International Journal of Advanced Research and Development
ISSN: 2455-4030
Impact Factor: RJIF 5.24
www.advancedjournal.com
Volume 3; Issue 1; January 2018; Page No. 277-282

Synthesis and spectroscopic characterization of new ONO donor AZO ligands and its Cu (II)-complexes

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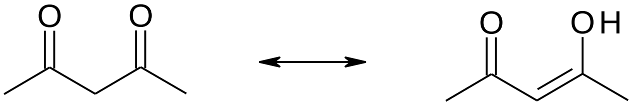
Abstract

Aryl diazonium salt of antranilic acid and 2-aminophenol are coupled with acetyl acetone to synthesize ONO donor tridentate ligands of the type R-C_6H_5-N=N-C(=C(OH)CH_3)$COCH_3$ (R = COOH [HL^1], OH [HL^2]). The ligands can show keto-enol tautomerism. The ^{1}H NMR spectra suggest that they exist in enol form. They can bind to the metal through O, N and O donor centers. The reaction of $Cu(NO_3)_2$ with HL^1 and HL^2 in presence ammonium hydroxide formed chelate complexes of the type $Cu_2L^1_2$ and $Cu_2L^2_2$. Copper (II) complexes have been confirmed by ^{1}H NMR, FT-IR spectra, magnetic moment and elemental analysis. The solution spectra complexes exhibit both ILCT and MLCT bands.

Keywords: keto-enol tautomerism, Cu(II) complexes, LMCT and ILCT

1. Introduction

Acetylacetone is a beta-diketone (1, 3-diketone) and two keto groups are separated by one carbon. The beta-diketone is stable as a conjugated enol rather than alpha-diketone due to the delocalization which makes the counterion more stable and less likely to regain the proton [1].



Acetylacetone contains active methylene groups which have relatively acidic alpha-protons due to H atom adjacent to two carbonyl groups. The reactivity of its methylene group provides the sequence of reactions of alkylation, benzylation, acylation, hydrolysis of the esters and decarboxylation resulting in substituted ketones [1, 2]. The methylene group can also be reacted to form amino-carbonyl compounds. Acetoacetates are important aliphatic parts adjoining azo dyes and pigments [3]. Moreover, the incorporation of acetyl acetonate in the ligand frame enhances the binding sites with mixed, soft and hard, centers and they can bind in different modes depending on soft and hardness of the metal centers. The coordination chemistry of transition metals with azo ligands is of interest due to the observation of several interesting properties [4-11]. The π-acidity and metal binding ability of azo nitrogen have drawn attention to the exploration of the chemistry of metal complexes incorporating azo ligands. Thus, the synthesis of ligands incorporating azo function in different backbone is an inspiring field of research. Notable examples of these ligands are arylazobenzene [12], arylazooxime [13], arylazophenol [14], arylazopyridine [10, 11, 15], arylazoimidazole [16], arylazopyrimidine [17], arylazoaniline [18] etc. Copper is second to iron in its usefulness in life and society. The metal and its compounds are used in every sphere of life. The potential role played by copper ions, present in the active sites of many metalloproteins having the CuN_2S_2 chromophore [19], has stimulated to design new ligand frame having N, S donor sets and their copper complexes as models for providing a better understanding of the biological system [20]. The copper (II)-N, S chelates have antineoplastic activities [21-23], efficient photosensitizer to cleave DNA [24] and antibacterial activity [25]. The Chemistry of metal complexes of azo function system is a field of greater attention for their stability, chemical and electrochemical activities and biological relevance [26, 27]. Besides, acetylacetone is a versatile molecule in chemistry and industry. My present purpose is to design azo functionalised molecule in the backbone of acetylacetone with azophenolate and azocarboxylate. Metal complexes of acetylacetonate derivatives are of effective industrial agent and catalyst [28]. This has encouraged me to synthesise copper (II) complexes of newly designed ligands. The ligands and complexes have been characterized by ^{1}H NMR, FT-IR, UV-Vis and elemental analysis.

2. Materials and Method

Anthranilic acid, 2-aminophenol, acetylacetone, Na_2CO_3, $NaNO_2$ were purchased from EMERK India Pvt. Ltd. $Cu(OAc)_2$, $CuNO_3$, $CuSO_4$ and all other organic chemicals and inorganic salts were available from Sisco Research Lab, Mumbai, India. Solvents were distilled over appropriate drying agents under appropriate condition as per literature under N_2 environment [29]. All other chemicals and solvents were of reagent grade and were used without further purification.

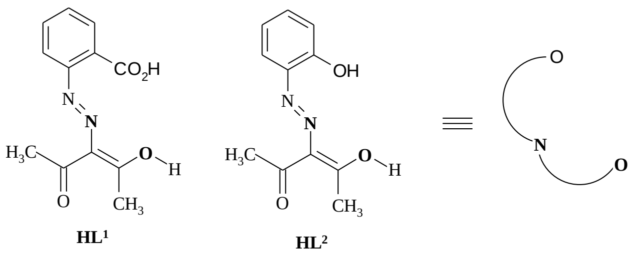
2.1 Physical measurements

Microanalytical data (C, H, N) were collected on Perkin-Elmer 2400 CHNS/O elemental analyzer. Spectroscopic data were obtained using the following instruments: UV-Vis spectra, Perkin Elmer; model Lambda 25. IR spectra (KBr disk, 4000-450 cm^{-1}), Perkin Elmer; model RX-1; ^1H NMR spectra, Bruker (AC) 300 MHz FTNMR spectrometer.

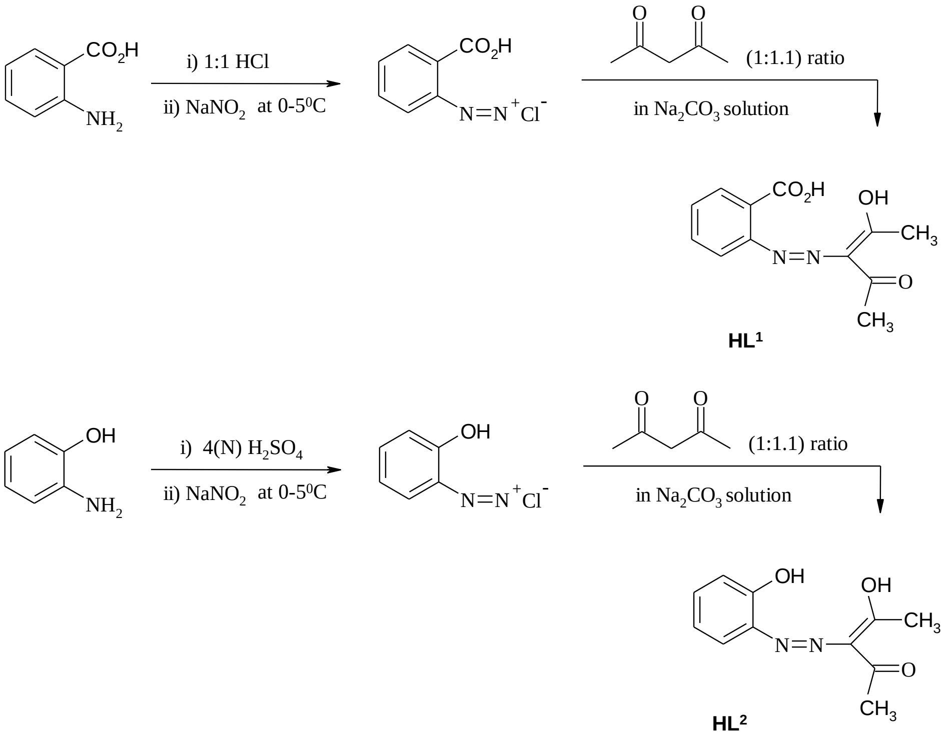
3. Result and discussion

3.1 Formulation of the ligands and the complexes

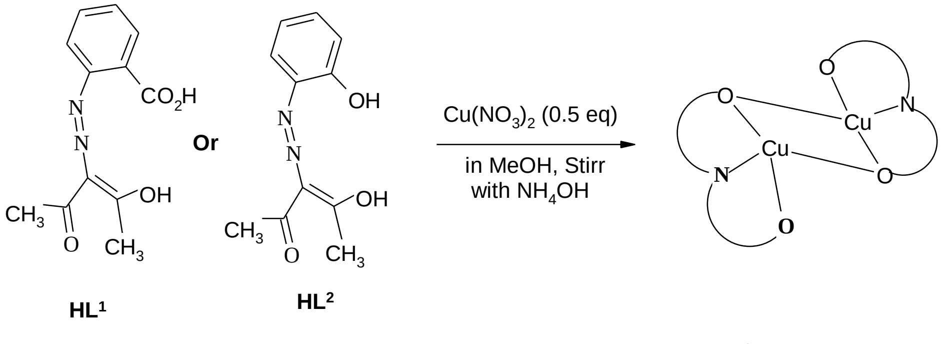
The ligands used in the present work is depicted in scheme-1 and generally abbreviated as HL^1 and HL^2. They are prepared by the coupling of aryl diazonium ion and acetyl acetone in alkaline medium (scheme-2). Copper(II) complexes are synthesized by adding methanolic solution of HL into ammonical blue solution of copper(II) nitrate and stirred for 2 hrs at room temperature in open air. Solution colour turned to brown immediately. Upon slow evaporation of the filtered solution has separated dark colored crystalline compound. The complexes are nonconducting and microanalytical data support the formulation of the compound, $[Cu_2L_2]$ (Scheme 3). The composition of the complexes is supported by microanalytical, IR, ^1H-NMR and mass spectrometric data. The complexes are sufficiently soluble in acetonitrile, DMF, DMSO but insoluble in hexane, benzene, toluene. They are non-conducting in solution of acetonitrile, DMF etc. At room temperature the effective magnetic moments are 1.64BM for $(Cu_2(C_{12}H_{10}N_2O_4)_2)$ and 1.60BM for $(Cu_2(C_{11}H_{10}N_2O_3)_2)$ per copper centre. The subnormal moment data may be due to magnetic exchange between Cu(II) (d^9) bridge centres *via* oxygen bridging.



Scheme 1: Arylazo-acetylacetonate ligands



Scheme 2: Preparation of ligands



Scheme 3: Complexsation with the ligands and probable structure of complexes

3.2 Spectral characterization

3.2.1 FT-IR spectra

Infrared spectra of the ligands (HL^1 and HL^2) exhibit large number of vibrations and the significant frequencies are υ(N=N), υ(C=O) and υ(O-H) at 1380-1412, 1673-1635 and 3280-3320 cm^{-1} respectively. In copper(II) complexes the stretching frequency of the υ(C=O) is almost same and the υ(N=N) appears at 1370-1380 and the OH frequency is gone.

3.2.2 Electronic spectra

The electronic spectra of the ligand HL^1 shows two significant transitions at 265 and 373 nm with a weak band at 382 nm, those are assigned to π-π^* and n–π^* (ILCT) transitions. The complex $Cu_2(L)_2$ has an intense broad band at 645 nm and a shoulder at 490-495 nm assigned to charge transfer and d-d transitions [30] and the π-π^* and n–π^* transitions were shifted to 274-275 and 404 nm (Fig. 1). The other ligand HL^2 shows transition at 260 and 402 nm with two shoulders at 385 and 430 nm those are assigned to π-π^* and n–π^* transitions. In the complex $Cu_2(L^2)_2$ have a broad band observed at 610-620 nm assigned to d-d transition and the π-π^* and n–π^* transitions were shifted to 275 and 474 nm (MLCT) with two additional bands at 315 and 368 nm (Fig.2).

^{1}H NMR spectra

The ^{1}H NMR spectra of the ligands are recorded in $CDCl_3$ and the assignment has been made on the basis of spin-spin interaction. Free ligands, HL^1/HL^2 may exist in keto-enol tautomeric form; a sharp resonance is observed at 14.59-15.54 ppm that is assigned to –OH frequency. Intensity of δ(OH) is compared with signals of other protons and has been inferred the presence of full form of enolic, –(C=C-)-OH, hydrogen. Two $–CH_3$ groups of aectylacetonyl part appear at 2.51-2.52 and 2.63-2.64 ppm. The phenolic OH proton appeared at 10.5ppm and the COOH proton at 15.2ppm.

4. Synthesis

4.1 Synthesis of ligands

(HL^1) Anthranilic acid (2gm, 0.0145 mol) was dissolved in 1:1 HCl and it was diazotized with 10 mL aq. solution of $NaNO_2$ (1gm, 0.0145 mol) was added dropwise to it at 0°C to 5°C. The diazotized solution was then coupled with acetyl acetone (1.5 mL, 0.0146 mol) in Na_2CO_3 solution. A shiny yellow precipitation was obtained; it was filtered and washed with cold water, dried over $CaCl_2$ desicators. Yield was 69.6%, m.p. 228°C. Microanalytical data: Calculated (Found): $C_{12}H_{12}N_2O_4$ (HL^1). C, 58.06 (57.82); H, 4.87(4.91); N, 11.29 (11.08). ^{1}H-NMR in $CDCl_3$ 15.49(1H, s); 8.17(1H, d); 8.05(1H, d); 7.66(1H, t); 7.25(1H, t); 7.2(1H, s); 2.63(3H, s); 2.52(3H, s). IR data in KBr disc 1681 (ν CO_2H); 1671 (ν CO); 1383 (ν N=N). Uv-Vis spectral data in DMF 382(12,831)^b; 373(13,551); 266(5,741).

(HL^2): The ligand HL^2 was prepared using the same method as HL^1, used 2-amino-phenol instead of anthranilic acid and 4(N) H_2SO_4 instead of (6N) HCl. Yield was 55.4%, m.p. Microanalytical data: Calculated (Found): $C_{11}H_{12}N_2O_3$ (HL^2). C, 59.99 (59.13); H, 5.49 (5.72); N, 12.72(12.25). ^{1}H-NMR in dmso-D^6 14.56(1H, s); 10.52(IH, s); 7.64(1H, d); 7.03(2H, t); 6.93(1H, d); 2.63(3H, s); 2.45(3H, s). IR data in KBr disc 3084 (ν OH); 1635 (ν C=O); 1517 (ν C-O); 1419 (ν N=N). Uv-Vis spectral data in DMF 430(8119)^b; 402(12649); 385(12146).

4.2 Synthesis of complexes $Cu_2(L^1)_2$.

Cu $(OAc)_2$. H_2O (82.3 mg, 0.41 mmol) in 15 mL MeOH was added to ammonical solution of HL^1 (102.9 mg, 0.41 mmol) into the same solvent in stirring condition and the stirring was continued for 1hour. A green colour solution was formed, it was filtered and after slow evaporation of the solvent a dark green mass was left. It was washed with 1:1 MeOH, H2O mixture and dried *in* ***vacuo.*** Yield was 62% Microanalytical data: Calculated (Found): $Cu_2(C_{12}H_{10}N_2O_4)_2$ C, 46.53 (47.09); H, 3.25 (3.42); N, 9.04 (8.86). IR data in KBr disc 1675 (ν CO); 1346 (ν N=N). Uv-Vis spectral data in DMF 644(196); 494(463); 404(16908); 386(15161)^b; 275(19443). $Cu_2(C_{12}H_{10}N_2O_4)_2$ via NO_3: C, 46.53 (45.87); H, 3.25 (3.06); N, 9.04 (9.34). IR data in KBr disc 1673 (ν CO); 1348 (ν N=N). Uv-Vis spectral data in DMF 644(187); 492(467); 404(13620); 372(9983)^b; 274(15314).

Other complexes were prepared with the identical procedure, yield were varied from 55-65%. Microanalytical data: Calculated (Found): $Cu_2(C_{11}H_{10}N_2O_3)_2$ C, 46.89 (46.42); H, 3.58 (3.71); N, 9.94 (9.78). IR data in KBr disc 1672 (ν CO); 1370 (ν N=N). Uv-Vis spectral data in DMF 611(488)^b; 473(14304); 383(7176)^b; 368(8028); 314(9003). Cu_2 $(C_{11}H_{10}N_2O_3)_2$ via NO_3: C, 46.89 (47.40); H, 3.58 (3.38); N, 9.94 (9.76). IR data in KBr disc 1671 (ν CO); 1372 (ν N=N). Uv-Vis spectral data in DMF 683(456)^b; 619(586)^b; 473(9333); 368(4987); 314(5741); 267(9621).

Table 1: Uv-vis and IR Data of the ligands and complexes^a

Compounds	λ_{max}(ε x 10^{-3} in $mole^{-1}cm^{-1}$)	IR data in KBr disc	
		$\nu_{C=O}$	$\nu_{N=N}$
$C_{12}H_{12}N_2O_4$ (HL^1)	382(12,831)^b; 373(13,551); 266(5,741).	1671	1383
$C_{11}H_{12}N_2O_3$ (HL^2)	430(8119)^b; 402(12649); 385(12146).	1635	1419
$Cu_2(C_{12}H_{10}N_2O_4)_2$	644(196); 494(463); 404(16908); 386(15161)^b; 275(19443).	1675	1346
$Cu_2(C_{12}H_{10}N_2O_4)_2$ via NO_3	644(187); 492(467); 404(13620); 372(9983)^b; 274(15314).	1673	1348
$Cu_2(C_{11}H_{10}N_2O_3)_2$	611(488)^b; 473(14304); 383(7176)^b; 368(8028); 314(9003)	1672	1370
$Cu_2(C_{11}H_{10}N_2O_3)_2$ via NO_3	683(456)^b; 619(586)^b; 473(9333); 368(4987); 314(5741); 267(9621)	1671	1372

^{a} Solvent: DMF, ^{b}Shoulder

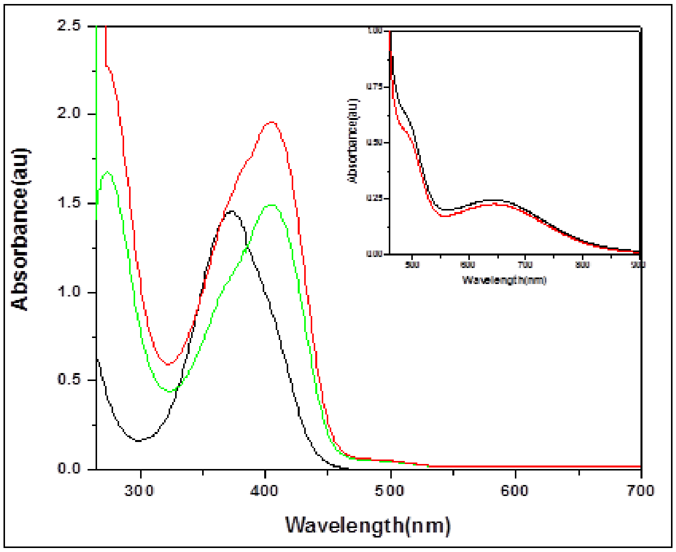


Fig 1: Uv-vis spectra of the $C_{12}H_{11}N_2O_4$ (HL^1) (——); [$Cu_2(C_{12}H_{10}N_2O_4)_2$ via $Cu(OAc)_2$] (——) and [$Cu_2(C_{12}H_{10}N_2O_4)_2$ via $Cu(NO_3)_2$] (——) in DMF solution. The inset picture show the higher wavelength spectra of [$Cu_2(C_{12}H_{10}N_2O_4)_2$ via $Cu(OAc)_2$] (——) and [$Cu_2(C_{12}H_{10}N_2O_4)_2$ via $Cu(NO_3)_2$] (——).

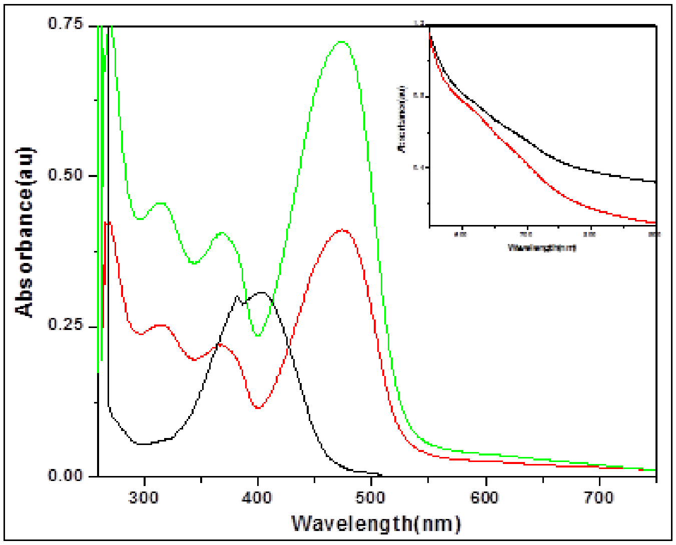


Fig 2: Uv-vis spectra of the $C_{11}H_{11}N_2O_3$ (HL^2) (——); [$Cu_2(C_{11}H_{10}N_2O_3)_2$ via $Cu(Oac)_2$] (——) and [$Cu_2(C_{11}H_{10}N_2O_3)_2$ via $Cu(NO_3)_2$] (——) in DMF solution. The inset picture show the higher wavelength spectra of [$Cu_2(C_{11}H_{10}N_2O_3)_2$ via $Cu(OAc)_2$] (——) and [$Cu_2(C_{11}H_{10}N_2O_3)_2$ via $Cu(NO_3)_2$] (——).

5. Conclussion

Although keto and enol are in equlibrium but in the prepared ligands after verification of ^{1}H-NMR spectra it mainly exist in enol form due to the chelation. The ligand may be used for identification of transition metal and may be used for cation as well as anion sensor.

6. Acknowlegement

Prof. (Dr.) C.R. Sinha, department of chemistry, Jadavpur University are greatfully acknowledge for his unconditional help. Financial support from the University Grants Commission New Delhi, are gratefully acknowledged.

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