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Pentanuclear Ba(II) Complex of a Macrocyclic Ligand

**Alberto Freiría, Rufina Bastida,* Mª del Carmen Fernández-Fernández, Alejandro Macías,
Laura Valencia,* and Manuel Vicente**

*Departamento de Química Inorgánica, Universidad de Santiago de Compostela,
Avda. de las Ciencias s/n 15782, Santiago de Compostela, Spain*

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We report here the first pentanuclear Ba(II) complex of a new tri-aza, tri-oxa macrocycle with two carboxymethyl “arms” pending from two N atoms, H_2L^2. The crystal structure corresponds to the formula $[Ba_5(H_{0.375}L^2)_4(ClO_4)(CH_3CH_2OH)(H_2O)_2](ClO_4)_{2.5}\cdot 9.5H_2O$ and reveals the presence of four molecules of the ligand surrounding five Ba(II) ions, giving rise to an unusual structure with the metal ions inside a spherical organic cavity.

1. Introduction

The literature features descriptions of the structures of several pentanuclear Ba(II) cluster compounds synthesized by reaction of barium derivatives with diketones[1−3] and phenolic compounds.[4] Many mono- and dinuclear complexes of macrocyclic ligands have also been reported,[5−7] but as far as we know the only endomacrocyclically coordinated pentanuclear complex of a macrocyclic ligand to have been characterized hitherto is a pentamanganese(II) complex of the [2+2] tetraimine derived from 2,6-diacetylpyridine and 1,3-diaminopropan-2-ol, which was obtained from the corresponding mononuclear Ba(II) complex by transmetalation.[8] Here, we describe the structure of a pentanuclear Ba(II) complex of a new macrocyclic ligand H_2L^2 (Scheme 1) in which four of the five Ba(II) ions are endomacrocyclically coordinated.

Although the macrocyclic skeleton of H_2L^2 is not large enough to accommodate multiple metal atoms, its carboxylic side chains enhance its capacity for coordination, and, in this case, an unusual structure having five Ba(II) metal ions inside a spherical organic cavity has been obtained.

2. Experimental Section

2.1. Physical Measurements. Elemental analyses were carried out by the University of Santiago de Compostela Microanalytical Service on Carlo Erba EA-1108 and Leco CNHS-932 Microanalyzers. IR spectra were recorded as KBr disks using Bruker IFS-66V and Bio-Rad 175C spectrophotometers. NMR spectra were recorded using Bruker DPX-250, AMX-300, and AMX-500 spectrometers. Positive-ion FAB mass spectra were recorded on a Micromass AUTOSPEC spectrometer using a 3-nitrobenzyl alcohol (NOBA) matrix.

2.2. Chemicals and Starting Materials. Pyridine-2,6-dicarbaldehyde,[9] 1,11-diamine-3,6,9-trioxaundecane,[10] and 6,9,12-trioxa-3,15,21-triazabicyclo[15.3.1]henicosa-1(20),17(21),18-triene (L) were prepared by published procedures.[11] All others chemicals were of reagent grade and used as supplied without further purification. The organic solvents were purified by standard methods.[12]

Caution: Although no problems were encountered in this work, all perchlorates are prone to explosion and must be handled with care.

2.3. Synthesis of L^1. To a refluxing solution of 6,9,12-trioxa-3,15,21-triazabicyclo[15.3.1]henicosa-1(20),17(21),18-triene, L (1.47 g, 5 mmol) and sodium carbonate (0.8 g, 15 mmol) in acetonitrile (400 mL) was added a solution of ethyl bromoacetate (1.4 mL, 11 mmol) in acetonitrile (40 mL) under an atmosphere of N_2. The

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* Author to whom correspondence should be addressed. E-mail: qilaura@usc.es.

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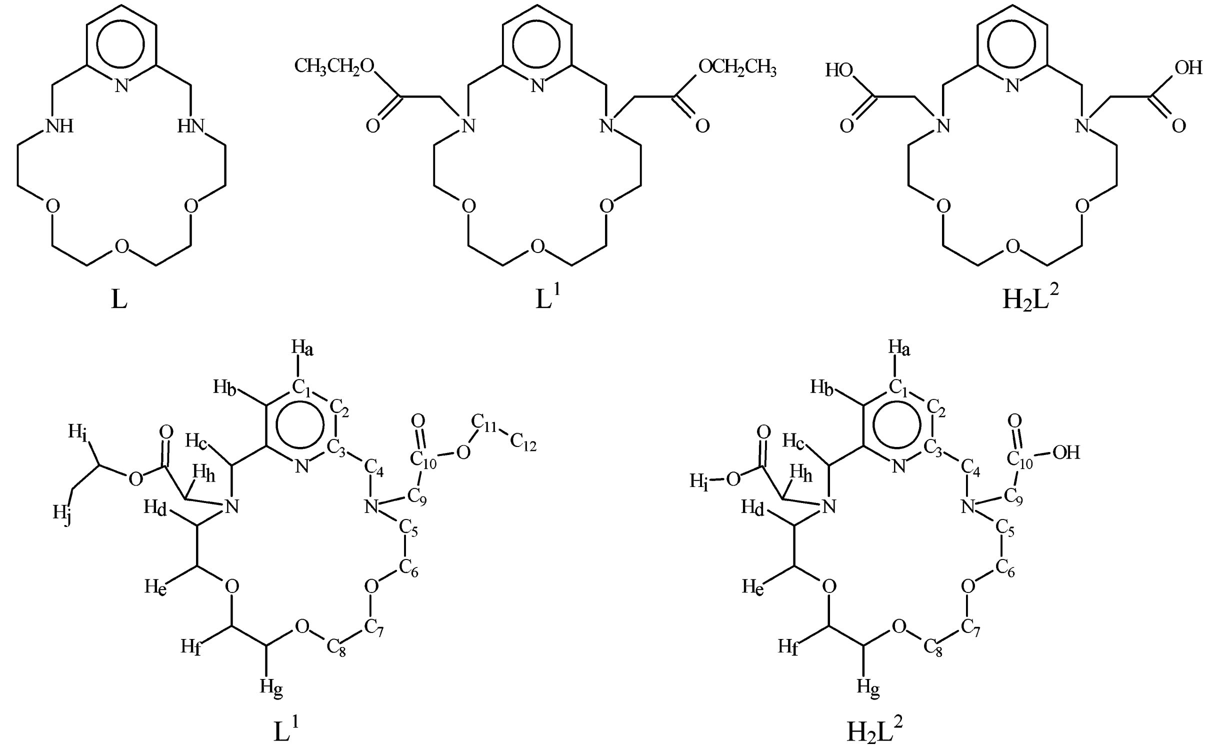
Scheme 1. The Macrocyclic Precursors L and L^1 and the Dicarboxylic Pendant-Armed Macrocycle H_2L^2



mixture was heated under reflux with magnetic stirring for 8 h. The reaction mixture was filtered and solvent evaporated on a rotary evaporator. The resulting residue was taken up in dichloromethane (50 mL) and washed with water (4 × 20 mL). The combined extracts were dried over $MgSO_4$, filtered, and evaporated under reduced pressure, to leave a brown oil. Yield: 81%. Anal. Calcd for $C_{23}H_{37}N_3O_7 \cdot 1.5H_2O$: C, 56.0; N, 8.5; H, 8.1. Found: C, 56.2; N, 8.3; H, 8.5. MS (FAB, *m/z*): 468 $[L^1 + H]^+$. IR (NaCl windows, cm^{-1}): ν(C=O) 1738, ν(Py) 1591, 1455. ^1H NMR ($CDCl_3$) δ(ppm): 7.60 (t, 1H, H_a), 7.30 (d, 2H, H_b), 4.16 (c, 4H, H_i), 4.01 (s, 4H, H_c), 3.47 (m, 16H, H_e, H_f, H_g, H_h), 2.90 (t, 4H, H_d), 1.26 (t, 6H, H_j). ^{13}C NMR ($CDCl_3$), δ(ppm): 137.4 (C_1), 122.2 (C_2), 159.3 (C_3), 60.9 (C_4), 70.9 (C_6, C_7, C_8), 57.2 (C_9), 53.9 (C_5), 172.2 (C_{10}), 60.9 (C_{11}), 14.8 (C_{12}). The compound is air stable, soluble in chloroform, dichloromethane, methanol, ethanol, water, and acetone, and insoluble in diethyl ether.

2.4. Synthesis of H_2L^2. The synthesis of the ligand H_2L^2 was achieved starting from L^1. L^1 (1 mmol, 0.47 g) was dissolved in water (60 mL), and sodium hydroxide (2.2 mmol, 0.10 g) was added. The solution was magnetically stirred at 60 °C for 9 h and allowed to cool. A 5% solution of HCl was added until pH 7, and the solution was concentrated to dryness. The residue was dissolved in ethanol, cooled to −20 °C, filtered, and the solution evaporated to dryness. The crude product was dissolved into a minimum volume of water and washed with dichloromethane (3 × 20 mL). Finally, the aqua layer was concentrated to dryness in a rotary evaporator to give the ligand H_2L^2, as the majority product, as a brown oil-solid, and dried under vacuum. The analytical data show that some trace amounts of NaCl impurities are present. Attempts to obtain the pure product were unsuccessful. MS (FAB, *m/z*): 412 $[H_2L^2 + H]^+$. IR (NaCl windows, cm^{-1}): ν(O−H) 3290 (sh); ν(C=O) 1711, 1638, ν(Py) 1454, 1593. ^1H NMR (D_2O), δ(ppm): 7.87 (t, 1H, H_a), 7.43 (d, 2H, H_b), 4.50 (sw, 4H, H_c), 3.42 (sw, 4H, H_d), 3.81 (m, 4H, H_e), 3.54 (sw, 4H, H_h), 3.66 (m, 8H, H_f, H_g). ^{13}C NMR (D_2O), δ(ppm): 142.7 (C_1), 127.9 (C_2), 154.8 (C_3), 61.1 (C_4), 57.4 (C_5), 67.9 (C_6), 58.5 (C_9), 72.8 (C_7, C_8), 175.3 (C_{10}). The compound is air stable, soluble in water, methanol, ethanol, and acetonitrile, and insoluble in diethyl ether and dimethyl sulfoxide.

2.5. Synthesis of $[BaH_2L^2](ClO_4)_2$. To an ethanolic solution (80 mL) of H_2L^2 (0.5 mmol, 0.1205 g) was added a solution of hydrated barium perchlorate (0.5 mmol) in ethanol (30 mL), and the solution was heated at reflux for 4 h. The solution was concentrated until 10−15 mL, and the precipitate was filtered off and dried in vacuo. The complex was found to be air stable and soluble in water, acetone, acetonitrile, low soluble in methanol and ethanol, and it is insoluble in diethyl ether, dimethyl sulfoxide dichloromethane, and chloroform.

Yield: 48%. Anal. Calcd for $C_{19}H_{29}N_3O_{15}Cl_2Ba$: C, 30.5; N, 5.6; H, 3.9. Found: C, 30.6; N, 5.7; H, 4.1. MS (FAB, *m/z*): 548 $[BaH_2L^2]^+$. IR (KBr, cm^{-1}): ν(C=O) 1705; ν(Py) 1585, 1449; $\nu(ClO_4^-)$ 1121, 1095, 636, 625. Λ_M (DMF): 159 Ω^{-1} cm^2 mol^{-1} (2:1 electrolyte). Color white.

2.6. Crystallographic Study of $[Ba_5(H_{0.375}L^2)_4(ClO_4)(CH_3CH_2OH)(H_2O)_2](ClO_4)_{2.5} \cdot 9.5H_2O$. Colorless prisms suitable for X-ray diffraction of $[Ba_5(H_{0.375}L^2)_4(ClO_4)(CH_3CH_2OH)(H_2O)_2](ClO_4)_{2.5} \cdot 9.5H_2O$ were obtained by recrystallization of $[BaH_2L^2](ClO_4)_2$ in ethanol/water. Measurements were made on a MACH3 Enraf Nonius using graphite monochromated Mo Kα radiation.

Crystal data, data collection parameters, and convergence results are listed in Table 1. All data were corrected by Lorentz and polarization effects. Empirical absorption correction was also applied.[13] Complex scattering factors were taken from the program package SHELXTL.[14] The structure was solved by direct methods using SHELX-97,[15] which revealed the position of all non-hydrogen

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Table 1. Crystallographic Data and Structure Refinement for $[Ba_5(H_{0.375}L^2)_4(ClO_4)(CH_3CH_2OH)(H_2O)_2](ClO_4)_{2.5}\cdot 9.5H_2O$

empirical formula	$C_{78}H_{92}Ba_5Cl_{3.50}N_{12}O_{54.50}$
formula weight	2880.41
temperature	293(2) K
wavelength	0.71073 Å
crystal system	monoclinic
space group	*P*21/*n*
a, Å	16.649(3)
b, Å	28.644(7)
c, Å	24.366(5)
β, deg	95.540(19)
volume	11 566(4) Å^3
Z	4
density (calculated)	1.654 Mg/m^3
absorption coefficient	1.853 mm^{-1}
final *R* indices [$I > 2\sigma(I)$]^a	$R_1 = 0.0604$, $wR_2 = 0.1456$
R indices (all data)	$R_1 = 0.2280$, $wR_2 = 0.1901$

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

atoms, and it was 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 generated using the CAMERON tool graphic.

3. Results and Discussion

3.1. Synthesis and Characterization of L^1. The new pendant-armed macrocycle L^1 has been synthesized by *N*-alkylation of the oxaazamacrocyclic precursor L with ethylbromoacetate in the presence of Na_2CO_3 in acetonitrile. The compound was isolated as a brown oil (81% yield) and was found to be stable in air and soluble in water and in most common organic solvents. The ligand was characterized by elemental analysis, FAB MS, and ^1H and ^{13}C NMR spectroscopy. Positive-ion FAB mass spectrometry provides evidence for the presence of the pendant-armed ligand (*m*/*z* 468, assignable to $[L^1 + H]^+$). The disappearance of the secondary amine stretch in the IR spectrum further confirms that alkylation took place; this band appears at 3245, 3324 cm^{-1} in the precursor ligand L. Due to the incorporation of ethyl acetate pendant arms into the macrocyclic backbone, the IR spectrum shows a strong band at 1738 cm^{-1} associated with the ν(C═O) vibration.

The ^1H and ^{13}C NMR spectra of L^1 have been recorded in $CDCl_3$ as solvent and confirm the integrity of the ligand and its stability in solution. The assignment of the proton signals was based upon standard 2D homonuclear (COSY) and $^1H/^{13}C$ heteronuclear spectra (HMQC). The ^1H NMR spectrum features the disappearance of the signal due to the amine protons at 2.99 ppm, present in L, and the appearance of new signals at 4.16, 3.47, and 1.26 ppm, corresponding to the pendant-arm protons.

3.2. Synthesis and Characterization of H_2L^2. The new ligand H_2L^2 was synthesized from the previously described armless parent compound L^1, by hydrolysis of the ester groups with sodium hydroxide in water. The new dicarboxylic ligand H_2L^2 was isolated as an air-stable brown oil as the majority product. The elemental analysis showed that some impurities of NaCl are present. Attempts to obtain the pure product were unsuccessful.

Positive-ion FAB mass spectrometry provides evidence for the presence of the new pendant-armed ligand (*m*/*z* 412, assignable to $[H_2L^2 + H]^+$). The spectrum shows a peak at higher molecular mass (*m*/*z* 434) that has been assigned to the fragment $[H_2L^2 + Na]^+$, indicative of some impurity of NaCl from the synthesis of the ligand. The IR spectrum shows bands corresponding to the carboxylic group at ca.1711 and 1638 cm^{-1}; the position of this last band could be indicative of intramolecular hydrogen-bond interactions.[16,17] Bands attributable to ν(OH) cannot be observed due to the existence of a broad band at ca. 3400 cm^{-1} with a shoulder at ca. 3290 cm^{-1} assignable to the stretching modes of water. The spectrum exhibits medium to strong bands at ca. 1593, 1454 cm^{-1} as expected for the two highest-energy ν(C═N)py and ν(C═C) vibrations.

The ^1H and ^{13}C NMR spectra were recorded in D_2O and confirm the integrity of the ligand and its stability in solution. The assignments of the proton signals were based upon standard 2D homonuclear (COSY) and $^1H/^{13}C$ heteronuclear spectra (HMQC). The ^1H NMR spectrum features the disappearance of the signals due to the $-CH_2-CH_3$ protons of the ester groups, present in L^1.

Reaction of H_2L^2 in methanol with hydrated barium perchlorate in a 1:1 mole ratio afforded a good yield of the analytically pure product $[BaH_2L^2](ClO_4)_2$, which was identified and characterized by analytical and spectroscopic techniques. Its mass spectrum exhibits a peak at 548 amu that is attributable to $[BaH_2L^2]^+$. Its IR spectrum, recorded from KBr disks, shows the ν(C═O) band at 1705 cm^{-1} (a position typical of non-hydrogen-bonded, undeprotonated carboxyl groups; cf. 1638 cm^{-1} in the spectrum of the free ligand H_2L^2, in which hydrogen bonding is suggested[17]) and shows neither the symmetric nor the antisymmetric vibrations expected of carboxylate groups. Unfortunately, the presumed ν(OH) vibrations are masked by a broad band around 3400 cm^{-1} that is attributed to trace amounts of water in the KBr disks.

In the ^1H NMR spectrum of the complex in deuterated water, coordination via the pyridine protons is shown by their appearing upfield of their positions in the spectrum of H_2L^2 (as a triplet at 7.38 and a doublet at 6.90 ppm). The aliphatic signals are very broad (because of fast conformational interconversion of the ethylene linkages), but are likewise shifted upfield, suggesting coordination of all of the donor atoms.

Although the macrocyclic skeleton of H_2L^2 is not large enough to accommodate multiple metal atoms, its carboxylic side chains enhance its capacity for coordination. Slow concentration of a solution of $[BaH_2L^2](ClO_4)_2$ in ethanol/water afforded colorless crystals that X-ray crystallography showed to be composed of supramolecular units of formula $[Ba_5(H_{0.375}L^2)_4(ClO_4)(CH_3CH_2OH)(H_2O)_2](ClO_4)_{2.5}\cdot 9.5H_2O$ in which four mononuclear endomacrocyclic complexes surround a central barium atom (Figures 1 and 2). The ligand molecules form two pairs as two pairs of hands holding an

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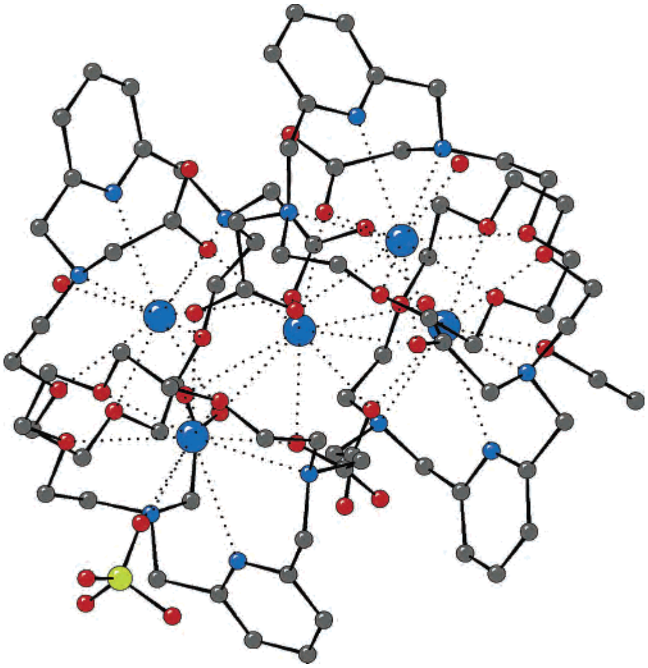

Figure 1. Crystal structure of $[Ba_5(H_{0.375}L^2)_4(ClO_4)(CH_3CH_2OH)(H_2O)_2](ClO_4)_{2.5}\cdot 9.5H_2O$.

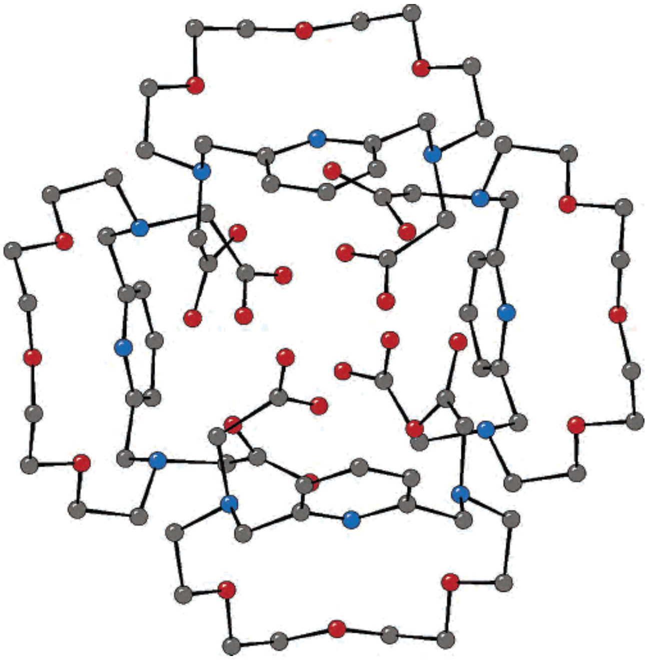

Figure 2. Arrangement of the four macrocycles in $[Ba_5(H_{0.375}L^2)_4(ClO_4)(CH_3CH_2OH)(H_2O)_2](ClO_4)_{2.5}\cdot 9.5H_2O$.

invisible ball with Ba(5) at its center. The molecules in each pair face each other with their pyridine rings closer than their oxoalkane fragments (the intercentroid distance between the two pyridine rings is 7.2 Å in one pair and 7.6 Å in the other, and the angle between these rings is 48.6° in the former case and 31.5° in the latter) and their carboxylic side chains pointing inward to form a hydrophilic core around Ba(5). The two pairs of ligands are mutually inverted, and their midplanes (the planes containing the two pyridine nitrogens and the corresponding *para* carbons of each pair) are almost at right angles to each other [dihedral angle 89.53(14)°].

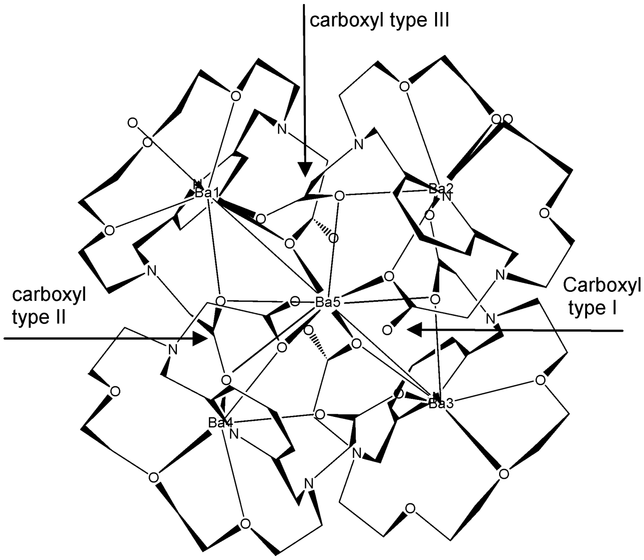

Figure 3. Schematic diagram showing the coordination pattern in the new complex when all carboxymethyls have their 75% occupancy conformation.

The geometries of the four ligand molecules are not identical but are very similar. None are folded or twisted, the average rms deviation of the six donor atoms in the macrocyclic skeleton from their least-squares plane being only 0.406 Å. The endomacrocyclic metal ions lie on the same side of this plane as Ba(5), at an average distance of 0.77 Å. Both of the side chains of each ligand are disordered, adopting two positions with occupancies of 75% and 25%, and the most-occupied positions are not the same for all four ligands. In each ligand, one carboxyl group forms a monodentate bridge between Ba(5) and the endomacrocyclic metal of that ligand (carboxyl type I), but the two ligand pairs differ with respect to the coordination of the other carboxyl group: in one pair, it chelates Ba(5) and at the same time coordinates, through different oxygens, to the endomacrocyclic metal atoms of both its own and a neighboring ligand (carboxyl type II); in the other pair, one of its oxygens coordinates to the endomacrocyclic metal of a neighboring ligand, while the other bridges between Ba(5) and its own endomacrocyclic metal (carboxyl type III) (see Figure 3).

The geometry of this pentanuclear cluster is intermediate between square planar and tetrahedral. The average distance between the endomacrocyclic Ba(II) ions and Ba(5) is 4.335 Å (cf., 4.22−4.37 Å in other polynuclear Ba(II) complexes).[3] All of the barium ions are 10-coordinated, and in no case does the coordination geometry correspond even approximately to any regular polyhedron. The endomacrocyclic ions are each bound to the six donors in the corresponding macrocycle, one carboxyl oxygen in each of the side chains of this molecule, one carboxyl oxygen belonging to an adjacent ligand, and another oxygen that belongs to a perchlorate anion for Ba(1), to an ethanol molecule for Ba(2), and to water molecules for Ba(3) and Ba(4) (Figure 3). Ba(5) is coordinated to one oxygen of each of the four carboxyl groups of one of the ligand pairs, and to three carboxyl oxygens of each of the other ligands. The Ba−N distances, 2.91−2.99 Å, are all within the expected range,[18−20] and all of the Ba−O distances are similar to those reported previously for this kind of ligand:[21−23] the shortest, 2.65(3) Å, binds Ba(1) to one of the oxygens of a Type III carboxyl, while the longest, 3.104(9) Å, binds Ba(5) to one of the oxygens of a Type II carboxyl.

The crystal exhibits disorder not only with respect to the positions of the ligand side chains, but also with respect to the numbers of uncoordinated molecules in the asymmetric unit, with an average of 9.5 water molecules and 2.5 perchlorate anions. This latter disorder further implies disorder with respect to the protonation status of the carboxyl groups, because it means that the neutrality of the complex requires an average 6.5 to be deprotonated. It was not possible to locate any hydrogen atoms crystallographically.

4. Conclusion

We report here an endomacrocyclically coordinated pentanuclear Ba(II) complex of a macrocyclic ligand, a new triaza, tri-oxa macrocycle with two carboxymethyl "arms" pending from two N atoms, H_2L^2. The complex shows an unusual spherical crystal structure with formula $[Ba_5(H_{0.375}L^2)_4(ClO_4)(CH_3CH_2OH)(H_2O)_2](ClO_4)_{2.5}\cdot 9.5H_2O$, in which four mononuclear endomacrocyclic Ba(II) complexes surround a central barium atom. The five barium ions are 10-coordinated, and in no case does the coordination geometry correspond even approximately to any regular polyhedron.

Acknowledgment. We thank Dr. Ricardo Alonso of the Department of Organic Chemistry, University of Santiago de Compostela, for assistance with the experimental work, and the Xunta de Galicia for financial support under contract PGIDT04PXIB20901PR. X-ray diffraction was performed in the facilities of RIAIDT (University of Santiago de Compostela).

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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