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ORIGINAL PAPER

Theoretical study on the complexation of the cesium cation with dibenzo-18-crown-6

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Abstract By using quantum mechanical calculations, the most probable structures of free dibenzo-18-crown-6 ligand and the cationic complex species of Cs^+ both with one and with two dibenzo-18-crown-6 ligands were derived. In these two complexes, the “central” cation Cs^+ is bound by strong bond interactions to the corresponding ethereal oxygen atoms of the parent crown ligand.

Keywords Crown ethers · Macrocycles · Complexation · Ab initio calculations · Complex structure

Introduction

In 1967, Pedersen published his first papers [1, 2] dealing with cyclic polyether compounds with the oxyethylene groups –CH_2–CH_2–O–, which are called crowns because of their structure. These electroneutral crown compounds form relatively stable complexes in nonaqueous solvents, especially with alkali and alkaline-earth metal cations, the cations being placed in the ligand cavities. The ratio of the size of the crown ligand cavity to the ion radius of the central cation is a decisive or at least an important factor in the stability of the complex species formed [3]. It is the complexing properties of the crowns that are due to the rapid development of the chemistry of these cyclic polyethers that we have witnessed in recent decades. At this point it should be noted that several reviews have covered many aspects of their chemistry [3–6].

Recently, protonation of valinomycin, some calixarenes, dibenzo-18-crown-6, and a hexaarylbenzene-based receptor has been investigated in detail [7–18]. Further, the interactions of benzo-18-crown-6 with NH_4^+ and dibenzo-18-crown-6 with Ag^+ have also been studied [19, 20]. Besides this, the solvent extraction of microamounts of cesium by a nitrobenzene solution of hydrogen dicarbollylcobaltate [21] in the presence of dibenzo-18-crown-6 (L, Scheme 1) has been reported [22]. The equilibrium data have been explained assuming that the complexes CsL^+ and CsL_2^+ are extracted into the organic phase [22]. However, up to now, the structures of the complexes CsL^+ and CsL_2^+ have not been solved by means of quantum mechanical theoretical calculations. Therefore, in the current work, applying quantum mechanical DFT calculations, the most probable structures of the considered CsL^+ and CsL_2^+ cationic complexes are derived.

Results and discussion

The quantum mechanical calculations were performed at the density functional level of theory (DFT, B3LYP/LanL2DZ) using the Gaussian 03 suite of programs [23]. The structural optimizations of L and its complexes with Cs^+ (i.e., CsL^+ and CsL_2^+) were fully unconstrained.

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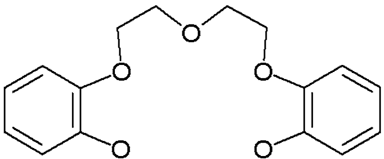

L

Scheme 1

Although a possible influence of a polar solvent on the detailed structures of L, CsL^+, and CsL_2^+ could be imagined, our quantum mechanical calculations in similar cases, carried out in an analogous way, showed very good agreement of the experiment with theory [24–29].

In the model calculations, we optimized the molecular geometries of the parent ligand L and its two complexes with Cs^+. The optimized structure of a free ligand L with C_2 symmetry is illustrated in Fig. 1. In Fig. 2, the structure obtained by the DFT-optimization of the CsL^+ complex also having C_2 symmetry is depicted, together with the lengths of the corresponding bonds (in Å; 1 Å = 0.1 nm). In the CsL^+ cationic complex species, which is most energetically favored, the "central" cation Cs^+ is bound by strong bond interactions to four (Ar–O–CH_2) ethereal oxygens (3.12, 3.12, 3.12, and 3.12 Å) and two (CH_2–O–CH_2) ethereal oxygen atoms (3.24 and 3.24 Å) of the parent crown ligand L.

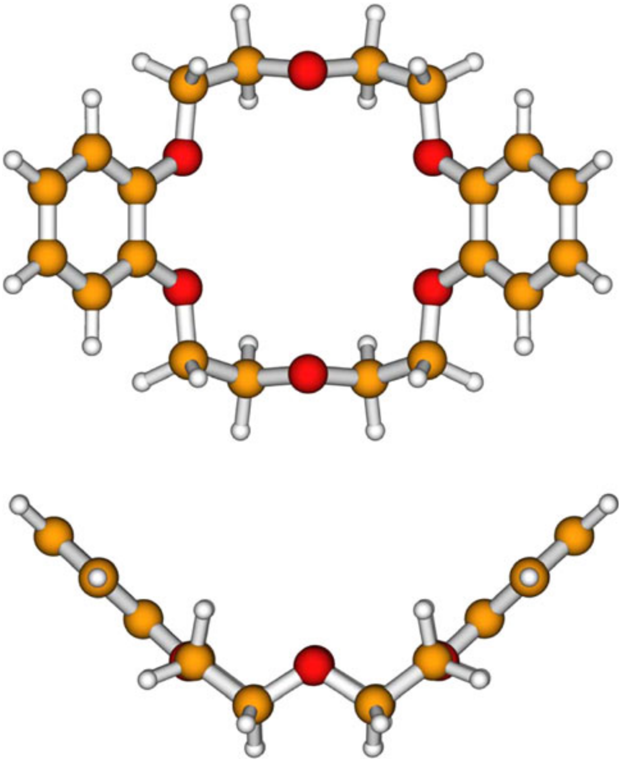

Fig. 1 Two projections of the DFT-optimized structure of a free ligand L (B3LYP/LanL2DZ)

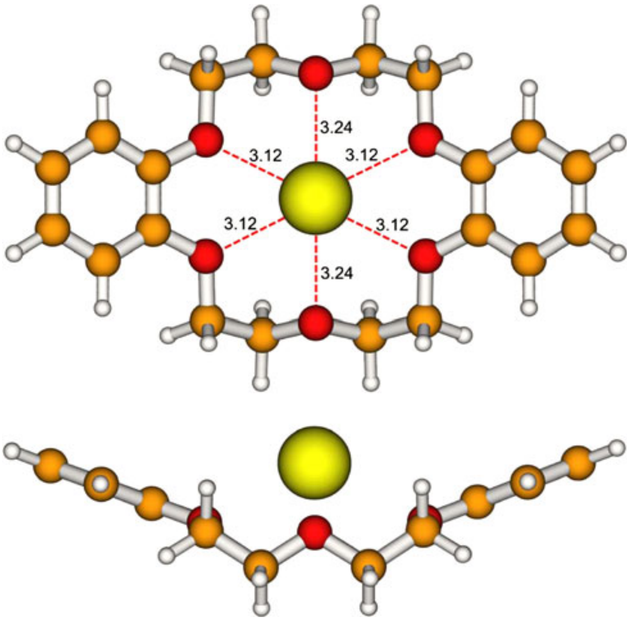

Fig. 2 Two projections of the DFT-optimized structure of the CsL^+ complex (B3LYP/LanL2DZ)

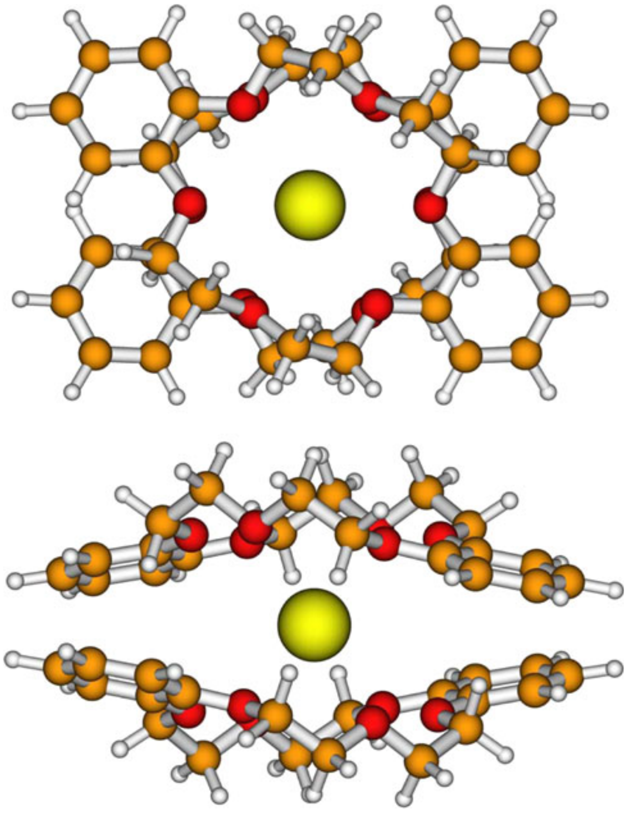

Fig. 3 Two projections of the DFT-optimized structure of the CsL_2^+ complex (B3LYP/LanL2DZ)

Moreover, the DFT-optimized CsL_2^+ structure, also called the "sandwich" structure, is shown in Fig. 3. In this case, the "central" Cs^+ is bound partly to eight (Ar–O–CH_2) oxygens (the $Cs^+ \cdots O$ distances are in the range of 3.27 to 3.44 Å) and partly to the remaining four (CH_2–O–CH_2) ethereal oxygen atoms (the $Cs^+ \cdots O$ distances are from 3.59 to 3.60 Å) of the two respective crown ligands.

Finally, the calculated interaction energies of the CsL^+ and CsL_2^+ complex species, denoted by the symbols $E_{int}(CsL^+)$ and $E_{int}(CsL_2^+)$ [calculated on the basis of the simple relations: $E_{int}(CsL^+) = E(CsL^+) - E(Cs^+) - E(L)$; $E_{int}(CsL_2^+) = E(CsL_2^+) - E(Cs^+) - 2\,E(L)$, where $E(CsL^+)$, $E(CsL_2^+)$, $E(Cs^+)$, and $E(L)$ are the pure electronic energies of the corresponding species given in the parentheses], are -231.4 and -342.2 kJ mol^{-1}, respectively, which confirm the formations of the considered cesium complexes.

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References

1. Pedersen CJ (1967) J Am Chem Soc 89:2495
2. Pedersen CJ (1967) J Am Chem Soc 89:7017
3. Kolthoff IM (1979) Anal Chem 51:1R
4. Christensen JJ, Eatough DJ, Izatt RM (1974) Chem Rev 74:351
5. Bradshaw JS, Izatt RM (1997) Acc Chem Res 30:338
6. Izatt RM, Pawlak K, Bradshaw JS (1991) Chem Rev 91:1721
7. Makrlík E, Vaňura P (2006) Monatsh Chem 137:157
8. Makrlík E, Vaňura P (2006) Monatsh Chem 137:1185
9. Dybal J, Makrlík E, Vaňura P (2007) Monatsh Chem 138:541
10. Kříž J, Dybal J, Makrlík E, Budka J, Vaňura P (2007) Monatsh Chem 138:735
11. Dybal J, Makrlík E, Vaňura P, Selucký P (2007) Monatsh Chem 138:1239
12. Dybal J, Makrlík E, Vaňura P, Budka J (2008) Monatsh Chem 139:1175
13. Dybal J, Makrlík E, Budka J, Vaňura P (2008) Monatsh Chem 139:1353
14. Makrlík E, Dybal J, Vaňura P (2009) Monatsh Chem 140:29
15. Makrlík E, Dybal J, Budka J, Vaňura P (2009) Monatsh Chem 140:1155
16. Makrlík E, Čajan M, Budka J, Vaňura P (2011) Monatsh Chem 142:5
17. Makrlík E, Vaňura P, Budka J (2009) Monatsh Chem 140:583
18. Toman P, Makrlík E, Vaňura P, Kašička V, Rathore R (2010) Monatsh Chem 141:737
19. Toman P, Makrlík E, Vaňura P (2010) Monatsh Chem 141:301
20. Makrlík E, Toman P, Vaňura P (2011) Monatsh Chem 142:137
21. Makrlík E, Vaňura P (1985) Talanta 32:423
22. Valentová Z, Vaňura P, Makrlík E (2006) J Radioanal Nucl Chem 267:241
23. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery Jr JA, Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA (2004) Gaussian 03, Revision C. 02, Gaussian, Wallingford
24. Kříž J, Dybal J, Makrlík E (2006) Biopolymers 82:536
25. Kříž J, Dybal J, Makrlík E, Vaňura P, Lang J (2007) Supramol Chem 19:419
26. Kříž J, Dybal J, Makrlík E, Vaňura P (2008) Supramol Chem 20:387
27. Kříž J, Dybal J, Makrlík E, Budka J, Vaňura P (2008) Supramol Chem 20:487
28. Kříž J, Dybal J, Makrlík E, Budka J (2008) J Phys Chem A 112:10236
29. Kříž J, Dybal J, Makrlík E, Budka J, Vaňura P (2009) J Phys Chem A 113:5896