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# 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 phtalic 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.

## 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. $CD_3CN$ and $CH_3CN$ 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 $CO_2$-free glove box.

### 2.1. Synthesis of CPhDA

A solution of (1.48 g, $1.0 \times 10^{-2}$ mol) 1,2-bis(2-aminoethoxy)ethane, (1.48 g, $1.0 \times 10^{-2}$ 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 ($3 \times 10$ ml). The chloroform solution was combined and evaporated under reduced pressure to dryness. The solid residue was purified by chromatography ($CHCl_3/CH_3OH$, 5:1) on silica gel (Fluka, type 60), yield – 420 mg, 15.1%. (See Scheme 1, method a.).

### 2.2. Synthesis of CPhDA–$LiClO_4$–$H_2O$ (1:1:1) complex

The appropriate lithium perchlorate (1.0 mmol) in warm acetonitrile (5 $cm^3$) was added to a solution of CPhDA (1.0 mmol) in warm acetonitrile (2 $cm^3$). 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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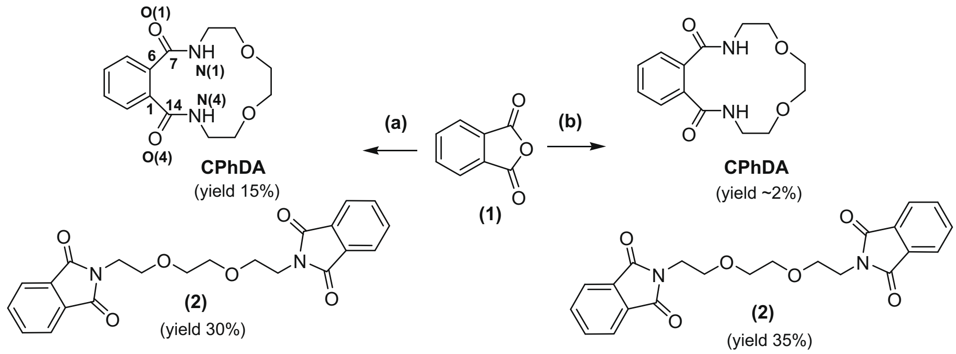

**Scheme 1.** Synthesis of cyclic diamide of *o*-phthalic acid (CPhDA). Reagent and conditions: (a) *o*-phthalic anhydride (**1**) (1.0 equiv), 1,2-bis(2-aminoethoxy)ethane (1.0 equiv), toluene, 100 °C, 24 h; (b) *o*-phthalic anhydride (**1**) (1.0 equiv), 1,2-bis(2-aminoethoxy)ethane (1.0 equiv), lithium 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–$LiClO_4$–$H_2O$ were obtained by recrystallisation from acetone: $M = 384.69$, monoclinic, space group $P2_1/c$ (No. 14), $a = 10.6095(9)$ Å, $b = 10.6336(9)$ Å, $c = 17.0492(14)$ Å, $\beta = 102.12(1)$ Å, $V = 1880.6(3)$ Å$^3$, $Z = 4$, $d_c = 1.359$ g cm$^{-3}$, $2\theta_{max} = 48.28$, $F(0\,0\,0) = 800$. 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 e Å$^{-3}$. The bond distances and angels 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 ($1.0 \times 10^{-5}$ 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 μl 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 dessolvation temperature was 300 °C. Nitrogen was used as the nebulizing and dessolvation gas at flow-rates of 100 and 300 1 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–$LiClO_4$–$H_2O$ 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) |

**Table 2**
Dimensions of the hydrogen bonds (Å and °) in CPhDA–$LiClO_4$–$H_2O$ crystal.

| D–H···A | d(D–H) | d(H···A) | d(D···A) | ∠(DHA) |
|---|---|---|---|---|
| N(1)–H(1N)···O(3CL) | 0.86 | 2.12 | 2.944(8) | 161 |
| N(2)–H(2N)···O(4CL) | 0.86 | 2.28 | 3.008(4) | 143 |
| O(W1)–H(W1)···O(2CL)$^{i}$ | 0.82(4) | 2.14(4) | 2.95(1) | 166(3) |
| O(W1)–H(W2)···O(2)$^{ii}$ | 0.78(6) | 2.23(6) | 2.91(2) | 145(5) |

Symmetry code: (i): $1 - x, -0.5 + y, 0.5 - z$; (ii): $-x, -0.5 + y, 0.5 - z$.

### 2.5. Spectroscopic measurements

The FT-IR spectra of CPhDA and its 2:1 and 1:1 complexes were recorded in KBr pellets (1.5/200 mg) as well as in acetonitrile at 300 K on a Bruker IFS 113v spectrometer (DTGS detector, resolution of 2 $cm^{-1}$). For the solution measurements, a cell with Si windows and a wedge-shaped layer was used to avoid interferences (mean layer thickness: 0.176 mm and the concentration of the samples 0.1 mol $dm^{-3}$). The Happ–Genzel apodization function was used.

The $^{1}H$ NMR measurement in $CD_3CN$ was carried out at the operating frequency 300.075 MHz; flip angle, pw = 45°; spectral width, sw = 4500 Hz; acquisition time, at = 2.0 s; relaxation delay, $d_1 = 1.0$ s; $T = 293.0$ K and using TMS as the internal standard. No window function or zero filing was used. Digital resolution = 0.2 Hz per point.

The $^{13}C$ NMR spectrum was recorded at the operating frequency 75.454 MHz; pw = 60°; sw = 19000 Hz; at = 1.8 s; $d_1 = 1.0$ s; $T = 293.0$ K and TMS as the internal standard. Line broadening parameters were 0.5 or 1 Hz. The error of chemical shift value was 0.01 ppm.

The $^{1}H$ and $^{13}C$ NMR signals were assigned independently for each species using one or two-dimensional (COSY, HETCOR) spectra.

### 2.6. PM5 calculations

PM5 semiempirical calculations were performed using the CAChe WorkSystem Pro 7.5.0.85 Version [10,11].

## 3. Results and discussion

### 3.1. Synthesis

The methods for the preparation of macrocyclic amides have been extensively reviewed [12]. Among these methods, the high dilution-techniques [12], the route based on the template effect [13] and the high pressure approach are frequently used [12,14]. In this work, we used two methods for synthesis of CPhDA. In the first method, the reaction was carried out under high dilution conditions in toluene using *o*-phthalic acid anhydride and 1,2-bis(2-aminoethoxy)ethane (Scheme 1) yielding CPhDA (15%) [15]. Furthermore, side products such as diimide (**2**) (30%) and an insoluble polymer have been obtained. It is interesting to note that using high dilution condition the reaction of *o*-phthaloyl dichloride with 1,2-bis(2-aminoethoxy)ethane under reflux in toluene gave essentially an insoluble polymer. The second method of macrocyclizations used to obtain CPhDA was metal-templated cyclization in acetonitrile solution between *o*-phtalic anhydride and 1,2-bis(2-aminoethoxy)ethane with addition of lithium perchlorate (Scheme 1) [13]. Unfortunately, the main product of this reaction was diimide (**2**) (35%) and polymers.

### 3.2. Spectroscopic and structural studies

The ESI mass spectra of 1:1 and 2:1 mixtures of CPhDA with lithium cation (Fig. 1(a) and (b)) shows the $m/z = 285$ and $m/z = 563$ signals, respectively, demonstrating the formation of the respective complexes.

Inspired by the mass spectrometry results, we have performed the spectroscopic ($^{1}H$ NMR and $^{13}C$ NMR, FT-IR) and structural investigation (X-ray, and semiempirical calculations) of these new lithium complexes. The crystals of 1:1 complex between CPhDA and $LiClO_4$ were obtained from acetonitrile solution as inclusion crystals with one water molecule [CPhDA–$LiClO_4$–$H_2O$ (1:1:1)] (Tables 1 and 2). Unfortunately, no suitable crystals for X-ray measurements of 2:1 complex of CPhDA with $LiClO_4$ were obtained.

The X-ray diffraction analysis revealed a lattice-type complexation of lithium, considerably different than that obtained by PM5 calculation. The CPhDA–$LiClO_4$ crystallizes as a hydrate, and the water molecule participates in the $Li^+$ complexation (Tables 2 and 3). The PM5 calculated and solid state conformations of the 14-membered ring are very similar, and therefore it can be assumed that the CPhDA molecule is not very flexible and favours this conformation. It can explain the complexation of $Li^+$ observed in the crystal (Figs. 2 and 3). The $Li^+$ cation is tetrahedrally coordinated by carbonyl O(4) and ether O(3) oxygen atoms of one CPhDA molecule, by carbonyl O(1) of the neighbouring molecule of CPhDA and by the oxygen O(W1) from the water molecule. These four oxygen atoms form a nearly ideal tetrahedron with edges (inter-oxygen distances) of 3.125–3.274 Å (see Table 3). These distances are commensurate with the sums of van der Waals radii of oxygen and small size of the $Li^+$ cation. Meanwhile in the calculated complexes the fourfold coordination tetrahedral are considerably dis-

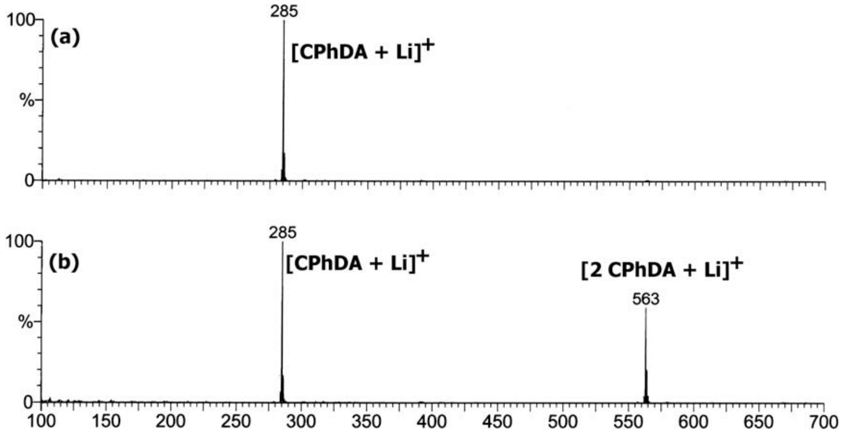

**Fig. 1.** The ESI positive ion mode mass spectra of: (a) 1:1 mixture of CPhDA with $LiClO_4$; (b) 2:1 mixture of CPhDA with $LiClO_4$ at $cv = 30$ V.

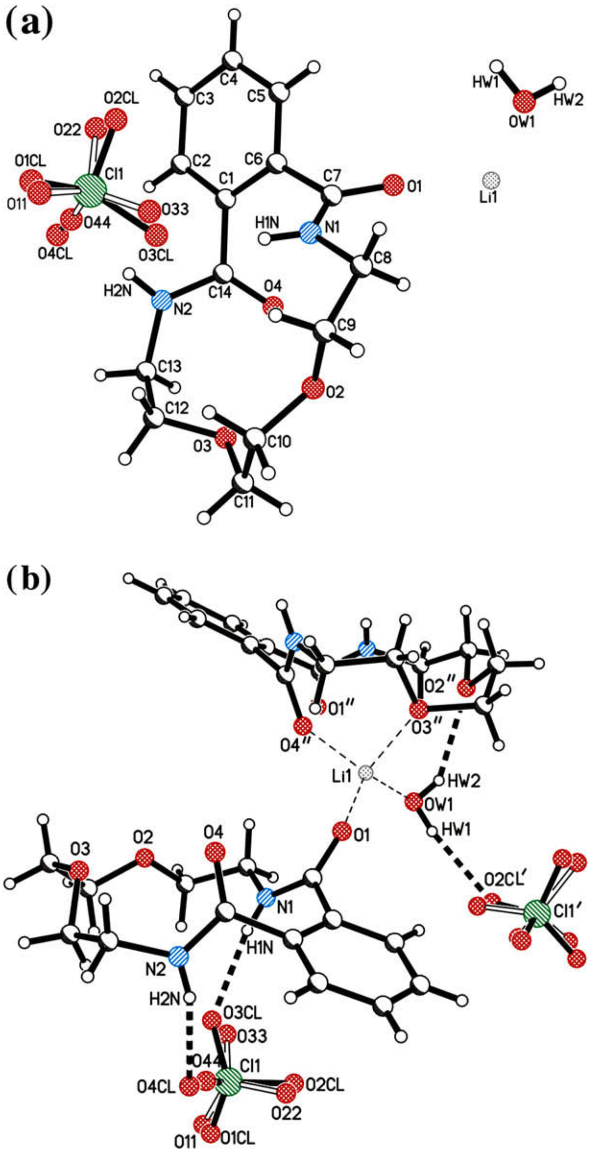

**Fig. 2.** (a) A perspective view of symmetry-independent part of the unit cell of the CPhDA–$LiClO_4$–$H_2O$ complex; (b) a perspective view of the coordination scheme of the $Li^+$ cation. The superscripts refer to the symmetry codes in Table 2. Two sites of the orientationally disordered perchlorate anions have been shown. The hydrogen bonds have been indicated by thick dashed lines and the coordination bonds by the thin dashed lines.

**Table 3**
Coordination schemes of the Li cation. Distances (Å) and angles (°) determined form X-ray studies and calculated by PM5 semiempirical method.

| Used method | Compound[a] | Distances (Å) and angles (°) | |
|---|---|---|---|
| X-ray | CPhDA–$LiClO_4$–$H_2O$ (in crystal) | Li···O(1) | 1.916(3) |
| | | Li···O(W1) | 1.940(4) |
| | | Li···O(4″) | 1.940(3) |
| | | Li···O(3″) | 2.047(3) |
| | | O(3″)···O(4″) | 3.125(2) |
| | | O(W1)···O(3″) | 3.145(2) |
| | | O(1)···O(3″) | 3.176(2) |
| | | O(W1)···O(4″) | 3.177(2) |
| | | O(1)···O(4″) | 3.258(2) |
| | | O(1)···O(W1) | 3.274(2) |
| | | O(1)···Li···O(W1) | 116.2(2) |
| | | O(1)···Li···O(3″) | 106.5(1) |
| | | O(1)···Li···O(4″) | 115.3(2) |
| | | O(W1)···Li···O(3″) | 104.1(1) |
| | | O(W1)···Li···O(4″) | 109.9(1) |
| | | O(3″)···Li···O(4″) | 103.2(1) |
| Semiempirical calculations | CPhDA–Li+ (1:1) | Li···O(1) | 1.95 |
| | | Li···O(2) | 2.02 |
| | | Li···O(3) | 2.07 |
| | | Li···O(4) | 2.01 |
| | | O(1)···Li···O(2) | 108.9 |
| | | O(1)···Li···O(3) | 159.2 |
| | | O(1)···Li···O(3) | 87.9 |
| | | O(2)···Li···O(3) | 89.7 |
| | | O(2)···Li···O(4) | 91.7 |
| | | O(3)···Li···O(4) | 81.2 |
| | CPhDA–$Li^+$ (2:1) | Li···O(1) | 1.94 |
| | | Li···O(4) | 1.95 |
| | | Li···O(1″) | 1.94 |
| | | Li···O(4″) | 1.95 |
| | | O(1)···Li···O(4) | 94.0 |
| | | O(1)···Li···O(1″) | 116.2 |
| | | O(1)···Li···O(4″) | 116.0 |
| | | O(4)···Li···O(4″) | 117.3 |
| | | O(4)···Li···O(1″) | 119.8 |
| | | O(1″)···Li···O(4″) | 94.1 |

[a] Structures of compound are showed in Fig. 2 and 6.

torted and the ligand oxygen–oxygen distances exceed 3.7 Å (O(1)···O(4) 3.733(2) Å, O(1)···O(3) 5.865(2) Å, O(4)···O(2) 3.977(2) Å). It demonstrates that the coordination schemes are much less efficient energetically and in filling the space around $Li^+$ than that observed in the crystal (Fig. 3).

The complex formation between CPhDA and lithium cation could be improved using the FT-IR spectroscopy. This improvement was due to the characteristic changes in ν(C=O) (amide I) and ν(C–N) (amide II) vibration upon complexation.

The spectrum of the crystals of CPhDA–$LiClO_4$–$H_2O$ (1:1:1) in a KBr pellet shown in Fig. 4 is compared with that of crystalline CPhDA–$H_2O$ (2:1) [15]. Fig. 4b shows the same spectra on the extended scales. The structure of CPhDA–$H_2O$ is known [15]. In its FT-IR spectrum the two bands at 3550 and 3475 $cm^{-1}$ are assigned to the OH stretching proton vibrations of the water molecules present in the crystal. The crystal structure of 2CPhDA–$H_2O$ showed that one N–H proton is hydrogen bonded with the carbonyl group, while the other one with the ether oxygen atom. Two bands assigned to the stretching vibrations of the N–H groups observed at 3301 and 3274 $cm^{-1}$ reflect their involvement in the intermolecular hydrogen bonds of different strength. The crystal structure demonstrates that one N–H proton is hydrogen bonded with the carbonyl group, while the other one- with the oxygen atom from the oxaalkyl moiety. The different involvement of the carbonyl groups in different intermolecular hydrogen bonds is reflected in the complex spectral feature of the ν(C=O) vibrations (amide I) as two bands at 1654 and 1629 $cm^{-1}$ are observed. Additionally, the band at 1654 $cm^{-1}$ shows a shoulder at 1662 $cm^{-1}$. The complex spectral feature of the amide I bands is also conserved in the spectral feature of the amide II bands because they are also observed as two bands at 1552 and 1539 $cm^{-1}$ [15]. In the spectrum of the CPhDA–$LiClO_4$–$H_2O$ (1:1:1) crystal (Fig. 4, solid line) two bands with maxima at ca. 3378 and 3305 $cm^{-1}$ are observed indicating the involvement of one of the N–H protons in the weak intermolecular hydrogen bond with perchlorate anion, which is consistent with the X-ray data (Table 2). According to these data the band assigned to ν(C=O) vibrations appears at ca. 1649 $cm^{-1}$ indicating that the carbonyl group interacts with the $Li^+$ cation (see Table 3).

The FT-IR spectra of 1:1 (solid line) and 2:1 CPhDA–$LiClO_4$ (dashed–dotted line) water free complexes and for comparison also the spectrum of CPhDA (dashed line), all in acetonitrile solutions, are compared in Fig. 5. The differences between these spectra are connected with the engagement of the carbonyl group in the coordination process of $Li^+$ cation in the structures of the complexes. In FT-IR spectrum of CPhDA (Fig. 5b, dashed line), the band at 1664 $cm^{-1}$ is assigned to the ν(C=O) vibrations (amide I band).

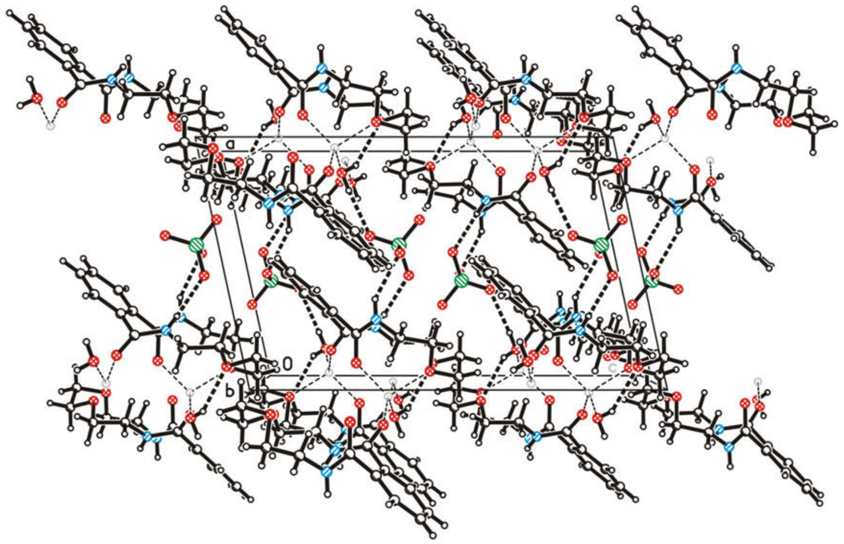

**Fig. 3.** Arrangement of complex CPhDA–$LiClO_4$–$H_2O$ (1:1:1) in the crystal lattice, projected along the [0 1 0] crystal direction.

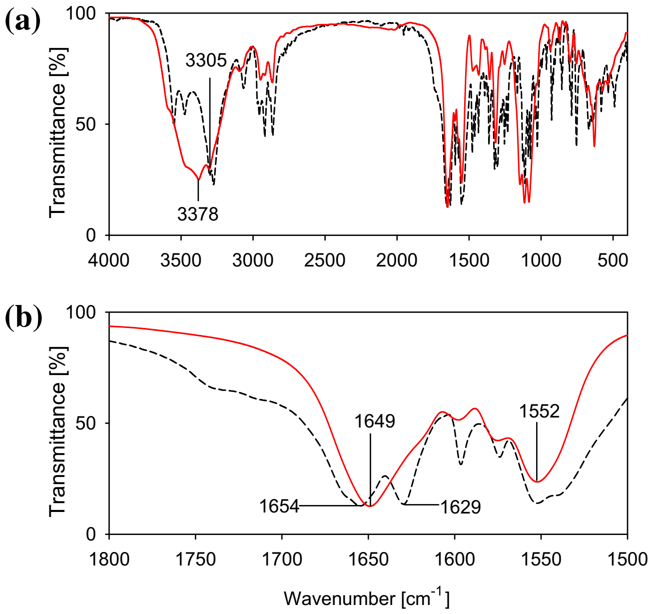

**Fig. 4.** The FT-IR spectra of crystal of [CPhDA–$LiClO_4$–$H_2O$ (1:1:1)] (—) and [CPhDA–$H_2O$ (2:1)] (- - -) recorded in KBr pallet: (a) 4000–400 cm$^{-1}$; (b) 1800–1500 cm$^{-1}$.

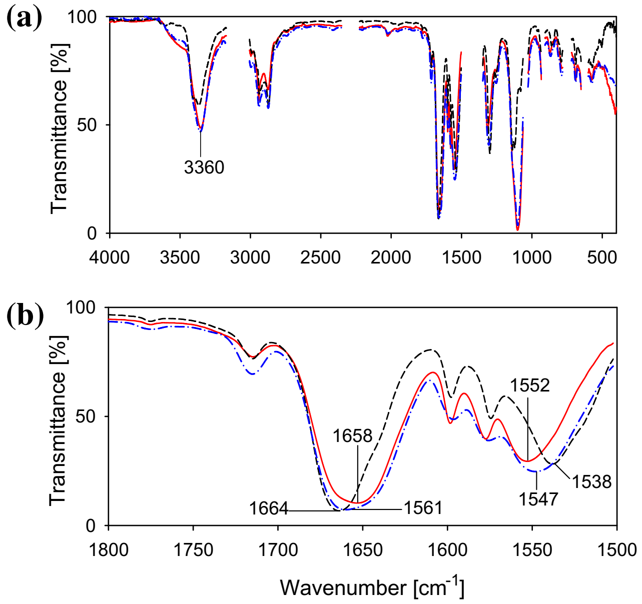

**Fig. 5.** The FT-IR spectra of crystal of 1:1 mixture of CPhDA with $LiClO_4$ (—), 2:1 mixture of CPhDA with $LiClO_4$ (– · –) and water free CPhDA (- - -) in the $CH_3CN$: (a) 4000–400 cm$^{-1}$; (b) 1800–1500 cm$^{-1}$.

The position and shape of the amide I bands in the spectra of 1:1 and 2:1 complexes are changed, i.e. these bands are shifted towards lower wavenumbers and become broadened, demonstrating that the oxygen atoms of the C═O amide groups are engaged in the complexation process of the $Li^+$ cation (Table 3). It is also interesting to note that the position of the amide II band in the spectra of the complexes is also very sensitive to this complexation process. In the FT-IR spectra of the 1:1 and 2:1 complexes, the amide II band observed in the spectrum of CPhDA at 1538 cm$^{-1}$, are shifted towards higher wavenumbers to about 1552 cm$^{-1}$ and 1547 cm$^{-1}$, respectively. The shift of the amide II band to higher frequencies is connected with the increase in the C–N bond order of the amide group.

The $^1H$ and $^{13}C$ NMR chemical shifts of CPhDA and its 1:1 complex with $LiClO_4$ are collected in Table 4. Comparison of the $^1H$ NMR data shows that the signals of the C(2,5)H and N(1,2)H protons are the most sensitive to complexation because of the involvement of the oxygen atom of amide groups in coordination of $Li^+$ cation. Comparison of the $^{13}C$ NMR chemical shifts in the spectra of the complex with those observed in the spectrum of CPhDA suggests not only that the oxygen atom of the carbonyl group takes part in the cation coordination but also indicates that the oxygen atom in the oxaalkyl moiety is also engaged in the complexation process to a small degree.

On the basis of the spectroscopic results, the structures of 1:1 and 2:1 complexes of CPhDA with $Li^+$ were calculated using the PM5 semiempirical method [10,11]. The inter-atomic distances between the coordinated $Li^+$ and the coordinating oxygen atoms within the respective structures are summarized in Table 3 and visualized in Fig. 6a and b, respectively. In the structure of the 1:1 complex, two oxygen atoms of the carbonyl groups and two oxygen atoms of the oxaalkyl moiety are involved in the coordina-

**Table 4**
$^{1}H$ and $^{13}C$ NMR chemical shifts (ppm) of proton and carbon atom signals of CPhDA and its (1:1) complex with $LiClO_4$ in $CD_3CN$.

| | $^{1}H$ NMR | | | $^{13}C$ NMR | | |
|---|---|---|---|---|---|---|
| | CPhDA | CPhDA:$LiClO_4$ (1:1) | Δ | CPhDA | CPhDA:$LiClO_4$ (1:1) | Δ |
| C(1,6)H | – | – | – | 136.11 | 135.72 | −0.39 |
| C(2,5)H | 7.57 | 7.53 | −0.04 | 129.14 | 128.74 | −0.40 |
| C(3,4) | 7.42 | 7.53 | 0.11 | 130.78 | 131.17 | 0.39 |
| C(7,14) | – | – | – | 169.31 | 170.86 | 1.55 |
| C(8,13)$H_2$ | 3.50 | 3.50 | 0.00 | 40.07 | 40.27 | 0.20 |
| C(9,12)$H_2$ | 3.60 | 3.62 | 0.02 | 69.77 | 69.53 | −0.24 |
| C(10,11)$H_2$ | 3.57 | 3.59 | 0.02 | 69.58 | 69.22 | −0.36 |
| N(1,2)H | 7.09 | 7.25 | 0.16 | – | – | – |

Δ = δCPhDA:$LiClO_4$ (1:1) − δCPhDA.

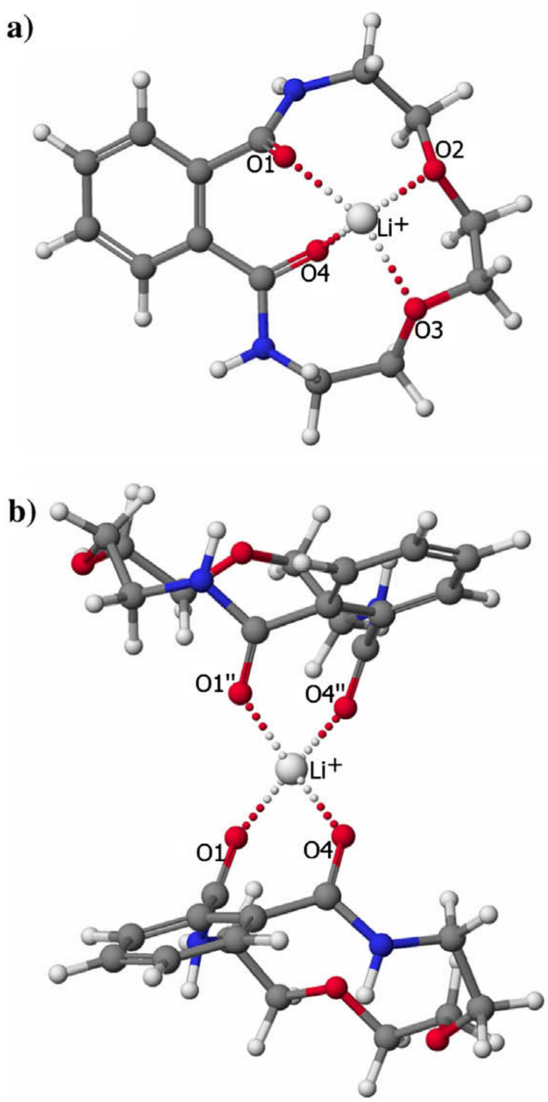

**Fig. 6.** The structure of: (a) CPhDA–$Li^+$ and (b) 2CPhDA–$Li^+$ complexes calculated by PM5 semiempirical method.

tion of the $Li^+$ cation. In contrast to the structure of the 2:1 complex, only the oxygen atoms of the carbonyl groups are engaged in this process.

## 4. Conclusions

Cyclic diamide of *o*-phthalic acid (CPhDA) was synthesised and it is demonstrated by ESI mass spectrometry that this compound forms 1:1 and 2:1 complexes with $Li^+$ cations. The 1:1 complex was obtained in the solid state and its structure is determined by X-ray diffraction method. The structure in the solid is compared with that in the solution using FT-IR, NMR and PM5 semiempirical methods. It is found that the structures of 1:1 complex in both states are different.

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