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Mass Spectrometric Characterization of a Barium Thiocyanate Complex with a New Macrocycle

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Abstract

The mass spectrometric characterization of the barium thiocyanate complex (L^1), $Ba(L)(SCN)_2$, where L is the macrocyclic ligand 7,16-dihydroxy-bis-[1′(pyridinyl-2″-methyl)[10,9-a][1,18-a]imidazolidine]-bis[5′-chloro[6,8-1′,3′][15,17-1′,3′]phenylene]1,4,10,13-tetrazacycloctadeca-4,13-diene is reported, as obtained by different ionization methods and metastable ion data. Positive fast atom bombardment experiments on this complex have shown either a proton extraction process, leading to $[M-H]^+$ or the formation of the ligand cation.

Introduction

Growing interest has been devoted to the design and synthesis of macrocycles selective for certain ions [1]; finding a macrocycle to fit a particular metal ion depends upon several parameters such as the size of the ring cavity and the type of binding atoms. Some metals prefer oxygen or nitrogen, others prefer sulfur, or phosphorus [2].

The link between metal ions and macrocycles works both ways: it is not just that macrocycles ring metal ions, thereby making them more soluble and more reactive but metal ions can be used to build up the macrocycles.

Barium and lead ions have been used as templating device for the preparation of macrocyclic Schiff bases, not otherwise obtainable, by condensation of polyamines and dicarbonyl compounds [3]. Once the macrocycle is made the template metal ion can be replaced by the desired metal ion (for instance copper(II)) [3] (Fig. 1).

These macrocycles are generally planar; this favours metal complexation but not always selectivity. Thus tridimensional macrocyclic ligands have been prepared, in order to increase selectivity; the disadvantage with these compounds is represented by the low rate of complexation and decomplexation [4].

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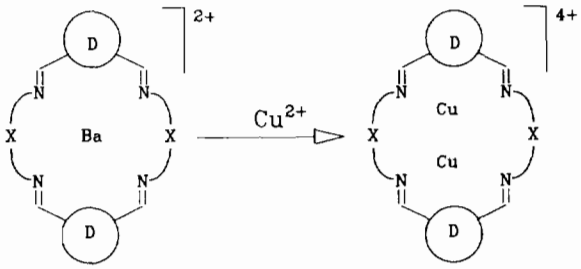

Fig. 1. Schematic representation of the binuclear copper(II) formation from the analogous mononuclear barium(II) macrocyclic complex.

A convenient compromise is represented by the macrocycles containing flexible pendant arms, which can coordinate or/not a metal ion also in the axial positions [5].

Accordingly we have prepared the barium thiocyanate complex $Ba(L)(SCN)_2$ (L^1) where L is the macrocyclic ligand 7,16-dihydroxy-bis[1′(pyridinyl-2″-methyl)[10,9-a][1,18-a]imidazolidine]-bis[5′-chloro[6,8-1′,3′][15,17-1′3′]phenylene]1,4,13-tetrazacycloctadeca-4,13-diene obtained by template condensation of 1-(2′-pyridyl)-2,5,8-triazaoctane (L^2) with 2,6-diformyl-4-chlorophenol in methanol (Scheme 1).

In the present paper we report the mass spectrometric characterization of the complex L^1, together with that of L^2, L^3 and L^4, the precursor synthons of macrocycle L, as obtained by different ionization methods and metastable ions data.

Experimental

2,6-Diformyl-4-chlorophenol [6] and the compounds L^1–L^4 were analytically pure samples synthesized and purified according to the literature [7].

All mass spectrometric measurements were performed on a VG ZAB-2F instrument operating in EI (70 eV, 200 μA, ion source temperature 200 °C)

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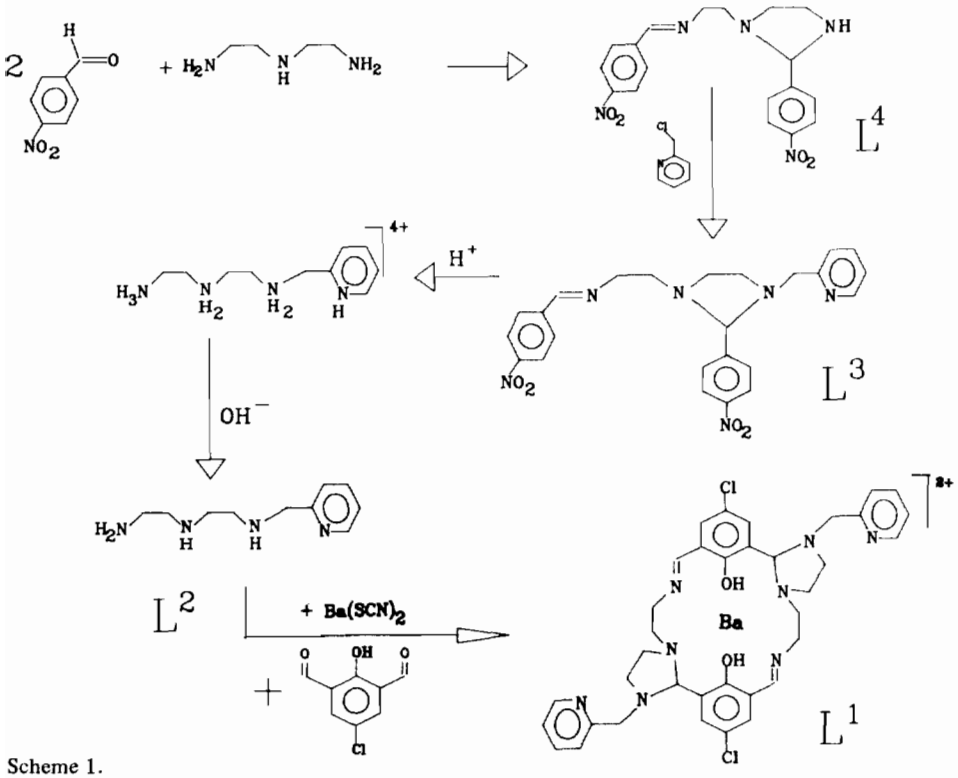


Scheme 1.

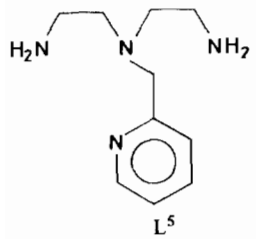
and FAB (8 keV Xe atoms bombarding tioglycerol solution of the sample) conditions.

Metastable transitions were detected by B/E linked scans [8].

Laser induced evaporation of compound L^1 was obtained by the device already described [9], consisting in the use of a ruby laser and of a fiber optics for the sample irradiation. The typical energy of the laser pulse was 2 Joule.

Results and Discussion

The reaction procedure described in Scheme 1 could, in principle, lead to the formation of the amine L^5, as an alternative product to L^2.



L^5

As a consequence the subsequent barium thiocyanate complex L^1 could also have a different structure, both amine and barium complex maintaining the same molecular weight. A mass spectrometric investigation was thus undertaken in order to characterize the possible structure of the compound L^1.

A parallel physicochemical study, together with X-ray structure determinations confirmed the ligands and the barium complex had to be described as reported in Scheme 1. It must be noted that, differently from other macrocycles obtained by direct synthesis of 2,6-diformyl-4-chlorophenol and polyamines, we were not able to obtain the macrocycle L. We were successful only by condensing the diformyl precursor and L^2 in methanol solution and in the presence of barium thiocyanate. Other ions with a smaller ionic radius (for instance copper(II) or lanthanides(III)) are not effective in the macrocycle formation. Ba^{2+}, in agreement with observations already reported for other cyclization reactions, has the more appropriate ionic radius for this reaction to take place. In the barium complex the macrocycle is bonded to the central metal ion through the two phenolic oxygens, the two iminic nitrogens and the two pyridinyl nitrogens. Two N-bonded thiocyanate groups complete the coordination polyhedron around the metal ion, giving rise to a distorted antiprism (Fig. 2).

Electron impact mass spectrometry of L^1 does not lead to any significative fragmentation pattern. The molecular ion is completely absent and most of

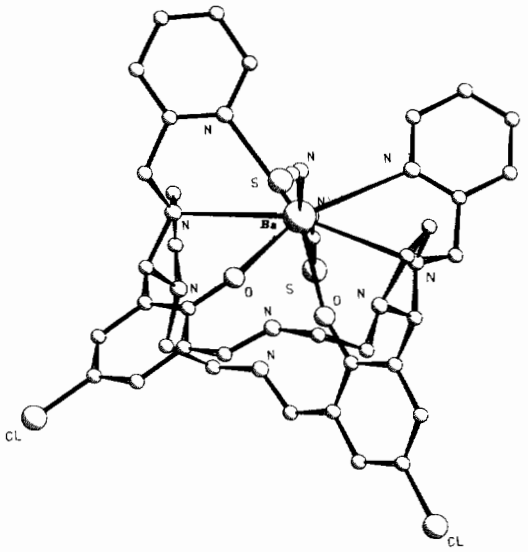


Fig. 2. The crystal structure of L^1.

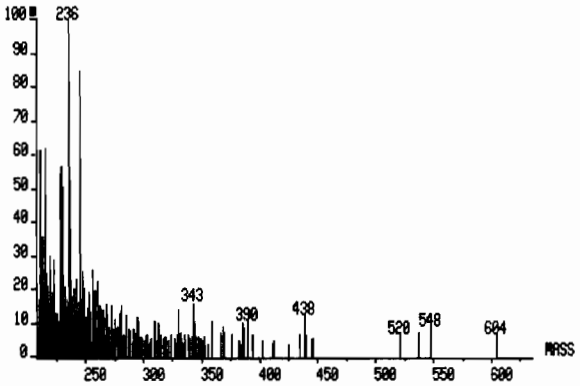
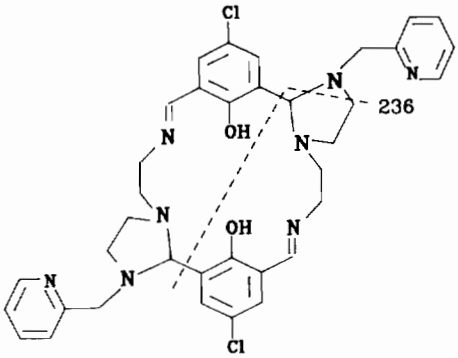


Fig. 3. Laser desoprtion mass spectrum of L^1.

the fragment ions are completely unrelated to the compound L^1 structure.

This frustrating result can be due in principle to two different reasons: (i) thermal lability; (ii) lability to EI conditions.



Scheme 2.

Looking at the exciting results obtained by laser induced evaporation in the field of thermally lable coordination compounds [10] we performed the laser desorption of compound L^1, using laser pulse up to 2 J energy. The result obtained is reported in the Fig. 3.

Unfortunately, also in these conditions, no molecular species are detectable at m/z 820–826. The base peak is due to ionic species at m/z 236, reasonably originating from a thermal degradation of the complex, followed by EI of the pyrolysis products (see Scheme 2). Hence these results seem to indicate a thermal lability of L^1 as is to be expected for a salt moiety.

In recent years, fast atom bombardment (FAB) has proved to be a valid analytical tool in organometallic and coordination compounds [11]. Consequently we performed FAB experiments on compound L^1.

The best results were obtained with tioglycerol solutions, as shown in Fig. 4. A well detectable molecular cluster is present in the mass range 818–825, which perfectely match with the theoretical one for $[M-H]^+$. It corresponds to the $[M-H]^+$ species, reasonably originating through a proton extraction, which leads to a singly charged molecular cation at m/z 821 (considering the ^{138}Ba isotope).

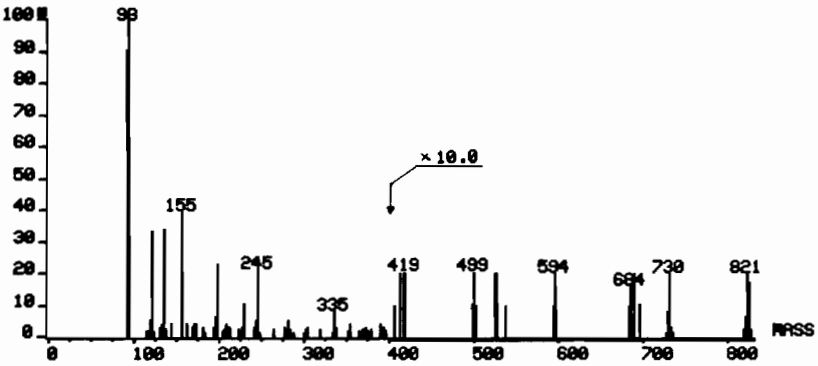
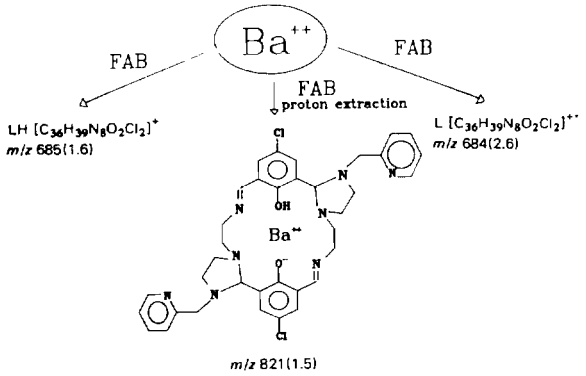


Fig. 4. FAB mass spectrum in tioglycerol solution of L^1.



Scheme 3.

Further FAB induced decomposition pathways lead to $[L]^+$ (m/z 688) and $[LH]^+$ (m/z 689) species (see Scheme 3).

Hence by FAB mass spectrometry characterization of the highly unstable crown moiety is possible.

The fragmentation patterns of these species are closely related to their structures. Cleavages of the macrocyclic structures (2 and 3 of Scheme 4) lead to complementary ions at m/z 162, 527 and 300, 389. In its turn the cleavage of the imidazolinic ring (cleavage 1 of Scheme 4) gives rise to the ionic species at m/z 135 and 553. Some other quite abundant fragments are difficult to explain and possibly originate by condensed-phase reaction with the FAB matrix. The base peak is due to the molecular ion of methyl pyridine (m/z 93).

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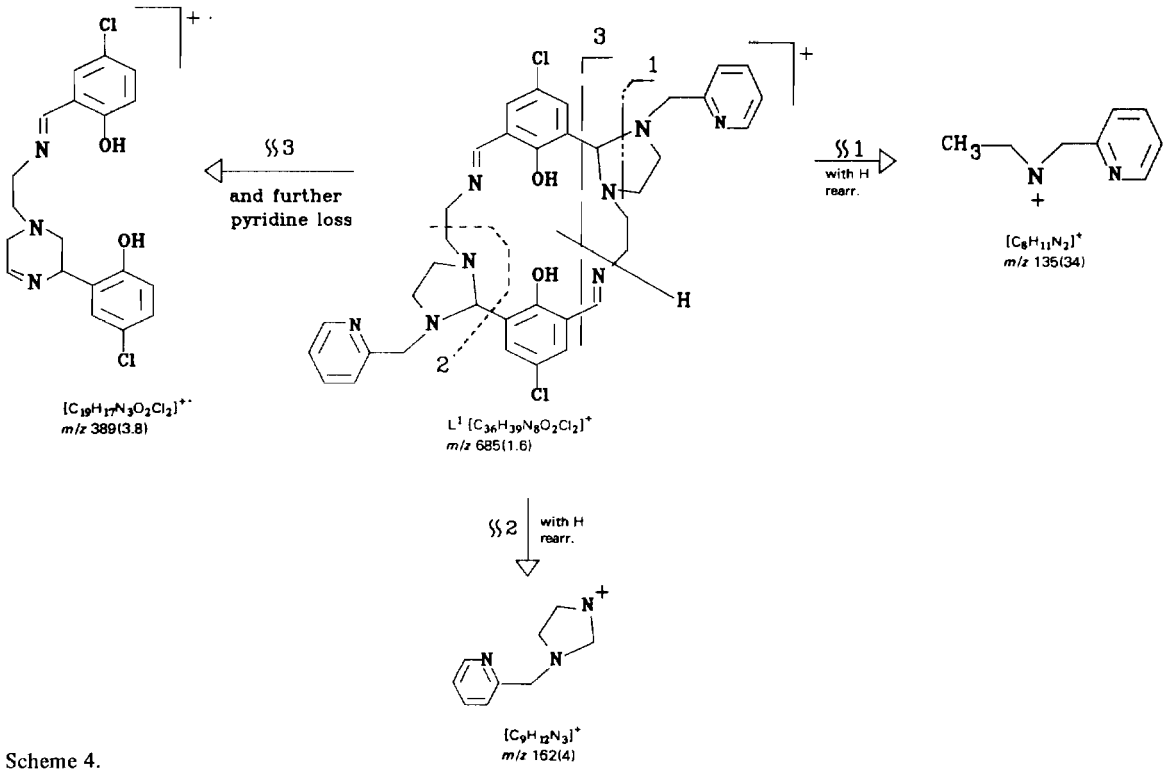

Scheme 4.

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