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Synthesis, spectral, molecular modeling, thermal analysis studies of orange (II) complexes

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ABSTRACT

Six Orange (II) metal complexes of Mn (II), Fe (III), Co (II), Ni (II), Cu (II) and Zn (II) were prepared and characterized by elemental analysis, IR, electronic spectra and magnetic susceptibility. The complexes were of different geometries: Octahedral and Tetrahedral. ESR was studied for copper complex. The prepared complex was of isotropic nature. Molecular modeling calculations were used to characterize the ligation sites of the free ligand. Furthermore, quantum chemical parameters of Orange (II) such as the energies of highest occupied molecular orbital (E_{HOMO}), energies of lowest unoccupied molecular orbital (E_{LUMO}), the separation energy ($\Delta E = E_{LUMO} - E_{HOMO}$), the absolute electronegativity, χ, the chemical potential, P_i, the absolute hardness, η and the softness, σ, were obtained for Orange (II). The thermal analyses of the complexes were studied by DTA, TGA and DSC techniques. The thermodynamic parameters, thermolysis and the thermal transitions, such as glass transitions, crystallization and melting temperatures for ligand and its complexes were evaluated and discussed. The entropy change values, $\Delta S^{\#}$, showed that the transition states are more ordered than the reacting complexes. Biological activity for Orange (II) and its complexes were done.

1. Introduction

Azo compounds containing two phenyl rings separated by an azo (-N=N-) bond, are versatile molecules and have received much attention in both fundamental and applied research areas. Azo dyes have been widely used in many practical applications such as printing systems, optical storage technology (DVDs and CDs), textile dyes as well as in many biological reactions [1], as therapeutic agents, chemosensors [2]. In analytical chemistry azo compounds are used as indicators in pH, redox, or complexometric titration [3]. In the metallosupramolecular polymers an azo group is considered an active unit, which may be photochromic, proton responsive and redox active, depending on the chemical constitution in the molecule [4]. The azo ligands with different functional groups like hydroxyl, amide, carboxyle, etc. have the ability to be complexed with many metals. Masoud et al. [5–18] published a series of papers and reviews about the chemistry of azo complexes.

Among dyes containing azo-aromatic groups, Orange (II) (commercial name AO7) (4-[(2-hydroxy-1-naphthy)azo] benzenesulphonate, monosodium salt) is an anionic monoazo textile dye of the acid class. It is resistant to light degradation, the action of O_2 and common acids or bases, so usually used in organic light emitting diodes, inks, soaps, textiles and wood stains [19]. It has been reported that it exists as azoenol and ketohydrazone forms (Scheme 1) [20–23]. In a water solution, the H-atom within the O–H···N intramolecular H-bond is shifted to the nitrogen site, making HYZ structure the most stable one (*ca.* 95%) [20,23].

Orange (II) was used for sensitive extraction-spectrophotometric determination of lorazepam (LOR) in pharmaceutical formulations [24]. The $LORH^+$ cation which is formed in an acidic solution can form an ion-pair with Orange (II) anionic dye, the $LORH^+ -$ Orange $(II)^-$ ion pair is quantitatively extracted into dichloromethane solvent and its absorption was measured at 482 nm. The calibration graph is linear over the LOR concentration range of 1.0–25.0 μg mL^{-1} and the regression coefficient is 0.9999. The relative standard deviation (RSD) of 10 replicate determination of 10.0 μg mL^{-1} of LOR is 1.6% and the limit of detection (LOD) of the method is 4.8×10^{-2} μg mL^{-1}. The method is successfully applied to the determination of LOR amount in pharmaceutical formations (1.0 and 2.0 mg tablets).

The coordination complexes of transition metals with acid dyes

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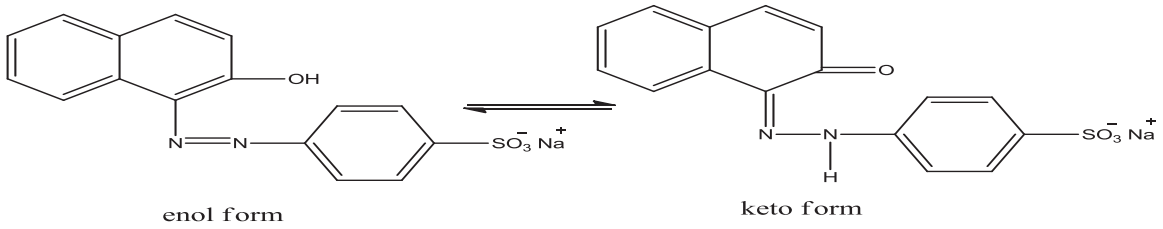

Scheme 1. Azoenol and ketohydrazone forms of Orange (II).

ligands are also focus of the current attraction due to the interesting physical, chemical, photophysical and photochemical, catalytic and different material properties. Metal complex dyes play a very important role in the textile industry. Chromium, Cr (III) and cobalt Co (III) complexes are used most frequently for the dyeing of wool and synthetic polyamides [25].

In the present work, six Orange (II) metal complexes of Mn (II), Fe (III), Co (II), Ni (II), Cu (II) and Zn (II) were prepared. The free ligand and its complexes were examined systematically in their solid state using physicochemical and computational studies.

2. Experimental

2.1. Synthesis of orange (II) metal complexes

Six simple metal-ligand complexes were prepared in a similar manner. A hot clear solution of 0.1 M of inorganic salts [Mn (II), Fe (III), Co (II), Ni (II), Cu (II) as chlorides] and [Zn (II) as sulphate] were dissolved in 25 mL a bidistilled water. Ammonia solution was added to 0.1 M solution of Orange (II) dissolved in 25 mL hot bidistilled water and then the solution of inorganic salt was added. The mixture was stirred for 30 min at 45 °C. The precipitated complexes were filtered, washed several times with bidistilled water and dried in an oven over $CaCl_2$. The metal contents were determined by two methods. (i) Atomic absorption technique (ii) Complexometrically with standard EDTA solution using the appropriate indicator as reported [26,27]. The carbon, hydrogen and nitrogen contents were determined. The analysis of chloride contents was determined by familiar Volhard method by titration with standard $AgNO_3$ solution using ferric alum as indicator. $BaCl_2$ test for qualitative analysis for sulphate group was performed for Zn-complex. The analytical data of the isolated complexes, Table 1 depict the formation of complexes with different stoichiometries. The proposed structures of synthesized metal complexes illustrated in Fig. 1.

2.2. Material and methods

Orange (II) was supplied by Sigma-Aldrich used without further purification. Analytical grade chemicals were utilized as received for all experiments. Infrared spectra for Orange (II) and its metal complexes were recorded as KBr disk on Perkin-Elmer 1430 spectrophotometer. The spectral studies in solution were measured using double beam UV–Visible spectrophotometry (T70-UV/Vis) PG instruments covering the wavelength range 190–600 nm. Molar magnetic susceptibilities corrected for diamagnetism using Pascal's constants were determined at room temperature (298 K) using faraday's method, the apparatus was calibrated with Hg [Co $(SCN)_4$]. The ESR spectra of the copper complex were recorded with a reflection spectrometer operating at 9.75 GHz (X-Band) in a cylindrical resonance cavity with 100 kHz modulation. The g-values were determined by comparison with DPPH signal ($g = 2.0037$) [28]. Differential thermal analysis (DTA), Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out using a Linseis STA PT-1000. The rate of heating was 5 and 10 °C/min under atmospheric oxygen.

2.3. Computer analysis programs

The molecular modeling calculations (bond lengths, angles, dihedral angles and charges) of the ligand and its complexes were performed with computer programs; ChemBioDraw Ultra 12.0 and ChemBio3D Ultra 12.0 [29]. Applying Hyper chemistry computer program version 8, using PM3 semi-empirical and Molecular Mechanics Force Field (MM+) methods to calculate theoretically the Quantum Chemical Parameters [30].

2.4. Biological activity

The antimicrobial and antifungal activities of the complexes were examined.

3. Results and discussion

3.1. IR spectra of orange (II) and its complexes

Table 2 represents the fundamental bands of Orange (II) and its complexes. The free ligand gave a very broad intense band at 3422 cm^{-1} due to νO—H stretching vibration mode, the broadness of the stretching band due to intramolecular hydrogen bond. The absence of a characteristic sharp band ν C=O at 1700 cm^{-1} and presence of intense bands at 1506 cm^{-1} and 1453 cm^{-1} due to asymmetric and symmetric stretching vibrations of N=N group

Table 1
Analytical data and physical properties of the prepared complexes.

Complexes	M.wt	Color	Formula	Calculated/(Found)%					
				C	H	N	S	M	Cl
$[Cu(HL)_2].6H_2O$	825.5	Dark Brown	$C_{32}H_{34}CuN_4O_{14}S_2$	46.51 (46.3)	4.15 (4.05)	6.78 (6.62)	7.76 (7.36)	7.69 (7.5)	–
$[Zn(HL)(H_2O)_2]$	428.4	Dark orange	$C_{16}H_{15}N_2O_6SZn$	44.82 (44.71)	3.53 (3.45)	6.53 (6.51)	7.48 (7.61)	15.25 (15.63)	–
$[Mn(HL)_2].6H_2O$	816.9	Pale orange	$C_{32}H_{34}MnN_4O_{14}S_2$	47.00 (47.8)	4.19 (4.22)	6.85 (6.9)	7.84 (7.75)	6.72 (6.79)	–
$[Co(H_2L)_3].2Cl.2(H_2O)$	1149.7	Pale orange	$C_{48}H_{40}CoN_6Cl_2O_{14}S_3$	50.1 (49.8)	3.47 (3.8)	7.3 (7.5)	4.17 (4.35)	5.12 (5.41)	6.17 (6.2)
$[(Fe)_2(L)_2(H_2O)_4].4H_2O$	907.6	Reddish	$C_{32}H_{36}Fe_2N_4O_{16}S_2$	42.3 (42.55)	3.96 (4.11)	6.17 (6.22)	3.52 (3.63)	12.30 (12.45)	–
$[Ni(HL)_2(H_2O)_2]\cdot 2(H_2O)$	784.7	Pale orange	$C_{32}H_{30}N_4NiO_{12}S_2$	48.93 (48.85)	3.82 (3.95)	7.13 (7.25)	4.07 (4.25)	7.48 (7.66)	–