Asian Journal of Chemistry; Vol. 29, No. 10 (2017), 2167-2170

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2017.20668

Synthesis, Spectral and Biological Studies of Cu(II), Ni(II), Fe(III), Co(II), Mn(II) and Cd(II) Complexes of 3-Acetyl-4-hydroxy-6-methyl-2*H*-pyran-2-one Schiff Base Derived from 3-Amino-1,2,4-triazole

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Received: 25 March 2017; *Accepted*: 28 June 2017; *Published online*: 31 August 2017; AJC-18513

The solid metal complexes of Cu(II), Ni(II), Fe(III), Co(II) Mn(II) and Cd(II) with novel Schiff base ligand derived from 3-acetyl-4-hydroxy-6-methyl-2*H*-pyran-2-one and aromatic primary amine, 3-amino-1,2,4-triazole were synthesized and characterized by elemental analysis, FTIR, UV-visible, ^{1}H NMR and XRD spectroscopic techniques. The signals of ^{1}H NMR spectra and important bands in IR spectra are considered and discussed in relation to molecular structure of ligand. The UV-visible absorption bands are assigned to corresponding electronic transitions, which are also studied by magnetic study. The biological (antibacterial and antifungal) activity of ligand and its metal complexes have been screened *in vitro* against *Bacillus subtilis*, *Staphylococcus aureus*, *Aspergillus niger* and *Candida albicans*. Schiff base ligand as well as all metal complexes have shown significant biological activities.

Keywords: 3-Acetyl-4-hydroxy-6-methyl-2*H*-pyran-2-one, Schiff bases, Metal complexes, Biological activity.

INTRODUCTION

3-Acetyl-4-hydroxy-6-methyl-2*H*-pyran-2-one (DHA) and its derivatives constitute an important class of compounds in organic synthesis, especially as starting material for the preparation of various heterocyclic systems *viz.* Schiff bases, Mannich bases, chalcones, *etc*. The Schiff bases are one of the most widely used chelating ligands in coordination chemistry.

Herein we describe the synthesis and characterization of the Schiff base derived from 3-acetyl-4-hydroxy-6-methyl-2*H*-pyran-2-one (DHA) and 3-amino-1,2,4-triazole as well as their synthesized metal complexes with Cu(II), Ni(II), Fe(III), Co(II), Mn(II) and Cd(II). The Schiff base and metal complexes were characterized by elemental analysis, FTIR, UV-visible, ^{1}H NMR, XRD spectroscopic techniques and their magnetic profiles are recorded and discussed herein. The biological (antibacterial and antifungal) activities of ligand and its metal complexes have been screened *in vitro* against *Bacillus subtilis*, *Staphylococcus aureus*, *Aspergilus niger* and *Candida albicans*.

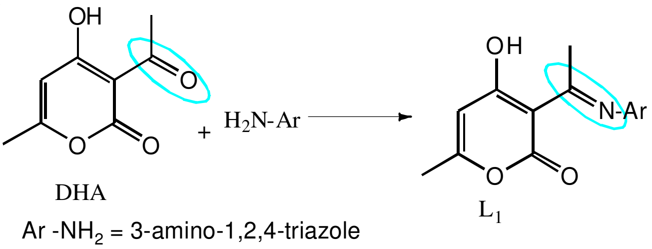
EXPERIMENTAL

3-Acetyl-4-hydroxy-6-methyl-2*H*-pyran-2-one (DHA) was procured from E-Merck, Germany, 3-amino-1,2,4-triazole was obtained from Avra. Metal chlorides were purchased from E. Merck as well as from Loba chemie Pvt. Ltd. The solvents were dried and distilled before use following the literature reported procedure [1].

The C, H and N analysis of the compounds were obtained on Perkins Elmer CHN Analyzer (2400). The IR spectra of ligand and the metal complexes were recorded by KBr pellet method on Perkin Elmer (1430) FTIR spectrophotometer in the range 4000-400 cm^{-1}. The ^{1}H NMR spectrum of ligand is recorded on Brucker FT-300 MHz NMR spectrophotometer in $CDCl_3$ by using TMS as reference. The electronic spectral measurements were made on Shimadzu UV-visible spectrophotometer UV160, Magnetic susceptibility measurements were carried out with on Gouy's balance at laboratory temperature by using $Hg[Co(CNS)_4]$ as standard. The TG and DT analysis were carried out in 25-1000 °C range. The biological (antibacterial and antifungal) activities of ligand and metal complexes were screened *in vitro* against *Staphylococcus aureus* (NCIM-2079) and *Bacillus subtilis* (NCIM from 24 h cultures of microorganisms were adjusted to 0.5 McFarland. Muller-Hinton Petri dishes-2063, *B. subtilis*) as bacterial strains and *Candida albicans* (MTCC-227) and *Aspergillus niger* (NCIM-545) as fungal strains were used. For the study of antibacterial activity suspensions in sterile peptone water of 90 mL were prepared and inoculated using these suspensions. Wells (6 mm in diameter) containing 100 μL of the substance to be tested (at a concentration of 1 mg/mL in DMSO) were formed in a circular pattern in each using a ruler. Streptomycin was used as a reference substance.

For antifungal activity, the same procedure was repeated with replacement of peptone water with phosphates buffered saline (PBS) and Muller-Hinton medium with yeast peptone dextrose (YPD) medium. Griesofulvin was used as reference. Incubation of the plates was done at 37 °C for 24 h. Reading of the results was done by measuring the diameters of the inhibition zones generated by the tested substances [2].

Synthesis of Schiff bases: Schiff base motif (L_1) was prepared by the addition of ethanolic solution of 3-amino-1,2,4-trizole (0.05 mol) into ethanolic solution of DHA (0.05 mol). The reaction mixture was subjected to reflux for 8 h on rotamantle. The yellowish coloured Schiff base separated out as solid upon cooling subsequently followed by filtration. The recrystallization is subsequently done in dry ethanol. The purity was ascertained by TLC technique and melting point [3].

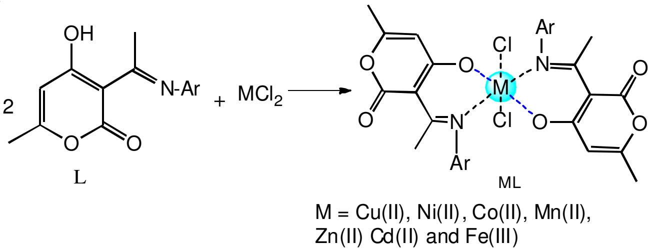


Synthesis of Schiff bases

Synthesis of metal complexes: Refluixing of methanolic solution (0.002 mol) of DHA Schiff base (L_1) treated with refluxing with methanolic solution (0.001 mol) of Cu(II), Ni(II), Fe(III), Co(II) and Mn(II) and Cd(II) metal chloride in 2:1 molar ratio yielded corresponding metal complexes (ML_1) after the addition of 10 % methanolic solution of ammonia at different pH values. Solid metal complexes were filtered, washed with hot methanol and petroleum ether and dried over anhydrous calcium chloride in vacuum desiccator.

RESULTS AND DISCUSSION

Synthesized Schiff base is yellowish solid, stable to air non-hygroscopic, insoluble in water and soluble in hot alcohols. The melting points were determined by open capillaries. All the metal complexes are coloured solids, stable to air non-hygroscopic (Table-1). They are insoluble in water, methanol, ethanol, but soluble in DMF and DMSO.



Synthesis of metal complexes

IR spectra: The characteristic IR frequencies of the ligand and metal complexes are shown in Table-2. The IR spectrum of synthesized free ligand revealed a broad weak absorption band at 3400 to 3100 cm^{-1} appear due to intramolecular hydrogen bonding of ν(O-H). The band at 1689 cm^{-1} is assigned to ν(C=O) lactone carbonyl, 1654 cm^{-1} is assigned to ν(C=N) (azomethine), 1360 cm^{-1} is assigned to ν(C-N) aryl azomethine and 1257 cm^{-1} is assigned to ν(C-O) enolic are in tune with the literature values. The disappearence of band at 3400-3100 cm^{-1} in the spectra of all the metal complexes indicates deprotonation of enolic oxygen and azomethine nitrogen due to coordination to the metal ion. It is further supported by downward shift in band due to ν(C=N) and upward shift in band due to ν(C-O) and ν(C-N) azomethine. This indicates the coordination of azomethine 'N' and enolic 'O' in complex formation. The IR spectra of the metal complexes showed new bands in the region 650-540 cm^{-1} and 580-450 cm^{-1}, which can be assigned to ν(M-O) and ν(M-N) vibrations, respectively [4].

TABLE-1
ANALYTICAL DATA OF SYNTHESIZED COMPOUNDS

Compound	Colour	f.w.	m.p. (°C)	Elemental analysis (%): Found (calcd.)			
				C	H	N	M
$C_{10}H_{10}N_4O_3$ (L_1)	Yellow	234.00	180	51.29 (51.28)	4.27 (4.27)	23.95 (23.93)	–
$Cu(C_{10}H_{10}N_4O_3)\ Cl_2$	Green	638.47	> 250	38.8) (37.59)	3.20 (3.13)	17.6 (17.54)	9.85 (9.95)
$Ni(C_{10}H_{10}N_4O_3)Cl_2$	Greenish	597.70	> 250	40.20 (40.15)	3.22 (3.35)	18.64 (18.74)	9.9 (9.82)
$Fe(C_{10}H_{10}N_4O_3)Cl_3$	Brown	630.21	> 250	39.00 (38.08)	3.27 (3.17)	18.00 (17.77)	8.88 (8.86)
$Co(C_{10}H_{10}N_4\ O_3)Cl_2$	Pink	705.93	> 250	33.38 (33.99)	2.68 (2.83)	14.93 (15.87)	8.74 (8.35)
$Mn(C_{10}H_{10}N_4O_3)Cl_2$	Yellowish	522.94	> 250	45.28 (45.89)	3.67 (3.83)	20.85 (21.42)	10.63 (10.51)
$Cd(C_{10}H_{10}N_4O_3)I_2$	Yellow	834.22	> 250	28.64 (28.76)	2.30 (2.39)	13.11 (13.42)	13.22 (13.47)

TABLE-2
CHARACTERISTICS IR FREQUENCIES (cm^{-1}) OF THE LIGAND AND ITS METAL COMPLEXES

Compound	ν(C=O)	ν(C=C)	ν(C=N)	ν(C–N)	ν(C–O)	ν(M–O)	ν(M–N)
$C_{10}H_{10}N_4O_3$ (L_1)	1689	1559	1654	1360	1257	–	–
Cu(II)L_1	1714	1566	1650	1361	1263	542	480
Ni(II)L_1	1717	1553	1642	1373	1262	566	465
Fe(III)L_1	1701	1579	1649	1365	1261	547	466
CO(II)L_1	1697	1577	1643	1375	1268	556	478
Mn(II)L_1	1694	1554	1648	1364	1267	553	480
Cd(II)L_1	1707	1573	1645	1368	1264	559	473

^{1}H NMR: The ^{1}H NMR spectra of ligand in $CDCl_3$ at laboratory temperature showed the signals at δ (ppm) values for L_1 2.28 (3H, s, C_6-CH_3), 16.00(1H, s, C_3-H), 5.94 (1H, s, C_5-H), 2.67 (3H, s, N = C-CH_3) methyl hydrogen linked carbon azomethine, for DHA moiety 13.30 (1H, s, NH) 7.27(1H, s, C_5-H) of triazole moiety.

Magnetic moment and electronic absorption spectra: The magnetic and electronic spectral data is given in Table-3. The data is of significance for the projected structure of complexes. The electronic spectra of the Cu(II) complex in DMSO shows the bands at 10976 and 15524 cm^{-1} due to $^2Eg \rightarrow {}^2T_{2g}$ transition which is characteristic of distorted octahedral geometry. This further supported by magnetic moment value (1.79 μ_{eff}) within the required range for d^9-system [5]. The electronic spectra of the Ni(II) complex shows three bands in the range 10476 (ν_1), 15234 (ν_2) and 24231 (ν_3) assigned to the transitions $^3A_{2g}(F) \rightarrow {}^3T_{2g}$ and a charge transfer transition, respectively, signifying square planar geometry of the complexes [6,7]. Also the diamagnetic nature supports to the above geometry by it's magnetic moment value (2.87 μ_{eff}). The electronic absorption spectrum of Co(II) complex has three bands in the range 12453 (ν_1), 18547 (ν_2) and 27472 (ν_3) which may be endorsed to three spin-allowed transitions $^4T_{1g}$ (F) $\rightarrow$ $^4T_{2g}$ (F), $^4T_{1g}$ (F) $\rightarrow$ $^4A_{2g}$ (F) and $^4T_{1g}$ (F) $\rightarrow$ $^4T_{2g}$(P), respectively, signifying an octahedral geometry [5]. The effective magnetic moment value (4.8 μ_{eff}) was found to be well within the range as expected for octahedral geometry. The electronic spectra Mn(II) complex showed two bands at 17456 cm^{-1} (ν_1) and 24756 cm^{-1} (ν_2) assigned to transition $^6A_{1g} \rightarrow {}^4T_{1g}$ and $^6A_{1g} \rightarrow {}^4T_{2g}$, respectively, indicating tetrahedral geometry. The magnetic moment value (5.07 μ_{eff}) which is slightly lower than the spin only value expected for tetrahedral Mn(II) complex [7]. This may be due to the presence of magnetic exchange and small traces of Mn(II) species [8]. In addition to metal analysis, this is an additional evidence for the dimeric nature of Mn(II) complex. The subnormal magnetic moment value is investigative of metal-metal interaction supporting dimeric nature. The electronic spectra of the Fe(III) complex showed three bands at 16984 (ν_1), 24258 (ν_2) and 31532 cm^{-1} (ν_3) assigned to transitions $^6A_{1g} \rightarrow {}^4T_{1g}$(D), $^6A_{1g} \rightarrow {}^4T_{1g}$ and $^6A_{1g} \rightarrow {}^4T_{1g}$, respectively and the magnetic moment value (5.8 μ_B) signifying high spin octahedral geometry [9-12].

TABLE-3
MAGNETIC AND ELECTRONIC ABSORPTION SPECTRAL DATA (DMSO) OF THE COMPLEXES

Compound	μ_{eff}	ν (cm^{-1})	Geometry
Cu(II)L_1	1.79	10976, 15524	Distorted octahedral
Ni(II)L_1	2.87	10476, 15234, 24231	Square planner
Fe(III)L_1	5.80	16984, 24258, 31532	Octahedral
CO(II)L_1	4.80	12453, 18547, 27472	Octahedral
Mn(II)L_1	5.07	17456, 24756	Octahedral
Cd(II)L_1	1.75	20400, 24378, 25700	Octahedral

XRD powder diffraction: The powder X ray diffraction of Cu and Ni complexes was screened in the range 5 to 70° at wavelength λ 1.543 Å The diffractogram and associated data depict the data 2θ values of each peak relative intensity and inter planar spacing (d-values). The diffractogram of Cu complex of L_1 ligand has 12 reflections with maxima at 2θ 14.19° corresponding to d value 6.2444. The diffractogram of Ni complex had 9 reflections with maxima at 2θ 12.78° corresponding to d value 8.3366. The X ray diffraction pattern of these complexes with respect to major peaks of relative intensity greater than 10 % has been indexed by using computer program [13]. The above indexing method also yields Miller indices (h k l), unit cell parameter and unit cell volume. The unit cell of Cu complex yielded values of lattice constant a = 14.7884 Å, b = 7.5475 Å and c = 5.8163 Å and unit cell volume V = 649.1889 $Å^3$. In concurrence with these cell parameters, the condition such that $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90°$ required for sample to be orthorhombic was tested and found to be satisfactory. The unit cell of Ni(II) complex yielded values of lattice constant a = 18.3652 Å, b = 4.7725 Å and c- = 9.4358 Å and unit cell volume V = 827.0282 $Å^3$. In concurrence with these cell parameters, the condition such that $a \neq b \neq c$ and $\alpha = \gamma = 90° \neq \beta$ required for sample to be monoclinic was tested and found to be satisfactory. Hence, it can be concluded that CuL_1 complex is orthorhombic crystal system while NiL_1 complex is monoclinic crystal system. The experimental density value of complexes were obtained by using specific gravity method [14,15] and found to be 2.4686 and 2.0478 g/cm^3 for CuL_1 and NiL_1 complexes, respectively.

TGA-DTA analysis: The consecutive TGA and DTA examination of Cu(II), Ni(II), Co(II), Mn(II) and Fe(III) metal complexes was studied from ambient temperature to 1000 °C under an inert nitrogen atmosphere using alumina as reference. The TG curve Cu(II) and Ni(II) metal complexes up to 220 °C showed no change indicating the absences of coordinated water [16,17]. Therefore, the complexes exhibit high thermal stability. The TG thermograms show single step exothermic peak at 323 °C which specify the decomp-osition temperature of the complexes. The complexes start decomposing partially giving metal oxide at 323 °C, the organic part completely decomposes in the temperature of range 335-483 °C as indicating by DTA curve. The TG curve of Co(II) complex shows two stages decomposition. The weight loss encountered at 90 °C supported by broad exothermic peak in TG curve which is characteristic of lattice water, second step was encountered at 190 °C where the organic constituent of the complex starts breaking and decomposes at 337 °C. It is supported by the two endothermic peaks at 310 and 391 °C in DTA curve. The constant weight after 391 °C corresponds to cobalt oxide as final product. The thermogram of Mn(II) complex shows decomposition temperature at 240 °C indicated by sharp peak the organic part completely decompose in the temperature range 230-280 °C which was supported by DTA curve. The TG curve of Fe(III) complex shows an exothermic peak at 180 °C which may be decomposition temperature of organic matter and exothermic peak at 390 °C indicate decomposition temperature of the complex. The FeO is obtained as the end product at 474 °C as showed in DTA curve. All the complexes finally decomposed to their metal oxides [9,10,18].

Biological evaluation: *in vitro* Antibacterial and antifungal activity was screened by considering zone of inhibition of growth. The synthesized compounds were screened and compared with standard antibiotics such as streptomycin (1 mg/mL) and griesofluvin (1 mg/mL). It was found that metal complexes have good activity than ligand under similar condition [19,20].

All the compounds were found moderate in growth inhibition against *B. subtilis* with maximum zone of inhibition 9 mm (compound L_1, FeL_1 and CoL_1) and minimum zone of inhibition 5 mm (CuL_1). Against *S. aureus*, the compounds L_1, CoL_1 and MnL_1 have showed 13, 13 and 14 mm zone of inhibition while compound CuL_1, NiL_1, FeL_1 and CdL_1 showed 12 mm zone of inhibition. Compound MnL_1 showed maximum zone of inhibition (14 mm). Compound L_1, CuL_1, FeL_1, CdL_1 and CoL_1 has showed 12 mm, 12 mm, 10 mm, 10 mm, and 13 mm, respectively. Lowest activity was showed by compound NiL_1 with 9 mm zone of inhibition against *A. niger*. Maximum zone of inhibitory zone was showed by compound CuL_1 (18 mm), moderate activity by compounds L_1, NiL_1 and FeL_1 (15 mm) and MnL_1 (14 mm) while compound CoL_1 and CdL_1 showed minimum zone of inhibition (12 mm) against human opportunistic pathogen, *C. albicans*.

TABLE-4
BIOACTIVITY SCREENING DATA

Sample	*B. subtilis*[a]	*S. aureus*[a]	*A. niger*[a]	*C. albicans*[a]
Streptomycin	16	19.5	NA	NA
Griesofluvin	NA	NA	25	22
L_1	9	13	12	15
CuL_1	5	12	12	18
NiL_1	6	12	9	15
FeL_1	9	12	10	15
CoL_1	9	13	13	12
MnL_1	8	14	14	14
CdL_1	6	12	10	12

[a]NA = Not applicable. [b]Zone of inhibition in m

Conclusion

From the analytical data, composition of Schiff base ligand and its metal complexes was determined. Structure of ligand was confirmed by its ^{1}H NMR and IR spectra and its metal complexes was confirmed from electronic, IR, XRD, TGA-DTA spectra and their magnetic moment values. The DHA Schiff base and its metal complexes were showed strong antifungal activity than antibacterial activity. Cobalt, copper and manganese complexes were among the stronger inhibitors of growth and least growth inhibitory activity was showed by iron and cadmium complexes against biological species.

ACKNOWLEDGEMENTS

The authors express their sincere thanks to UGC (WRO) for the award of TRF under UGC 11th plan period. The authors are also grateful to Director, BCUD, SRTM University, Nanded and Head of the Department of Chemistry & Analytical Chemistry. Special thanks to Dr. S.H. Kathwate, Department of Microbiology, Savitribai Phule Pune University, Pune, India and Dr.V.S. Shembekar, Department of Biotechnology, Rajarshi Shahu Mahavidyalaya (Autonomous) Latur, India for useful suggestions.

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