



Structural, spectroscopic and semiempirical characterisation of the calcium cation complexes with 14-membered macrocyclic ligand of cyclic oxalkyl diamide of *o*-phthalic acid

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ABSTRACT

Cyclic oxalkyl diamide of *o*-phthalic acid (CPhDA) has been obtained and its ability to form complexes with calcium cation has been studied by X-ray, ESI MS, ¹H and ¹³C NMR, FT-IR and PM5 semiempirical methods. The ESI MS measurements have proved that in gas phase the 3:1, 2:1 and 1:1 CPhDA–Ca²⁺ as well as 3:1 and 2:1 CPhDA–Ca(ClO₄)⁺ complexes are formed. In the solid state a 3:1 complex between CPhDA and calcium perchlorate of the CPhDA–Ca(ClO₄)₂–H₂O (3:1:0.5) stoichiometry crystallises as hemihydrate in centrosymmetric space group (R-3) of the rhombohedral system. In crystal, the central Ca²⁺ cation is coordinated by the three CPhDA ligands via the carbonyl oxygen atoms in a distorted trigonal antiprism. The cationic [Ca(CPhDA)₃]²⁺ complex exhibits a threefold symmetry. Two [Ca(CPhDA)₃]²⁺ cations related by an inversion centre interact with oxygen atom of water molecule that statistically occupies two positions around the inversion centre along the Ca...Ca axis. The FT-IR spectra show the characteristic changes in the frequencies of the amide I and amide II bands upon complexation. The structures of the CPhDA and its complexes with calcium cation are visualised using DFT and PM5 methods and discussed in detail.

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1. Introduction

Calcium cations are of special interest, particularly due to their biochemical importance. Calcium plays versatile role within cells in all living creatures, predominantly as a second messenger transmitting signals between the plasma membrane and intracellular machinery [1–6]. Recently, considerable attention has been focused on synthesis of ligands able to bind calcium cations [7–11]. It is well established that the presence of polar amide donors in the ligand's molecule plays an important role in enhancement of selectivity in cation binding [7,11]. Some structural aspects of toward alkaline earth metal cations complexation with macrocyclic amide–ether receptors have been reported on the basis of crystallographic and spectroscopic studies. It has been shown that macrocyclic ligands containing additional ethereal oxygen atoms exhibit selectivity toward alkaline earth metal cations [10,11]. In those studies, secondary amide-based macrocycles containing additional etheric oxygen atoms and pyridine groups have been used for complexation of Ca²⁺ cations [11]. Recently it was shown that some phthalic acid diamides activate ryanodine-sensitive Ca²⁺ release channels in insects [12]. These interesting results as well as the results obtained in our previous papers, demonstrating that cyclic

oxalkyl diamide of *o*-phthalic acid (CPhDA) ligand is able to form complexes with Li⁺ and Na⁺ cations [13,14], stimulated us to check whether the CPhDA molecule is able to form complexes with Ca²⁺ cation. In the present paper we report the X-ray crystal structure, and spectroscopic studies of a new 3:1 complex of CPhDA with calcium perchlorate. In addition, the conformation of the free CPhDA ligand obtained by the DFT calculations is compared to that in the crystalline calcium complex. The structures of all calcium complexes with CPhDA ligands detected in the ESI MS experiment are visualised using PM5 semiempirical method and discussed in detail.

2. Experimental

1,2-Bis(2-aminoethoxy)ethane, *o*-phthalic acid anhydride as well as calcium perchlorate were purchased from Sigma–Aldrich and were used without any further purification. CD₃CN and CH₃CN spectral-grade solvents were stored over 3 Å molecular sieves for several days.

2.1. Synthesis of CPhDA

CPhDA was obtained according to our method described previously [13]. The purity of this compound was controlled by elemental analysis, FT-IR, ¹H and ¹³C NMR spectroscopic methods.

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Table 1
Crystal data and structure refinement.

Empirical formula	(C ₁₄ H ₁₈ N ₂ O ₈) ₃ Ca(H ₂ O) _{0.5} (ClO ₄) ₂
Formula weight (g mol ⁻¹)	1081.89
Crystal system, space group	rhombohedral, R-3
<i>a</i> = <i>b</i> = <i>c</i> (Å)	14.1857(16)
$\alpha = \beta = \gamma$ (°)	87.795(17)
<i>V</i> (Å ³)	2848.5(6)
<i>Z</i>	2
<i>D</i> _{calc} / <i>D</i> _{obs} (g cm ⁻³)	1.261/1.26
μ (mm ⁻¹)	0.277
<i>F</i> (0 0 0)	675
Crystal size (mm)	0.24 × 0.20 × 0.18
Radiation type, wavelength, λ (Å)	Mo K α , 0.71073
<i>T</i> (K)	295(2)
θ range (°)	2.90–29.0
Absorption correction	Numerical, CrysAlis Red
<i>T</i> _{minimum} / <i>T</i> _{maximum}	0.9365/0.9518
Reflections collected/unique/observed	38 459/4 982/2 778
<i>R</i> _{int}	0.0657
Refinement on	<i>F</i> ²
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.0637
<i>wR</i> (<i>F</i> ² all reflections)	0.1443
Goodness-of-fit (GOF), <i>S</i>	1.006
$\Delta\rho$ _{maximum} , $\Delta\rho$ _{minimum} (e Å ⁻³)	+0.319, -0.143

$$wR = \{\sum[w(F_o^2 - F_c^2)^2] / \sum w F_o^4\}^{1/2}; w^{-1} = (\sigma^2(F_o^2) + (0.0540P)^2) \text{ where } P = (F_o^2 + 2F_c^2) / 3.$$

Table 2
Selected bond lengths (Å) and angles (°).

Ca–O1	2.3447 (17)	Ca–O4	2.3556 (17)
Ca–O5	2.686 (5)	C1–C2	1.378 (3)
C2–C3	1.384 (3)	C3–C4	1.347 (3)
C4–C5	1.359 (3)	C5–C6	1.384 (3)
C1–C6	1.372 (3)	C6–C7	1.494 (3)
C7–O1	1.219 (3)	C7–N1	1.363 (3)
N1–C8	1.433 (3)	C8–C9	1.504 (3)
C9–O2	1.398 (3)	O2–C10	1.381 (3)
C10–C11	1.488 (4)	C11–O3	1.442 (3)
O3–C12	1.407 (3)	C12–C13	1.519 (3)
C13–N2	1.456 (3)	N2–C14	1.314 (3)
C14–O4	1.243 (4)	C1–C14	1.509 (3)
O1–Ca–O4	77.24 (6)	O1–Ca–O4 ⁱ	87.98 (6)
O1–Ca–O4 ⁱⁱ	164.70 (7)	O1–Ca–O5	126.75 (4)
O1–Ca–O1 ⁱ	87.88 (6)	O4–Ca–O4 ⁱ	105.44 (5)
O4–Ca–O5	66.75 (5)		

Symmetry code: (i) *y*, *z*, *x*; (ii) *z*, *x*, *y*.**Table 3**
Geometry of the hydrogen bonds (Å and °).

D–H...A	D–H	H...A	D...A	D–H...A
N1–H1...O14 ⁱ	0.86	2.07	2.900(6)	162
N1–H1...O18 ⁱ	0.86	2.20	3.053(7)	173
N2–H2A...O3 ⁱⁱ	0.86	2.01	2.870(4)	173

Symmetry code: (i) = *x* + 1, *y*, *z* (ii) –*x* + 2, –*y* + 1, –*z* – 1.

2.2. Synthesis of CPhDA–Ca(ClO₄)₂–H₂O (3:1:0.5) complex

The appropriate calcium perchlorate (1.0 mmol) was dissolved in warm dry acetonitrile (10 cm³) and added to the solution of CPhDA (3.0 mmol) in warm dry acetonitrile (5 cm³). Then the solution was cooled and left at room temperature. After several days the colourless crystals suitable for X-ray crystallography were obtained.

2.3. X-ray measurements

A colourless single crystal of CPhDA–Ca(ClO₄)₂–H₂O (3:1:0.5) with the edges of 0.24 × 0.20 × 0.18 mm was measured on a

KUMA KM-4 CCD diffractometer with graphite monochromatised Mo K α ($\lambda = 0.71073$ Å) radiation at room temperature. The unit cell parameters were refined by the least-square method on the basis of 1211 reflections. 38,459 reflections (4982 independent, *R*_{int} = 0.0657) were measured up to 59° in 2 θ covering over 99% of the Ewald sphere. Data collections were made using the CRYSLIS CCD program [15], integration, scaling of the reflections and absorption corrections were performed with CRYSLIS RED program [15]. The structure was solved by direct methods using the SHELXS-97 and refined using the SHELXL-97 program [16]. The hydrogen atoms were located from the $\Delta\rho$ maps, but in the final refinement they were constrained. The final differences Fourier maps showed no peaks of chemical significance. Details of the data collection parameters, crystallographic data and final agreement parameters are collected in Table 1. Selected bond lengths and angles are listed in Table 2, and the hydrogen bonding geometries are collected in Table 3. Visualisation of the structure was made with the DIAMOND 3.0 program [17].

2.4. NMR measurements

The NMR spectra were recorded in CD₃CN using a Varian Gemini 300 MHz spectrometer. All spectra were locked to deuterium resonance of CD₃CN. The error in ppm values was 0.01. All ¹H NMR measurements were 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 TMS as the internal standard. No window function or zero filling was used. Digital resolution = 0.2 Hz/point. ¹³C NMR spectra were 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.

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

2.5. FT-IR measurements

In the mid infrared region the FT-IR spectra of CPhDA and CPhDA–Ca(ClO₄)₂–H₂O (3:1:0.5) were recorded in potassium bromide as pellets and in acetonitrile solution. A cell with Si windows and wedge-shaped layers was used to avoid interferences (mean layer thickness 170 μ m). The spectra were taken on an IFS 113v FT-IR spectrophotometer (Bruker, Karlsruhe) equipped with a DTGS detector; resolution 2 cm⁻¹, NSS = 64. The Happ-Genzel apodization function was used.

2.6. ESI mass spectrometry

The ESI (Electrospray Ionisation) 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. The measurements were performed for the solutions of 3:1 CPhDA–Ca(ClO₄)₂ mixture. The samples were infused into the ESI source using a Harvard pump at a flow rate of 20 μ l min⁻¹. The ESI source potentials were: capillary 3 kV, lens 0.5 kV and extractor 4 V. In the case of standard ESI mass spectra the cone voltage was 30 V. Nitrogen was used as the nebulising and desolvation gas at flow-rates of 100 and 300 dm³ 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.

2.7. DFT and PM5 calculations

Full geometry optimisation for the CPhDA macrocyclic ligand was accomplished applying the GAUSSIAN03 programme package

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