

# Synthesis, characterization and theoretical study of some transition metal complexes with N-(4-(dimethyl amino benzylidene)benzo[d] thiozal-2-amine)

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**Abstract.** In this paper, the cobalt(II), nickel(II), copper(II) and zinc(II) complexes were prepared with a new Schiff bases ligand and the three complexities were identified using infrared spectroscopy, UV and UV spectroscopy and atomic absorption spectrometry to diagnose the ratio of prepared elements and accurate diagnosis of carbon elements Hydrogen and nitrogen. The physical properties of the record and its complexities such as color, temperature, electrical conductivity and magnetic properties were also studied. The ligand preparation was 2: 1 and all the prepared complexes were eight distorted surfaces. A theoretical study was also carried out to calculate the physical energies of the transitions.

## 1. Introduction

Schiff bases are compounds that contain a ( $\text{>C=N}$ ) bond where product from condensation primary amines with carbonyl compounds (aldehyde or ketone), Schiff bases reported by Hugo Schiff et.al. (1864). The most structural of these compounds is the azomethine group with a general formula  $\text{RN=CH-R1}$ , where R and R1 are alkyl, aryl, cyclo alkyl or heterocyclic groups. Azomethine compounds have different names such as imine, ketimines when it is derived from ketone or aldimine when it is derived from aldehyde, Benzylidene aniline, benzanil, and anil [1,2].

Schiff bases metal complexes play important role in coordination chemistry as ligands because of their excellent donor abilities. Their metal complexes have wide applications such as antibacterial, antifungal and other biological as well as clinical, industrial uses especially in catalysis, dyeing, and analytical chemistry [3,4]. Because of perfect selectivity, sensitivity and stability of Schiff bases for specific metal ions.

## 2. Preparation of The Ligand

A mixture of equimolar amount (0.09) mol of 2-amino benzothiazole and Dimethyl amino benzaldehyde in absolute ethanol (15 ml) with (3) drops of glacial acetic acid was refluxed in water bath for (3) hours. The reaction mixture was then allowed to cool room temperature, and the precipitate was filtered and dried, recrystallized from ethanol to give yellow crystals. [5]

## 3. Preparation of Complexes

An amount of (0.321 g of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , 0.277 g of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , 0.122 g  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and 0.234 g  $\text{ZnCl}_2$  were dissolved in 10 ml of ethanol for each one and mixed with (0.93 g of ligand dissolved in 15 ml ethanol) in a molar ratio 1:2 refluxed for 3 hrs. The colored precipitates were filtered then washed with hot ethanol and dried by using desiccator at 60 °C. Elemental micro analysis data, color and yield for the complexes are given in Table (1).



#### 4. Results and Discussion

Some physical properties of the ligand and new complexes are listed in Table (1), elemental microanalysis (C.H.N.), were in a good agreement with the calculated values.

**Table 1.** Elemental microanalysis and some physical properties of the complexes.

Comp.	Color	Melting point (°C)	Elemental Analysis found%, Calc.				
			Yield %	C	H	N	M
L (C <sub>16</sub> H <sub>15</sub> N <sub>3</sub> S)	Deep yellow	160-163	84%	52.33 (52.01)	3.44 (3.2)	9.78 (9.92)	----
L-Co (C <sub>32</sub> H <sub>32</sub> O <sub>2</sub> N <sub>6</sub> S <sub>2</sub> Co)	Deep Brown	210	73%	44.62 (43.77)	3.32 (3.5)	7.55 (8.32)	8.70 (8.90)
L-Ni (C <sub>32</sub> H <sub>31.5</sub> O <sub>2</sub> N <sub>6</sub> S <sub>2</sub> N)	Brown	222	65%	43.89 (43.97)	2.34 (2.9)	6.82 (7.22)	8.86 (8.02)
L-Cu (C <sub>32</sub> H <sub>33</sub> O <sub>2</sub> N <sub>6</sub> S <sub>2</sub> Cu)	Dark yellow	211	73%	44.78 (43.94)	3.57 (3.9)	7.44 (7.99)	9.61 (9.95)
L-Zn (C <sub>32</sub> H <sub>32</sub> O <sub>2</sub> N <sub>6</sub> S <sub>2</sub> Zn)	Light Yellow	230	70%	42.66 (41.55)	3.88 (4.0)	6.96 (7.11)	9.12 (9.67)

##### 4.1 The FTIR Spectrum of Ligand [L] and Complexes

The ligand [L] exhibited a strong high intensity bands appeared at 1662 and 1122.57 cm<sup>-1</sup> which were ascribed to the stretching mode of  $\nu(\text{C}=\text{N})$  and  $\nu(\text{C}-\text{N})$  groups. The weak absorption bands appeared at 3047.53cm<sup>-1</sup> assigned to  $\nu(\text{C}-\text{H})$  aromatic and 2904.80-2819  $\nu(\text{C}-\text{H})$  aliphatic, Table (2) shows the FTIR of ligand. Schiff base behaved as a tetra- dentate ligand, which was been coordinating with the metal via nitrogen of azomethane group. FTIR spectra of the complexes.

abroad bands were observed a round (3353, 3435, 3322, 3455) cm<sup>-1</sup> in each of Co(II), Ni(II),Cu(II) and Zn(II) complexes spectra, which are assigned to the  $\nu(\text{O}-\text{H})$  (H<sub>2</sub>O), results led to a suggestion for the presence of coordinated water molecules[6]. New bands at (513.7,509.5, 543and 555) cm<sup>-1</sup> for metal complexes Co(II), Ni(II),Cu(II) and Zn(II) respectively. Refer to the coordination of the ligand to the central metal ion through nitrogen atom of imine group (M-N).

**Table 2.** Infrared data of Ligand and metal complexes (cm<sup>-1</sup>).

Comp.	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{N})$	$\nu(\text{C}-\text{H})$ Ar	$\nu(\text{C}-\text{H})$ Al	$\nu(\text{O}-\text{H})$ H <sub>2</sub> O	$\nu(\text{M}-\text{N})$
L	1662	1122.57	3047.53	2904.8	----	----
L-Co	1658.7	1126.4	3080	2912.5	3353	513.7
L-Ni	1597.06	1130.3	3089.9	2980	3435	509.5
L-Cu	1658.9	1122.9	3090	2908	3322	543
L-Zn	1654	1127	3088	2907	3455	555

##### 4.2 Electronic Spectra of Ligand [L] and Complexes

The ultraviolet visible electronic spectrum of the ligand and complexes are given in Table (3). Electronic spectra of the all compounds were recorded in the range 190-1100 nm. The absorption spectrum of the one ligand observes absorption at 240 nm, which can be attributed to  $\pi \rightarrow \pi^*$  transitions of the Schiff base ligand [7]. The electronic spectra of Co(II) complexes show bands at 780,650 , 430 and 320nm, which may be attributed to 4T<sub>1</sub>g(F)→4T<sub>2</sub>g(F),4T<sub>1</sub>g(F) →4A<sub>2</sub>g(f), 4T<sub>1</sub>g(F) → 4T<sub>1</sub>g (p), and charge transfer transitions, respectively.[8]

The electronic spectrum of the Ni(II) complex shows four absorption bands at 920,570,370 and 460nm.which ascribed to the transitions 3A<sub>2</sub>g→3T<sub>2</sub>g(f) , 3A<sub>2</sub>g(f)→3T<sub>1</sub>g(f) , 3A<sub>2</sub>g(f)→3T<sub>1</sub>g(p) and charge transfer transitions respectively. The electronic spectra of Cu(II)ion complexes showed two

transitions at 750 and 450 nm, which are attributed to the electronic transition of  $2B_{1g}$   $2B_{2g}$  and because the distorted in octahedral geometry [9], Zn (II) ion complex showed one transitions at 320 nm to charge transfer, all complexes are octahedral geometry.

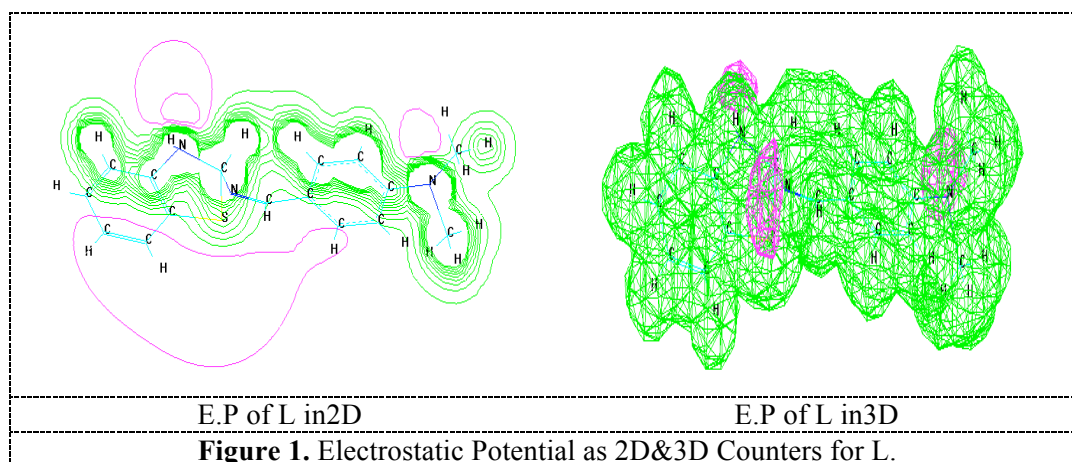
**Table 3.** Electronic spectral data of [L] and complexes.

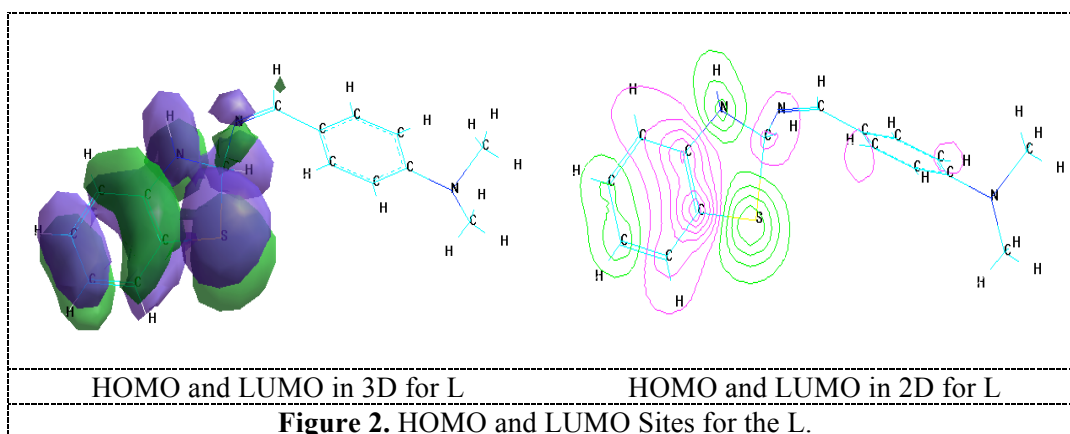
Compounds	Absorption bands ( $\text{cm}^{-1}$ )	Assigned transition
L	41,666	$\pi-\pi^*$
	27,027	$n-\pi^*$
	12,820	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$
L- Co	15,384	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(f)$
	23,255	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(p)$
	31,250	Charge Transfer
	10,869	${}^3A_{2g} \rightarrow {}^3T_{2g}(f)$
L-Ni	17,543	${}^3A_{2g}(f) \rightarrow {}^3T_{1g}(f)$
	27,027	${}^3A_{2g}(f) \rightarrow {}^3T_{1g}(p)$
	21,739	Charge Transfer
	13,333	${}^2B_{1g} \rightarrow {}^2B_{2g}$
L-Cu	22,222	Charge Transfer
L-Zn	31,250	Charge Transfer

## 5. Theoretical study

### 5.1 Electrostatic potential

It designates the interaction of energy of the molecular system with a positive charge point, in order to find the most neactive sites of reaction in molecule positive charge species. They tend to attack a molecule wherever the E.P is powerfully negative electrophilic attach. The E.P of the free ligand is measured and plotted as 2D and 3D contour to inspect the reactive sites of the molecules and can be shown in Figure (1). The results of calculation illustrate that the LUMO of transition metal ion choose to react with the HOMO of donor atoms in ligand [10, 11], as represented in Figure (2) via adopting Hyperchem.-8.07 program.



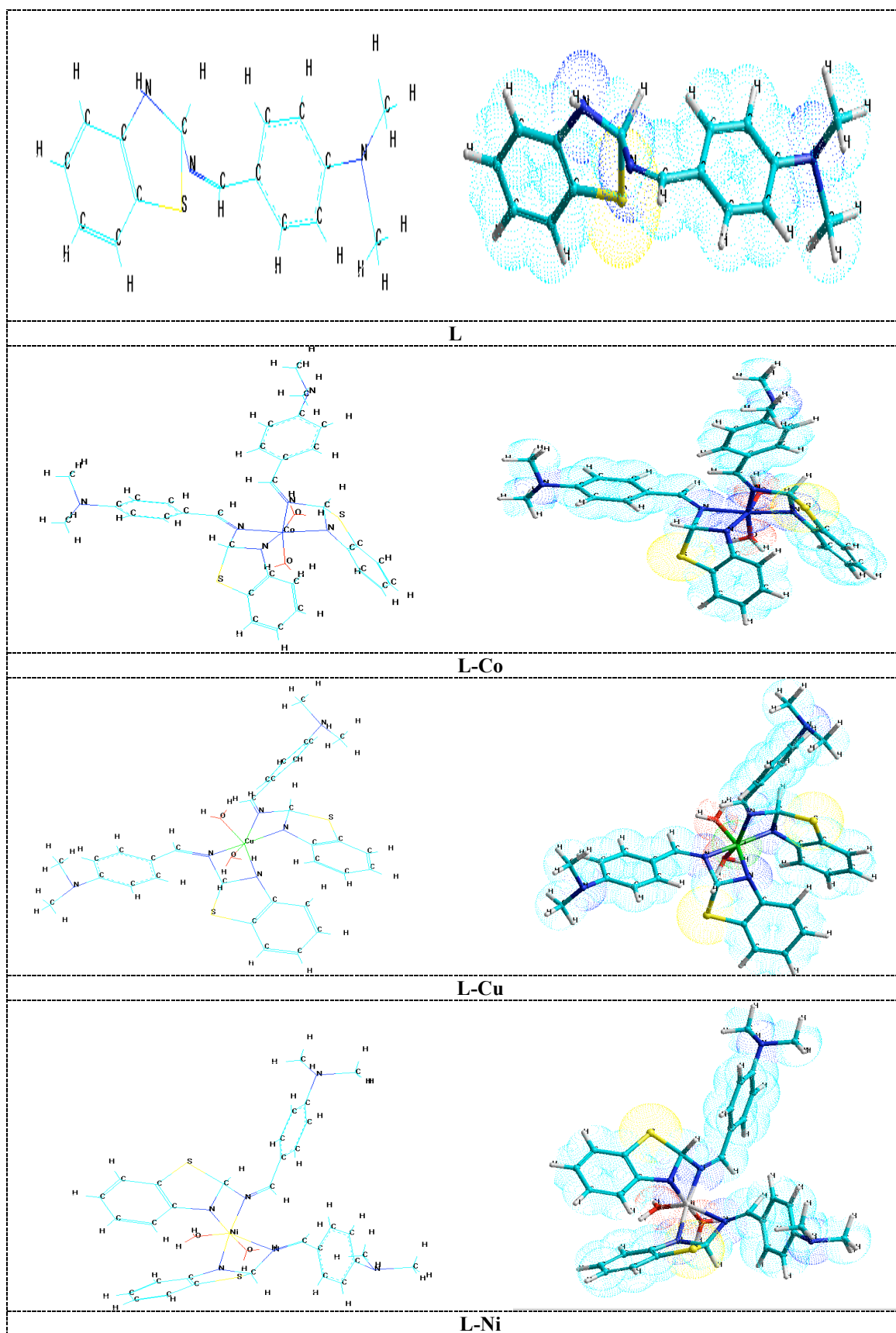


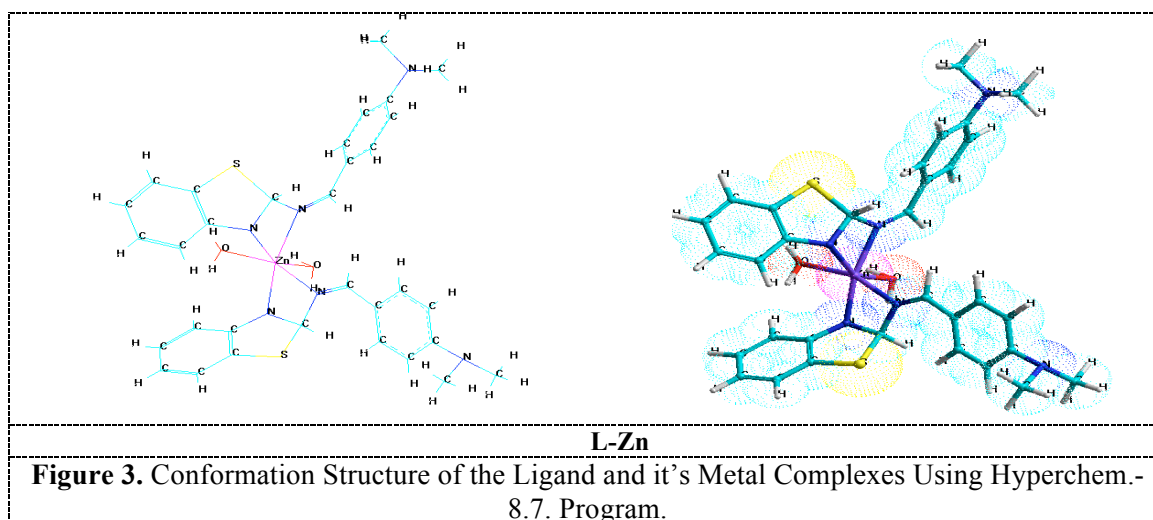
### 5.2 Optimized geometries and energy of ligand its Metal Complexes:

The program HyperChem-8.7 is used for the semi-empirical calculation at optimized geometries energies. The results of PM3 methods of calculation in gas phase for heat of formation ( $\Delta H^{\circ}_f$ ), binding energy ( $\Delta E_b$ ) and total energy ( $\Delta E_T$ ) for the ligand and its complexes are calculated and tabulated in Table (4) [12,13,14]. Theoretically probable structures of metal complexes with ligand have been calculated to find the most possible model building stable structure [15]. The shapes appearing in Figure (3) indicate the calculation optima geometries for the imines and its complexes.

**Table 4.** Conformation Energetic in (KJ.mol<sup>-1</sup>) and for the Ligand and its Metal Complexes.

Compound	PM3		
	$\Delta H^{\circ}_f$	$\Delta E_b$	$\Delta E_T$
L	347.27	-16506.16	-273161.78
L-Co	-1131.33	-36201.94	-682988.88
L-Ni	-635.46	-35707.74	-707052.15
L-Cu	-137.47	-35117.22	-720740.19
L-Zn	482.12	-34290.25	-608643.17





### 5.3 Optimized vibrational spectra for the Ligand and it's Metal Complexes

Theoretically calculated wave numbers for the molecular show some deviations from the experimental values [16, 17, 18]. These deviations are generally acceptable in theoretical calculation and are described in (Table 5).

**Table 5.** A Comparison between Experimental and Theoretical Vibrational Frequencies data for the Ligand and it's Metal Complexes (cm-1).

Compound	$\nu\text{C}=\text{N}$	$\nu\text{C-H}$ Aliph.	$\nu\text{C-H}$ Arom.	$\nu\text{C-N}$	$\nu(\text{O-H})$ H <sub>2</sub> O	$\nu\text{M-N}$
L	1662	2904.80	3047.53	1122.57		
	1892 <sup>a</sup>	3067 <sup>a</sup>	3081.46 <sup>a</sup>	1140 <sup>a</sup>	----	----
	12.156 <sup>b</sup>	5.288 <sup>b</sup>	1.101 <sup>b</sup>	1.528 <sup>b</sup>		
L-Co	1658.7	2912.5	3080	1126.4	3353	513.7
	1636 <sup>a</sup>	2910 <sup>a</sup>	3085	1136 <sup>a</sup>	3617 <sup>a</sup>	517 <sup>a</sup>
	-1.387 <sup>b</sup>	-0.085 <sup>b</sup>	-0.162	0.845 <sup>b</sup>	7.298 <sup>b</sup>	0.638 <sup>b</sup>
L-Ni	1597.06	2980	3089.9	1130.3	3435	509.5
	1618 <sup>a</sup>	2973 <sup>a</sup>	3078 <sup>a</sup>	1125 <sup>a</sup>	3683 <sup>a</sup>	504 <sup>a</sup>
	1.294 <sup>b</sup>	-0.235 <sup>b</sup>	-6.884	-0.471 <sup>b</sup>	6.733 <sup>b</sup>	-1.091 <sup>b</sup>
L-Cu	1658.9	2908	3090	1122.9	3322	543
	1684 <sup>a</sup>	3030 <sup>a</sup>	3078 <sup>a</sup>	1126 <sup>a</sup>	3721 <sup>a</sup>	561 <sup>a</sup>
	1.490 <sup>b</sup>	4.026	-0.389 <sup>b</sup>	0.275 <sup>b</sup>	10.722 <sup>b</sup>	3.208 <sup>b</sup>
L-Zn	1654	2907	3088	1127	3455	555
	1621 <sup>a</sup>	2825 <sup>a</sup>	3080 <sup>a</sup>	1123 <sup>a</sup>	3804 <sup>a</sup>	577 <sup>a</sup>
	-2.035 <sup>b</sup>	-2.902 <sup>b</sup>	-0.259	-0.356	9.174 <sup>b</sup>	3.812 <sup>b</sup>

Experimental frequencies:

<sup>a</sup> Theoretical frequencies

<sup>b</sup> Error %

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