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Spectral and thermal characterization of 3-acetyl-5-azophenyl-4-hydroxy-6-methyl-pyran-2-one and its metal complexes

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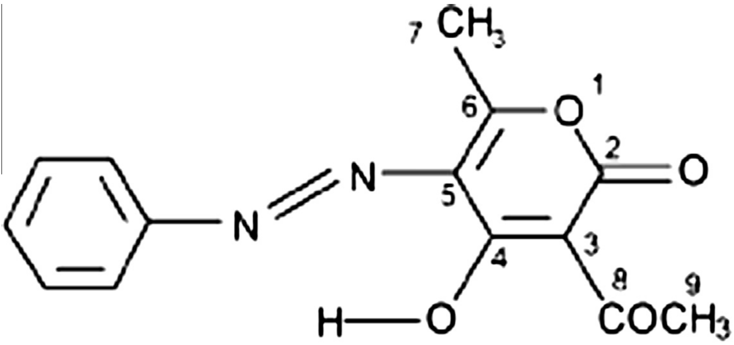
HIGHLIGHTS

- A novel diazo-coupled compound with phenylazo group at a rather unusual position.
- The synthesized compound was found to be acting as a potential ligand.
- Five chelates of phenylazo dehydroacetic acid were synthesized and characterized.
- Analytical, spectral and thermal data confirm the structure of the compounds.

GRAPHICAL ABSTRACT



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ABSTRACT

Five chelates of 3-acetyl-5-azophenyl-4-hydroxy-6-methyl-pyran-2-one (phenylazo dehydroacetic acid) with Cr(III), Fe(III), Ni(II), Cu(II) and Zn(II) have been synthesized and characterized by elemental analysis, magnetic susceptibility measurements, electronic, ^{1}H NMR, FAB mass, IR-spectral and thermal (TG/DTG) analytical techniques. In the present work it has been found that oxygen of the deprotonated —OH group and one of the azo-nitrogens of the ligand take part in coordination. The Cr(III), Fe(III) and Ni(II) complexes were found to be having octahedral geometry and the Cu(II) and Zn(II) tetrahedral.

Introduction

Dehydroacetic acid, 3-acetyl-4-hydroxy-6-methyl-*2H*pyran-2-one (DAA) is found to be occurring in anthers of *Solandra nitida* (solanaceae). It possesses interesting biological properties such as fungicidal and antibacterial activity and is used as a cosmetic preservative too. It can also act as a complexing ligand. Furthermore, this compound has several reactive functional groups and can serve as a reagent in organic synthesis. The synthesis and characterization of two macrocyclic ligands, by the condensation of dehydroacetic acid with 1,2-phenylenediamine and 1,3-propylenediamine [1] have also been reported. DAA in solution exists as a completely enolised species [2]. Like phenols, it can couple with diazonium salts at C-5 and some reports [3,4] are available on the condensation of DAA with diazotised derivatives of aniline, substituted anilines, benzidine, etc. Even though some studies are available on metal chelate of DAA [5], no work has so far been

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reported on chelates of azo dehydroacetic acid (ADAA). ADAA formed stable complexes with Cr(III), Fe(III), Ni(II), Cu(II) and Zn(II). In all the complexes one of the azo nitrogens took part in coordination together with oxygen of the enolic OH. The Zn(II) complex was diamagnetic and all others showed expected magnetic moment values. All complexes were deep red/brown in color.

Experimental

Materials and methods

All the chemicals used for synthetic purposes were of Analar grade. Solvents like methanol, acetic acid, acetone, dichloromethane and chloroform were purchased from E Merck and used as received. Commercial ethanol was purified by distillation and used. The metal salts used for the synthesis of complexes were acetate of Ni(II) and Cu(II) and chlorides of Cr(III), Fe(III) and Zn(II).

Synthesis of phenylazo dehydroacetic acid (ADAA)

Aniline (0.01 mol) was diazotised and this solution of diazonium salt was added slowly drop wise to a well cooled alkaline solution of DAA (0.02 M). The mixture was allowed to stand for 0.5 h. The product, phenylazo dehydroacetic acid, (ADAA) was filtered, washed successively with very dilute HCl and water, recrystallized from methanol and stored over anhydrous $MgSO_4$ in a desiccator.

Synthesis of metal complexes

To a methanolic solution of ADAA, the metal salt solution, also in methanol was added drop wise with stirring. The mixture was refluxed on a steam bath for about 1 h. The metal salt to ligand ratio was kept at 1:2/1:3 for bivalent/trivalent metals, respectively. The precipitated complexes were filtered, washed with water, methanol and dried. These were recrystallized from CH_2Cl_2—CH_3OH mixture and stored over anhydrous $MgSO_4$ in a desiccator.

Physical measurements

The elemental percentage analyses of C, H and N were carried out using Vario EL III CHN analyzer. Some of the metal percentage analyses were conducted using ICP-AES spectrometer using argon as the conductor gas for plasma state at a core temperature of 9000 K. The other metal percentages were determined by adopting standard [6] procedure. UV–visible spectra were recorded using 10^{-3} M solutions of ligands and complexes in methanol. IR spectra of the compounds were recorded by their thin KBr discs. The FAB mass spectra were obtained using argon as the FAB gas, accelerating voltage, 10 kV and *m*-nitrobenzyl alcohol (NBA) as matrix. The metal percentage analyses in some cases were conducted using ICP-AES spectrometer using argon as the conductor gas for plasma state at a core temperature of 9000 K. The other metal percentages were determined by adopting standard procedure. The NMR spectra were obtained using $CDCl_3$ as solvent and TMS as internal standard. Magnetic susceptibility was determined at room temperature on Sherwood Magway susceptibility instrument which was calibrated using $Hg[Co(NCS)_4]$. Thermogravimetric studies, TG/DTG were carried out in nitrogen atmosphere with a heating rate of 10 °C/min.

Results and discussion

The elemental percentages of the ligand, ADAA were found to be in fine agreement with molecular formula $C_{14}N_2O_3H_{12}$. ADAA formed stable complexes with Cr(III), Fe(III), Ni(II), Cu(II) and Zn(II). In all the complexes one of the azo nitrogens took part in coordination together with oxygen of the enolic OH. The Zn(II) complex was diamagnetic and all others showed expected magnetic moment values. All complexes were deep red/brown in color. The molar conductivity of the complexes in DMF solutions (10^{-3} M) at room temperature indicated that these are non-electrolytes. The analytical data are entered in Table 1.

Spectral studies

Electronic spectra and magnetic moment interpretation

The electronic spectrum of ADAA was conspicuous with the band at 278 nm which is characteristic of an azo form. The other bands of importance were at 260 nm (carbonyl) and 370 nm (N═N—). The magnetic moment value of 3.76 B.M. for the Chromium(III) complex suggested [7] an octahedral geometry. The prominent electronic spectral bands include 380 nm ($^4T_{1g}(F) \rightarrow A_{2g}(F)$) and 570 nm ($^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$) which also pointed to an octahedral geometry Fe(III) complex spectrum was difficult to interpret due to CT bands. The magnetic moment value of 5.85 B.M. indicated an octahedral geometry. The spectrum of Ni(II) complex had almost all of the peaks expected for an octahedral geometry. The bands at 376 nm ($^3A_{2g} \rightarrow {}^3T_{1g}(P)$) and 680 nm ($^3A_{2g} \rightarrow {}^3T_{1g}(F)$) were very conspicuous. The magnetic moment value of 2.92 B.M. also confirmed the octahedral geometry. The copper(II) complex exhibited bands at 316 nm and 682 nm which were characteristic overlapped bands of copper complexes. The band at 420 nm was typical [8] of a tetrahedral geometry. The

Table 1
Analytical and physical data of the ligand (LH) and its metal complexes.

Sl. No.	Compound	Color	Yield (%)	MP (°C)	Elemental analysis found (calc.)%					Magnetic moment μ B.M.	Electronic spectral data λ_{max} (nm)
					C	H	N	M	Cl		
1	$C_{14}N_2O_4H_{12}$ (LH)	Brick red	60	50	61.70 (61.77)	4.26 (4.41)	9.95 (10.29)				260, 278, 370
2	$[Cr(L)_2Cl(H_2O)]$	Dark brown	65	80	51.53 (51.89)	4.10 (4.32)	8.98 (8.65)	8.65 (8.03)	5.69 (5.48)	3.76	276, 314, 380, 570
3	$[Fe(L)_2Cl(H_2O)]$	Dark brown	65	140	51.15 (51.58)	4.26 (4.29)	8.14 (8.59)	8.13 (8.58)	5.71 (5.45)	5.85	278, 310, 370, 514
4	$[Ni(L)_2(H_2O)_2]$	Dark brown	70	160	52.72 (52.75)	4.82 (4.71)	8.84 (8.79)	9.74 (9.22)	–	2.82	278, 312, 376, 680
5	$[Cu(L)(OAc)H_2O]$	Dark brown	70	>300	46.64 (46.60)	4.12 (3.88)	6.79 (6.90)	15.38 (15.42)	–	2.10	278, 316, 377,420, 682
6	$[Zn(L)_2]$	Maroon	65	210	55.01 (55.32)	3.55 (3.62)	9.76 (9.22)	10.25 (10.76)		D[a]	278, 310, 370,445, 512

[a] Diamagnetic.

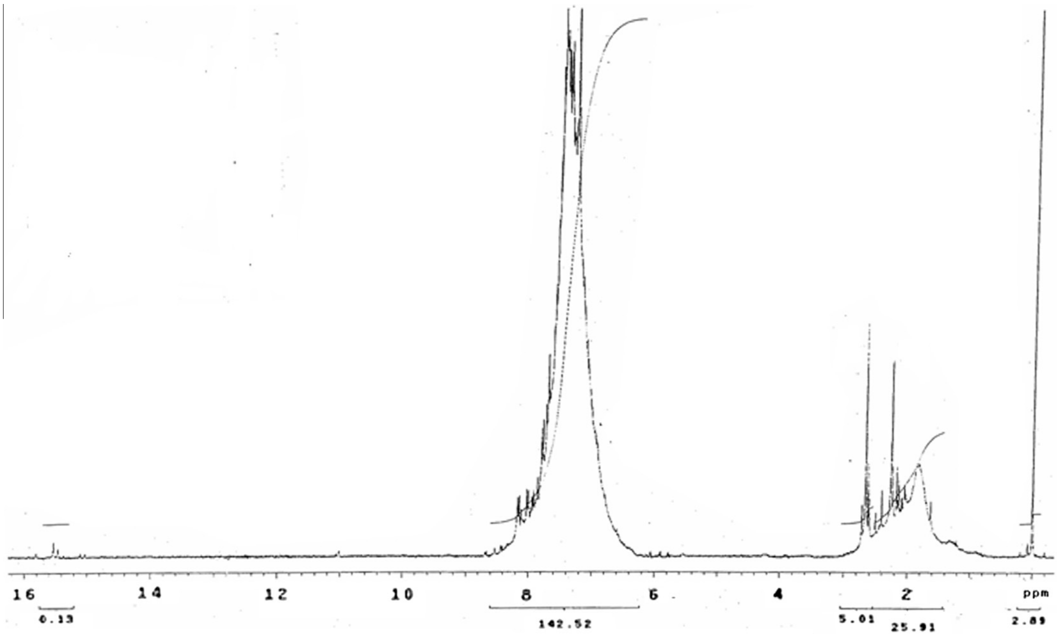

Fig. 1. ^{1}H NMR Spectrum of phenylazo dehydroacetic acid.

magnetic moment value of the Cu(II) complex 2.10 B.M was an additional support to the tetrahedral geometry. The Zn(II) complex exhibited conspicuous bands at 375 nm and 445 nm which suggested [9] the tetrahedral nature of the complex.

FTIR spectra

In FTIR spectra, the broad band at 3445 cm^{-1} in the ligand showed the presence of hydrogen bonded OH. The band at 1599 cm^{-1} is typical of an —N=N— group. The free acetyl carbonyl absorption was found at $\sim$720 cm^{-1} and the ring C=O at 1657 cm^{-1}. The band due to C—O—C stretch of the pyrone was observed at 1125 cm^{-1}. The FTIR spectra of all complexes showed the acetyl carbonyl stretch more or less at the same position indicating the absence of coordination through this carbonyl oxygen. The N=N stretch also has lowered from $\sim$1600 to 1570 cm^{-1} pointing to coordination through azo nitrogen. The appearance of two new bands at lower wave numbers around 580 and 440 cm^{-1} may be an indication of M—N and M—O bonds, respectively.

^{1}H NMR spectra

^{1}H NMR spectrum of ADAA (Fig. 1) showed all the peaks expected of dehydroacetic acid [10] except the peaks at C-5 where the proton has been substituted by a phenylazo group. The peak at 15.68 ppm belonged unmistakably to the acidic proton of OH at C-4 and other prominent peaks were 7.48 nm (unsymmetrical pattern, aromatic), 2.7 ppm for H_S on C-8 and 2.4 ppm for H_S on C-9.The ^{1}H NMR spectrum of the diamagnetic Zn(II) complex exhibited all the peaks of the ligand except the enolic OH peak at $\sim$15.58 ppm. This indicated the coordination through enolic oxygen where the metal has replaced H leading to the formation of a six membered chelate. Other peaks of importance were at 2.48 (s) (acetyl proton) and 2.62 ppm (s) (methyl protons).

Mass spectra

The mass spectrum of ADAA showed the M$^+$ peaks at m/z 272. The peaks at 244 pertained to $(M—N_2)^+$ which is very characteristic of an azo group. The base peak at m/z 149 indicated the fragment $[M—(C_6H_5N_2 + OH)]^+$. So, based on the above evidences the probable structure of ADAA was found to be as depicted in Fig. 1, which is in conformity with other findings. The mass spectrum of the Cu(II) complex showed M + 1 peak at 413 which confirmed the formula $[CuL(OAc)(H_2O)]$. Other prominent peaks were 394 $(M—H_2O)$, 375 $[M—(H_2O + N_2)]$ which supports the azo structure. The peaks at 244, 168, 149 were the same as those in the spectrum of the ligand.

Thermal data

The thermal decomposition curves of the complexes $[Cu(L)(OAc)(H_2O)]$ and $[Ni(L)_2(H_2O)_2]$ were in conformity with the formulae. The decomposition pattern is summarized in Table 2. It can be observed from the data that both of the complexes are stable up to 150 °C. Above this temperature, decomposition begins slowly. After the loss of coordinated OAc/H_2O, the final stage is attained at a very high temperature of $\sim$1000 °C. This is a clear

Table 2
Thermal decomposition data of copper and nickel complexes from TG/DTG.

Complex	F.W.	Decomposition stage	Decomposition temperature (°C)	Mass loss% TG (calc.)	Decomposition pattern
		Stage 1	181.9	3.8 (4.4)	Loss of H_2O
$[Cu(L)(OAc)(H_2O)]$	412	Stage 2	281.5	18.5 (18.6)	Loss of $(H_2O + OAc)$
		Stage 3	1000.1	86.1 (80.7)	Final residue CuO
$[Ni(L)_2(H_2O)_2]$	636	Stage 1	160.6	9.2 (5.7)	Loss of two H_2O
		Stage 2	1001.2	88.2 (88.3)	Final residue NiO

indication of the strong binding nature of the ligand ADAA. The degradation pattern strongly supports the proposed molecular formulae as the percentages of mass loss at different stages are very close to the calculated values.

Conclusion

In all the synthesised complexes, ADAA (LH) was found to be acting as a bidentate mono-anionic ligand. All complexes except the Zn(II) complex were found to be accommodating other ligands to satisfy co-ordination number/electrovalency. Zinc was found to be attached to two ligand moieties, thus satisfying both primary and secondary valencies. The Cr(III), Fe(III) and Ni(II) complexes were found to assume octahedral geometry and the Cu(II) and Zn(II) complexes, tetrahedral geometry.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2013.04.046.

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