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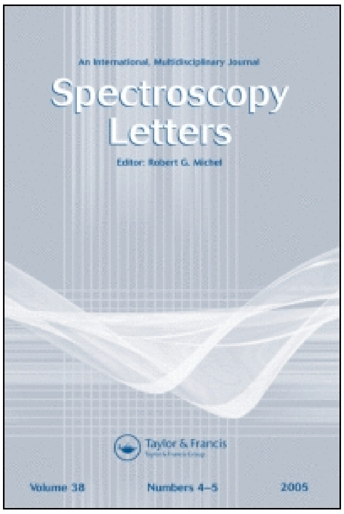

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A STUDY ON SOME BARIUM (II) COMPLEXES BY SPECTRAL TECHNIQUES

Key words: Macrocycle, Barium Complex, NMR, Mass Spectrum.

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ABSTRACT

The structure of three complexes $[BaL^1(ClO_4)_2]\cdot 3H_2O$, $[BaL^2(ClO_4)_2(H_2O)]\cdot MeOH\cdot 1.5H_2O$ and $[BaL^3(ClO_4)_2(H_2O)]\cdot MeOH\cdot 1.5H_2O$ have been studied by ES-MS spectra and ^{1}HNMR spectrum in methanol solutions. The barium (II) ion was coordinated by nitrogen atoms of macrocycle, perchlorate and water. The perchlorate anion coordinates to barium (II) in same side of the macrocyclic plane with imidazole rings.

INTRODUCTION

Application of barium(II) and other alkaline earth metal ions template procedures for cyclic condensation reactions between dicarbonyl compounds and diprimary amines have developed as one of the main methods in synthesizing macrocyclic complexes.[1-3] Mononuclear alkaline earth metal complexes of (2+2) macrocycles provide interesting chemical features, as well as serving through the transmetallation reactions, as useful synthetic reagents.[4] The macrocyclic compounds with different structures were synthesized by different reactional conditions. We report briefly here the syntheses and

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* The corresponding author

structural studies on barium(II) complexes of macrocycles by spectral methods. The ligands of the complexes are shown in Scheme I.

EXPERIMENTAL

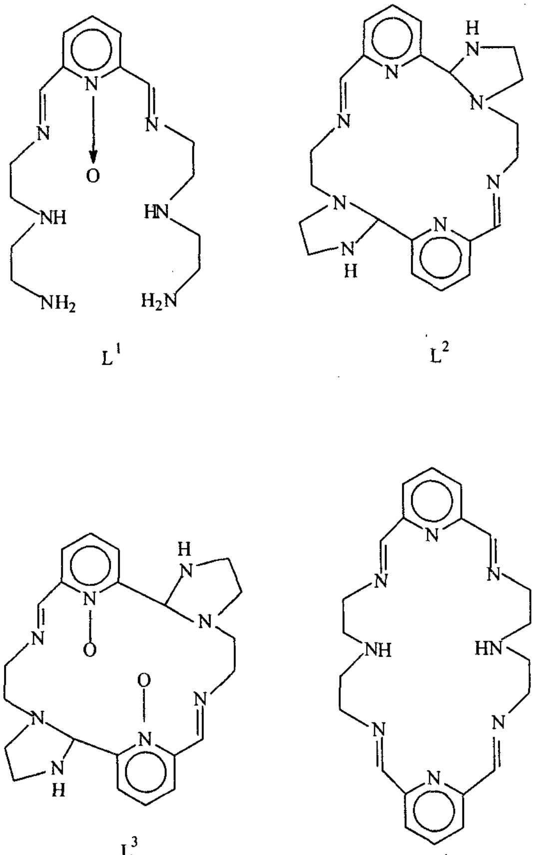
$[BaL^1(ClO_4)_2]\cdot 3H_2O$ was synthesized by condensation of diethyltriamine with 2, 6-diformylpyridine-N-oxide in 4:1 ratio in the presence of barium(II) perchlorate. $[BaL^2(ClO_4)_2(H_2O)]\cdot MeOH\cdot 1.5H_2O$ was obtained by adding 2,6-diformylpyridine to a hot methanol solution of the $[BaL^1(ClO_4)_2]\cdot 3H_2O$. $[BaL^3(ClO_4)_2(H_2O)]\cdot MeOH\cdot 1.5H_2O$ was synthesized by template condensation between diamine and dialdehyde. The elemental analyses and physical constants are in agreement with the structural formulas.

IR spectra were measured as KBr disc using a Nicolet 5DX FT-IR spectrophotometer. Thermoanalyses of the complexes were performed on a SDT 2960 TA thermoanalyser under an argon atmosphere with a rate of 10 ^{0}C min^{-1}. ^{1}HNMR spectrum of $[BaL^2(ClO_4)_2(H_2O)]\cdot MeOH\cdot 1.5H_2O$ was obtained using a BRUKER ARX-500 NMR spectrometer at 25^{0}C with TMS as the internal standard. Electrospray mass spectra (ES-MS) of the complexes were determined on a Finnigan LCQ mass spectrograph.

RESULTS AND DISCUSSION

$[BaL^1(ClO_4)_2]\cdot 3H_2O$ can be soluble in methanol and poorly soluble in other solvents such as acetonitrile. It exhibited two fairly strong bonds at 3310 and 3260 cm^{-1} attributable to the ν (N-H) vibrations of a primary and secondary amine, a strong bond at 1590 cm^{-1} is a characteristic of the coordinated C=N group vibration. The vibrations of the ClO_4^- group occurring at its positions are split (Table 1), which suggests that they are coordinating to barium (II).

The IR spectra of $[BaL^2(ClO_4)_2(H_2O)]MeOH\cdot 1.5H_2O$ $[BaL^3(ClO_4)_2(H_2O)]MeOH\cdot\cdot 1.5H_2O$ are similar to the $[BaL^1(ClO_4)_2]\cdot 3H_2O$, but differ in the following important respects. Only a sharp single band at 3310 cm^{-1} occurs in the NH stretching region. These observations are taken as evidence for the absence of primary amine groups and the presence of secondary amine groups. Well defined splitting in the two absorption



L^1 L^2

L^3 L^4

Scheme I The structural formulas of the ligands

characteristics of ClO_4^-, being the same as $[BaL^1(ClO_4)_2]\cdot 3H_2O$, indicate that the perchlorate anions were coordinated to barium (II).

Thermogravitric analyses show that the number of exocyclic solvent molecules exist in the complexes. When $[BaL^2(ClO_4)_2(H_2O)]\cdot MeOH\cdot 1.5H_2O$ was dried in vacuum, the complex lost one methanol molecule. In the thermogram of complex $[BaL^2(ClO_4)_2(H_2O)]$ $\cdot MeOH\cdot 1.5H_2O$ there are two weight loss processes from room temperature to 400 °C.

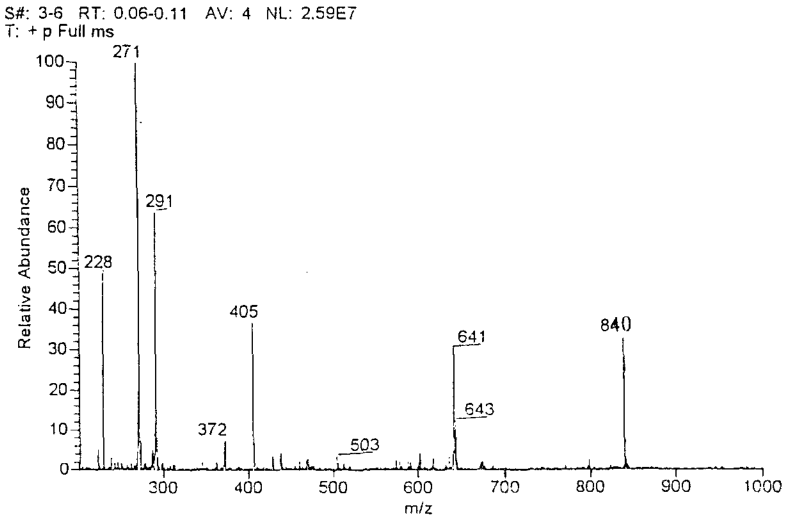


Fig. 1 The ES mass spectrum of $[BaL^2(ClO_4)_2(H_2O)]\cdot MeOH\cdot 1.5H_2O$ in methanol

The complex began to lose 5.7% of its weight at about 42-50 °C corresponding to 2.5 water molecules (calc. 5.5%), which indicates that water coordinates to barium (II) weakly. However, the exact temperature at which loss of coordinated water and uncoordinated water occurred could not be determined because their endothermic peaks in the DTA curve overlapped with each other. The second process was over 255 °C corresponding to decomposition of the complex. The thermogram of the complex $[BaL^3(ClO_4)_2(H_2O)]\cdot MeOH\cdot 1.5H_2O$ is analogous to that of $[BaL^2(ClO_4)_2(H_2O)]\cdot MeOH\cdot 1.5H_2O$. It began to lose 9.0% of its weight at about 30-100 °C corresponding to all solvent molecules. The second process was from 100 to 200 °C, 3.80% of total weight was lost which corresponded to loss of two oxygen atoms from the macrocycle (calc. 3.76%). Finally, the complex was decomposed over 200 °C.

The relatively new technique of electrospray mass spectrometry (ES-MS) allows pre-existing ions in solution to be transferred very gently into the gas phase with minimal fragmentation.[5] Figure 1 shows the position-ion ES-MS spectrum of the complex $[BaL^2(ClO_4)_2(H_2O)]\cdot MeOH\cdot 1.5H_2O$ in methanol. Several peaks are observed. The mass

Table 1 The elemental analyses and physical constants for the complexes

complexes	Analysis[a](%)				IR absorption			Λ_m (298K)
	C	H	N	Ba	ν(NH)	ν(C=N)	ClO_4	S cm^2mol^{-1}
$[BaL^1(ClO_4)_2]3H_2O$	25.61	5.10	14.20	19.01	3310, 3260	1590	1098, 1080	305
$C_{15}H_{33}N_7BaCl_2O_{12}$	(25.30)	(4.68)	(13.78)	(19.26)				
$[BaL^2(ClO_4)_2(H_2O)]$ MeOH1.5H_2O	33.56	4.22	14.03	16.95	3225	1640	1119, 1058	336
$C_{23}H_{37}N_8BaCl_2O_{11.5}$	(33.77)	(4..56)	(13.70)	(16.79)				
$[BaL^3(ClO_4)_2(H_2O)]$ MeOH1.5H_2O	33.00	4.58	13.50	16.05	3300	1620	1119, 1056	304
$C_{23}H_{37}N_8BaCl_2O_{113.5}$	(32.51)	(4.39)	(13.19)	(16.16)				

a Calculated values for formula of complexes were given in parentheses

spectrum is dominated by the peak at m/z 271 which is due to $[BaL]^{2+}$ indicating that the barium (II) ion is still encapsulated in the macrocycle. The other main peaks can be assigned to new species formed by solvation or protonation of the complex, loss of perchlorate ligand or hydrogen molecule. The peak at m/z 840 is due to the formation of the new complex $[Ba(L^2\text{-}H_2)(ClO_4)_2(MeOH)_2(H_3O)(H_2O)]^+$, a hydrogen molecule is lost from the five-membered ring and a proton is added to the nitrogen atom of the ring. The peak at m/z 291 is assigned to $\{[BaL^2(MeOH)]_2(H_2O)\}^{4+}$ which is formed by water linked with two molecules of the complex $[BaL^2(MeOH)]^{2+}$. The peak due to the fragmentation of the macrocycle was observed at m/z 228 corresponding to $[HL^2(MeOH)(H_3O)]^{2+}$. The mass spectrum of $[BaL^1(ClO_4)_2]\cdot 3H_2O$ gives only a peak at m/z 322 which is due to $[BaL^1(ClO_4)(H_3O)(H_2O)_2(MeOH)]^{2+}$, indicating that the complex ion is still existing in solution. No peaks due to the fragmentation of the complex were observed (Table 2). It shows that the complex is rather stable in methanol solution. Several peaks are observed in the ES mass spectrum of $[BaL^3(ClO_4)_2(H_2O)]$. The mass spectrum is dominated by the peak at m/z 322 which is due to $[BaL^1(ClO_4)(H_3O)(H_2O)_2\text{-}(MeOH)]^{2+}$ indicating that the complex $[BaL^3(ClO_4)_2(H_2O)]\cdot MeOH\cdot 1.5H_2O$ is unstable in methanol solution, its two five-membered dinitrogen rings broke. The corresponding peak at m/z 222, which is corresponded to $[Ba(L^1\text{-}O)]^{2+}$ further proved its insability. The peak at m/z 305 can be assigned to $[BaL^3(H_2O)_2]^{2+}$ which lost two water molecules and an oxygen atom corresponding to the peak at m/z 279. The other main peaks can be assigned

Table 2 The m/z values and relative abundants (r. a.) of the complexes in ES mass spectra

$[BaL^1(ClO_4)_2]3H_2O$ m/z (r. a.)	$[BaL^2(ClO_4)_2(H_2O)]MeOH1.5H_2O$ m/z (r. a.)	$[BaL^3(ClO_4)_2(H_2O)]MeOH1.5H_2O$ m/z (r. a.)
322 (100%)	437 (55%)	840 (36%)
	419 (28%)	641 (32%)
	401 (11%)	405 (39%)
	322 (100%)	291 (64%)
	305 (29%)	271 (100%)
	222 (61%)	228 (49%)
	279 (15%)	

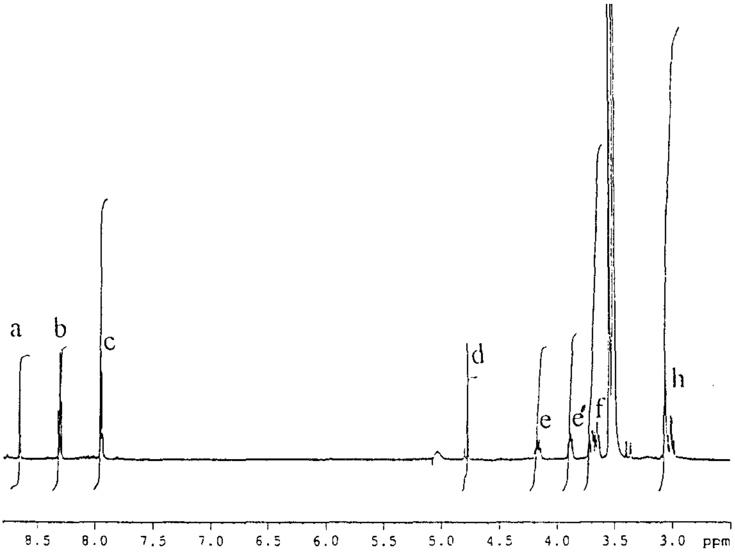


Fig. 2 The ^{1}HNMR spectrum of the complex $[BaL^2(ClO_4)_2(H_2O)]$

to new species formed by solvation or protonation and dissociation of barium(II) ion from the complex.

Neither chemical analysis nor IR spectra and mass spectra allow a distinction to be made between L^4 and the isomeric form L^2 (Scheme I) which was the expected five - membered ring-closure product. The ^{1}HNMR spectrum can supply some usable evidence. The ^{1}HNMR spectrum of $[BaL^2(ClO_4)_2(H_2O)]$ (Figure 2) shows a singlet at 8.65 and

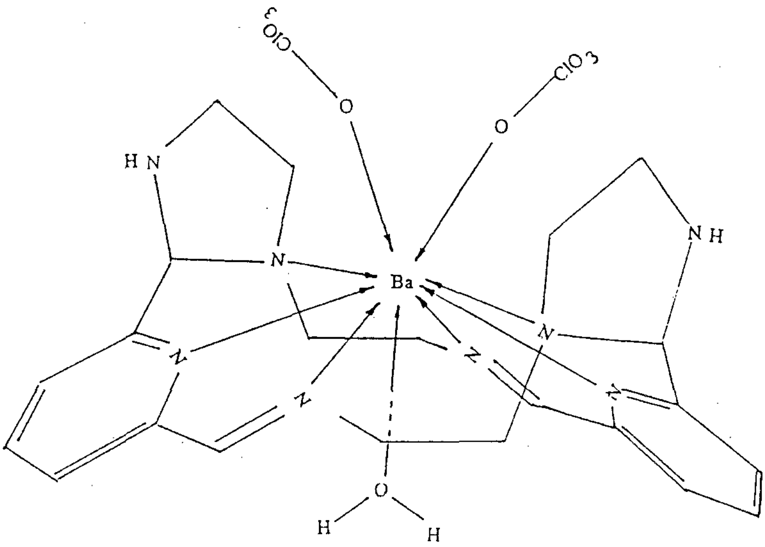


Fig. 3 The deduced structure of the complex $[BaL^2(ClO_4)_2(H_2O)]$.

triplet at 8.40, as well as a doublet at 7.95 ppm. The coupling constants of the triplet and doublet, all being 8.0 Hz, suggests that they derive from the *para* and *meta* proton of pyridine rings, respectively. The signal at 8.65 ppm is observed as a singlet or doublet, it is assigned the proton of Schiff-based groups, which indicates that the nitrogen of the Schiff base is coodinated to barium (II). The signal at 7.95 ppm is observed as a doublet of doublets. On close examination of this doublet it is concluded that a doublet of doublets arises from long-distance coupling of a proton attached to the imino with a meta-proton of the pyridine ring. The coupling constants 1.34 Hz of them can act as evidence. The proton H(d) gives a sharp singlet (*d*, Figure 2) demonstrate that there is no transformation of conformation of the five-membered rings, which is different from the macrocycle synthesized by Martell.[6] It implies that the two five-membered rings and two perchlorate anions are located at the same side of the macrocycle, which inhibits the conformation changes of the rings. The multiplets *e-h* have not been completely assigned, however a few conclusions are possible. Assignment was attempted through the use of the results of the decoupling experiment. The multiplets at *h* containing three proton signals are probably a complex mixture of overlapping signals arising from a proton H(g) of methylene in imidazole ring and two protons H(h) of the methylene groups attached to the ring. The two broad multiplets *e* and *e'* may be the signals arising from the two protons H(e) of methylene attached to the Schiff-base due to the different chemical environments and the fluxionality [7] of them. The multiplets *f* containing three proton signals are probably a complex mixture of overlapping signals accounted for by the protons H(f), and H(g) of methylene in the imidazole ring. The complex signals of $[BaL^2(ClO_4)_2(H_2O)]$ may arise from the barium (II) atom on the macrocyclic plane, the contracted rings, and the two perchlorate anions coordinated to barium (II) on the same side of the macrocyclic plane. These make the protons in the same methylene to be in different chemical environments showing different chemical shifts. The deduced structure is given in Figure 3.

To examine the stability of the complex $[BaL^2(ClO_4)_2(H_2O)]$, different ^{1}HNMR spectra were recorded in a temperature range of 0-50 $^\circ$C. The results show that there are not significant changes in the ^{1}HNMR spectra.

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