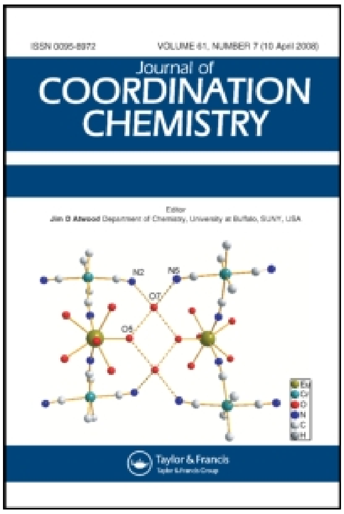

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Synthesis and crystal structure of alkaline-earth metal cryptates of a ligand derived from 2,6-diformyl-pyridine

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New alkaline-earth metal cryptates $[ML](ClO_4)_2 \cdot$ solvent ($M = Ca^{2+}$, Sr^{2+}, Ba^{2+}; L = 1,4,12,15,18,26,31,39,42,43,44-undecaazapentacyclo-[13.13.13.$1^{6,10}$.$1^{20,24}$.$1^{33,37}$]-tetratetraconta-4,6,8,10(44),11,18,20,22,24(43),25,31,33,35,37(42),38-pentadecaene) were synthesized by [2 + 3] template condensation of tris(2-aminoethyl)amine with 2,6-diformylpyridine and characterized by physical methods. The crystal structure of the calcium cryptate was determined. The central atom is nine coordinate with three pyridyl and six imino nitrogen atoms. The coordination polyhedron can be described as slightly distorted tricapped trigonal prism.

Keywords: Alkaline-earth metal; Cryptate; Crystal structure

1. Introduction

Cryptates receive considerable attention for their special properties [1] and potential applications in molecule recognition [2], catalysis [3, 4], and molecular devices [5, 6]. A pytren polyazacryptand derived from [2 + 3] condensation of pyridyl dicarboxylaldehyde with tris(2-aminoethyl)amine (tren) had a cage-like structure [7, 8] and has been extensively investigated for complexing properties transition metal, alkali metal and lanthanide ions [9–16], but only a few reports about its alkaline earth metal cryptates [17] have appeared; calcium cryptates were seldom reported. Calcium is a biologically essential element and calcium transport plays an important role in biological systems. Cryptands were shown to mimic the ion transport of natural systems [18, 19] because they contain appropriate binding sites, suitable size and the cryptates formed had special thermodynamic and kinetic properties. Therefore the studies of synthesis and the crystal structure of alkaline earth cryptates had both theoretical and practical significance. In this work, we synthesized three alkaline earth metal cryptates $[ML](ClO_4)_2 \cdot$ solvent ($M = Ca^{2+}$, Sr^{2+}, Ba^{2+}, L denotes the macrocyclic ligand, scheme 1) by [2 + 3] condensation of tren with 2,6-diformylpyridine in the presence of the alkaline earth metal ion. X-ray crystal structure analysis showed that in

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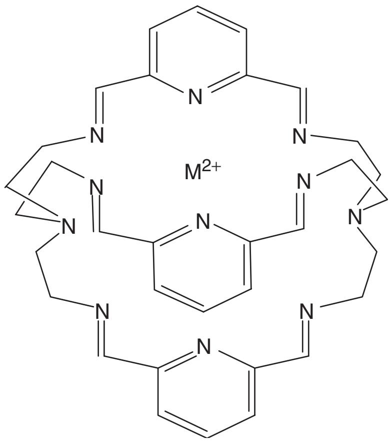

Scheme 1. The chemical formula of the complex cation (M = Ca, Sr, Ba).

the calcium complex the central ion has a tricapped prism structure, nine-coordinate. The structure was different from the asymmetrical structure of sodium cryptate with the same ligand [12].

2. Experimental

2.1. *Materials and methods*

All starting chemicals were of reagent grade; alkaline earth perchlorates were prepared by the reaction of corresponding carbonate and $HClO_4$ (70%); tris(2-aminoethyl)amine [20] and 2,6-diformyl-pyridine [21] were prepared by the literature methods. Their physical constants and spectroscopic data were in agreement with literature values. Elemental analyses (C, H and N) were performed on a Perkin–Elmer 240c analytical instrument. The molar electrical conductivities in CH_3CN solution containing $10^{-4}\,\mathrm{mol\,dm^{-3}}$ complex were measured at $25 \pm 0.1^\circ\mathrm{C}$ using a BSD-A conductometer (Jangsu, China). Electronic spectra were recorded on a UV-3100 spectrophotometer. IR spectra were measured using KBr discs with a Vector 22 FT–IR spectrophotometer. Electrospray mass spectra (ES–MS) were determined on a Finnigan LCQ ES–MS mass spectrograph using methanol as mobile phase with sample concentration about $1.0\,\mathrm{mmol\,dm^{-3}}$. The diluted solution was electrosprayed at a flow rate of $5 \times 10^{-6}\,\mathrm{dm^3\,min^{-1}}$ with needle voltage of +4.5 kV. The temperature of the heated capillary in the interface was 200°C and a fuse silica sprayer was used.

2.2. *Preparation of the compounds*

$[CaL](ClO_4)_2 \cdot 2MeOH$ (1). To a stirred solution of 2,6-diformyl-pyridine (0.405 g, 3 mmol) and calcium perchlorate (0.263 g, 1.1 mmol) in 60 mL absolute methanol solution was added an absolute methanol solution (40 mL) containing tris (2-aminoethyl)amine (0.292 g, 2 mmol). After refluxing for 2 h, the solution was cooled and the yellow crystals were filtered out and recrystallized from methanol, yields 0.60g (67%). Found: C, 47.48; H, 4.87; N, 17.49%; Calcd for $C_{35}H_{47}N_{11}Cl_2O_{10}Ca$ (Mw 892.81): C, 47.09; H, 5.31; N, 17.26%; IR (cm^{-1}): 1648 (s, ν(C=N)); 1089 (s, $\nu(C1O_4^-)$); UV–Vis (λ_{max}/nm (ε/$dm^3\,mol^{-1}\,cm^{-1}$), CH_3CN): 213(59,300), 237(39,400), 301(14,500), 318(10,600); Λ_M (CH_3CN, 293 K): 241 $S\,cm^2\,mol^{-1}$. Colorless cubic crystals $[CaL](ClO_4)_2$ suitable for X-ray diffraction were obtained by diffusion of Et_2O into MeCN solution over 1 week.

$[SrL](ClO_4)_2 \cdot 2MeOH$ (**2**) and $[BaL](ClO_4)_2 \cdot 4MeOH$ (**3**) were prepared by a similar procedure as described for **1**.

$[SrL](ClO_4)_2 \cdot$ 2MeOH (2). yellow crystals, yield 63%. Found: C, 44.33; H, 5.31; N, 16.75%; Calcd for $C_{35}H_{47}N_{11}Cl_2O_{10}Sr$ (Mw 940.35): C, 44.71; H, 5.04; N, 16.39%. IR (cm^{-1}): 1648 (s, ν(C=N)); 1089 (s, $\nu(ClO_4{}^-)$). UV–Vis (λ_{max}/nm (ε/$dm^3\,mol^{-1}\,cm^{-1}$), CH_3CN): 213(58,500), 237(41,500), 301 (15,800), 318(11,700). Λ_M (CH_3CN, 293 K): 237 $S\,cm^2\,mol^{-1}$.

$[BaL](ClO_4)_2 \cdot$ 4MeOH (3). yellow crystals, yield 58%. Found: C, 42.53; H, 5.55; N, 14.85%; Calcd for $C_{37}H_{55}N_{11}Cl_2O_{12}Ba$ (Mw 1054.14): C, 42.16; H, 5.26; N, 14.62%. IR (cm^{-1}): 1648 (s, ν(C=N)); 1089 (s, $\nu(C1O_4^-)$). UV–Vis (λ_{max}/nm (ε/$dm^3\,mol^{-1}\,cm^{-1}$), CH_3CN): 213(57,800), 237(40,700), 301 (15,100), 318(10,900). Λ_M (CH_3CN, 293 K): 235 $S\,cm^2\,mol^{-1}$.

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with care. The complexes described in this report have, so far, been found to be safe in small quantities.

2.3. *Crystal structure determination*

Intensity data were collected on a SAMRT CCD diffractometer with monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation. Data reduction and cell refinement were performed by SMART and SAINT programs [22]. An empirical absorption correction was applied using the SADABS [22] program with $T_{max} = 0.935$ and $T_{min} = 0.924$. The structure was solved by direct methods (Bruker Shelxtl) and refined on F^2 by full-matrix least-squares (Bruker Shelxtl) using all unique data [22]. The non-H atoms in the structure were anisotropic. Hydrogen atoms were located geometrically (C–H 0.93 to 0.97 Å) and refined in riding mode with U(H) = 1.2 times Ueq of the parent atom. The occupation factor of $C1O_4^-$ was constrained to 2/3 because it was located at a special position with a C3 axis passing through it, and the charge of the central cation was +2. A summary of crystallographic data and additional data collection parameters is given in table 1.

3. Results and discussion

3.1. *Synthesis and characterization*

Based on the conductivities of the three cryptates, they behave as 1 : 2 electrolytes [23], which are consistent with the chemical formula predicated by elemental analysis. The intense absorptions in the electronic spectra of the cryptates at 200–250 nm and 310–330nm are π–π* transitions of the pyridyls and C=N groups, respectively. The IR spectra show the characteristic C=N stretch (1648 cm^{-1}) and ionic perchlorate (1089 cm^{-1}). Upon formation of cryptates, the frequencies of the C=N do not move

Table 1. Crystal data and structure refinement for the complex $[CaL](ClO_4)_2$.

Empirical formula	$C_{33}H_{39}Cl_2\ N_{11}O_8Ca$
Crystal system	Trigonal
Space group	R-$3c$
a, c (Å, °)	15.246(1), 31.824(2)
α, γ (Å, °)	90, 120
V (Å^3)	6406.2(7)
D_{Calcd} (g cm^{-3})	1.290
Temperature (K)	293(2)
F(000)	2595
Crystal size (mm)	$0.20 \times 0.20 \times 0.30$
μ(Mo-Kα) (mm^{-1})	0.331
2θ range (°)	2.7–25.0
Reflections collected	10,280
Independent reflections	1255 ($R_{\mathrm{int}} = 0.037$)
Observed reflections	711
Refined parameters	93
Number of restrains	0
Index ranges	$-15 \le h \le 0;\ 0 \le k \le 18;\ 0 \le l \le 37$
w^{-1}	$w = 1/[\sigma^2(F_o{}^2) + (0.0500P)^2]\ P = (F_o{}^2 + 2F_c{}^2)/3$
Goodness of fit on F^2	1.049
Rinal R_1, wR_2 for all reflections	0.0677, 0.1354
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0475, 0.1323
Largest diff. peak and hole (e Å^3)	0.78, −0.20

in comparison to the free ligand (1647 cm^{-1}) [8], this indicates a weak interaction between the hard alkaline metal ions and the soft imino nitrogen atoms.

3.2. *Electrospray mass spectra*

The positive-ion ES mass spectrum of **1** in methanol is shown in figure 1. The base peak at $m/z = 314.8$ is assigned to $[CaL]^{2+}$, and the peaks at $m/z = 728.4$ can be assigned to $[Ca^{2+}L(C1O_4^-)]$. The peaks at $m/z = 590.3$ and at $m/z = 612.5$ are to monoprotonated cryptand and $[NaL]^+$, respectively, implying that Ca^{2+} is dissociated and replaced by Na^+ ion. The Na^+ is present in trace amount. The peaks at $m/z = 612.5$ were also observed in the ES–MS spectra of the previous synthesized neodymium cryptate $[NdL](NO)_3 \cdot H_2O$ [14]. The isotopic distribution of the peaks at $m/z = 612.5$ is shown in figure 1(a). From the numbers and isotopic abundances of the atoms in $[NaL]^+$, a revised program is used to calculated the pattern (figure 1b) which is in agreement with the experimental one. No fragment of the cryptand is observed, showing the cryptand is very stable. Compounds **2** and **3** have similar ES mass spectra with that of **1**, but no peaks at $m/z = 590.3$ are observed and the abundances of the peaks at $m/z = 612.5$ are lower than that of **1**, implying that **1** is the least stable of the three complexes. Assignments of the ES mass spectra of the three cryptates are given in table 2.

3.3. *Crystal structure of the cryptate*

The structure of the complex is shown figure 2(a) and important bond distances and angles are listed in table 3. The cation lies on a special position a of the space group R-$3c$ with multiplicity 6 and site symmetry 32 (hexagonal axes). Ca1 is located in the

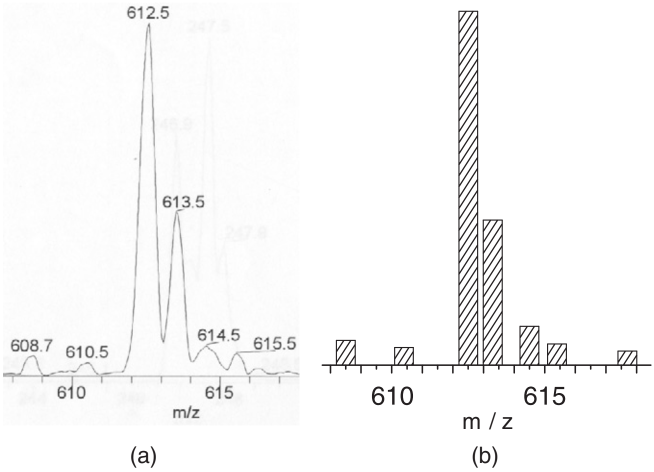

Figure 1. The isotopic distribution of the peak at $m/z = 612.5$. (a) Experimental; (b) calculated.

Table 2. Assignments of the ES mass spectra of the three cryptates.

No.	Cryptate	Peak (m/z)	Relative abundance (%)	Assignment
1	$[CaL](ClO_4)_2 \cdot 2MeOH$	314.8	100	$[CaL]^{2+}$
		590.3	5	$[HL]^{+}$
		612.5	25	$[NaL]^{+}$
		728.4	16	$[CaL(ClO_4)]^{2+}$
2	$[SrL](ClO_4)_2 \cdot 2MeOH$	338.5	100	$[SrL]^{2+}$
		612.5	18	$[NaL]^{+}$
		776.6	13	$[SrL(ClO_4)]^{2+}$
3	$[BaL](ClO_4)_2 \cdot 4MeOH$	363.8	100	$[BaL]^{2+}$
		612.5	13	$[NaL]^{+}$
		826.3	10	$[BaL(ClO_4)]^{2+}$

Table 3. Selected bond distances (Å) and angles (°) of **1**.[a]

Ca1–N2	2.644(3)	Ca1–N3	2.582(3)
Ca1 ··· N1	3.926(5)		
N2–Ca1–N2A	78.87(10)	N2–Ca1–N3	62.11(7)
N2–Ca1–N2C	150.40(9)	N2–Ca1–N3A	136.32(6)
N2–Ca1–N2E	87.38(9)	N2–Ca1–N3B	75.20(8)
N2–Ca1–N2D	124.25(12)	N3–Ca1–N3A	120.00(4)

[a] Symmetry transformation used to generate equivalent atoms: i: $1-y, x-y, z$ (N2A, N3A); ii: $1-x+y, 1-x, z$ (N2B, N3B); iii: $1/3+y, -1/3+x, 1/6-z$ (N2C, N1A); iv: $1/3+x-y, 2/3-y, 1/6-z$ (N2D); v: $4/3-x, 2/3-x+y, 1/6-z$ (N2E).

center of the macrocycle and coordinated by three pyridyl nitrogen atoms and six imino nitrogens. The lone pairs of the two bridgehead nitrogens of the tren moieties are directed toward the central Ca1, but there is no interaction between Ca1 and the bridgehead nitrogen atoms because the Ca1–N1 (or N1A) distance (3.926(5) Å) is too long for coordination. The coordination polyhedron around Ca1 can be described as a nine-coordinate distorted tricapped trigonal prism in which the three pyridyl nitrogen atoms (N3, N3A and N3B) are the caps (figure 2b). The upper and basal triangular

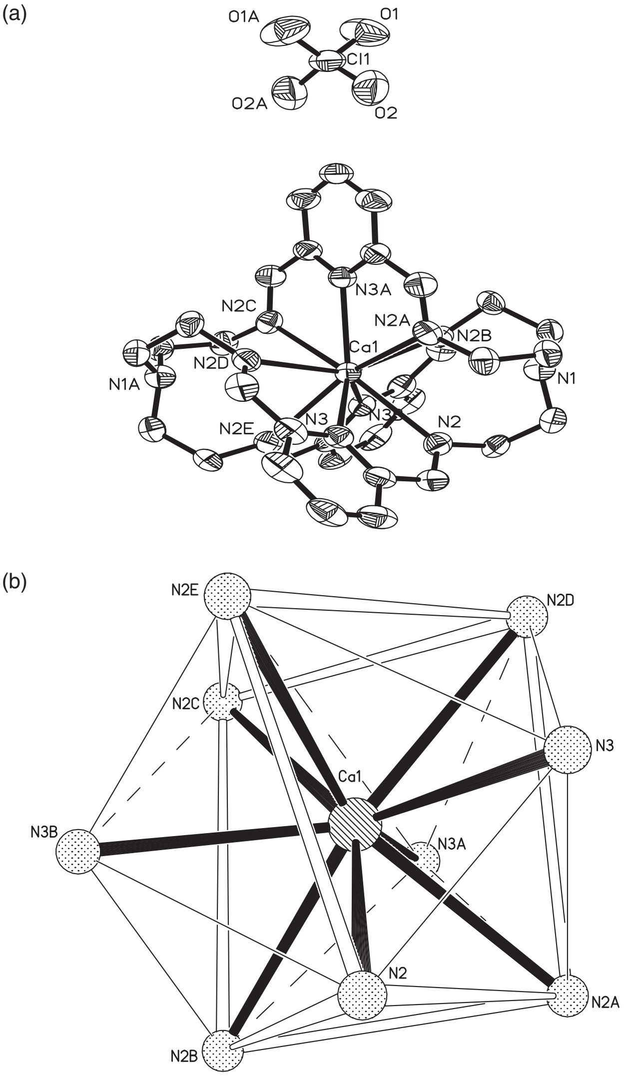

Figure 2. (a) A perspective view of $[\mathrm{CaL}]^{2+}$; (b) the structure of coordination polyhedron.
Notes: Symmetry transformation used to generate equivalent atoms: i: $1-y$, $x-y$, z (N2A, N3A); ii: $1-x+y$, $1-x$, z (N2B, N3B); iii: $1/3+y$, $-1/3+x$, $1/6-z$ (N2C, N1A); iv: $1/3+x-y$, $2/3-y$, $1/6-z$ (N2D); v: $4/3-x$, $2/3-x+y$, $1/6-z$ (N2E).

planes of the prism, which are approximately parallel, are composed of the imino nitrogen atoms (the upper plane: N2, N2A, N2B; the basal plane: N2C, N2D, N2E). Ca1 is located in the symmetrical center of the prism. The distance of Ca1 to each of the three lateral least-squares plane is 0.956 Å (N2, N2A, N2D, N2E: mean deviation 0.2801 Å; N2A, N2B, N2C, N2D; mean deviation 0.2801 Å; N2, N2B, N2C, N2E: mean deviation 0.2801 Å). The distance of Ca1 to the upper (or basal) plane is 1.797 Å. Distortion from idealized geometry arises from rotation of one of the two triangular planes by 19.20° along the axis passing through Ca1, the two bridged nitrogens and the centers of the two triangular plans. This distorted tricapped prism structure is also adopted by previously reported Eu [13], Nd [14] and Ba [17] analogues. Hosting one lanthanide or alkaline-earth metal ion (Eu^{3+}, Nd^{3+}, Ca^{2+} or Ba^{2+}) or two Cu(I) [10] ions, the cryptand has a symmetric convergent conformation in contrast to the divergent structure of the metal-free cryptand in which all lone pairs on the imino nitrogens point outside of the cavity [7, 8]. In other mononuclear Na [12], Fe [15] and Ag [16] complexes with the same cryptand, the central ions locate in one end of the macrocycle and are coordinated by three pyridyl nitrogen atoms and three imino nitrogen atoms to form a asymmetric conformation in which the three coordinated imino nirtogens are convergent and the uncoordinated imino ones are divergent. Ca ion like Ba, Eu or Nd ions locates in the symmetrical center of the macrocycle to make best use of the nine sp^2 nitrogens due to its bigger volume and the requirement of higher coordination number.

Supplementary material

CCDC-208552 contains the supplementary crystallographic data for this article. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0)1223-336033; Email: deposit@ccdc.cam.ac.uk].

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