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Synthesis and Characterization of Boron Complex of Calix[4]arene

Kui LU, Yang Jie WU*, Zhi Xian ZHOU

Department of Chemistry, Zhengzhou University, 450052

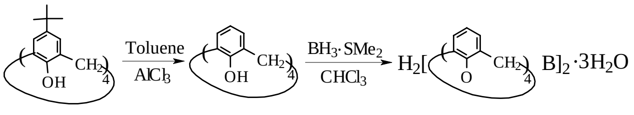
Abstract: A new boron complex of calix[4]arene was synthesized by the reaction of calix[4]arene with BMS; and the structure of the product was characterized by IR, ^{1}HNMR, ^{13}CNMR, ^{11}BNMR and MS spectra.

Keywords: Boron complex; calix[4]arene; synthesis; characterization.

It has been shown that calixarenes can perform selective ion transport and form neutral complexes with cations through proton loss[1]. Olmstead reported[2] the synthesis and X-ray crystal structures of Titanium (IV), Iron (III) and Cobalt (II) complexes of *p-tert*-butylcalix[4]arene and found that a complete exchange of all four OH groups in *p-tert*-butylcalix[4]arene took place when treated with Ti $(NMe_2)_4$ to give the aryloxo complex [{Ti (*p-tert*-butylcalix[4]arene)}$_2$]·6PhMe which may be formally described as a centro-symmetric titanium aryloxide dimer consisting of two Ti (*p-tert*-butylcalix[4]arene) units.

We have studied on the synthesis and properties of a series of calixarenes bearing boronic acid units on the lower rim and on the upper rim, and found that they had special coordination with carbohydrates[3]. In our attempt to conduct researches further into structures and properties of calix[4]arenes containing boron moiety and to find the highly selective and effective ligand for coordination with some special compounds, a new boron complex of calix[4]arene **3** was obtained as a white solid in 90% yield by the reaction of calix[4]arene **2** with $BH_3{\cdot}SMe_2$ (BMS) in $CHCl_3$ (**Scheme 1**).

Scheme 1



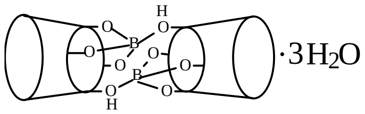
1 **2** **3**

The structure of **3** was confirmed by elemental analysis, IR, MS, ^{1}HNMR, ^{13}CNMR, ^{11}BNMR spectra and DSC, DTG analysis[4].

By comparing the ^{1}HNMR spectrum of **3** with that of **2**, it was found that the peak for ArO*H* at δ10.22 was absent. The ^{11}BNMR spectrum of **3** displayed a peak at δ21.77, indicating that a reaction of **2** with BMS had occurred. The data of elemental analysis of

3 were consistent with the proposed structure; and the mass spectrum (APCI−) of **3** showed a peak at m/z 863.6, confirming that **3** was a dimer. An analysis of DSC and DTG showed that **3** lost water at 188.9℃–239.4℃, and the weightloss was 5.69%, indicating that there were three molecules of water of crystallization in **3**. The IR spectrum of **3** displayed a wide and strong band at 3200cm^{-1} which was indicative of water. From the data specified above, it can be seen that the structure of **3** may be such a centrosymmetric dicalix[4]arene as depicted in **Figure 1**.

Figure 1.



Compound **3** probably has special selectivity for cation because there are two cavities in its molecule. A preliminary study of ion-selective electrode analysis has shown that **3** has very high selectivity for lithium cation.

Acknowledgments

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References and Notes

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2. M. M. Olmstead, G. Sigel, H. Hope, *et al. J. Am. Chem. Soc.*, **1985**, *107*, 8087.
3. K. Lu, Y. J. Wu, Z. X. Zhou, *et al.* to be publish.
4. ^{1}HNMR (CD_3COCD_3): δ 7.269-7.250 (d, J=7.6Hz, 16H, ArH), 6.809-6.771 (t, J=7.6Hz, 8H, ArH), 4.020 (s, 16H, $ArCH_2Ar$). ^{13}CNMR (CD_3COCD_3): δ 148.78, 128.96, 128.36, 121.91 (Ar-C), 30.71 ($ArCH_2Ar$). ^{11}BNMR (CD_3COCD_3): δ 21.77. IR (KBr): 3200 (s), 1608 (w), 1466 (vs), 1450 (vs), 1299 (m), 1245 (s), 1198 (s), 1078 (m) cm^{-1}. MS (APCI–): m/Z 863.6. mp 310-313 ℃. Anal. Calcd for $C_{56}H_{42}O_8B_2{\cdot}3H_2O$: C, 73.22, H, 5.27. Found: C, 73.32, H, 5.37.

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