

Research Article



Synthesis, Characterization and Theoretical Studies of Transition Metal Complexes of 1,2Phenyl(4-Carboxy)Benzylidene

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Accepted on: 05-04-2016; Finalized on: 30-04-2016.

ABSTRACT

New Schiff base chelate of Mn(II), Co(II), Ni(II) and Cu(II) derived from benzene 1,2 dicarboxylic aldehyde with o-amino benzoic acid have been prepared, and characterized by elemental analysis, magnetic and spectroscopic measurements IR, UV-Vis, CHN and spectral studies have been carried out to suggest the structures for the complexes. The data show these complexes have general composition of $[ML_2 \cdot 2H_2O]$ type. The works also include a theoretical treatment of the formed complexes in the gas phase. This was done using the (hyperchem-8) program for the molecular mechanics and semi-empirical calculations. The heat of formation (ΔH_f°), binding energy (ΔE_b) and total energy (ΔE_T) for ligand and its complexes were calculated by (PM3) method at 298 K. The electrostatic potential of the free ligand (L) was calculated to investigate the reactive sites of the molecules. The theoretical results agreed with those found experimentally.

Keywords: 1,2Phenyl(4-Carboxy)Benzylidene, synthesis, characterization.

INTRODUCTION

Metal complexes of Schiff bases have played a central role in the development of coordination chemistry. Schiff bases, named after Hugo Schiff¹ are formed when any primary amine reacts with an aldehyde or a ketone under specific conditions. Schiff bases have also been shown to exhibit a broad range of biological activities including antifungal, antibacterial, antimalarial, antiproliferative, anti-inflammatory, anti-inflammatory, antiviral, and antipyretic properties^{2,3}. Nowadays, the research field dealing with Schiff base coordination chemistry has expanded enormously. The importance of Schiff base complexes for bioinorganic chemistry, biomedical application, supramolecular chemistry, catalysis and material science, separation and encapsulation processes, and formation of compounds with unusual properties and structures have been well recognized and reviewed. It is well known from the literature that much work has been done on the synthesis and characterization of this compounds^{4,5}.

Experimental

All the chemical used were of analar grade and procured from sigma-Aldrich.

The solvents were dried and distilled before use according to standard procedures. IR spectra were recorded in KBr medium on a shimadzu FTIR-8300 spectrophotometer.

The UV-Vis spectra of all the complexes were recorded in ethanol on a Shimadzu UV-1650PC spectrophotometer in the range (200-1000) nm.

Magnetic Susceptibility measurements for complexes were obtained at room temperature using (magnetic susceptibility balance) Johnson Matthey catalytic system division.

Synthesis of the ligand (L)

The Schiff base (L), fig1 was been prepared according to the following procedure. An ethanolic solution of **benzene 1,2 dicarboxylic aldehyde** (0.020ml, 2.68g) was added to an ethanolic solution of **o-amino benzoic acid (anthranilic acid)** (0.020ml, 2.14g) and refluxed for 6 hours in water bath. After concentration of the solution, the precipitate was separated, filtered, and dried over anhydrous calcium chloride under vacuum, the yield of product 83% yields.

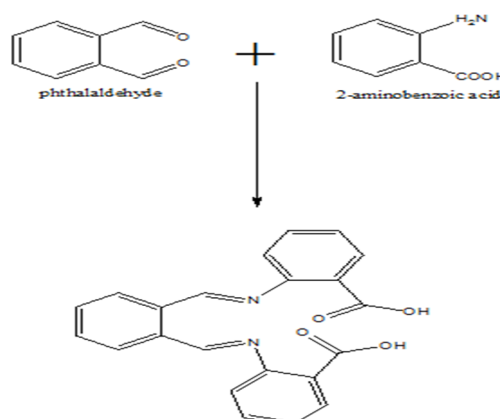


Figure 1: Synthesis route of ligand (L).

Preparation of metal ion complexes

The metal ion complexes of organometallic compounds were prepared by mixing ethanolic equimolar concentration (0.02M) Of(L) ligand with (0.04M) aqueous



solution of metal acetate of **manganese(II)**, **cobalt (II)**, **Nickel(II)** and **copper(II)** salts were used for preparation these complexes. Then the solutions were mixed in 1:1 ratio and refluxed for 6 hours using water condenser. After that, the solution were cooled at room temperature, solid of complexes were appeared then, it will filtered, washed with ethanol and dried. The yields is obtained in between 60-82%.

RESULTS AND DISCUSSION

The physical and analytical properties data of the organometallic compound and their complexes is given in table 1. The ligand (L), on interaction with Mn(II), Co(II), Ni(II) and Cu acetates, yields complexes corresponding to general formula $[ML(H_2O)]$. The analytical data show that the metal to ligand ratio is 1:1. They are soluble in common organic solvents. The low molar conductance values of the complexes reveal their non-electrolytic nature⁶.

Table 1: Physical and Analytical data of the ligand and its complexes (*Experimental values)

Compound/complexes	yield%	MP/C	C%	N%	H%	M%	Mol ⁻¹ cm ⁻² Ω	BM.μeff
C ₂₂ H ₁₆ N ₂ O ₄	80	243-245	70.89 70.50*	7.52 7.50*	4.33 4.25*	-----	-----	-----
[Mn(C ₂₂ H ₁₆ N ₂ O ₄).2H ₂ O]	71	223-226	56.98 56.44*	6.04 6.00*	3.45 3.35*	11.85 11.67*	18	5.90
[Co(C ₂₂ H ₁₆ N ₂ O ₄).2H ₂ O]	63	218-220	56.49 56.40*	5.99 5.89*	3.42 3.35*	12.61 12.58*	22	3.38
[Ni(C ₂₂ H ₁₆ N ₂ O ₄).2H ₂ O]	70	217-220	56.52 56.50*	5.99 5.87*	3.42 3.39	12.56 12.50*	19	2.90
[Cu(C ₂₂ H ₁₆ N ₂ O ₄).2H ₂ O]	68	212-214	55.98 55.88*	4.24* 4.20*	3.39 3.30*	13.46 13.40*	23	1.90

Table 2: Infrared Spectral Data of ligand and its complexes

Compound/complexes	OH acidU	C=NU	M-NU	uM-O	2H ₂ O
C ₂₂ H ₁₆ N ₂ O ₄ (3390	1680	-	-	-
[Mn(C ₂₂ H ₁₆ N ₂ O ₄).2H ₂ O]	-	1622	533	455	3495,3422
[Co(C ₂₂ H ₁₆ N ₂ O ₄).2H ₂ O]	-	1628	547	459	3490,3445
[Ni(C ₂₂ H ₁₆ N ₂ O ₄).2H ₂ O][--	1637	538	465	3520,3437
[Cu(C ₂₂ H ₁₆ N ₂ O ₄).2H ₂ O]		1640	552	451	3511,3432

Table 3: Conformation energetic (in Kcal.mol⁻¹) for ligand and its metal complexes

Compd.No.	H _A (Kcal/mol)	E _{tot} (Kcal/mol)	E _b (Kcal/mol)	HOMO (ev)	LUMO (ev)
1.L	77.7101	-4979.733	-95214.812	-7.32928	-2.079906
2.NiL	-410.562	-138047.362	-5689.928	-9.490167	-1.029562
3.CoL	-404.044	-132528.571	-5735.112	-9.223408	-1.469652
4.MnL	-123.190	-123876.942	-5523.762	-9.573216	-0.970663
5.CuL	-243.231	-141621.885	-5552.599	-9.358659	-0.893238

IR spectra

The infrared spectra of organometallic ligand (C₂₂H₁₆N₂O₄) and their complexes were recorded [Mn(C₂₂H₁₆N₂O₄).2H₂O], [Co(C₂₂H₁₆N₂O₄).2H₂O], [Ni(C₂₂H₁₆N₂O₄).2H₂O] and [Cu(C₂₂H₁₆N₂O₄).2H₂O] and compared with substituted moieties. The bands were observed in the organometallic ligands at 3700 cm⁻¹ for ν(OH), which was found to have disappeared in all the respective complexes that mean its bonding with metal

ions through deprotonation⁷, band observed at 1680 cm⁻¹ for azomethan (>C=N-) group, due bonding with metal ions in between 1640-1622cm⁻¹. The two new bands were observed at 3520-3490 and 3445-3422cm⁻¹ due to two coordinated water molecules present in the coordination sphere. The bands were observed far infrared region at 552-533cm⁻¹ due to metal-nitrogen bonding (M←N)linkage and 465-451cm⁻¹ due to metal-oxygen bonding (M→O). The central metal ions have six



coordination numbers and ligand behaves as a monodentate ligand^{8,11}. IR bands values of the organometallic compound and their complexes were reported in table 2.

Electronic spectra

Upon the electronic spectrum of the L schiff base ligand, the two essential absorption bands were observed at 310nm, (360 and 550) nm due to the transitions $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, respectively. These transitions were existed also in the spectra of the complexes, but they shifted to different lower intensities, confirming the coordination of the ligand to the metal ions. In UV-Vis. spectra, the weak band should be at 400-500nm are due to charge-transfer (ct) band in the complexes, which is absence in the ligand. However, the weak broad band at 500-700nm is due to d-d transition of the metal ions as mentioned. The electronic absorption spectra of Mn (II) complexes were recorded at room temperature using ethanol as solvent show four medium intensity bands assigned to ${}^6A_{1g} \rightarrow {}^4T_{1g}$, ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$ and ${}^6A_{1g} \rightarrow {}^4E_g(G)$, ${}^4A_{1g}(G)$ respectively, for Mn(II) ion in an distorted octahedral field¹². The electronic spectrum of octahedral Co(II) complex has three types of transitions due to ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$, and ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$ ¹². The diffuse reflectance spectrum of copper (II) complex is expected to show two allowed transitions namely ${}^2B_{1g} \rightarrow {}^2E_g$ and ${}^2B_{1g} \rightarrow {}^2B_{2g}$. These bands suggested distorted octahedral geometry around Cu(II)[12]. The electronic spectrum of the Ni(II) complex could be assigned to octahedral geometry. The solid reflectance spectrum of the Ni(II) complex showed two identified bands at 16722 and 2272cm⁻¹, assigned to the transitions ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ respectively¹³.

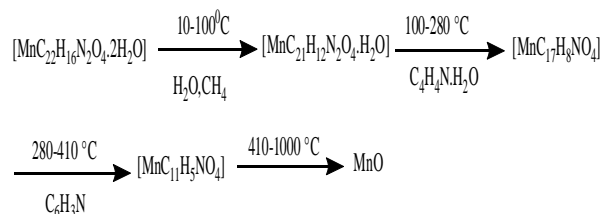
Magnetic properties

The effective magnetic moment values of the complexes are presented in table 1. The **Mn(II)** complex has μ_{eff} value of 5.90 μ_B , which suggests a spin-free complex. The **Co(II)** complex has a magnetic moment of 3.38 μ_B which is typical of Co(II) ion in an octahedral environment^{14,15}. A magnetic moment value of 2.90 μ_B is observed for the **Ni(II)** complex, expected for octahedral geometry^{16,17}. The magnetic moment value of Cu(II) complex is 1.90 μ_B which suggest a distorted octahedral geometry^{18,19}.

Thermal Analysis of [Mn(C₂₂H₁₆N₂O₄).2H₂O] complex

Thermogravimetric study of **Mn(II)** complex shows weight losses in the temperature range 90-140°C, which is corresponding to the loss of one water molecule present in the coordination sphere and some part of complex were loosed. The experimental percentage loss, which has calculated from Thermogravimetric analysis curve, is 7.55%. The value were comparing with actual theoretical percentage loss of the complex. The differential thermal analysis peak is endothermic²⁰. In second step at 150-470°C, the second coordinated molecule will loss and some part of complex were losses. The major part of complex agent were lost at 480-580°C. The experimental

percentage loss values are 33.72%, which is obtained from Thermogravimetric analysis curve. The experimental percentage loss values which were comparable with theoretical percentage loss value i.e. 36.17%. The Differential thermal analysis peak is exothermic²¹. The probable leaving part of complex is C₁₀H₁₀. The temperature range 600-910°C leading to the formation of Manganese oxide. The decomposition scheme of the complex as shown below.



According to the results obtained an octahedral structure has been suggested to these complexes.

Structure of complex

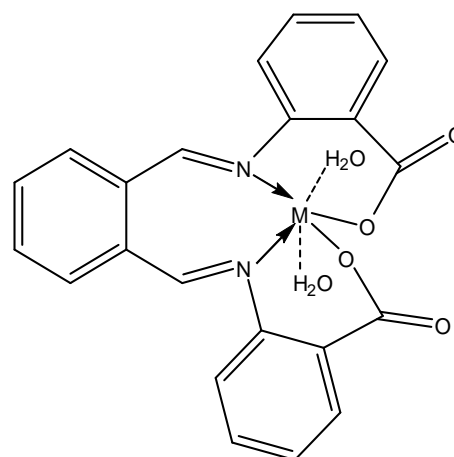


Figure 2: The suggested structure of complexes

where M=Mn, Co, Ni, and Cu

ligand=1,2phenyl(4-carboxy)benzylidene.

Study of complexes in gas state (Theoretical studies)

Electrostatic potentials

Electron distribution governs the electrostatic potential of the molecules. The electrostatic potential (E.P.) is useful for finding sites of reaction in a molecule; positively charged species tend to attack a molecule, where the electrostatic potential is strongly negative (electrophilic attack)²². The E.P. of the free ligand (**L**) was calculated and plotted as 2D contour to investigate the reactive sites of the molecules (Fig. 3). Also one can interpret the stereochemistry and rates of many reactions involving "soft" electrophiles and nucleophiles in terms of the properties of frontier orbital (HOMO, highest occupied molecular orbital) and (LUMO, lowest unoccupied molecular orbital). The results of calculations show that the LUMO of transition metal ions prefer to react with the HOMO of two-donor atoms of oxygen and nitrogen of the ligand (**L**)²³.

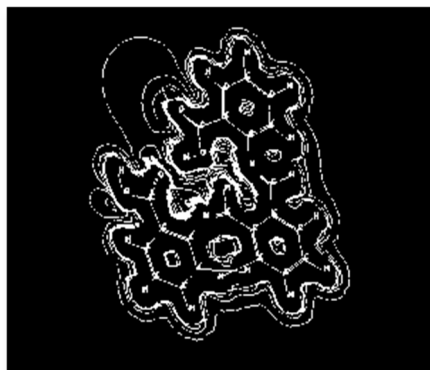


Figure 3: Electrostatic potential(HOMO and LUMO)as 2D contours for (L)

Optimized energies

The program Hyperchem-8 was used for the semi-empirical and molecular mechanics calculations.

The heat of formation (ΔH_f°) and binding energy (ΔE_b) for free ligand (**L**) and their metal complexes (**1-5**).

REFERENCES

1. H. Schiff (1864) Justus Liebigs Ann.Chem.Vol 131, 118.
2. D.N.Dhar and C.L.Taploo.J.Sci.Ind.Res, Vol41, 1982, 501.
3. N. Dixit, L. Mishra, S.M. Mustafi, K.V.R.Chary and H.Houjou, spectrochimica Acta part A:Molecular and Biomolecular
4. L.A. Bigelow and H. Eatough, Org.synth., 1, 1967, 80.
5. L.G. Marzilli, P.A.Marzilli and J.Halpern, 93, 1971, 1374.
6. Geary Wj Coord.Chem.Rev. 7, 1971, 81.
7. K. Nakamoto, Infrared Spectro of Inorganic and Coordination Compounds, 6th Ed., Wiley, Inter Science, New York(1997).
8. Abulsamath S, Raman M, Raman N, Complexes of Cu(II) cinnamalidene. Trans Metal Chem, 17, 1993, 13-20.
9. Roik NV, Belyakova LR, Infrared Spectroscopy, X-Ray Diffraction and Thermal Analysis Studies of Solid b-Cyclodextrin-para-Aminobenzoic Acid Inclusion Complex, phyChem Solid State, 12(1), 2011, 168-173.
10. Krishan B, Prakash O, Synthesis characterization and spectral studies of gold complex with gliclazide, Ori j Chem, 29(1), 2013, 381-88.
11. Ferraro JF, Low Frequency Vibrations of Inorganic and Co-ordination Compounds. Plenum press:New York, 1991, 153-57.
12. Lever, A.B.P. The electronic spectra of tetragonal metal complexes analysis and significance. Coord.chem.Rev., 3(2), 1968, 119-140.
13. Singh D.P; Kumar K.; Sharma C. Synthesis, Characterization and Antimicrobial activities of Macrocyclic Complexes of Divalent Transition Metal Ions 14.Synth.Reac.Inorg.Met-Org.Chem., 40(6), 2010, 385-387.
14. Krishna C H, Mahapatra C M and Dush K C J.Inorg. Nucl. Chem. 39, 1977, 1253.
15. Lever, A.B.P. The electronic spectra of tetragonal metal complexes analysis and significance. Coord.Chem.Rev., 3(2), 1968, 119-140.
16. Konig E1971 Structure and bonding (Berlin: Springer Verlag) p.175.
17. Rana A K and Shah JR, Indian JChem.A20, 1981, 120.
18. Cotton FA and Wilkison G1962 Advanced inorganic Chemistry (New Delhi: Wiley Intescience).
19. Figgis B. N., 1976 An introduction to ligand fields (New Delhi: Wiley Eastern). chemistry (New York: Wiley Interscience)
20. Sabastiyam A and Venkappayya D, J. Indian Chem. Soc. 67, 1990, 584.
21. K. Nagesha and A. Kotove, Concepts in Theoretical Chemistry Elsevier Publishing Company, NewYork, London (1978).
22. R. A. AL-Hassani, O. Niff and A. Mahmood, Acta Chimica and Phamaceutica Indica: 5(3), 2015, 129-142.

Source of Support: Nil, **Conflict of Interest:** None.