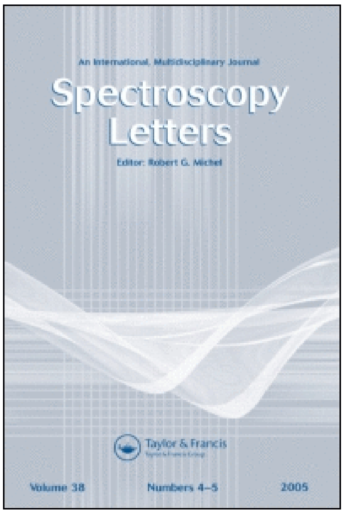

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A STUDY ON A NEW BARIUM (II) CRYPTATE BY NMR SPECTRA AND MOLECULAR DYNAMICS METHOD

Key words: NMR, Barium, Cryptate, Molecular Dynamics.

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ABSTRACT

The structure and conformation of the complex $[BaL](ClO_4)_2 \cdot MeCN$ have been studied by NMR spectra and molecular dynamics method in CD_3CN solution. The coordination geometry of barium(II) is distorted, tricapped trigonal prism, in which the six nitrogen atoms of the imine compose the prism and three pyridyl nitrogen atoms are capping atoms forming nine coordinated structure.

INTRODUCTION

It is well known that cryptands have special host-guest chemical behavior and potential application in molecular catalysis and supramolecular divices [1-3], the conformation information of cryptates obtained by using NMR and molecular dynamics a e important[4-7] for designing and synthesizing new cryptates. Herein we reported briefly a new Ba(II) cryptate $[BaL](ClO_4)_2 \cdot MeCN$ ($L = C_{39}H_{51}N_{11}$) (Figure

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1) synthesized by (2+3) Schiff base condensation of tris(3-aminopropyl)amine (trpn) with 2,6-diformylpyridine (dfp) in the presence of barium perchlorate as the template. The structure of the $[BaL]^{2+}$ cation was studied by NMR and molecular dynamics method. The results show that the coordination number of Ba(II) is nine. The coordination geometry of Ba(II) is approximately tricapped trigonal prism with six imine nitrogen atoms at vertexes and three nitrogen atoms of pyridyls at capping positions. The ^{13}C NMR spectrum shows that the complex $[BaL](ClO_4)_2{\cdot}MeCN$ has a D_3 geometrical symmetry in solution.

EXPERIMENTAL

Tris(3-aminopropyl)amine and 2,6-diformylpyridine were synthesized by the literature methods [8,9]. The physical constants agree with literature values. The $[BaL](ClO_4)_2{\cdot}MeCN$ was obtained by (2+3) condensation of trpn with dfp in the presence of barium perchlorate as the template in methanol solution followed by recrystalization from MeCN/ Et_2O. The characteristic results are in agreement with the structure in Figure 1.

A 2D phase-sensitive ^1H - ^{13}C HMQC measurement was carried out on a BRUKER ARX-500 NMR spectrometer. The solution of $[BaL](ClO_4)_2{\cdot}MeCN$ in CD_3CN was about 3.8×10^{-3} mol·dm^{-3} containing TMS as internal standard, the spectrum was recorded using the simple four-pulse sequence with GARP[10] decoupling detection. J(C,H) Assumed to be 145Hz and 3.45ms was used for polarization transfer. The relaxation delay was 2s. The acquisition points were 512×256 ($f_1 \times f_2$). The hydrogen and carbon chemical shifts were referenced to the CD_3CN peaks which were set to 2.00 ppm for hydrogen atom and 0 as well as 117 ppm for two carbon atoms. The NOESY spectrum was recorded from the same solution. The spectral parameters was as follows: mixing time, 800ms; data points, 1025×512 and 1024×1024 for Fourier transformation; scan number, 32; relaxation delay, 2s; chemical shifts were referenced to CD_3CN and set hydrogen atom for 2.00 ppm.

Modeling and molecular dynamics simulation were carried out on SGI Indigo workstation. A preliminary molecular model was sketched using the standard bond lengths and angles. The MM2 method with conjugate-gradient minimizer selection

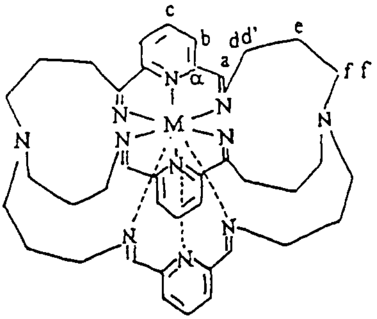

Figure 1. The structure of L

was used to make a primitive geometry optimization with molecular dynamics program package of the SYBYL 6.0[11]. Energy optimization was carried out with Powell[11] method. The simplex initial set-up was made before the energy optimization. Boltzmann distribution was used and a time step of 0.5 fs was chosen. The cut-off value was set as 1.0 nm for Van der Waals interaction of non-bond. Electrostatic interaction was not considered. The energy optimization structure was used as the original input structure for further refining with the simulate annealing molecular dynamic method employed with the SYBYL 6.0. Tripos force field, the temperature range from 2000 to 200K and the exponential ramping anneal function, were set and 100 cycles were processed. The 100 refined conformations retained by simulate annealing were further minimized directly with the energy minimization (EM) program[11]. During the geometry optimization calculations, only the distance constraints of Ba - N were imposed on the structure.

RESULTS AND DISCUSSION

Figure 2 shows the contour plot of ^1H -^{13}C HMQC spectrum of $[BaL]^{2+}$ cation. The ^1H NMR (top) and ^{13}C NMR (side) spectra of the complex show eight and seven peaks respectively. Three proton signals labeled a, c and b appear in downfield, which arise from strong deshielding effects of protons at imino and pyridyl groups; analogously, four carbon signals labeled a', α, c' and b' appear in downfield which

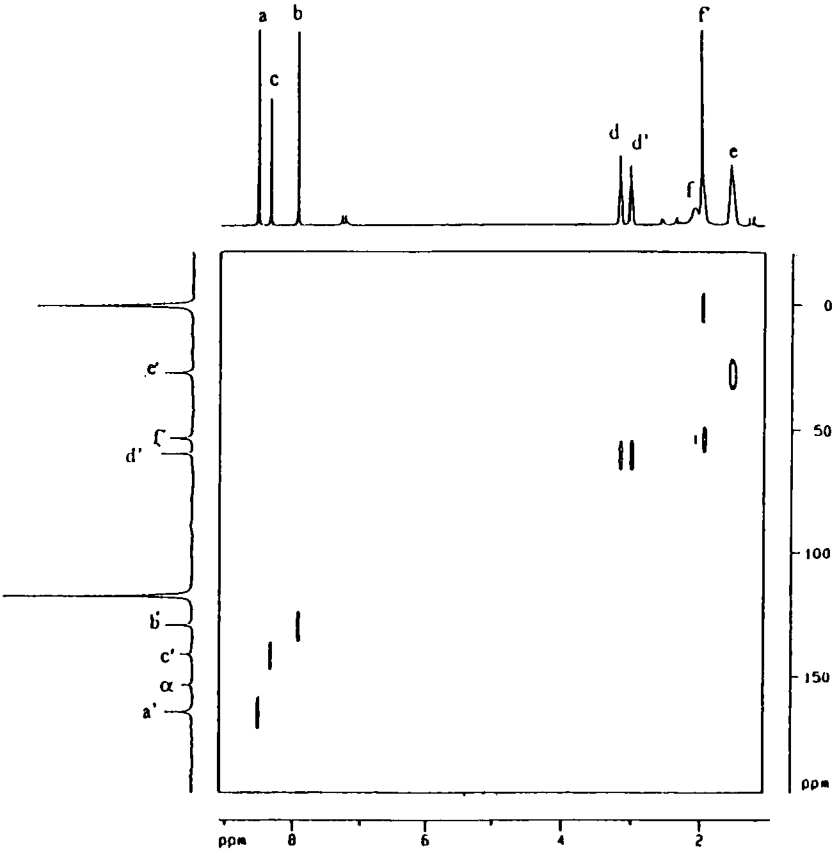

Figure 2. The phase -sensitive ^{1}H -^{13}C HMQC spectrum of $[BaL]^{2+}$ cation.

were assigned to carbons of imino and pyridyl groups. The simple seven peaks in ^{13}C NMR spectrum show that the complex has a geometry symmetry of D_3 in MeCN solution.

The correlativities between protons are detected in NOESY spectrum which displays eight cross signals. From analysis of NOE intensities, the H - H distances are obtained.

The solution structure of $[BaL]^{2+}$ is obtained by molecular dynamics method. The calculated geometrical structure of the complex is shown in Figure 3. The

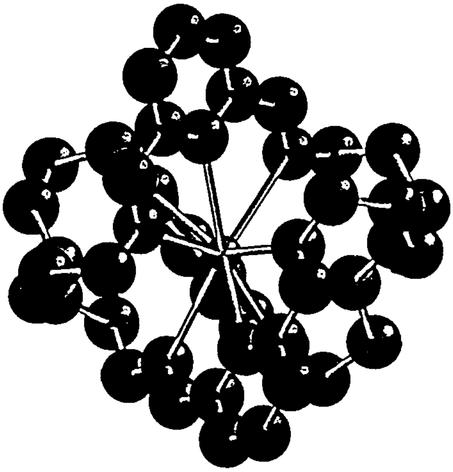

Figure 3. The calculated structure of the $[BaL]^{2+}$ cation.

Table 1. Selected bond distances (A) by calculating

bond lengths (A)	
Ba(1) - N(12)	3.022
Ba(1) - N(10)	2.998
Ba(1) - N(7)	3.047
Ba(1) - N(11)	3.081
Ba(1) - N(14)	3.036
Ba(1) - N(16)	2.999
Ba(1) - N(13)	3.014
Ba(1) - N(18)	2.993
Ba(1) - N(15)	2.992
N(8) - C(34)	1.453
N(8) - C(33)	1.278

Table 2. Selected bond angles (°) of the complex $[BaL]^{2+}$ by calculation

bond angles		bond angles	
N(12)-Ba(1)-N(16)	132.592	N(16)-Ba(1)-N(10)	79.844
N(16)-Ba(1)-N(13)	103.128	N(15)-Ba(1)-N(14)	132.784
N(12)-Ba(1)-N(7)	137.509	N(10)-Ba(1)-N(7)	77.230
N(12)-Ba(1)-N(8)	97.345	N(10)-Ba(1)-N(8)	146.933
N(7)-Ba(1)-N(8)	70.317	N(16)-Ba(1)-N(11)	132.592
N(13)-Ba(1)-N(11)	69.408	N(8)-Ba(1)-N(11)	150.142
N(16)-Ba(1)-N(15)	112.362	N(13)-Ba(1)-N(15)	143.787
N(8)-Ba(1)-N(15)	83.886	N(12)-Ba(1)-N(14)	78.616
N(10)-Ba(1)-N(14)	143.888	N(7)-Ba(1)-N(14)	119.974
N(11)-Ba(1)-N(14)	119.986	N(12)-Ba(1)-N(10)	111.075
N(12)-Ba(1)-N(13)	63.451	N(10)-Ba(1)-N(13)	96.415
N(16)-Ba(1)-N(7)	56.285	N(13)-Ba(1)-N(7)	159.035
N(16)-Ba(1)-N(8)	77.106	N(13)-Ba(1)-N(8)	111.652
N(12)-Ba(1)-N(11)	55.290	N(10)-Ba(1)-N(11)	55.929
N(7)-Ba(1)-N(11)	119.967	N(12)-Ba(1)-N(15)	82.756
N(10)-Ba(1)-N(15)	83.325	N(7)-Ba(1)-N(15)	56.150
N(11)-Ba(1)-N(15)	81.111	N(16)-Ba(1)-N(14)	84.888
N(13)-Ba(1)-N(14)	55.565	N(8)-Ba(1)-N(14)	56.465

conformation parameters are listed in Tables 1 and 2. The perspective and label views of the predicted $[BaL]^{2+}$ is plotted in Fig. 4a. The structure of coordination polyhedron of $[BaL]^{2+}$ cation can be described approximately as a tricapped trigonal prism (Fig. 4b), while each of the three pyridyl-nitrogen atoms locates at the capping position in each side square respectively and the trigonal prism composed of six imino nitrogen atoms is distorted. The least-square plane (I) composed of N(8),

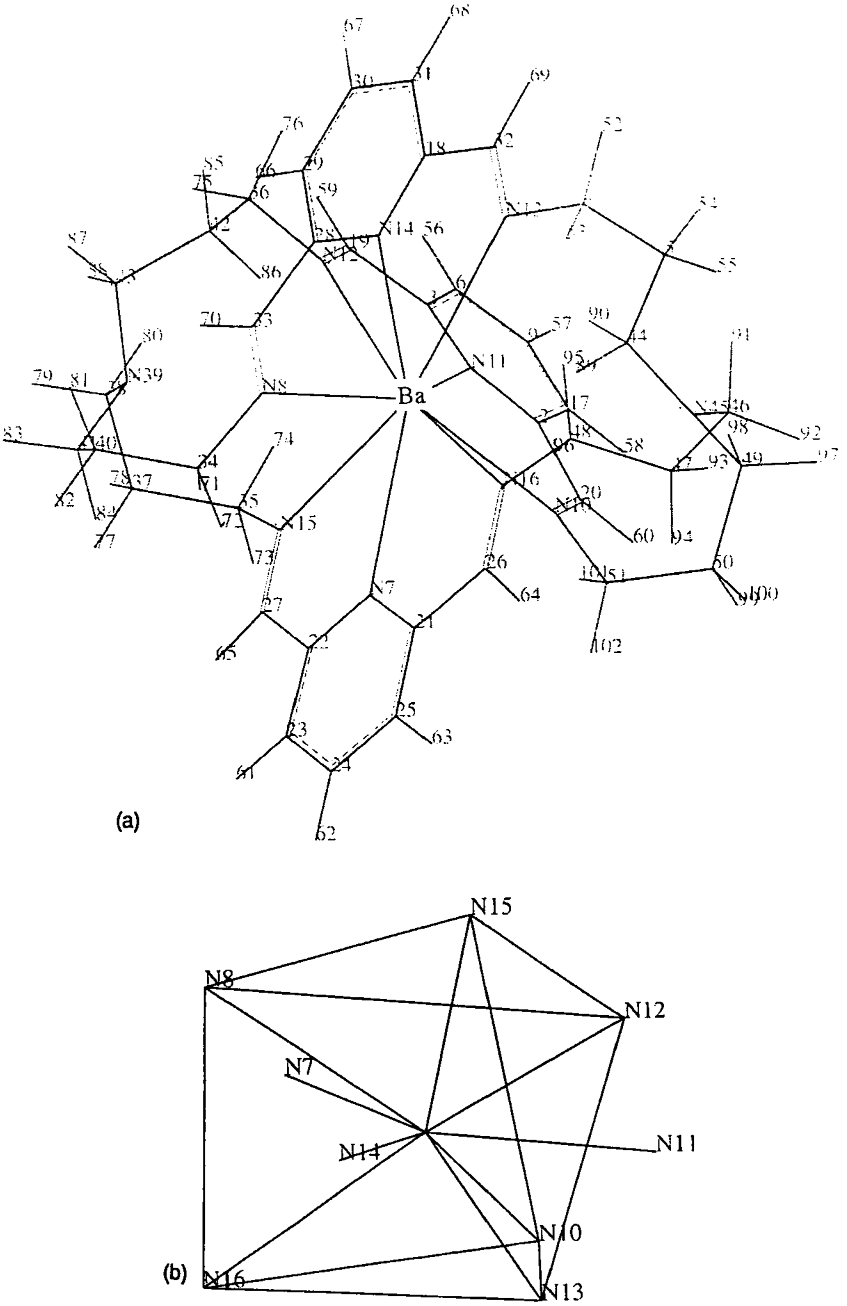

Figure 4. The perspective and label views of the predicted $[BaL]^{2+}$ cation.

(a). labeling atoms structure of the $[BaL]^{2+}$ cation, (b) the structure of coordination polyhedron of $[BaL]^{2+}$ cation.

Table 3. Selected H - H distances (Å) by calculating

Label atom	Calc.	Label atom	Calc.
61-62	2.494	61-63	4.298
61-64	5.765	61-65	2.455
61-73	3.930	61-74	5.254
61-77	5.148	61-78	5.937
61-80	7.558	61-79	6.699
62-63	2.490	62-64	4.958
62-65	4.993	62-74	6.289
62-73	5.057	62-78	6.898
62-77	7.744	62-79	7.811
62-80	9.034	63-64	2.466
63-65	5.866	63-74	5.823
63-73	5.136	63-77	7.450
63-78	7.993	63-79	7.734
63-80	9.072	73-74	1.744
77-78	1.759	79-80	1.763
64-65	6.603	64-74	5.214
64-73	5.307	64-77	7.699
64-78	7.793	64-79	7.523
64-80	8.734	65-73	2.331
65-74	3.638	65-77	4.423
65-78	4.189	65-79	6.218
65-80	6.429	73-77	2.794
73-78	2.711	74-78	2.417
74-77	2.861	73-79	3.083
73-80	3.712	74-79	3.072
74-80	4.043	77-79	2.420
78-79	3.024	78-80	2.339

Table 4. The comparison of selected H - H distances between calculation conformation and the NOESY experimental results

No.	calc.(Å)	exp.(Å)	label atom
1	2.455	2.442	65-61
2	2.480	2.482	61-62
3	1.774	1.800	73-74
4	2.794	2.595	73-77
5	2.861	2.998	74-77
6	2.785	2.686	65-73
7	3.638	3.541	65-74
8	3.024	3.455	78-79
9	2.339	2.390	78-80
10	1.763	1.700	79-80

N(12) and N(15) is approximately parallel with plane (II) composed of N(10), N(13) and N(16). The two planes are upper and lower basis of the prism respectively. The distance between Ba(II) and plane (I) is 1.711 Å and the distance between Ba(II) and plane (II) is 1.553 Å. The angle between plane (III) (average derivation 0.436 Å) composed of N(8), N(12), N(13) and N(16) and plane (IV) (average derivation 0.355 Å) composed of N(10), N(12), N(13) and N(15) is 55.15°; The angle between plane (III) and plane (V) (average derivation 0.355 Å) composed of N(8), N(10), N(15) and N(16) is 118.89°;The angle between plane (IV) and plane (V) is 63.78°. The distance between N(11) and its base plane (IV) is 1.206 Å, the distance between N(14) and its base plane (III) is 1.383 Å and the distance between N(7) and its base plane (V) is 1.174 Å. The three pyridyl nitrogen atoms and Ba^{2+} are coplanar in the complex and all three angles between two Ba - N (Py) bonds approximately being 120°. The Ba - N bond lengths for nine nitrogen atoms (3.00 - 3.08 Å) show that the bonds between Ba(II) and coordinated nitrogen atoms are weak in the complex. The Ba - N bond lengths for imino groups are shorter than those for pyridyl groups. It indicates that the coordination ability of imino-nitrogen atoms is stronger than that of pyridyl-nitrogen atoms, which agrees with the conjugated structure of pyridine and imine.

Based on the MD method, the H - H distances are obtained which are listed in Table 3. Results in Table 3 and NOESY show that the strong NOE across peaks occur only when H - H distances being shorter than 3.000 Å.

To identify the calculated results, we evaluated the structure derivation of the conformation with RMSD (Root-Mean-Square-Derivation) and the average derivation factor between the calculated H - H distances and measured distances in NMR 2D NOESY spectrum. The RMSD is less than 0.005 and R factor is less than 0.0045. The comparison of calculated and experimental H - H distances are listed in Table 4. It can be seen that the calculated H - H distances are agreement with those of experimental results. The studies are in progress.

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