSCN complex.

Rb(1)—C(14), Rb(1)—C(15) and Rb(1)—C(16) are 3.46(1), 3.33(1) and 3.44(1) Å, respectively) to give a 1:1 complex where the Rb(1)⁺ ion is six-co-ordinated. The bond lengths between Rb⁺ ions and heteroatoms in both complexes are comparable (see caption of Fig. 3), thus, the presence of two kinds of the dihedral angles N(ring)—Rb—N(SCN)—C(SCN) would make the complex formed the two kinds of structures in a unit cell.

As we reported before, the RbSCN complex of **1** having two methyl groups at positions 3' and 5' forms a polymer-like (1:1)_n complex [2]. Therefore, molecular structures of the RbSCN complexes with a series of N-(4-hydroxy-3',5'-dialkylbenzyl)-monoaza-15-crown-5 ethers (**1**, **2** and **3**) were systematically changed depending upon the size of the R groups at positions 3' and 5' in the side arm; **1** (R = Me), a polymer-like (1:1)_n complex; **2** (R = *i*-Pr), a mixture of 1:1 complex and polymer-like (1:1)_n complex; **3** (R = *t*-Bu), a dimeric 1:1 complex. Further studies of the new armed-monoaza crown ethers having various phenol derivatives as a side arm are in progress.

Acknowledgements

The authors wish to thank Professor Jerald S. Bradshaw (Brigham Young University, USA) for helpful discussions. This work was partially

supported by a Grant-in Aid for Scientific Research (No. 09640698 and 12640566) from the Ministry of Education, Culture, Sports, Science and Technology (Japan) and the Mitsubishi Material Foundation for the Promotion of Chemical Research (Japan).

References

- [1] Gluzinski, P., Krajewski, J. W., Urbanczyk-Lipkowska, Z., Andreetti, G. D. and Bocelli, G. (1984). *Acta Crystallogr., Sec. C*, **C40**, 778; Shu, M. P., Shim, B. Y. and Yoon, T. S. (1994). *Inorg. Chem.*, **33**, 5509; Sibert, J. W., Lange, S. J., Williams, D. J., Barrett, A. G. M. and Hoffman, B. M. (1995). *Inorg. Chem.*, **34**, 2300; Olsher, U., Frolow, F., Weiming, J., Yu, Z., Knobeloch, J. M. and Bartsch, R. A. (1991). *J. Am. Chem. Soc.*, **113**, 6570.
- [2] Habata, Y. and Akabori, S. (1996). *J. Chem. Soc., Dalton Trans.*, 3871.
- [3] Reviews for the Mannich reaction. Bricke, F. F. (1949). *Org. React.*, **5**, 301; Tramontini, M. and Angiolini, L. (1990). *Tetrahedron*, **46**, 1791; Trost, B. M., Fleming, I. and Heathcock, C. H. (1991). *Comprehensive organic synthesis*. Oxford: Pergamon Press, pp. 893–1109.
- [4] A review for the syntheses of armed-aza crown ethers using the Mannich reaction. Bordunov, A. V., Bradshaw, J. S., Pastushok, V. N. and Izatt, R. M. (1996). *Synlett*, 966 and references cited therein.
- [5] Compounds **2**, **3** and their RbSCN complexes were synthesized according to the reported method. [2] Satisfactory spectroscopic and analytical data for compounds **2**, **3**, 2-RbSCN and 3-RbSCN have been obtained.
- [6] Crystal data for 2-RbSCN and 3-RbSCN. X-ray diffraction measurements were made on a Rigaku AFC5S four-circle diffractometer with graphite-monochromated Mo-K α radiation (10.71069 Å) at 23°C and a 12 kW rotating-anode generator.