

Cyclic oxaalkyl diamide of *o*-phthalic acid as a new macrocyclic ligand for complexation of Li⁺ cation

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ABSTRACT

Cyclic diamide of *o*-phthalic acid (CPhDA) was synthesised in the reaction between phthalic anhydride and 1,2-bis(2-aminoethoxy)ethane in high dilution conditions and its ability to form the 1:1 and 2:1 complexes with Li⁺ cations was detected by ESI mass spectrometry. The 1:1 complex was obtained in the solid state and studied by X-ray diffraction, FT-IR, NMR and PM5 semiempirical methods. The structure of 1:1 complex was also studied in acetonitrile. It was found that the structures of 1:1 complex are different in the solid and in solution.

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1. Introduction

Macrocycles are possibly the widest used family of host compounds in supramolecular chemistry [1]. Among different areas of supramolecular chemistry, the synthesis of cyclic diamides has been a subject of intensive studies because of their wide applications in chemistry, biology, molecular recognition, medicine, industry and agriculture [1,2]. They are highly capable of selective and effective complexation of various transition and heavy metal cations as well as some neutral molecules and anions [3]. Macrocyclic diamides are valuable intermediates for the preparation of aza-crown compounds and more complicated ligands such as cryptands [4]. Some diamide-containing macrocycles have been used as new catalysts [5] or molecular receptors for molecular recognition of biologically interacting substrates including anti-HIV active drugs [6]. Designing of an efficient ionophore for lithium cation presents a considerable problem because of its relatively small ionic diameter with the respect to the other alkali metal cations [7]. We report here the ionophoric properties of cyclic benzo-substituted diamide (CPhDA) (Scheme 1) toward lithium cations.

2. Experimental

1,2-Bis(2-aminoethoxy)ethane, *o*-phthalic acid anhydride and phthaloyl dichloride were purchased from Sigma–Aldrich. The lithium perchlorate was commercial product of Sigma and was used

without any further purification. CD₃CN and CH₃CN spectral-grade solvents were stored over 3 Å molecular sieves for several days. All manipulations with the substances were performed in a carefully dried and CO₂-free glove box.

2.1. Synthesis of CPhDA

A solution of (1.48 g, 1.0 × 10⁻² mol) 1,2-bis(2-aminoethoxy)ethane, (1.48 g, 1.0 × 10⁻² mol) phthalic acid anhydride in the 300 ml of anhydrous toluene was stirred under reflux for 24 h under argon atmosphere. After this time the solvent was evaporated under reduced pressure and the solid residue was washed with chloroform (3 × 10 ml). The chloroform solution was combined and evaporated under reduced pressure to dryness. The solid residue was purified by chromatography (CHCl₃/CH₃OH, 5:1) on silica gel (Fluka, type 60), yield – 420 mg, 15.1%. (See Scheme 1, method a.).

2.2. Synthesis of CPhDA–LiClO₄–H₂O (1:1:1) complex

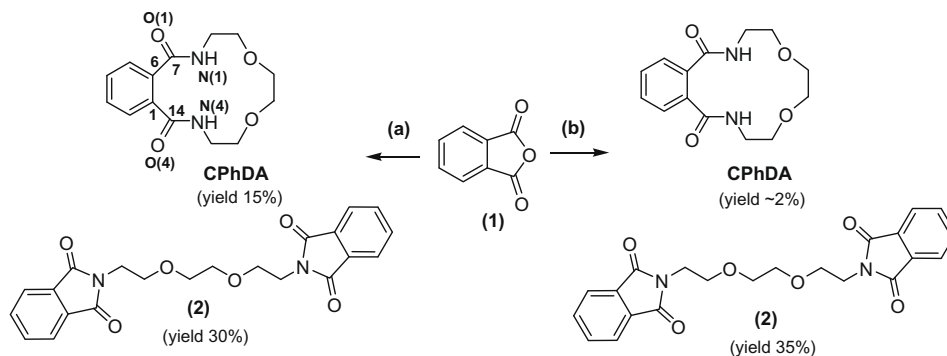
The appropriate lithium perchlorate (1.0 mmol) in warm acetonitrile (5 cm³) was added to a solution of CPhDA (1.0 mmol) in warm acetonitrile (2 cm³). Crystals suitable for X-ray crystallography were grown by slow crystallization from acetone solutions.

2.3. X-ray crystal structure analysis

The X-ray diffraction measurements were carried out on a Kuma KM-4 CCD diffractometer at 293 K. The structure was

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Scheme 1. Synthesis of cyclic diamide of *o*-phthalic acid (CPhDA). Reagent and conditions: (a) *o*-phthalic anhydride (**1**) (1.0 equiv), 1,2-bis(2-aminoethoxy)ethane (1.0 equiv), toluene, 100 °C, 24 h; (b) *o*-phthalic anhydride (**1**) (1.0 equiv), 1,2-bis(2-aminoethoxy)ethane (1.0 equiv), lithium perchlorate (2.0 equiv), acetonitrile, 80 °C, 24 h.

solved by direct method with SHELXS-97 [8] and refined with SHELXL-97 [9]. All on-hydrogen atoms were anisotropically refined. Two H-atoms at O(W1) were located from the difference Fourier maps and refined with isotropic temperature factors. All other H-atoms were calculated from the molecular geometry, and their U_{iso} 's were related to the thermal vibrations of their carriers. The crystallographic-information-file (CIF) has been deposited with Cambridge Crystallographic Database Centre as a supplementary Publication No. CCDC 714396. A copy can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44(12) 23336 033, e-mail: deposit@ccdc.cam.ac.uk.

Crystals of CPhDA–LiClO₄–H₂O were obtained by recrystallisation from acetone: $M = 384.69$, monoclinic, space group $P2_1/c$ (No. 14), $a = 10.6095(9) \text{ \AA}$, $b = 10.6336(9) \text{ \AA}$, $c = 17.0492(14) \text{ \AA}$, $\beta = 102.12(1)^\circ$, $V = 1880.6(3) \text{ \AA}^3$, $Z = 4$, $d_c = 1.359 \text{ g cm}^{-3}$, $2\theta_{max} = 48.28$, $F(000) = 800$. A total of 13,592 reflections were measured, 4729 unique. The final cycle of full-matrix least squares refinement was based on all observed reflections, 293 variable parameters, with factors of $R = 0.067$, $wR_2 = 0.145$, $GOF = 0.958$,

max./min. residual electron density $0.28/-0.44 \text{ e \AA}^{-3}$. The bond distances and angles are listed in Table 1 and hydrogen-bonds geometry is described in Table 2.

2.4. ESI mass spectrometry

The electrospray ionization (ESI) mass spectra were recorded on a Waters/Micromass (Manchester, UK) ZQ mass spectrometer equipped with a Harvard Apparatus syringe pump. All sample solutions were prepared in acetonitrile ($1.0 \times 10^{-5} \text{ mol dm}^{-3}$). The measurements were performed for the solutions of KTA-TBD complex. The samples were infused into the ESI source using a Harvard pump at a flow rate of $20 \mu\text{l min}^{-1}$. The ESI source potentials were: capillary 3 kV, lens 0.5 kV, extractor 4 V. In the case of standard ESI mass spectra the cone voltage was 70 V. The source temperature was 120 °C and the desolvation temperature was 300 °C. Nitrogen was used as the nebulizing and desolvation gas at flow-rates of 100 and 300 l h^{-1} , respectively. Mass spectra were acquired in the positive ion detection mode with unit mass resolution at a step of 1 m/z unit.

Table 1
Selected bond lengths (Å) bond angles (°) and torsion angles (°) determined from X-ray measurement of CPhDA–LiClO₄–H₂O crystal.

Bond lengths (Å)	Bond angles (°)	Torsion angles (°)			
O(1)–C(7)	1.2407(18)	C(10)–O(2)–C(9)	112.88(13)	C(6)–C(1)–C(2)–C(3)	–0.4(3)
O(2)–C(10)	1.432(2)	C(12)–O(3)–C(11)	113.42(14)	C(14)–C(1)–C(2)–C(3)	–175.58(16)
O(2)–C(9)	1.436(2)	C(7)–N(1)–C(8)	123.12(13)	C(4)–C(5)–C(6)–C(7)	–178.39(15)
O(3)–C(12)	1.438(2)	C(14)–N(2)–C(13)	124.84(14)	C(2)–C(1)–C(6)–C(5)	0.7(2)
O(3)–C(11)	1.450(2)	C(5)–C(6)–C(7)	115.68(14)	C(14)–C(1)–C(6)–C(7)	–6.4(2)
O(4)–C(14)	1.2422(19)	C(1)–C(6)–C(7)	124.91(13)	Li(1)–O(1)–C(7)–N(1)	–19.5(4)
N(1)–C(7)	1.333(2)	O(1)–C(7)–N(1)	123.06(15)	Li(1)–O(1)–C(7)–C(6)	156.1(3)
N(1)–C(8)	1.467(2)	N(1)–C(7)–C(6)	116.74(13)	C(8)–N(1)–C(7)–O(1)	0.4(2)
N(2)–C(14)	1.344(2)	N(1)–C(8)–C(9)	110.75(13)	C(8)–N(1)–C(7)–C(6)	–175.29(14)
N(2)–C(13)	1.475(2)	O(2)–C(9)–C(8)	107.81(13)	C(5)–C(6)–C(7)–O(1)	–56.6(2)
C(1)–C(2)	1.402(2)	O(2)–C(10)–C(11)	107.72(14)	C(1)–C(6)–C(7)–O(1)	125.41(17)
C(1)–C(6)	1.408(2)	O(3)–C(11)–C(10)	112.42(15)	C(5)–C(6)–C(7)–N(1)	119.22(16)
C(1)–C(14)	1.504(2)	O(3)–C(12)–C(13)	109.30(15)	C(1)–C(6)–C(7)–N(1)	–58.7(2)
C(2)–C(3)	1.395(3)	N(2)–C(13)–C(12)	114.27(15)	C(7)–N(1)–C(8)–C(9)	–159.31(15)
C(3)–C(4)	1.378(3)	O(4)–C(14)–N(2)	123.59(15)	C(10)–O(2)–C(9)–C(8)	–157.28(15)
C(4)–C(5)	1.388(3)	N(2)–C(14)–C(1)	114.90(14)	N(1)–C(8)–C(9)–O(2)	9.86(18)
C(5)–C(6)	1.403(2)	O(44)–Cl(1)–O(33)	119(3)	C(9)–O(2)–C(10)–C(11)	170.99(15)
C(6)–C(7)	1.511(2)	O(44)–Cl(1)–O(22)	86.3(18)	C(12)–O(3)–C(11)–C(10)	–80.8(2)
C(8)–C(9)	1.512(2)	O(33)–Cl(1)–O(22)	116(2)	O(2)–C(10)–C(11)–O(3)	–58.9(2)
C(10)–C(11)	1.500(3)	O(1CL)–Cl(1)–O(2CL)	106.4(12)	C(11)–O(3)–C(12)–C(13)	176.10(14)
C(12)–C(13)	1.509(3)	O(44)–Cl(1)–O(11)	118.1(15)	C(14)–N(2)–C(13)–C(12)	86.7(2)
Cl(1)–O(44)	1.143(18)	O(33)–Cl(1)–O(11)	97.6(17)	O(3)–C(12)–C(13)–N(2)	–83.67(19)
Cl(1)–O(33)	1.26(2)	O(22)–Cl(1)–O(11)	122.0(12)	C(13)–N(2)–C(14)–O(4)	–2.6(3)
Cl(1)–O(1CL)	1.389(11)	O(1CL)–Cl(1)–O(4CL)	104.2(6)	C(13)–N(2)–C(14)–C(1)	174.11(16)
Cl(1)–O(22)	1.417(15)	O(2CL)–Cl(1)–O(4CL)	119.6(10)	C(2)–C(1)–C(14)–O(4)	127.64(17)
Cl(1)–O(2CL)	1.422(8)	O(1CL)–Cl(1)–O(3CL)	116.7(16)	C(6)–C(1)–C(14)–O(4)	–47.4(2)
Cl(1)–O(11)	1.47(2)	O(2CL)–Cl(1)–O(3CL)	106.8(5)	C(2)–C(1)–C(14)–N(2)	–49.1(2)
Cl(1)–O(4CL)	1.495(10)	O(4CL)–Cl(1)–O(3CL)	103.8(4)	C(6)–C(1)–C(14)–N(2)	135.81(16)
Cl(1)–O(3CL)	1.498(11)	HW1–OW1–HW2	100(4)	C(7)–O(1)–Li(1)–OW1	–68.3(4)

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