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Synthesis and characterization of new copper(II) and palladium(II) complexes with azo-, bisazo-5-pyrazolones

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ABSTRACT

New copper(II) and palladium(II) complexes were synthesized by the interaction of metal acetates and azo-, bisazo-5-pyrazolones in a methanolic medium. The mononuclear copper(II) and palladium(II) complexes were obtained from the ligands, HAP/HL^{1a-b} and HAP/HL^{2} (Azo-5-Pyrazolone Ligand), and the binuclear copper(II) complexes were obtained from the ligands, HBAP/HL^{2a} and HBAP/HL^{1c} (BisAzo-5-Pyrazolone Ligand). The resulting complexes were characterized on the basis of spectroscopic techniques such as infrared, mass spectra, nuclear magnetic resonance and UV–visible absorption spectra as well as thermal analyses. The spectral data show that the ligands coordinated via the carbonyl oxygen of 5-pyrazolone and via the azo group of the nitrogen atoms of the azo-, bisazo-5-pyrazolones, except for the complex [Pd(HL^{1a})$_2$] which coordinated from the carbonyl oxygen of 5-pyrazolone and the hydroxyl oxygen of the azo-substituted aromatic ring.

1. Introduction

Pyrazolones constitutes a group of organic compounds that have been extensively studied due to their properties and applications. Since the synthesis of *Antipyrine* in 1883, a great deal of attention has been paid to the analgesic and antipyretic properties of these compounds and they have been extensively investigated on account of their wide range of pharmacological activities [1–4].

Moreover, azo compounds which are highly coloured, enjoy widespread use as dyes and pigments in a variety of applications that include textile dyeing as well as nonlinear and Photo electronics, especially in optical information storage [5]. Regarding the industrial importance of metallized azo dyes relative to their structures, they can be classified into two main types: those in which the azo group participates in coordination with the metal ion for formation of the chelate ring and those in which it does not [1,6].

5-Pyrazolone derivatives, mainly 4-acylpyrazol-5-ones have been employed extensively as ligands in coordination compounds. Surprisingly, structural information concerning azo- and bisazo-5-pyrazolone complexes with palladium(II) and copper(II) are rather scarce, although their interaction with palladium has been used in the analysis of metal, in extraction chemistry and in the preparation of a selective hydrogenation catalyst [7–9]. Apart from the activation of molecular oxygen by copper, these complexes play a central role in synthetically useful stoichiometric and catalytic oxidative conversions of organic molecules and in biological systems [10,11]. These complexes have also attracted special attention as endonuclease mimics due to their labile coordination spheres [12].

Over the last few years, we have focused part of our research on the synthesis of 5-pyrazolones and azo-, bisazo-5-pyrazolone dyes [13–15], which constitute many prospective biologically active molecules, using spectral data and their dyeing properties. In the present paper, we wish to describe the synthesis and, the spectroscopic and thermal investigations of copper(II) and palladium(II) complexes and identify their probable structures.

2. Results and discussion

The azo- and bisazo-5-pyrazolone ligands were prepared by coupling the appropriate 5-pyrazolone with diazonium salt derived from the appropriately substituted aniline, as we recently published [15]. The molecular structures of these ligands are such that they can exist in different tautomeric forms as has been shown by many researchers [14,16–18]: some ligands prefer the hydrazo and some the enol tautomeric structures for complex formation (Scheme 1). Palladium(II) acetate did not react with bisazo-5-pyrazolones, although different reaction conditions were used. This might be due to the electronic nature of palladium(II) ion since the bisazo-5-pyrazolone ligands are too bulky for coordination.

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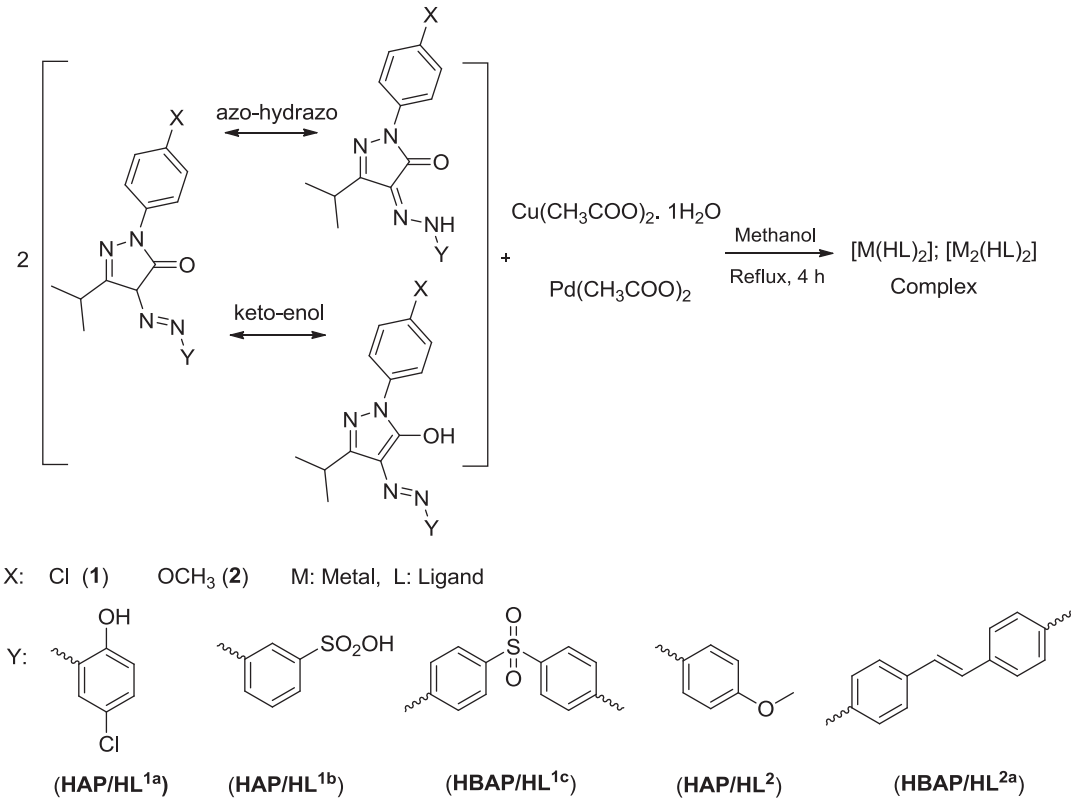

Scheme 1. Synthesis of copper(II) and palladium(II) complexes.

The complexes were prepared by reaction of the relevant metal(II)acetate with the azo- or bisazo-5-pyrazolone in methanol at reflux for 4 h (Scheme 1). The resulting precipitates were purified by recrystallization or by rinsing the formed solid with an appropriate cold solvent.

The metal complexes were found to be stable at room temperature and were insoluble in some organic solvents such as methanol, methylene chloride and acetone, but soluble in coordinating solvents like DMF and DMSO. The copper(II) complexes, $[Cu(HL^{1b})_2]$ and $[Cu_2(HL^{1c})_4]$, with the palladium(II) complexes, $[Pd(HL^{1a})_2]$ and $[Pd(HL^{1b})_2]$, are water soluble. This is an important aspect for our ongoing investigation on their catalytic activity in water.

Single crystals of the compounds could not be isolated from any organic solution, thus no definite structures can be described. However, the structure of all new metal(II)-azo complexes were evaluated according to FTIR, ^1H, ^{13}C NMR, APT, ESI-MS, UV–Vis and TGA/DSC analyses. The spectral data and thermal investigations agree well with their proposed formulae. Schemes 2 and 3 show the suggested structure of the copper(II) and palladium(II) complexes, respectively.

2.1. FT-IR spectral studies

IR Spectral studies are very useful for structural determination of the complexes with the aid of other spectral and thermal techniques. Metal complexes show significant differences from ligands [15], with weak bands in the 501–682 cm^{-1} and 405–505 cm^{-1} range, which may be attributed to ν(M–O) and ν(M–N) stretching [6,19].

The IR spectra of the copper(II) and palladium(II) complexes show the ligands coordinating with the metal ion from carbonyl oxygen with azo-nitrogen. For the azo-complexes, the absence of carbonyl absorption bands regarding the ligands indicates the enolization of the carbonyl followed by coordination of the oxygen to the metal ion, except for the ligands of $[Cu(HL^{1b})_2]$, and the bisazo-5-pyrazolone copper(II) complexes, $[Cu_2(HL^{1c})_2]$.MeOH and, $[Cu_2(HL^{2a}),(MeOH)_4]$, which tend to be in the hydrazo tautomeric form for coordination. This suggestion is supported by the appearance of bands at 3356, 3352 and 3340 cm^{-1}, respectively assigned to the ν(N–H) vibration.

In the palladium complexes, $[Pd(HL^{1a})_2]$ coordinated differently than its counterparts because of the ortho substituted hydroxyl group on the aromatic ring of the ligand, although $[Cu(HL^{1a})_2]$ did not tend to follow this kind of coordination. This finding can be seen in the IR spectrum of the palladium complex. The characteristic band of the azo group did not change significantly (from 1490 to 1492 cm^{-1}) after complexation and the band assigned to the ν(O–H) vibration (3390 cm^{-1}) disappeared with the complex formation.

After coordination between the bisazo-5-pyrazolone ligands and copper(II) salt, the carbonyl stretching frequencies shift slightly to a lower wave number region: from 1662, 1655 to 1647, 1650 cm^{-1} and the complexes coordinate to the copper ion directly from the carbonyl oxygen and nitrogen of the hydrazo tautomeric structure. The coordinated methanol in $[Cu_2(HL^{1c})_2]$.MeOH and the bonded methanol in $[Cu_2(HL^{2a}),(MeOH)_4]$ exhibit bands at 3441, 3444 cm^{-1}, respectively due to the ν(O–H) vibration [20,21].

The presence of multiple bands at 2924–2970 cm^{-1} in the ligands and at 2924–2993 cm^{-1} in their complexes with only marginal shifting suggests the presence of the aliphatic isopropyl group of 5-pyrazolones.

2.2. MS spectral studies

The mass spectra of the complexes support the suggested structures, revealing a molecular ion peak or monoisotopic exact mass of molecular ion adducts which are often observed in ESI mass spectra [22], consistent with the molecular weight of the