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Synthesis, experimental and theoretical characterizations of cobalt (II) complex of 4-nitro-N^2-pyridin-2-ylmethylene-benzene-1,2-diamine

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Herein, a cobalt (II) complex of the 4-nitro-N2-pyridin-2-ylmethylene-benzene-1,2-diamine=HL Schiff base has been newly synthesized. The complex was characterized using several experimental and theoretical methods. Structure of the complex is octahedral with [CoL2] formula. The HL Schiff base loses a proton of the –NH2 amine group. Two deprotonated L- moieties act as tridentate ligands, occupy six coordination positions of the octahedral complex. In addition to optimized geometry, assignment of the IR spectrum of the complex was calculated using density functional theory (DFT) methods. In the optimized geometry of the free ligand, the aromatic rings are not in the same plane. But, the Co(II) complex has octahedral geometry in which two deprotonated Schiff bases act as N3-tridentate ligands. The DFT-predicted vibrational frequencies are in good agreement with the experimental values, approving suitability of the optimized geometry for synthesized Co(II) complex.

Keywords: Cobalt(II); 2-pyridinecarboxaldehyde; Schiff base; DFT; Assignment

1. INTRODUCTION

The Schiff bases are condensation product of an carbonyl group as electrophile and an amino group as nucleophile. Due to variety in their structure, ease of preparation, different of coordination mode and so on, the Schiff bases are the most versatile studied ligands in coordination chemistry. In addition, this important class of organic ligands shows useful biological activities such as antibacterial, antifungal, anticancer and antiviral activities [1-4]. Coordination to the metal ions improves their biological and catalytic activities [5-10].

On the other hands, the Cobalt (II) complexes of the Schiff bases have several useful biological applications such as activated protein inhibitor [11], oxygen carrier [12], cyanide scavenging [13], carbon dioxide fixation [14] and so on. Also, the cobalt-Schiff base complexes show important catalytic activities [15-17].

Schiff bases derived from 2-pyridinecarboxaldehyde and their metal complexes have received much attention [18-22]. A complex prepared from a Schiff-base of the 2-pyridinecarboxaldehyde showed high super oxide dismutase activities [23]. Since, hopping to beneficial biological and catalytic activities, we attempted to synthesis, experimental and theoretical characterizations of a Co(II) complex of 4-nitro-N^2-pyridin-2-ylmethylene-benzene-1,2-diamine =**HL** Schiff base.

2. EXPERIMENTAL

In this work, all of used chemicals were prepared from the Merck Company and were used without any further purification. The melting points were determined by using a Stuart SMP3 melting point apparatus. The FT-IR spectra were obtained on a Bruker Tensor 27 as KBr discs.

2.1. Synthesis of the cobalt (II) complex

The **HL** Schiff base ligand was synthesized according to a reported procedure [24]. A metanolic solution of the **HL** ligand (1 mmol in 3 mL) was added dropwise to a solution of $Co(OAc)_2.4H_2O$ (1 mmol, 0.249g) in 3 mL methanol. The mixture was refluxed for 4 h. The products formed were filtered and washed with diethyl ether. Finally, the dark-green complex was left to dry at room temperature. (Yield: 87 %, m.p.: 300 ºC)

3. THEORETICAL CHARACTERIZATION

The DFT calculations have been performed using the Gaussian 03 software package [25], the B3LYP [26] functional and the 6-31+G(d,p) basis set. Geometry of the complex was fully optimized, which was confirmed to have no imaginary frequency. The frequency calculation was carried out on the optimized geometry of the Co complex. Generally, the DFT-vibrational frequencies are higher than the experimental values. Herein, the computed vibrational frequencies were scaled using a factor of 0.9614 [27]. All of the structures were imagined by employing the Chemcraft 1.7 program [28].

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4. RESULTS & DISCUSSION

4.1. Geometry optimization

The Schiff bases, which contain a similar structure than the investigated **HL** ligand, make usually an octahedral geometry with the Co^{2+} metal ion [29-33]. Since, an octahedral geometry has been considered for the investigated Co(II) complex. Optimized geometry of the [Co**L**$_2$] complex is shown in Fig.1 in two different views. For more clarification, the hydrogen atoms are omitted in the right-side structure.

For complexation, the **HL** ligand loses one of its amine protons to produce a **L**$^-$ moiety as an anionic ligand. In structure of the Co complex, the **L**$^-$ acts as a tridentate-anionic ligand. Donor atoms of two **L**$^-$ occupy coordination position of octahedral geometry. Donating atoms of the ligand are: the N2 atom of the pyridine ring as well as the N1 and N3 amine nitrogens. This structure is in agreement with the proposed geometry for similar compounds.

Selected bond lengths, angles and dihedral angles are gathered in Table 1. In the optimized geometry of the complex, each of the **L**$^-$ ligands has planar structure; the pyridine and benzene rings as well as chelating rings are in a same plane. For example, all of the calculated N2-C2-C1-N1, C1-N1-C7-C9, C1-N1-C7-C9, Co-N3-C9-C11 and Co-N2-C5-C6 dihedral angles are about 178 to 180.0°. These dihedral angles confirm planarity of each of the **L**$^-$ ligand.

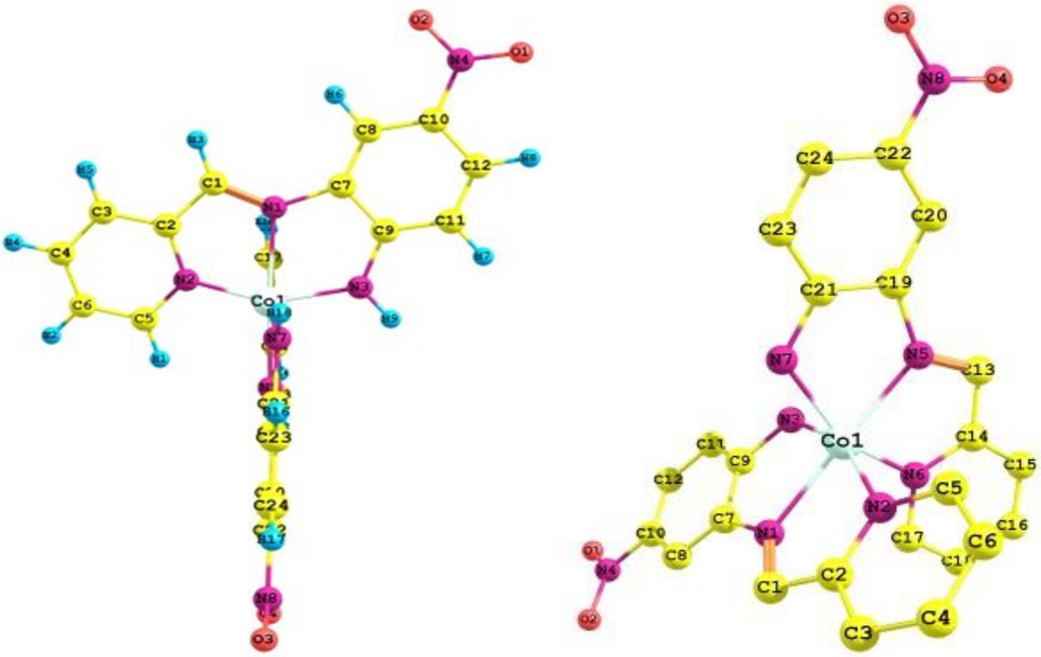

Fig 1. Optimized geometry of the investigated cobalt complex in two different views.

As seen in Table 1, the C1=N1 and C13=N5 azomethine groups are roughly in the same plane with their corresponding pyridine and benzene rings. All of the aromatic rings with their substitution together with two chelating rings lie in a same plane. In complexation, the –NH$_2$ amine groups lose a proton, firstly, which increases electron density in the C9-N3 and C21-N7 bond regions.

The calculated structural parameters for the Co(II) complex are in consistent with the corresponding data reported for the similar compounds [10,29-34], confirming suitability of the optimized geometry of the investigated [Co**L**$_2$] complex.

4.2. Vibrational spectroscopy

The IR spectrum of the Co(II) complex is shown in Fig. 2. The vibrational frequencies of the complex were assigned by comparison of the experimental and the DFT-computed vibrational frequencies. The important obtained results are gathered in Table 2.

An intensive band in the 1660-1500 cm^{-1} region is as a fingerprint region of the IR spectra of the Schiff bases, energy value of which determines coordination mode of the Schiff bases to metals [34]. The symmetrical stretching modes of the C1=N1 and C13=N5 bonds of the azomethine groups are assigned to a strong band at 1596 cm^{-1} of the IR spectrum of the complex [34].

Overlapping of the O-H, N-H and C-H stretching vibrations in the 3600-2000 cm^{-1} spectral region of the IR spectra, results in a band broading [34, 36, 37, 39-50]. Deconvolution of this region of the IR spectrum of complex has been given in Table 2. As can be seen, the strongest band of this region is attributed to the N3-H9 and N7-H18 stretching vibrations of the amine groups.

Table 1. Selected structural parameters of the CO(II) complex.

Bond length (ppm)		Angle (°)		Dihedral angle (°)	
Co-N1	218.2	N1-Co-N2	76.0	Co-N2-C2-C1	2.1
Co-N2	191.1	N1-Co-N2	77.3	Co-N3-C9-C7	1.9
Co-N3	196.7	N2-Co-N3	152.9	C2-N2-Co-N6	-107.6
Co-N6	190.8	N1-Co-N5	174.0	C9-N3-Co-N2	-0.9
C5-N2	134.8	N1-Co-N6	95.7	C9-N3-Co-N2	-108.3
C2-N2	139.3	N1-Co-N7	107.8	N6-Co-N7-C21	1.7
C2-C3	141.2	Co-N1-C1	114.7	N1-C1-N2-C2	0.0
C3-C4	139.9	Co-N1-C7	112.2	C7-N1-C1-H3	180.0
C2-C1	144.6	C1-N1-C7	131.6	N1-C7-C9-N3	-0.1
C1-H3	109.1	C5-N2-C2	119.5	C7-C9-N3-H10	180.0
C1-N1	131.6	N2-C2-C1	113.8	N4-C10-C8-C7	-180.0
C7-N1	141.5	N1-C1-C2	116.1	C8-C10-N4-O1	-180.0
C7-C9	140.4	C1-N1-C7	130.7	C3-C2-C7-C8	0.6
C9-N3	132.3	N1-C7-C9	110.7	C2-C1-N1-C7	1.3
N3-H10	103.4	C7-C9-N3	115.3	C1-N1-C7-C8	0.3
C9-C11	141.6	C9-N3-H10	119.5	C3-C2-N1-C1	178.8
C10-N4	144.9	C11-C9-N3	127.1	C1-C2-C3-C4	-180.0
N4-O1	123.6	C9-C11-C12	120.9	C2-C3-C4-C6	0.0
		C7-C8-C10	117.9	C7-C8-C10-C12	0.0
		C8-C10-N4	119.3		
		C10-N4-O1	118.3		

Table 2. Selected experimental and calculated IR vibrational frequencies (cm^{-1}) of the **L3** ligand and its Co(II) complex.

Experimental frequencies	Calculated frequencies		Vibrational assignment
	Frequency	Intensity (km.mol^{-1})	
647 (w)	623	14	υ_{sym}(N2-Co-N3)
819, 772 (w)	801, 757	30, 49	$\delta_{on\ plane}$ (C-H) of the aromatic rings
1076 (m)	1061	198	$\delta_{in\ plane}$ (C-H) of the aromatic rings
1157 (s)	1192	74	υ(C7-N1) + υ(C19-N5)
1254 (vs)	1339	107	υ(C9-N3) + υ(C21-N7)
	1303	1421	[υ(C10-N4) + υ(C22-N8)] of the C–NO$_2$ substitutions
1442 (s)	1526	403	υ_{asym}(O-N-O) of the –NO$_2$ substitutions
1503 (s)	1576	211	υ(C=N, C=C) of the aromatic rings
	1507, 1438	79, 448	υ(C=C) of the benzene ring + υ(C-N) of the substitutions of the benzene ring
1596 (s)	1589	179	υ(C1=N1) + υ(C13=N5)
3144 (m, br) 3251 (m)	3048	13	υ(C1-H3) + υ(C13-H12)
	3128-3073	2-11	υ(C-H) of the aromatic hydrogens
3415 (m)	3483	58	υ(N3-H9) + υ(N7-H18)

Abbreviation: op, out-of-plane; ip, in-plane; w, weak; m, medium; s, strong; vs, very strong; br, broad.

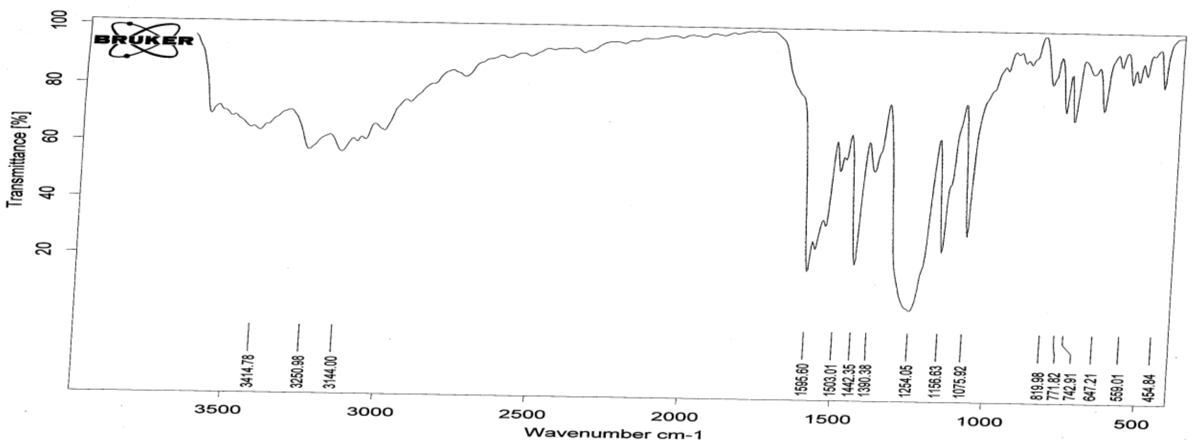

Fig 2. The FTIR spectrum of the Co(II) complex.

The FT-IR spectrum of the free **HL** Schiff base ligand involves absorption peaks at 1647 cm^{-1} and 3276-3362 cm^{-1} for the azomethine group and $–NH_2$ groups, respectively [24]. But, the FT-IR spectrum of the Co(II) complex don't show the absorption peaks of $–NH_2$ group (Fig. 2), confirming deprotonation of the $–NH_2$ amine group and coordination of the –NH amine group. The symmetrical stretching modes of C=N azomethine groups shifts from 1647 cm^{-1} for the free **HL** [24] to 1596 cm^{-1} for the [Co**L**$_2$] complex, which confirms coordination of the ligand *via* the azomethine nitrogen.

5. CONCLUSION

We previously reported synthesis and characterization of the 4-nitro-N^2-pyridin-2-ylmethylene-benzene-1,2-diamine Schiff base [24]. In this work, a Co(II) complex of this Schiff base has been newly synthesized and characterized experimentally. In addition, the valuable DFT methods were employed to obtain better insight into the geometry and spectral properties of the synthesized complex. Based on the experimental data and considering previous researches on the similar compounds, the [Co**L**$_2$] formula was proposed for the complex.

Structure of the complex is octahedral. The HL is deprotonated, firstly, loses one of the –NH2 protons. The anionic **L**$^-$ acts as a three dentate ligand, coordinates to the Co^{2+} metal ion *via* three nitrogen atoms of the pyridine ring, azomethine group and –NH amine group. Optimized geometry of the octahedral complex is more planar than the free **HL** ligand.

The vibrational IR frequencies of the Co(II) complex are computed theoretically. There is good agreement between the experimental and computational-DFT values, which approves validity of the optimized geometry for the investigated cobalt complex.

REFERENCES

1. H. Amiri Rudbari, M.R. Iravani, V. Moazam, B. Askari, M. Khorshidifard, N. Habibi, G. Bruno, *J. Mol. Structure,* **11, 75,** 113 (2016).
2. Ö. Güngör, P. Gürkan, *J. Mol. Structure*, **10**, 74 6270 (2014).
3. J.A. Makawana, J. Sun, H.-L. Zhu, *Bioorgan. Medic. Chem. Lett.*, **23** 6264 (2013).
4. K.S. Kumar, S. Ganguly, R. Veerasamy, E. De Clercq, *Eur. J. Medic. Chem*., **45**, 5474 (2010).
5. H. Mobley, R. Hausinger, *Microbiol. Rev*., **53,** 85 (1989).
6. R. Kurtaran, L.T. Yıldırım, A.D. Azaz, H. Namli, O. Atakol, J. Inorg. Biochemistry, **99**, 1937 (2005).
7. L. Yıldırım, R. Kurtaran, H. Namli, A. Azaz, O. Atakol, *Polyhedron,* **26**, 4187 (2007).
8. Y.-T. Liu, G.-D. Lian, D.-W. Yin, B.-J. Su, *Spectrochim. Acta, Part A*, **100**, 131 (2013).
9. L.H. Abdel-Rahman, R.M. El-Khatib, L.A. Nassr, A.M. Abu-Dief, F.E.-D. Lashin, *Spectrochim. Acta, Part A,* **111**, 266 (2013).
10. O.M.I. Adly, *Spectrochim. Acta*, Part A, **95,** 483 (2012).
11. S.A.B. Morteza Yavari, A. Morsali, M.R. Bozorgmehr, M. Khashi, *J. Mol. Structure,* (2016)
12. D. Chen, A.E. Martell, Y. Sun, *Inorg. Chem*., **28**, 2647 (1989).
13. E. Lopez-Manzano, A.A. Cronican, K.L. Frawley, J. Peterson, L.L. Pearce, *Chem. Res. Toxicol*., **29**, 1011 (2016).
14. G. Fachinetti, C. Floriani, P.F. Zanazzi, A.R. Zanzari, *Inorg. Chem.*, **18**, 3469 (1979).

15. I. Iwakura, T. Ikeno, T. Yamada, *Org. Lett.*, **6**, 949 (2004).
16. S. Förster, A. Rieker, K. Maruyama, K. Murata, A. Nishinaga, *J. Org. Chem.*, **61**, 3320 (1996).
17. N. Kleigrewe, W. Steffen, T. Blömker, G. Kehr, R. Fröhlich, B. Wibbeling, G. Erker, J.-C. Wasilke, G. Wu, G.C. Bazan, *J. Amer. Chem. Soc.*, **127**, 13955 (2005).
18. T. Campbell, F. Urbach, *Inorg. Chem.*, **12**, 1836 (1973).
19. W. Potter, L. Taylor, *Inorg. Chem.*, **15**, 1329 (1976).
20. A.N. Vlček, *Coord. Chem. Rev.*, **230**, 225 (2002).
21. J. García-Tojal, T. Rojo, *Polyhedron*, **18**, 1123 (1999).
22. J. García-Tojal, A. García-Orad, A.A. Díaz, J.L. Serra, M.K. Urtiaga, M.A.I. Arriortua, T. Rojo, J. Inorg. Biochem., **84**, 271 (2001).
23. C.-M. Liu, R.-G. Xiong, X.-Z. You, Y.-J. Liu, K.-K. Cheung, *Polyhedron*, **15**, 4565 (1996).
24. S.A.B. Mohammad Habibi, S. Allameh, M. Khashi, A. Morsali, M. Pordel, *J. Mol. Struct.*, (2016)
25. M. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, J. Montgomery Jr, T. Vreven, K. Kudin, J. Burant, Gaussian 03, revision B. 05; Gaussian, Inc., Pittsburgh, PA, 12478 (2003).
26. C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B*, **37**, 785 (1988).
27. D.C. Young, Computational Chemistry: A Practical Guide for Applying Techniques to Real World Problems, Wiley Online Library (2001).
28. G. Zhurko, D. Zhurko, ChemCraft, version 1.7, URL: http:// www. chemcraftprog. com, (2009).
29. K. Das, A. Datta, P.-H. Liu, J.-H. Huang, C.-L. Hsu, W.-T. Chang, B. Machura, C. Sinha, *Polyhedron*, **71**, 85 (2014).
30. S. Kundu, S. Roy, K. Bhar, R. Ghosh, C.-H. Lin, J. Ribas, B.K. Ghosh, *J. Mol. Struct*., **10**, 38 78 (2013).
31. M.A. Ali, A.H. Mirza, H.J.H.A. Bakar, P.V. Bernhardt, *Polyhedron*, **30**, 556 (2011).
32. A.-N.M.A. Alaghaz, M.E. Zayed, S.A. Alharbi, R.A.A. Ammar, A. Elhenawy, Synthesis, characterization, biological activity, *J. Mol. Struct*., **10**, 84, 352 (2015).
33. A. Sousa-Pedrares, N. Camiña, J. Romero, M.L. Durán, J.A. García-Vázquez, A. Sousa, *Polyhedron*, **27**, 3391 (2008).
34. P. Tyagi, M. Tyagi, S. Agrawal, S. Chandra, H. Ojha, M. Pathak, *Spectrochim. Acta, Part A*, **171**, 246 (2017).