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Metal complexes with pendant-armed oxaazamacrocycles. The crystal structures of dimeric Ca(II) and Sr(II) complexes

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ABSTRACT

A new series of alkaline-earth and transition metal complexes of Ca(II), Sr(II), Ba(II), Co(II), Ni(II) and Cu(II) with two pendant-arm oxaaza macrocyclic ligands, L^1 and L^2, with N_4O_2 and N_4O_3 donor sets, respectively, were synthesized by reaction of the ligand and the appropriate perchlorate salt in refluxing acetonitrile. The reactions gave analytically pure products that were characterized by elemental analysis, FAB mass spectrometry, IR and ^1H NMR spectroscopy. The crystal structure of $L^1 \cdot 3H_2O$, $[Sr_2(L^2-H)_2(ClO_4)_2]$ and $[Ca_2(L^2-H)_2(ClO_4)_2] \cdot 2.5CH_3CN$ could be also determined.

The crystal structures of the Ca(II) and Sr(II) complexes with L^2 show similar dimeric compounds with the two metal ions joined through the deprotonated phenolic oxygen from two salicylaldehyde groups. Both metal ions are in a seven coordination environment. In these dimeric compounds each metal ion is exomacrocyclicly bonded to the four nitrogen atoms from one ligand molecule, one oxygen atom from a monodentate perchlorate anion and the bridge oxygen atom of the salicylaldehyde group from both ligand molecules.

1. Introduction

The detection of metal cations continues to be a very vigorous area of research, mainly due to the important roles in chemistry, biology, medicine, biochemistry, marine chemistry and environmental sciences. In particular, oxaaza ligands have been extensively investigated in the last decades [1] mainly owing to their ability to form complexes with different metal ions with considerable potential as selective extractants for transition and post-transition metal ions, as isotope separation system [2], as components active electrode ion selective membrane, and in recent years, as chemical sensors and logic gates [3].

Interest in pendant-armed macrocycles is growing on account of their unique coordination and structural properties [4], their bioinorganic applications [5], their utility as contrast reagents in MRI [6–8], their use as tumor-directed radioisotope carriers [9], and their ability to carry out controlled molecular movements and translocations [10]. Furthermore, this type of functionalized amino pendant-armed macrocycle provides opportunities for the synthesis of a wide range of derivatives, by a Schiff-base condensation with a suitable carbonyl compound, leading to precursors for polynuclear complexation. In this way, tris(2-aminoethyl)amine (tren) can be used as a precursor for the design and synthesis of functionalized pendant-armed macrocycles [11–14].

We have recently reported the synthesis of oxaaza macrocyclic ligands L^1 and L^2 [15] (Scheme 1) derived from *1,4*-bis(2′-formylphenyl)-1,4-dioxabutane and tren. L^1 and L^2 may act as N_4O_2 and N_4O_3 donor ligands, respectively. L^2 has one phenolic group pendant-arm, which can be deprotonated leading to the mono-anionic ligand. Structurally, L^2 derives from L^1 by condensation with salicylaldehyde. The presence of additional donor atoms in the pendant group can be used to enhance the coordination potential of these ligands and/or to build polynuclear structures.

This paper describes the synthesis, structure and properties of complexes with the aforementioned pendant-armed macrocycles. The X-ray crystal structures of ligand L^1 and calcium(II) and strontium(II) perchlorate complexes are also reported.

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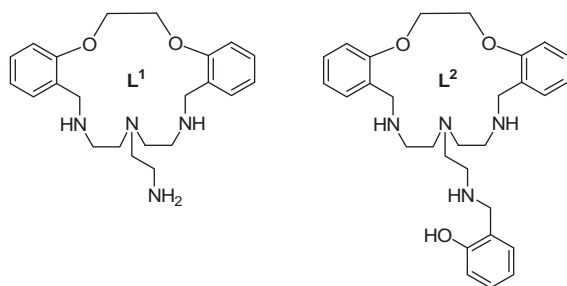
Scheme 1. Ligands L^1 and L^2.

2. Experimental

2.1. Chemicals and starting materials

The synthesis of macrocyclic ligands L^1 and L^2 [15] were achieved following the literature method. The others reagents employed in the synthesis were purchased from Aldrich/Panreac and they were used without further purification. Solvents were of reagent grade and were purified by standard methods.

Caution! Although problems were not encountered during the course of this work, attention is drawn to the potentially explosive nature of perchlorates salts.

2.2. Physical measurements

Elemental analyses were performed on a Carlo-Erba EA1108 CHNS-O and LECO CNHS-932 microanalyser by the Universidade de Santiago de Compostela. Infra-red spectra were recorded as a KBr discs on a Bruker IFS-66V. FAB mass spectra were recorded

using a Kratos- MS-50T spectrometer connected to a DS90 data system using 3-nitrobenzyl alcohol as the matrix. NMR spectra were recorded on a Bruker 500 MHz spectrometer.

2.3. Crystal structure determination

The details of the X-ray crystal structure solution and refinement are given in Table 1. Crystals suitable for X-ray diffraction were obtained for L^1·3H$_2$O, [Sr$_2$(L^2-H)$_2$(ClO$_4$)$_2$] and [Ca$_2$(L^2-H)$_2$ (ClO$_4$)$_2$]·2.5CH$_3$CN. Measurements were made on a Bruker SMART CCD Area Detector for Graphite monochromated Mo K$_\alpha$ was used. All data were correct for Lorentz and polarization effects. Empirical absorption corrections were also applied for all the crystal structures obtained [16]. Complex scattering factors were taken from the program package SHELXTL [17]. The structures were solved by direct methods using SHELX-97 [18], which revealed the positions of all non-hydrogen atoms. All the structures were refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms were located in their calculated positions and refined using a riding model. Molecular graphics were obtained with ORTEP-3 [19].

2.4. Synthesis of the metal complexes – general procedure

The reactions were carried out in 1:1 metal:ligand molar ratio in all cases. The appropriate metal salt (0.5 mmol) was disolved in acetonitrile (50 mL) and added to a stirred solution of the corresponding macrocyclic ligand (0.5 mmol) in the same solvent (5 mL). The resulting solution was refluxed with magnetic stirring for 6–3 h and concentrated in a rotary evaporator until *ca.* 10 mL. The solution was allowed to precipitate; in some cases diethyl

Table 1
Crystal data and structure refinement for L^1·3H$_2$O, [Sr$_2$(L^2-H)$_2$(ClO$_4$)$_2$] and [Ca$_2$(L^{2}H)$_2$(ClO$_4$)$_2$]·2.5CH$_3$CN.

	L^1·3H$_2$O	[Sr$_2$(L^2-H)$_2$(ClO$_4$)$_2$]	[Ca$_2$(L^2-H)$_2$(ClO$_4$)$_2$]·2.5CH$_3$CN
Empirical formula	C$_{22}$H$_{36}$N$_4$O$_5$	C$_{29}$H$_{37}$ClN$_4$O$_7$Sr	C$_{34}$H$_{44.5}$ClN$_{6.5}$O$_7$Ca
Formula weight	436.55	676.70	731.79
T (K)	293(2)	293(2)	293(2)
λ (Å)	0.71073	0.71069	0.71073
Crystal system	triclinic	orthorhombic	triclinic
Space group	$P\bar{1}$)	$Pbca$	$P\bar{1}$)
Unit cell dimensions			
a (Å)	9.0553(13)	12.265(5)	11.734(3)
b (Å)	10.8132(16)	20.877(5)	13.159(3)
c (Å)	12.4085(18)	24.554(5)	13.339(3)
α (°)	99.119(3)	90.000(5)	78.585(4)
β (°)	92.182(3)	90.000(5)	81.065(5)
γ (°)	91.854(3)	90.000(5)	64.391(4)
V (Å^3)	1197.9(3)	6287(3)	1814.8(8)
Z	2	8	2
D_{calc} (g/cm^3)	1.210	1.430	1.339
Absorption coefficient (mm^{-1})	0.086	1.850	0.302
$F(000)$	472	2800	774
Crystal size (mm^3)	0.59 × 0.34 × 0.32	0.61 × 0.30 × 0.16	0.36 × 0.18 × 0.07
θ (°)	1.66–26.37	1.95–26.37	1.56–26.42
Index ranges	$-11 \leqslant h \leqslant 11, -13 \leqslant k \leqslant 13, 0 \leqslant l \leqslant 15$	$0 \leqslant h \leqslant 15, 0 \leqslant k \leqslant 26, 0 \leqslant l \leqslant 3$	$-14 \leqslant h \leqslant 14, 15 \leqslant k \leqslant 16, 0 \leqslant l \leqslant 16$
Reflections collected	8636	25470	20518
Independent reflections (R_{int})	4878 (0.0226)	6439 (0.0356)	7392 (0.0428)
Completeness to theta	(99.4%) 26.37	(100%) 26.37	(99.1%) 26.42
Absorption correction	empirical	empirical	empirical
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	4878/15/317	6439/0/380	7392/0/469
Goodness-of-fit on F^2	1.016	1.010	1.022
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0707$, $wR_2 = 0.2206$	$R_1 = 0.0414$, $wR_2 = 0.1009$	$R_1 = 0.0612$, $wR_2 = 0.1538$
R indices (all data)	$R_1 = 0.1167$, $wR_2 = 0.2629$	$R_1 = 0.0687$, $wR_2 = 0.1136$	$R_1 = 0.0969$, $wR_2 = 0.1820$
Largest difference peak and hole (e Å^3)	0.682 and −0.262	0.855 and −0.525	2.253 and −0.716