

Barium Templating Schiff-Base Lateral Macrobicycles

David Esteban,[†] Daniel Bañobre,[†] Rufina Bastida,[‡] Andrés de Blas,^{*,†} Alejandro Macías,[‡] Adolfo Rodríguez,[‡] Teresa Rodríguez-Blas,^{*,†} David E. Fenton,[§] Harry Adams,[§] and José Mahía^{||}

Departamento de Química Fundamental e Industrial, Universidade da Coruña, Campus da Zapateira s/n 15071 La Coruña, Spain, Departamento de Química Inorgánica, Universidad de Santiago, Avda. de las Ciencias s/n 15706, Santiago de Compostela, Spain, Chemistry Department, The University, Sheffield S3 7HF, U.K., and Servicios Xerais de Apoio á Investigación, Universidade da Coruña, Spain

Received September 17, 1998

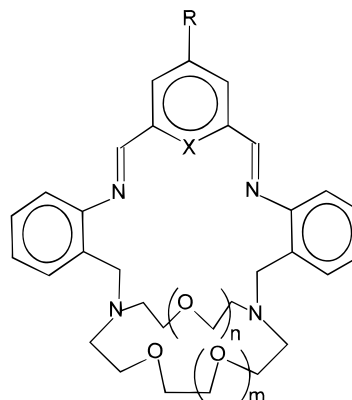
Schiff-base lateral macrobicycles containing two different binding units, a rigid and unsaturated N_2X set (X : N, O) and a flexible and cyclic N_2O_n set, linked by two aromatic bridges, have been prepared by reaction of the appropriate bibrachial diamines N,N' -bis(aminobenzyl)-diazacrown and diformyl precursors in the presence of Ba(II) as templating agent. The expected cryptands do not form in the absence of the cation; the presence of this metal ion is necessary to orient the diamine precursor in a syn conformation. Comparison of the X-ray crystal structures of the barium complex of the bibrachial diamine N,N' -bis(2-aminobenzyl)-1,10-diaza-15-crown-5 and the barium complex of the cryptand derived from it incorporating a pyridine unit indicates that the encapsulation of the metal ion is clearly more effective in the case of the cryptand. The coordination of Ba(II) ion to the pyridine nitrogen atom promotes the displacement of the metal into the cavity of the cryptand as well as important changes in the conformation of the crown unit, although the fold of the pendant arms remains practically unchanged. The cryptands reported constitute the first example of a novel family of macrobicycles.

Introduction

The design and synthesis of macropolycyclic molecules containing various binding subunits have received considerable attention in the past few years. Particularly, they can act as receptors binding more than one guest metal ion in close proximity; this fact may allow magnetic interaction or electron transfer studies depending on the nature of the encapsulated cations. According to the number of connecting bridges used for their construction and to the nature of the subunits used as building blocks, a variety of macropolycyclic structures may be envisaged: bis-macrocycles, axial macrobicycles, lateral macrobicycles, cylindrical macrotricyclic systems, and so on.¹

The potential of Schiff-base macrocyclic ligands in the selective coordination of metals is also of considerable current interest in the chemical literature,² and there has been an increase in interest in Schiff-base-derived cryptands and cryptates.^{3–8} Although numerous symmetric, and axial, cryptands have

Chart 1



L^3 : $m = n = 1$; $R = H$; $X = N$

L^4 : $m = n = 1$; $R = CH_3$; $X = C-OH$

L^5 : $m = 1$, $n = 2$; $R = H$; $X = N$

L^6 : $m = 1$, $n = 2$; $R = CH_3$; $X = C-OH$

previously been described, there is a deficiency of information concerning their lateral analogues.⁹ Herein, we present the novel family of Schiff-base cryptands shown in Chart 1, which constitutes the first example of lateral macrobicycles containing imine groups. They contain two different binding units, a rigid and unsaturated N_2X set (X : N, O, S, ...) and a flexible and cyclic N_2O_n set, linked by two aromatic bridges; since the former subunit is softer than the second one, this confers a heteroditopic character on the macrobicycles.

* Corresponding author, E-mail: ucambv@udc.es.

[†] Dpto. Q. Fundamental e Industrial, Universidade da Coruña.

[‡] Universidad de Santiago.

[§] The University, Sheffield.

^{||} Servicios Xerais de Apoio á Investigación, Universidade da Coruña.

- (1) (a) The term bibrachial lariet ether describes molecules that contain a crown ether ring with two pendant arms attached. Lateral macrobicycles are dissymmetrical molecules structurally based on the combination of two different binding subunits, a chelating one and a macrocyclic one; (b) Lehn, J.-M. *Pure Appl. Chem.* **1980**, *52*, 2441.
- (2) Guerriero, P.; Tamburini, S.; Vigato, P. A. *Coord. Chem. Rev.* **1995**, *139*, 17.
- (3) Timken, M. D.; Marritt, W. A.; Hendrikson, D. N.; Gagné R. A.; Sinn, E. *Inorg. Chem.* **1985**, *24*, 4202.
- (4) Jazwinski, J.; Lehn, J.-M.; Lilienbaum, D.; Ziessel, R.; Guilhem, J.; Pascard, C. *J. Chem. Soc., Chem. Commun.* **1987**, 1691.
- (5) MacDowell, D.; Nelson, J. *Tetrahedron Lett.* **1988**, *29*, 385.
- (6) Tsubomura, T.; Sato, T.; Yasaku, K.; Sakai, K.; Kobayashi, K.; Morita, M. *Chem. Lett.* **1992**, 731.
- (7) Kumar, M.; Arán, V. J.; Navarro, P. *Tetrahedron Lett.* **1995**, *36*, 2161.

(8) Sato, T.; Suzuki, A.; Sakai, K.; Tsubomura, T. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 379.

(9) Nelson, J.; McKee, V.; Morgan, G. *Prog. Inorg. Chem.* **1998**, *47*, 167.

Experimental Section

Materials. The bibracchial lariat ethers *N,N'*-bis(*o*-aminobenzyl)-1,10-diaza-15-crown-5 (**L**¹) and *N,N'*-bis(*o*-aminobenzyl)-4,13-diaza-18-crown-6 (**L**²) were prepared as described previously.¹⁰ 2,6-Diformylpyridine^{11,12} and 2,6-diformyl-4-methylphenol¹³ were prepared according to literature methods. All other chemicals were purchased from commercial sources and used without further purification. Solvents were of reagent grade purified by the usual methods.

Caution! Although we have experienced no difficulties with the perchlorate salts, these should be regarded as potentially explosive and handled with care.

Preparation of the Complexes. [BaL¹](ClO₄)₂ (1a**).** A solution of Ba(ClO₄)₂·3H₂O (0.10 g; 0.25 mmol) in absolute ethanol (5 mL) was added with stirring to a solution of the ligand **L**¹ (0.11 g; 0.25 mmol) also in absolute ethanol (10 mL). The reaction mixture was stirred and refluxed for 6 h. During the reaction, a white precipitate appeared, which was collected by filtration, washed with absolute ethanol, and air-dried. Slow diffusion of diethyl ether into a solution of **1a** in acetonitrile gave crystals suitable for X-ray crystallography. Yield: 0.17 g (82%). Mp 280 °C dec. Anal. Calcd for C₂₄H₃₆N₄O₁₁BaCl₂: C, 37.7; H, 4.7; N, 7.3. Found: C, 37.7, H, 4.7; N, 7.3. ¹³C NMR (500 Mz, CD₃CN; δ, ppm): 144.3 (C₁), 134.0 (C₅), 130.6 (C₃), 124.8 (C₆), 122.3 (C₄), 120.9 (C₂), 69.95, 69.5, 68.4 (C₉, C₁₀, C₁₂), 58.4 (C₇), 54.5 (C₈), 53.9 (C₁₁). MS-FAB (*m/z*): 665 (**1a** - ClO₄), 565 (**1a** - 2ClO₄). IR (KBr disks): 3368, 3310 (NH₂), 1614, 1588, 1498, 1460 (C=C), 1140, 1109, 1088, 1065, 636, 625 (ClO₄) cm⁻¹.

[BaL¹](SCN)₂ (1b**).** The white complex was prepared as described for **1a** by using Ba(SCN)₂·3H₂O (0.07 g; 0.25 mmol). Yield: 0.14 g (85%). Mp 251 °C dec. Anal. Calcd for C₂₆H₃₆N₆O₃BaS₂: C, 45.7; H, 5.3; N, 12.3; S, 9.4. Found: C, 45.5, H, 5.3; N, 12.2; S, 9.8. ¹³C NMR (200 Mz, CD₃CN; δ, ppm): 145.0 (C₁), 133.8 (C₅), 130.5 (C₃), 124.6 (C₆), 121.75 (C₄), 120.4 (C₂), 69.9, 69.8, 68.7 (C₉, C₁₀, C₁₂), 59.2 (C₇), 55.1 (C₈), 54.0 (C₁₁). MS-FAB (*m/z*): 624 (**1b** - SCN), 565 (**1b** - 2SCN). IR (KBr disks): 3315, 3260 (NH₂), 1610, 1583, 1496, 1457 (C=C), 2059, 484 (SCN) cm⁻¹.

[BaL²](ClO₄)₂·2H₂O (2a**).** A solution of Ba(ClO₄)₂·3H₂O (0.08 g; 0.20 mmol) in absolute ethanol (30 mL) was added with stirring to a solution of the ligand **L**² (0.09 g; 0.20 mmol) also in absolute ethanol (45 mL). The solution was stirred and refluxed for 24 h. During the reaction, a white precipitate appeared, which was collected by filtration, washed with absolute ethanol, and air-dried. Yield: 0.13 g (75%). Anal. Calcd for C₂₆H₄₀N₄O₁₂BaCl₂·2H₂O: C, 36.9; H, 6.6; N, 5.2. Found: C, 36.6; H, 6.4; N, 5.0. MS-FAB (*m/z*): 709 (**2a** - ClO₄), 609 (**2a** - 2ClO₄). IR (KBr disks): 3330, 3220 (NH₂), 1601, 1575, 1496, 1445 (C=C), 1100, 625 (ClO₄) cm⁻¹.

[BaL²](SCN)₂ (2b**).** A solution of Ba(SCN)₂·3H₂O (0.16 g; 0.50 mmol) in absolute ethanol (30 mL) was added with stirring to a solution of the ligand **L**² (0.25 g; 0.50 mmol) also in absolute ethanol (125 mL). The solution was stirred and refluxed for 24 h. The solution was evaporated in vacuo until the appearance of a precipitate, which was repeatedly and alternately washed with diethyl ether and *n*-hexane. Yield: 0.27 g (75%). Mp: 142–145 °C. Anal. Calcd for C₂₈H₄₀N₆O₄-BaS₂: C, 46.3; H, 5.5; N, 11.6; S, 8.8. Found: C, 46.0, H, 5.3; N, 11.8; S, 8.7. MS-FAB (*m/z*): 668 (**2b** - SCN), 609 (**2b** - 2SCN). IR (KBr disks): 3385, 3250 (NH₂), 1603, 1504, 1464 (C=C), 2050, 470 (SCN) cm⁻¹.

[BaL³](ClO₄)₂ (3**).** A solution of Ba(ClO₄)₂·3H₂O (0.10 g; 0.25 mmol) in absolute ethanol (50 mL) was added with stirring to a solution of the bibracchial lariat ether **L**¹ (0.11 g; 0.25 mmol) also in absolute ethanol (120 mL). The mixture was vigorously stirred and heated while a solution of 2,6-diformylpyridine (0.04 g; 0.25 mmol) in absolute ethanol (60 mL) was added dropwise over 1 day. After the addition

was complete, the resulting pale yellow solution was stirred and refluxed for 3 h. The solution was filtered while hot and the filtrate half evaporated in vacuo. Upon cooling of the filtrate to room temperature, a pale yellow microcrystalline precipitate formed, which was collected by filtration. X-ray quality crystals were grown by slow diffusion of diethyl ether into a solution of **3** in acetonitrile. Yield: 0.20 g (88%). Mp 296 °C dec. Anal. Calcd for C₃₁H₃₇N₅O₁₁BaCl₂: C, 43.1; H, 4.3; N, 8.1. Found: C, 42.8; H, 4.2; N, 8.3. ¹³C NMR (500 Mz, CD₃CN; δ, ppm): 167.7, 165.1 (C₁) 152.1 (C₄), 151.8 (C₁₀), 140.5 (C₂), 132.5 (C₉), 130.7 (C₃), 130.5 (C₁₁), 129.5 (C₇), 127.1 (C₈), 120.4 (C₆) 69.0, 68.9, 68.7 (C₁₄, C₁₅, C₁₇), 59.3 (C₁₂), 59.3 (C₁₃), 51.0 (C₁₆). MS-FAB (*m/z*): 764 (**3** - ClO₄), 665 (**3** - 2ClO₄). IR (KBr disks): 1634 (C=N_{imi}), 1583, 1492, 1458 (C=N_{py}), (C=C), 1110 (ClO₄) cm⁻¹.

[BaL³](ClO₄)₂·EtOH (4**).** A solution of Ba(ClO₄)₂·3H₂O (0.10 g; 0.25 mmol) in absolute ethanol (50 mL) was added with stirring to a solution of the bibracchial lariat ether **L**¹ (0.11 g; 0.25 mmol) also in absolute ethanol (120 mL). The mixture was vigorously stirred and heated while a solution of 2,6-diformyl-4-methylphenol (0.04 g; 0.25 mmol) in absolute ethanol (60 mL) was added dropwise over 1 day. After the addition was complete, the resulting orange solution was stirred and refluxed for 2 h. The solution was filtered while hot and the filtrate evaporated in vacuo to 20 mL. Upon cooling of the filtrate to room temperature, a dark orange microcrystalline precipitate formed, which was collected by filtration. Yield: 0.17 g (70%). Mp 230 °C dec. Anal. Calcd for C₃₃H₄₀N₄O₁₂BaCl₂: C, 44.7; H, 5.9; N, 4.9. Found: C, 44.2; H, 5.8; N, 5.1. ¹³C NMR (200 Mz, CD₃CN; δ, ppm): 172.5, 164.5, 69.7, 68.9, 68.3, 57.8, 55.2, 53.9, 19.8. MS-FAB (*m/z*): 793 (**4** - ClO₄), 693 (**4** - 2ClO₄). IR (KBr disks): 1634 (C=N_{imi}), 1597, 1531, 1487, 1447 (C=C), 1187, 1090, 625 (ClO₄) cm⁻¹.

[BaL³](ClO₄)₂ (5a**).** The bibracchial lariat ether **L**² (0.20 g; 0.43 mmol) and Ba(ClO₄)₂·3H₂O (0.17 g; 0.43 mmol) were dissolved in absolute ethanol (400 mL). The mixture was vigorously stirred and heated while a solution of 2,6-diformylpyridine (0.06 g; 0.43 mmol) in 75 mL of absolute ethanol was added dropwise over 3 h. After the addition was complete, the resulting pale yellow solution was stirred and refluxed for 4 h. The solution was filtered while hot and the filtrate half evaporated in vacuo. Upon cooling of the filtrate to room temperature, a pale yellow precipitate formed, which was collected by filtration. Yield: 0.25 g (65%). Anal. Calcd for C₃₃H₄₁N₅O₁₂BaCl₂: C, 43.7; H, 4.5; N, 7.7. Found: C, 43.5; H, 4.8; N, 7.8. ¹³C NMR (200 Mz, CD₃CN; δ, ppm): 166.4 (C₁) 153.9 (C₄), 152.2 (C₁₀), 141.6 (C₂), 133.4 (C₉), 132.1 (C₃), 131.5 (C₁₁), 130.8 (C₇), 127.9 (C₈), 121.3 (C₆) 69.7, 69.0 (C₁₄, C₁₅), 59.3 (C₁₂), 60.4 (C₁₂), 57.6 (C₁₆). MS-FAB (*m/z*): 808 (**5a** - ClO₄), 709 (**5a** - 2ClO₄). IR (KBr disks): 1645 (C=N_{imi}), 1625, 1585, 1490, 1457 (C=N_{py}), (C=C), 1121, 1097, 1080, 623 (ClO₄) cm⁻¹.

[BaL³](SCN)₂·4H₂O (5b**).** The bibracchial lariat ether **L**² (0.12 g; 0.3 mmol) and Ba(SCN)₂·3H₂O (0.09 g; 0.3 mmol) were dissolved in absolute ethanol (150 mL). The mixture was vigorously stirred and heated while a solution of 2,6-diformylpyridine (0.04 g; 0.3 mmol) in 30 mL of absolute ethanol was added dropwise over 10 h. After the addition was complete, the resulting pale yellow solution was stirred and refluxed for 12 h. The solution was filtered while hot and the filtrate half evaporated in vacuo. Upon cooling of the filtrate to room temperature, a pale yellow precipitate formed, which was collected by filtration. Yield: 0.25 g (88%). Anal. Calcd for C₃₅H₄₁N₇O₄BaS₂·4H₂O: C, 46.9; H, 5.6; N, 10.9; S, 7.1. Found: C, 46.4; H, 5.3; N, 11.2; S, 7.1. MS-FAB (*m/z*): 767 (**5b** - SCN), 709 (**5b** - 2SCN). IR (KBr disks): 1645 (C=N_{imi}), 1625, 1584, 1487, 1456 (C=N_{py}), (C=C), 2051, 470 (SCN) cm⁻¹.

[BaL⁶](SCN)₂·2H₂O (6**).** The bibracchial lariat ether **L**² (0.16 g; 0.35 mmol) and Ba(SCN)₂·3H₂O (0.11 g; 0.35 mmol) were dissolved in absolute ethanol (300 mL). The mixture was vigorously stirred and heated while a solution of 2,6-diformyl-4-methylphenol (0.06 g; 0.35 mmol) in 65 mL of absolute ethanol was added dropwise over 1 day. After the addition was complete, the resulting pale yellow solution was stirred and refluxed for 2 days. The solution was filtered while hot and the filtrate half evaporated in vacuo. Upon cooling of the filtrate to room temperature, a pale yellow precipitate formed, which was collected by filtration. Yield: 0.15 g (48%). Anal. Calcd for C₃₇H₄₄N₆O₅-BaS₂·2H₂O: C, 50.0; H, 5.4; N, 9.5; S, 7.2. Found: C, 50.2; H, 5.4;

- (10) Esteban, D.; Bañobre, D.; Bastida, R.; De Blas, A.; Macias, A.; Rodriguez, A.; Rodriguez-Blas, T.; Mahía J.; Fenton, D. E.; Adams, H. *J. Chem. Soc., Dalton Trans.*, submitted for publication.
 (11) Papadopoulos, E. P.; Jarrar, A.; Issidorides, C. H. *J. Org. Chem.* **1966**, *31*, 615.
 (12) Jerchel, D.; Heider, J.; Wagner H. *Justus Liebigs Ann. Chem.* **1958**, *613*, 153.
 (13) Taniguchi, S. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2683.

Table 1. Crystallographic Details for Complexes [BaL¹(ClO₄)](ClO₄) (**1a**) and [BaL⁵(ClO₄)₂] (**3**)

	1a	3
empirical formula	C ₂₄ H ₃₆ BaCl ₂ N ₄ O ₁₁	C ₃₁ H ₃₇ BaCl ₂ N ₅ O ₁₁
fw	764.81	863.90
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>Pbca</i>
cryst system	monoclinic	orthorhombic
<i>Z</i>	4	8
<i>a</i> , Å	14.040(5)	20.600(1)
<i>b</i> , Å	14.042(6)	15.933(1)
<i>c</i> , Å	15.556(7)	22.487(1)
α, deg	90	90
β, deg	91.75(3)	90
γ, deg	90	90
<i>V</i> , Å ³	3065(2)	7380.8(2)
ρ(calc), g/cm ³	1.657	1.555
μ _{calc} , mm ⁻¹	1.532	1.283
radn (Mo Kα), Å	0.710 73	0.710 73
<i>T</i> , K	293(2)	298(2)
final <i>R</i> indices ^a	R1 = 0.0408	R1 = 0.0467
[<i>I</i> > 2σ(<i>I</i>)]	wR2 = 0.1002	wR2 = 0.0938
final <i>R</i> indices	R1 = 0.0576	R1 = 0.0919
(for all data)	wR2 = 0.1107	wR2 = 0.1097

^a R1 = $\sum||F_o| - |F_c||/\sum|F_o|$ and wR2 = $\{\sum[w(|F_o|^2 - |F_c|^2)]^2/\sum[w(F_o^4)]\}^{1/2}$.

N, 9.6; S, 6.9. MS-FAB (*m/z*): 737 (**6** - 2SCN). IR (KBr disks): 1624 (C=N_{im}), 1587, 1531, 1482, 1457 (C=C), 2052, 470 (SCN) cm⁻¹.

Measurements. Elemental analyses and FAB mass spectra were carried out by Servicios Xerais de Apoio á Investigación of the Universidade da Coruña: elemental analyses were carried out on a Carlo Erba 1180 elemental analyzer, and FAB mass spectra were recorded on a FISIONS QUATRO mass spectrometer with a Cs ion gun using 3-nitrobenzyl alcohol as matrix. ¹H and ¹³C NMR spectra were run on a Bruker AC 200 F or a Bruker WM-500 spectrometer. IR spectra were recorded, as KBr disks, using a Perkin-Elmer 1330 spectrophotometer. UV-vis spectra were run on a Uvikon 942 Plus spectrophotometer. Melting points were measured on a Gallenkamp instrument. Conductivity measurements were carried out with a Crison Micro CM 2201 conductivitymeter using 10⁻³ M solutions of the complexes in acetonitrile.

Crystal Structure Determination of Complex 1a. Three-dimensional, room temperature X-ray data were collected in the range 3.5° < 2θ < 50° on a Siemens P4 diffractometer by the ω scan method. Of the 6632 reflections measured, all of which were corrected for Lorentz and polarization effects and for absorption by the analysis of 10 azimuthal scans (minimum and maximum transmission coefficients 0.146 and 0.893), 4255 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$. The structure was solved by direct methods and refined by full-matrix least-squares methods on *F*². Hydrogen atoms were included in calculated positions and refined in the riding mode. Refinement converged at a final R1 = 0.0408 (wR2 = 0.1107 for all 5381 unique data, 379 parameters, mean and maximum δ/σ 0.000, 0.000), with allowance for the thermal anisotropy of all non-hydrogen atoms. Maximum and minimum final electron density: 0.805 and -0.822 e Å⁻³. A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0628P)^2 + 1.7380P]$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXL93¹⁴ as implemented on the Viglen 486dx computer. Crystal data and details on the data collection and refinement are summarized in Table 1.

Crystal Structure Determination of Complex 3. Room temperature X-ray data were collected in the range 5.4° < 2θ < 50° on a Siemens CCD SMART diffractometer by the ω scan method. Of the 37 454 reflections measured, all of which were corrected for Lorentz and polarization effects and for absorption using the SADABS program (minimum and maximum transmission coefficients 0.584 and 1.000), 3999 independent reflections exceeded the significance level $|F|/\sigma$

($|F|$) > 4.0. The structure was solved by direct methods and refined by full-matrix least-squares methods on *F*². Hydrogen atoms were included in calculated positions and refined in the riding mode. Refinement converged at a final R1 = 0.0467 (wR2 = 0.1097 for all 3999 unique data, 452 parameters, mean and maximum δ/σ 0.000, 0.000), with allowance for the thermal anisotropy of all non-hydrogen atoms. Maximum and minimum final electron density 0.551 and -1.378 e Å⁻³. A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0463P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXL97¹⁵ as implemented on a PC computer. Crystal data and details on the data collection and refinement are summarized in Table 1.

Results

Synthesis and Characterization of Complexes of the Bibracchial Lariat Ethers.¹ The reaction of the ligands **L**¹ or **L**² with barium salts (perchlorate or thiocyanate) in absolute ethanol gives white products with formulas [BaL¹]X₂ (X = ClO₄⁻, **1a**; SCN⁻, **1b**) and [BaL²]X₂ (X = ClO₄⁻, **2a**; SCN⁻, **2b**). Slow diffusion of diethyl ether into a solution of **1a** in acetonitrile gave crystals suitable for X-ray crystallography.

In the region 3500–3100 cm⁻¹, the infrared spectra of solid samples of complexes (KBr disks) show two bands at 3368 and 3310 cm⁻¹ for **1a**, 3315 and 3260 for **1b**, 3330 and 3220 for **2a**, and 3385 and 3250 cm⁻¹ for **2b**, corresponding to the ν_{as}(NH₂) and ν_s(NH₂) stretching frequencies of the coordinated amine groups, respectively. The absorption bands at ca. 1100 and 630 cm⁻¹ present in the spectra of the perchlorate compounds are assignable to the asymmetric ν_{as}(Cl–O) stretching and δ_{as}(O–Cl–O) bending modes of the perchlorate group, respectively. The highest energy band shows considerable splitting with four maxima at 1140, 1109, 1088, and 1065 cm⁻¹ for **1a**. Also the lowest energy band due to the bending mode splits, showing two maxima at 636 and 625 cm⁻¹ for **1a**, because of the coordination to the metal which results in distortion from tetrahedral symmetry. The band corresponding to ν_{as}(Cl–O) of the perchlorate group in the case of **2a** is uninformative with respect to the coordinate mode of this group as it appears as a very broad band centered at 1093 cm⁻¹. The position of the thiocyanate stretch at 2059 cm⁻¹ for **1b** and 2050 cm⁻¹ for **2b** suggests that this group is coordinated to the metal atom in both cases.^{16,17}

Conductivity measurements were carried out in 10⁻³ M acetonitrile solutions at 20 °C. The molar conductivity of the thiocyanate complexes (Λ_M = 173 and 172 cm² Ω⁻¹ mol⁻¹ for **1b** and **2b**, respectively) revealed that they behave as 1:1 electrolytes in acetonitrile.¹⁸ The molar conductance data in the same solvent for the perchlorate complexes (Λ_M = 286 and 307 cm² Ω⁻¹ mol⁻¹ for **1a** and **2a**, respectively) are in the range reported for 2:1 electrolytes,¹⁸ indicating that these complexes are completely dissociated in acetonitrile solution. On these data, it is clear that the structure of the complexes in solution must be different from that in the solid state in light of the X-ray crystal structure of **1a** discussed later.

The UV-vis spectra of **1** and **2** in acetonitrile solutions exhibit three intense charge transfer bands with λ_{max} at 209, 229, and 277 nm (**1a**), 214, 231, and 281 nm (**1b**), 209, 230, and 279 nm (**2a**), and 214, 230, and 280 nm (**2b**) due to π → π* transitions of the coordinated aniline pendant arms of the ligand.

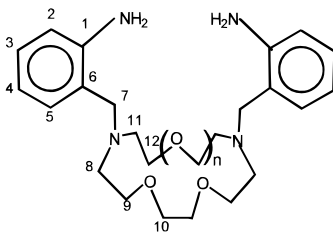
(15) Sheldrick, G. M. *SHELXL97, An integrated system for solving and refining crystal structures from diffraction data*; University of Göttingen: Göttingen, Germany 1997.

(16) Tandon, S. S.; McKee V. J. *Chem. Soc., Dalton Trans.* **1989**, 19.

(17) Habata Y.; Akabori S. *J. Chem. Soc., Dalton Trans.* **1996**, 3871.

(18) Geary, W. J. *Coord. Chem. Rev.* **1971**, 7, 81.

(14) Sheldrick, G. M. *SHELXL93, An integrated system for solving and refining crystal structures from diffraction data*; University of Göttingen: Göttingen, Germany, 1993.

Table 2. ^1H NMR Data for the Complexes **1a**, **1b**, **2a**, and **2b**

compd	NH ₂	H ₂	H ₄	H ₃	H ₅	H ₈ , H ₁₁	H ₇	H ₉	H ₁₀	H ₁₂
1a ^a	4.36 (s, br), 4H	7.07 (d), 2H	6.96 (t), 2H	7.31 (t), 2H	7.18(d), 2H	← 2.70 (m), 8H →	← 3.59 (m), 16H →			
1b ^b	4.55 (s, br), 4H	7.07 (d), 2H	6.91 (t), 2H	7.28 (t), 2H	7.16 (d), 2H	← 2.72 (m), 8H →	← 3.62 (m), 16H →			
2a ^c	4.29 (s), 4H	7.04 (d), 2H	6.94 (t), 2H	7.29 (t), 2H	7.20 (d), 2H	2.84–2.67 (br), 8H	← 3.57 (m), 12H →		3.70 (d), 8H	
2b ^d	4.69 (s), 4H	← 7.29 (d), 4H →		← 7.05 (t), 4H →		2.97 (t), 8H	3.89 (s), 4H	3.77 (t), 8H	3.28–3.10 (m) 8H	

^a Conditions: Assignment supported by 2D H,H COSY, HMQC, and HMBC experiments at $T = 293$ K, CD_3CN , 500 MHz. $J_{2,3} = 7.08$ Hz, $J_{4,3} = J_{4,5} = 7.48$ Hz, $J_{3,2} = J_{3,4} = 7.48$ Hz, $J_{5,4} = 7.35$ Hz. Chemical shifts (without assignment) of the different multiplets for crown protons are given only. ^b Conditions: $T = 293$ K, CD_3CN , 200 MHz. $J_{2,3} = 7.33$ Hz, $J_{4,3} = J_{4,5} = 7.33$ Hz, $J_{3,2} = J_{3,4} = 7.33$ Hz, $J_{5,4} = 7.33$ Hz. Chemical shifts (without assignment) of the different multiplets for crown protons are given only. ^c Conditions: $T = 293$ K, CD_3CN , 200 MHz. $J_{2,3} = 7.32$ Hz, $J_{4,3} = J_{4,5} = 7.32$ Hz, $J_{3,2} = J_{3,4} = 7.32$ Hz, $J_{5,4} = 7.81$ Hz. Chemical shifts (without assignment) of the singlet and triplet for protons 7 and 9 are given only. ^d Conditions: $T = 293$ K, CD_3CN , 500 MHz. Chemical shifts (without assignment) of the different multiplets for aromatic and crown protons are given only.

The proton (Table 2) and ^{13}C NMR spectra of **1a**, **1b**, **2a**, and **2b** were run in CD_3CN solution. Significant changes in the chemical shifts, the structures of the signals, and even the number of signals compared with those of the uncoordinated ligands¹⁰ can be observed in the ^1H NMR spectra of the complexes. While signals corresponding to the aromatic rings are shifted downfield, the singlet signal of amine protons is shifted upfield by 0.63 ppm for **1a**, 0.44 ppm for **1b**, 0.68 ppm for **2a**, and 0.28 ppm for **2b**, confirming the coordination of the amine groups to the metal. The most complicated region of these spectra is that corresponding to the chemical shifts of the protons of the ethylenic and methylenic chains. The coordination to the metal makes the ligand, usually, more rigid, limiting the interchange, and so the protons fail to be equivalent, appearing as more signals. Even so, the spectra of the barium complexes are simpler than the spectra of lead(II) and cadmium(II) compounds,¹⁰ and those of L^2 also are simpler than those of L^1 .

X-ray Crystal Structure of 1a. Table 3 summarizes selected bond and angles. Crystals of **1a** contain the cation $[\text{BaL}^1(\text{ClO}_4)]^+$ and a well-separated perchlorate anion. Figure 1 illustrates the structure of the cation. It contains a BaN_4O_5 core with the seven heteroatoms of L^1 coordinated to the barium as well as to a perchlorate group in a bidentate mode. The metal ion is almost symmetrically placed with respect to the cavity of the ligand and situated 1.781 Å above the plane defined by the three oxygen atoms of the bibracchial lariat ether and the pivotal nitrogen atom N(3) (deviation from planarity is 0.009 Å). Both aniline pendant arms are orientated on the same side, resulting a syn conformation, unlike the anti conformation found for the free ligand.¹⁰ Angles N(4)–C(11)–C(12) and N(3)–C(18)–C(19) are very similar, with values of 114.4° and 112.7°, respectively. Planes containing the aromatic rings form a dihedral angle of 42.8°. In this barium compound there are no hydrogen bonds between amine hydrogen atoms and perchlorate groups as occurs in the corresponding lead(II) complex.¹⁰

Synthesis and Characterization of Complexes of Schiff-Base Lateral Macrobicycles.¹ The reactions between equimolar amounts of 2,6-diformylpyridine and N,N' -bis(2-aminobenzyl)-1,10-diaza-15-crown-5 (L^1) or N,N' -bis(2-aminobenzyl)-4,13-diaza-18-crown-6 (L^2) in the presence of barium perchlorate in absolute ethanol under the conditions described in the Experimental Section gave analytically pure products $[\text{BaL}^3](\text{ClO}_4)_2$

(**3**) and $[\text{BaL}^5](\text{ClO}_4)_2$ (**5a**) with yields of 88% and 65%, respectively. Reaction between 2,6-diformyl-4-methylphenol and L^1 also in the presence of barium perchlorate led to the expected $[\text{BaL}^4](\text{ClO}_4)_2 \cdot \text{EtOH}$ (**4**) in a yield of 70%. X-ray quality crystals were grown by slow diffusion of diethyl ether into an acetonitrile solution of **3**.

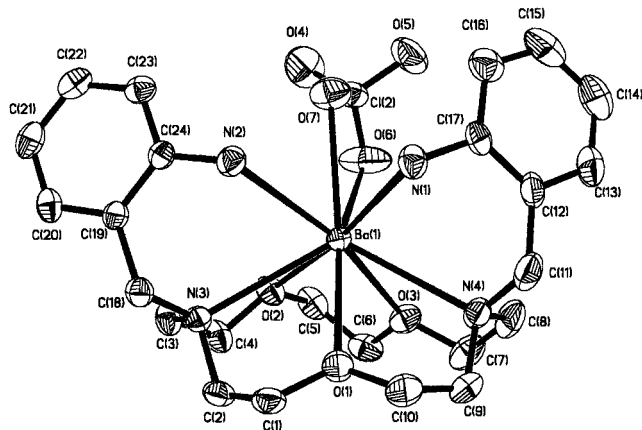
The presence of an absorption at 1634 cm^{-1} for **3** and **4**, 1645 cm^{-1} for **5a**, attributable to the $\nu(\text{C}=\text{N})_{\text{imine}}$ stretching frequency in their infrared spectra (KBr disks), as well as the absence of carbonyl and amine bands confirms that condensation and cyclization has occurred. The perchlorate stretch is broadened and, in some cases, split due to either coordination or the presence of a hydrogen bond, making assignments of coordination mode unreliable. Further evidence for the formation of the expected Schiff-base lateral macrobicycles comes from the fast atom bombardment mass spectra in which the peak due to the respective [1 + 1] lateral macrobicyclic formed appears at m/z 528 in **3**, 557 in **4**, and 572 in **5a**. These spectra also show the peak for the mononuclear complex $[\text{BaL}^n(\text{ClO}_4)]^+$ at m/z 764 for **3**, 793 for **4**, and 808 for **5a**, as well as the corresponding loss of the perchlorate group at m/z 665, 693, and 709, respectively.

Successive reactions between 2,6-diformyl-4-methylphenol and L^2 in the presence of barium perchlorate under different experimental conditions did not yield the expected complex of the Schiff-base macrobicyclic L^6 . In all cases, the infrared spectra of the products exhibited bands attributable to $\nu(\text{C}=\text{N})_{\text{imine}}$ together with those of carbonyl and/or amine groups indicating the presence of acyclic compounds.

The use of barium thiocyanate to template the above reactions was only effective when the diamine precursor L^2 was employed. Reactions between L^2 and 2,6-diformylpyridine or 2,6-diformyl-4-methylphenol in the presence of this barium salt under the experimental conditions described in the Experimental Section and using absolute ethanol as solvent gave the complexes of formulas $[\text{BaL}^5](\text{SCN})_2 \cdot 4\text{H}_2\text{O}$ (**5b**) and $[\text{BaL}^6](\text{SCN})_2 \cdot 2\text{H}_2\text{O}$ (**6**) with yields of 88% and 48%, respectively. Again, infrared and FAB mass spectra provide evidence for the formation of the expected Schiff-base lateral macrobicycles L^5 and L^6 . On the basis of the presence of an absorption band at 1645 cm^{-1} for **5b** and 1624 cm^{-1} for **6** assignable to the $\nu(\text{C}=\text{N})_{\text{imine}}$ stretching mode in their infrared spectra as well as the absence of bands due to amine and carbonyl groups, it can

Table 3. Selected Distances (Å) and Angles (deg) of Complexes **1a** and **3**

Complex 1a					
Ba(1)–O(1)	2.742 (4)	O(3)–Ba(1)–N(2)	167.50 (13)	O(7)–Ba(1)–N(2)	67.89 (13)
Ba(1)–O(3)	2.804 (4)	N(1)–Ba(1)–N(2)	67.72 (13)	O(1)–Ba(1)–O(6)	155.69 (14)
Ba(1)–N(2)	2.931 (4)	O(2)–Ba(1)–O(6)	70.7 (2)	O(3)–Ba(1)–O(6)	71.75 (13)
Ba(1)–O(6)	2.968 (6)	O(7)–Ba(1)–O(6)	45.74 (13)	N(1)–Ba(1)–O(6)	106.9 (2)
Ba(1)–N(3)	3.056 (4)	N(2)–Ba(1)–O(6)	109.76 (14)	O(1)–Ba(1)–N(4)	59.23 (13)
Ba(1)–O(2)	2.783 (4)	O(2)–Ba(1)–N(4)	117.05 (12)	O(3)–Ba(1)–N(4)	59.81 (12)
Ba(1)–O(7)	2.898 (4)	O(7)–Ba(1)–N(4)	123.08 (14)	N(1)–Ba(1)–N(4)	68.75 (13)
Ba(1)–N(1)	2.926 (4)	N(2)–Ba(1)–N(4)	128.93 (12)	O(6)–Ba(1)–N(4)	107.4 (2)
Ba(1)–N(4)	2.997 (4)	O(1)–Ba(1)–N(3)	60.59 (12)	O(2)–Ba(1)–N(3)	59.21 (11)
O(1)–Ba(1)–O(2)	96.39 (12)	O(1)–Ba(1)–O(3)	83.98 (12)	O(3)–Ba(1)–N(3)	103.00 (11)
O(2)–Ba(1)–O(3)	60.65 (12)	O(7)–Ba(1)–O(7)	158.13 (13)	O(7)–Ba(1)–N(3)	117.22 (13)
O(2)–Ba(1)–N(7)	100.24 (13)	O(3)–Ba(1)–O(7)	116.60 (12)	N(1)–Ba(1)–N(3)	119.93 (12)
O(1)–Ba(1)–N(1)	87.69 (13)	O(2)–Ba(1)–N(1)	174.07 (12)	N(2)–Ba(1)–N(3)	65.43 (11)
O(3)–Ba(1)–N(1)	124.27 (13)	O(7)–Ba(1)–N(1)	74.77 (14)	O(6)–Ba(1)–N(3)	122.8 (2)
O(1)–Ba(1)–N(2)	93.62 (13)	O(2)–Ba(1)–N(2)	107.62 (12)	N(4)–Ba(1)–N(3)	118.54 (12)
Complex 3					
Ba–O(6)	2.845(5)	O(6)–Ba–O(28)	76.99(18)	O(6)–Ba–O(25)	69.04(15)
Ba–O(25)	2.853(4)	O(28)–Ba–O(25)	56.33(15)	O(6)–Ba–O(19)	150.39(14)
Ba–O(2)	2.932(4)	O(28)–Ba–O(19)	83.95(18)	O(25)–Ba–O(19)	81.57(14)
Ba–O(4)	3.022(4)	O(6)–Ba–O(2)	135.54(13)	O(28)–Ba–O(2)	123.29(15)
Ba–N(8)	3.038(4)	O(25)–Ba–O(2)	155.28(13)	O(19)–Ba–O(2)	74.02(12)
Ba–N(16)	3.188(5)	O(6)–Ba–N(1)	71.11(12)	O(28)–Ba–N(1)	130.14(17)
Ba–O(28)	2.850(4)	O(25)–Ba–N(1)	135.72(13)	O(19)–Ba–N(1)	137.56(12)
Ba–O(19)	2.865(4)	O(2)–Ba–N(1)	66.13(11)	O(6)–Ba–O(4)	123.72(13)
Ba–N(1)	2.934(4)	O(28)–Ba–O(4)	159.05(18)	O(25)–Ba–O(4)	124.20(12)
Ba–N(38)	3.023(4)	O(19)–Ba–O(4)	75.78(12)	O(2)–Ba–O(4)	45.75(10)
Ba–N(22)	3.119(4)	N(1)–Ba–O(4)	66.32(11)	O(6)–Ba–N(38)	64.60(13)
O(28)–Ba–N(38)	135.68(16)	O(25)–Ba–N(38)	88.52(12)	O(2)–Ba–N(22)	105.27(11)
N(1)–Ba–N(22)	117.63(10)	N(38)–Ba–N(22)	65.42(11)	O(6)–Ba–N(16)	124.21(16)
O(19)–Ba–N(38)	119.74(10)	O(2)–Ba–N(38)	100.07(10)	O(25)–Ba–N(16)	104.17(14)
N(1)–Ba–N(38)	56.94(10)	O(4)–Ba–N(38)	61.87(11)	O(2)–Ba–N(16)	66.36(12)
O(6)–Ba–N(8)	81.78(15)	O(28)–Ba–N(8)	82.75(15)	O(4)–Ba–N(16)	106.05(13)
O(25)–Ba–N(8)	133.41(12)	O(19)–Ba–N(8)	118.31(11)	N(8)–Ba–N(16)	63.38(12)
O(2)–Ba–N(8)	64.72(11)	N(1)–Ba–N(8)	55.91(10)	O(4)–Ba–N(22)	67.26(11)
O(4)–Ba–N(8)	102.08(11)	N(38)–Ba–N(8)	111.24(10)	N(8)–Ba–N(22)	169.29(11)
O(6)–Ba–N(22)	104.75(15)	O(28)–Ba–N(22)	106.82(15)	O(28)–Ba–N(16)	57.56(17)
O(25)–Ba–N(22)	57.30(12)	O(19)–Ba–N(22)	59.41(11)	O(19)–Ba–N(16)	58.80(12)
N(1)–Ba–N(16)	113.83(12)	N(38)–Ba–N(16)	166.42(12)	N(22)–Ba–N(16)	117.35(12)

**Figure 1.** X-ray crystal structure of the cation of **1a** showing the atomic numbering scheme. Hydrogen atoms are omitted for clarity. The ORTEP plot is at the 30% probability level.

be confirmed that condensation and cyclization have taken place. Likewise, parent-ion peaks in the mass spectra are as expected for the mononuclear complexes of a [1 + 1] diimine-containing macrobicyclic product, and peaks corresponding to the sequential loss of counterions are also present at m/z 767 (**5b** – SCN), 709 (**5b** – 2SCN), and 737 (**6** – 2SCN).

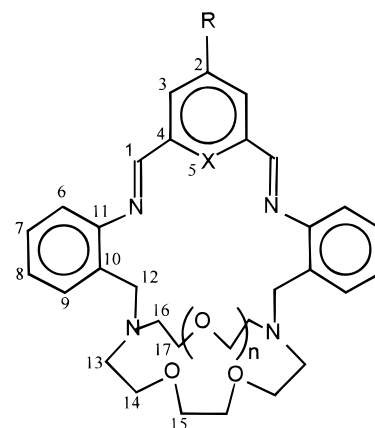
Conductivity measurements for 10^{-3} M solutions of complexes **3**, **4**, **5a**, **5b** and **6** in acetonitrile at 20 °C, with values of $\Lambda_M = 286$, 274, 241, 201 and 132 $\text{cm}^2 \Omega^{-1} \text{mol}^{-1}$, respectively, revealed that the thiocyanate complexes (**5b** and

6) behave as 1:1 electrolytes in acetonitrile¹⁸ while the perchlorate complexes (**3**, **4**, and **5a**) behave as 2:1 electrolytes.¹⁸ Again, the perchlorate complexes are completely dissociated in acetonitrile solution and, in light of the X-ray crystal structure of **3** discussed later, it is clear that the structure in solution must be different from that present in the solid state.

Besides bands due to $\pi \rightarrow \pi^*$ transitions of the aromatic rings, the UV–vis spectra in acetonitrile solutions of complexes **3–6** [λ_{max} 211, 226, 276, and 339 nm (**3**); 216, 232, 257, 315, and 458 nm (**4**); 216, 225, 244, and 326 nm (**5a**); 215, 230, and 331 nm (**5b**); and 215, 233, 283, 380, and 450 nm (**6**)] present a band in the region 330–460 nm corresponding to the imine groups and responsible for the color of these complexes.

Chemical shifts and assignments of the signals for the ¹H NMR of **3**, **4**, **5a**, **5b**, and **6** run in CD₃CN solutions are presented in Table 4. For each complex the spectrum confirms the integrity of the ligand in this solvent; resonances attributable to amino or aldehydic functions are absent; and imine resonances appear as a singlet at 8.61 ppm for **3**, 8.56 ppm for **4**, 8.78 ppm for **5a**, 8.62 ppm for **5b**, and 8.76 for **6**, which indicates that both imine bonds of the respective macrobicyclic are magnetically equivalent. Signals due to the ethylenic protons of the crown moiety appear at high field as a complicated multiplet as expected due to the coordination of the metal to the oxygen atoms of the crown. Assignments in this region were achieved for **3** with the aid of ¹H–¹H COSY, HMBC, and HMQC.

X-ray Crystal Structure of 3. Figure 2 displays a view of the structure of the complex and gives the atom-labeling scheme.

Table 4. ^1H NMR Data for the Complexes **3**, **4**, **5a**, and **5b**

	OH	H ₁	H ₂	H ₃	H ₆	H ₇	H ₈	H ₉	R	H ₁₃ , H ₁₆	H ₁₂	H ₁₄ , H ₁₇	H ₁₅
3^a		8.61 (s), 2H	8.38 (t), 1H	8.08 (d), 2H	7.06 (d), 2H	7.50 (td), 2H	7.33 (td), 2H	7.38 (dd), 2H		2.47 (d), 2H; 2.50 (d), 2H; 2.96 (m), 2H; 3.17 (m), 2H	4.01 (d), 2H; 3.34 (d), 2H	3.9 (m), 2H; 3.51 (m), 4H; 2.82 (s), 2H	3.44 (m) 4H
4^b	17.08 (s), 1H	8.56 (s), 2H		7.68 (s), 2H	← 7.50 (m) 8H →				2.20 (s), 3H	← 3.94 (m), 24H →			
5a^c		8.78 (s), 2H	8.48 (t), 1H	8.28 (d), 2H	← 7.53 (m), 4H →			← 7.32 (m), 4H →		← 3.73–3.50 (br), 28H →			
5b^d		8.62 (s), 2H	8.35 (t), 1H	8.09 (d), 2H	← 7.60–7.25 (m), 8H →					3.36 (m), 8H	3.55 (m), 4H	2.90 (m), 8H	2.60 (m), 4H

^a Conditions: uncoordinated ligand assignment supported by 2D H,H COSY, HMQC and HMBC experiments at $T = 293$ K, CD_3CN , 500 MHz. $J_{2,3} = 7.76$ Hz, $J_{3,2} = 7.76$ Hz, $J_{6,7} = 7.50$ Hz, $J_{7,6} = 7.50$ Hz, $J_{7,9} = 1.36$ Hz, $J_{8,7} = J_{8,9} = 7.50$, $J_{8,6} = 1.02$ Hz, $J_{9,8} = 7.40$ Hz, $J_{9,7} = 1.36$ Hz. Chemical shifts (without assignment) of the different multiplets for crown protons are given only. ^b Conditions: $T = 293$ K, CD_3CN , 200 MHz. Chemical shifts (without assignment) of the different multiplets for aromatic protons, crown protons, and proton H₁₂ are given only. ^c Conditions: $T = 293$ K, acetone-*d*₆, 200 MHz. Chemical shifts (without assignment) of the different multiplets for crown protons H₁₃, H₁₄, and H₁₅ and proton H₁₂ are given only. ^d Conditions: $T = 293$ K, CD_3CN , 200 MHz. Chemical shifts (without assignment) of the different multiplets for aromatic protons are given only.

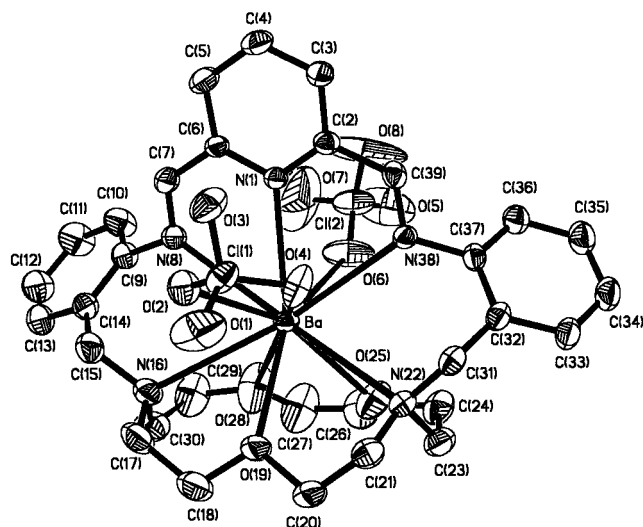


Figure 2. X-ray crystal structure of complex **3** showing the atomic numbering scheme. Hydrogen atoms are omitted for clarity. The ORTEP plot is at the 30% probability level.

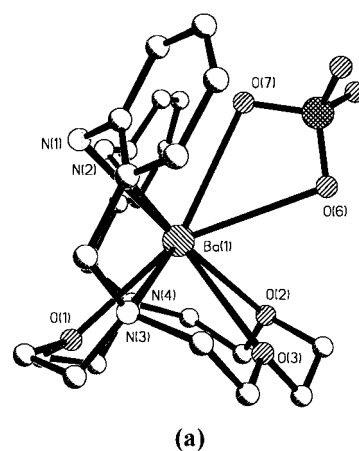
Table 3 summarizes selected distances and angles. In complex **3** the barium ion is coordinated to the eight donor atoms of the Schiff-base lateral macrobicyclic ligand with the metal ion almost symmetrically placed with respect to the ligand. Bond lengths from imine nitrogen atoms to the barium ion are almost equal (Ba–N(8) 3.038(4) Å, Ba–N(38) 3.023(4) Å) as well as those found from the three oxygen atoms, O(19), O(25), and O(28), with values of 2.865(4), 2.853(4), and 2.850(4) Å, respectively. The distances between Ba and both pivotal nitrogen atoms are slightly different (0.069 Å). The corresponding value for Ba–N(1)_{pyridine} is 2.934(4) Å. All distances are in the range found in the literature.^{6,19} Barium completes its coordination core with three oxygen atoms of the perchlorate groups, one of these groups acting as monodentate whereas the other acts as bidentate. The coordination polyhedron is best described as an icosahedron with an unoccupied site.

Angles N(22)–C(31)–C(32) and N(16)–C(15)–C(14) differ only by 1.1°, with values of 115.2(4)° and 114.1(5)°, respectively. Lateral aromatic rings are in different planes which intersect at 49°. The pyridine ring and both imine groups are in the same plane, which forms a dihedral angle of 68.1° with the plane containing the benzene ring bound to N(8) and of 64.3° with the plane containing the other aromatic ring.

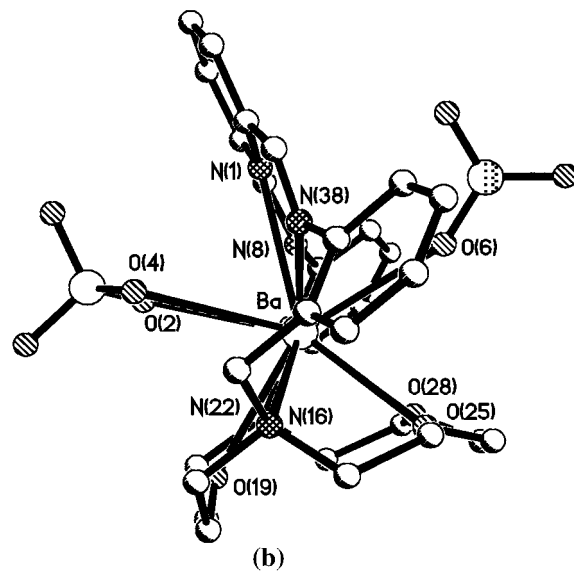
Discussion

The new family of lateral macrobicycles presented here cannot be prepared by a direct reaction between the organic precursors. We have carried out the condensation reaction of diamines N,N'-bis(2-aminobenzyl)-1,10-diaza-15-crown-5 (**L**¹) or N,N'-bis(2-aminobenzyl)-4,13-diaza-18-crown-6 (**L**²) and the corresponding dicarbonyl precursors under different experimental conditions using different solvents and concentrations, but in all cases results were unsuccessful. The IR spectra of the products exhibited bands corresponding to imine groups together with others due to amine and/or carbonyl groups, suggesting the presence of acyclic compounds.

The data presented under Results indicate that the presence of the barium cation in the reaction medium allows recovery of the expected macrobicyclic ligand in very high yields. The reason for it emerges from the conformation that the bibracchial



(a)



(b)

Figure 3. Side view of (a) the cation of **1a** and (b) complex **3**.

diamine possesses in solution; an anti arrangement leads to acyclic products as the majority ones, whereas the syn conformation favors the cyclization. In a previous publication¹⁰ we reported that both diamines **L**¹ and **L**² dispose the aniline groups in an anti arrangement. To force them to the syn conformation requires the presence of ionic species which place both amine groups pointing in the same direction either by the capability of the ionic species to coordinate them or by the formation of hydrogen bonds. From the X-ray crystal structure of the barium complex **1a** we found that the metal ion coordinates both amine nitrogen atoms and forces the ligand to adopt a syn arrangement. This conformation must be maintained also in solution since the presence of barium in the reaction medium leads to the expected Schiff-base macrobicycles in almost quantitative yields. From all of this it is clear that the barium acts as an effective template agent in the synthesis of these new Schiff-base cryptands and, in this case, the template effectiveness of any cation comes from its capability to orient the pendants of the diamines to a syn conformation. The cation must be big enough to lie out of the hole of the crown and to prefer high coordination numbers. Our results also show that the nature of the counterion (SCN⁻ or ClO₄⁻) is also important in the templating process, because the coordinating character of the anion will determine the extent of dissociation of the barium salt in the reaction medium.

X-ray crystal structures of complexes **1a** and **3** show the unexpected coordination of perchlorate anions to the metal ion.

(19) Adams, H.; Bailey, N. A.; Collinson, S. R.; Fenton, D. E.; Harding, C. J.; Kitchen, S. J. *Inorg. Chim. Acta* **1996**, *246*, 81.

As this group generally coordinates weakly to metal ions, its coordination has often been described as "semi-coordination".²⁰ In fact, in the complexes here presented perchlorate groups remain uncoordinated in solution, unlike thiocyanates. Comparison of the crystal structures of complexes **1a** and **3** on their side views (Figure 3) allows one to appreciate the effect that the embodiment of the pyridine fragment causes over both the arrangement of the diamine fragment and the position of the Ba(II) ion. The encapsulation of the metal ion is clearly more effective in the case of the cryptate **3**. The coordination of Ba(II) to the pyridine nitrogen promotes the displacement of the metal into the hole of the cryptand as well as important changes in the conformation of the crown. Nevertheless, the fold of the arms practically remains unchanged and the angle

(20) Gowda, M. N.; Naikar, S. B.; Reddy, G. K. *Adv. Inorg. Radiochem.* **1984**, 28, 255.

formed by the two planes containing aromatic rings is only 6.2° more open in **3**.

Concluding Remarks. We have probed the high efficiency of the barium(II) ion as a templating agent in the synthesis of a novel family of heteroditopic cryptands which are the first examples of Schiff-base lateral macrobicycles. Further work will include the synthesis and characterization of binuclear complexes of transition metals with these new ligands as well as their potential to encapsulate toxic heavy metals.

Acknowledgment. The authors thank the Universidade da Coruña for generous financial support.

Supporting Information Available: X-ray crystallographic files in CIF format for **1a** and **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC9811190