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Design, synthesis and physico-chemical investigation of a dinuclear zinc(II) complex with a novel 'end-off' compartmental ligand

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Abstract. A novel dinucleating pentadentate Schiff base, resulting from the condensation of 2,6-diformyl-*p*-cresol and N-methyl-indolyl-3-thiohydrazide, and its Zn complex have been prepared and characterized on the basis of elemental analysis, IR, UV-Visible, ^{1}H NMR and ^{13}C NMR studies. The ligand is acyclic and consists of a phenolate head unit, with two inbuilt azomethine shoulders and two indole thiohydrazide arms forming SNONS coordinating sites. NMR and IR spectral studies show that the ligand exists in thioketo form. Each Zn ion in the dinuclear core is in tetrahedral environment with endogenous phenolate bridging and exogenous acetate bridging. The zinc complex in DMF exhibits fluorescence.

Keywords. N-methyl-indolyl-3-thiohydrazone; compartmental ligand; Zn(II) complex of thiohydrazone; 2,6-diformyl-*p*-cresol.

1. Introduction

Phenol-based compartmental ligands of 'end-off' type, possessing two chelating arms attached to the 2- and 6-positions of the phenolate ring, have often been used to provide -phenoxo bridged dinuclear core complexes, keeping option for varying exogenous bridge [1]. Zinc-containing, carboxylate-bridged bimetallic centres are widespread structural motifs in hydrolytic metalloenzymes such as phosphatase and amino peptidases and some synthetic dinuclear Zn(II) complexes are found to have functions in RNA hydrolyse and dephosphorylation[2–7].

Considerable research has been carried out on N/O multidentate ligands to mimic synthetic analogues of nitrogen-rich zinc enzymes [8] but little is known about metal chelates of multidentate ligands having N/O/S donors, particularly those based on indole thiohydrazide moiety [9–12]. These observations were the impetus for us to build a thiohydrazide moiety on N-methyl indole and extending its framework to construct compartmental ligand by condensing it with dicarbonyl compound and synthesize zinc complex to study its coordinating behaviour.

2. Experimental

2,6-Diformyl-*p*-cresol and N-methyl-indole-3-dithiocarboxylate were respectively synthesized by a slight modification of the literature method [13–15]. Reactions are outlined in scheme 1.

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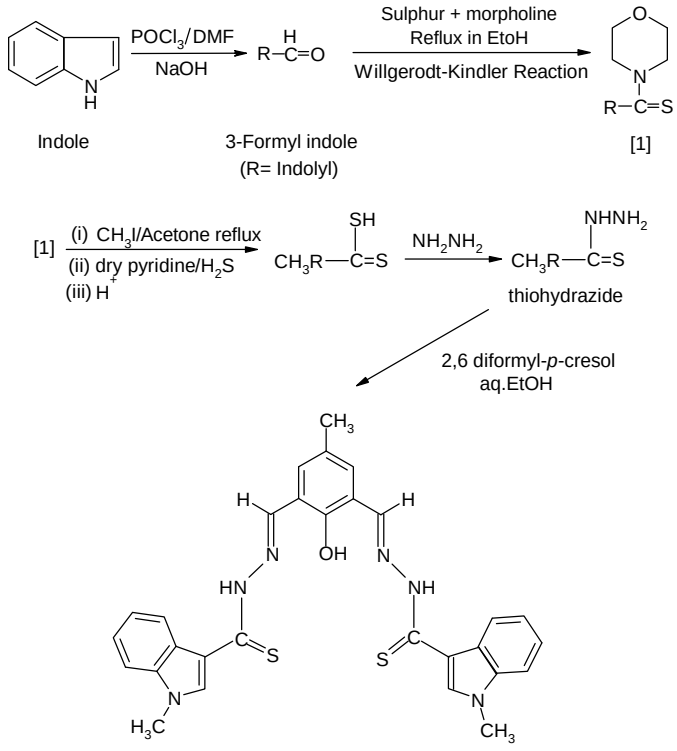

2,6-Diformyl-*p*-cresol-bis[N-methyl indolyl-3-thiohydrazone]

Scheme 1.

2.1 *Preparation of N-methyl indolyl-3-thiohydrazide*

An ethanolic solution (15 cm^3) of hydrazine hydrate (0·68 g, 0·01 mole) was slowly added with stirring to an ethanolic (35 cm^3) solution of N-methyl indole-3-dithiocarboxylate (2·07 g, 0·01 mole). The mixture was refluxed for 1 h and then the clear solution allowed to cool to room temperature. The colourless crystals that separated were filtered, washed with EtOH and dried (yield 50%, m.p. 160°C).

2.2 *Preparation of 2,6 diformyl-p-cresol-bis[N- methyl indolyl-3-thiohydrazone]*

Thiohydrazide (4·38 g, 0·02 mole) and 2,6-diformyl-*p*-cresol (1·64 g, 0·01 mole) in aq. EtOH (50 cm^3, 1 : 1 by vol.) were refluxed for 1 h. The pale yellow needles that crystallized out from the clear solution after cooling were filtered, washed with EtOH and dried in *vacuo*. Yield 80%, m.p. 219°C. Analysis: Calc. for $C_{29}H_{26}N_6OS_2$: C, 64·18; H, 4·75; N, 15·88; S, 11·48%. Found: C, 64·66; H, 4·86; N, 15·60; S, 11·91%.

2.3 *Preparation of complex*

Zinc acetate (0·439 g, 0·002 mole) in EtOH (15 cm^3) was added with stirring to an ethanolic solution (20 cm^3) of the ligand (0·538 g, 0·001 mole) and refluxed for 2 h. The

dark yellow compound that precipitated was filtered, washed with EtOH and dried in *vacuo*. Analysis: Calc. for $Zn_2(C_{31}H_{26}N_6O_3S_2).2H_2O$: C, 48·69; H, 3·79; N, 11·11; S, 8·42: Zn, 11·27%. Found: C, 48·89; H, 3·97; N, 11·04; S, 8·42; Zn, 11·17%.

2.4 *Physical measurements*

The complex was analysed for its metal content by EDTA titration after decomposition with a mixture of $HClO_4$ and HCl, followed by HCl alone. Sulphur was estimated as $BaSO_4$. Carbon, hydrogen and nitrogen were estimated on a Thermoquest CHN analyser. Electronic spectra were recorded on a Hitachi 2001 spectrophotometer in DMF. Fluorescence study was done on an F-2000 Hitachi Fluorescence spectrophotometer. IR spectra were recorded in the 4000–400 cm^{-1} region (KBr disc) on a Nicolet 170 SX FT-IR spectrophotometer. The ^1H and ^{13}C spectra were obtained in d_6-DMSO using TMS as an internal reference. D_2O exchange is also recorded. Conductance measurements were determined in DMF using an Elico-CM82 conductivity bridge.

3. Results and discussion

The complex contains 2 : 1 metal to ligand ratio. It is formed by the loss of three protons. It is insoluble in water, EtOH and MeOH but is soluble in polar organic solvents such as DMF, DMSO and CH_3CN. Molar conductivities in DMF suggest that the complex is non-electrolytic.

3.1 *Electronic and fluorescence spectral studies*

Maxima at 250 nm and 275 nm in the case of the ligand are due to p–p^* transitions. These bands are almost unchanged in the spectra of the complex. The ligand also shows a broad band at 325 nm with a shoulder at lower energy, due to the n–p^* transition associated with the azomethine linkage. This band in the complex has shown a bathochromic shift due to the donation of a lone pair of electrons to the metal and hence the coordination of azomethine [16–17]. The broad shoulder centred around 365 nm in the ligand was assigned to n–p^* of the thioamide chromophore which suffers a blue shift in the complex due to thioenolisation.

The moderately intense broad band for the complex in the region 350–425 nm is assigned to S → Zn(II) ligand to metal charge transfer transition (LMCT). The LMCT maxima for the phenolate complex shows line broadening, with a tail running into the visible part of the spectrum. This may result from a phenolate to Zn(II) LMCT band being superimposed on the low energy side of S→Zn(II) LMCT. Except this the complex shows no appreciable absorptions in the region above 450 nm in DMF solution, in accord with the d^{10} electronic configuration of the Zn(II) ion.

Fluorescence spectra of the complex show (figure 1) a strong emission band at 486 nm when excited with 350 nm radiation, at room temperature with sample concentration of 0·1 mmol in DMF. Generally fused-ring systems like indole and its derivatives show fluorescence. The free ligand shows an enhanced fluorescent intensity on complexation with diamagnetic zinc ion. The emission is neither MLCT (metal-to-ligand charge transfer) nor LMCT in nature. We tentatively assign it to the intraligand (p–p^*) fluorescence, since a similar emission is also observed for the free ligand, but with reduced intensity. It is known that lone pairs of electron on nitrogen and on thioamide

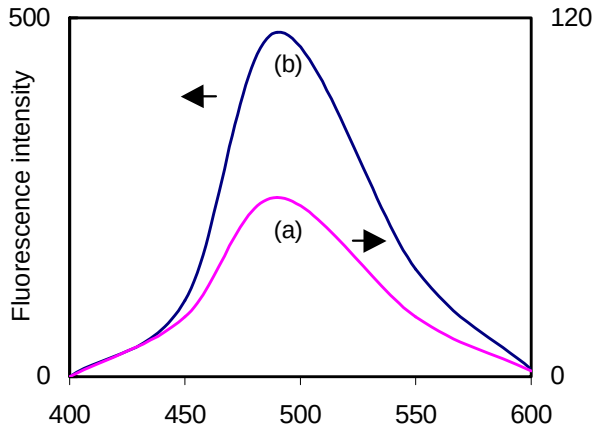

Figure 1. Fluorescence spectra of (a) free ligand (b) zinc complex (0·1 mmol) in DMF with excitation at 350 nm.

chromophore can quench the fluorescence of indole moiety through photo-induced electron transfer [18–21]. Draining out of these pairs of electrons on to the metal orbital via complex formation causes a suppression of this fluorescence quenching and therefore results in increase in fluorescence intensity [20]. The formation of metal chelates with metal ions, in general, also promotes fluorescence by promoting rigidity and minimizing internal vibrations. At higher concentration (1 mmol) the fluorescence intensity decreases considerably due to self-quenching.

3.3 *IR spectral studies*

The spectra of the ligand show a band of medium intensity at 3215 cm^{-1} which is assigned to *v*(NH). Absence of any band around 2400–2600 cm^{-1} confirms that the ligand exists in thioketo form [22]. ^{1}H NMR further confirms this, which shows no signal for the –SH group. The sharp band at 1618 cm^{-1} which was assigned to *v*(C=N) in the ligand has shifted to lower energy suggesting coordination of both the N atoms to metal. The *v*(OH) broad band of the ligand around 3406 cm^{-1} has disappeared in the complex suggesting deprotonation of phenolic oxygen on coordination to metal.

In complex, the *v*(NH) band disappears and there appears a weak band at 674 cm^{-1} assigned to *v*(C–S) stretching. Vibrational coupling among the thioamide groups are distributed at around 1535, 1422, 1374 and 749 cm^{-1} identified as thioamide bands I, II, III and IV in the ligand [23]. Bands at 1374 and 749 cm^{-1}, which have major contribution from *v*(C=S), also appear in the complex but with reduced intensity. Asymmetric and symmetric stretching vibrations of the acetate group appear at 1585 cm^{-1} and 1442 cm^{-1} respectively. The difference between ν_{asym}(COO) and ν_{sym}(COO) is 144 cm^{-1}, which is smaller than 164 cm^{-1} observed in ionic acetate, reflects the bidentate bridging coordination mode [3]. A medium intensity band at 3339 cm^{-1} indicates presence of non-coordinated water.

3.4 *^{1}H NMR and ^{13}C spectral studies*

Signals at 12·4 and 11·8 ppm are due to –OH and –NH protons, which disappear on D_2O exchange. Protons of N–CH_3 and Ph–CH_3 are observed at 3·35 and 2·31 ppm respectively [24,25]. A singlet at 8·58 ppm is due to the azomethine proton. A doublet around 7·12 ppm is due to protons adjacent to the –CH_3 in the *p*-cresol moiety and the protons of the pyrrole ring of indole. Protons of the phenyl ring of indole are found between 7·46 to 8·25 ppm. The signals at 20, 40, 143, 147 and 160 ppm in ^{13}C spectra are due to carbons of the –CH_3, N-CH_3, –C=N, –C–OH and –C=S groups respectively[24,26–28]. In the Zn complex, signals due to –OH and –NH are absent, supporting deprotonation and thioenolisation. Signals due to the protons of the phenyl ring of the indole show splitting. This may be due to the dissymmetry caused by the non-planarity of the ligand on complexation [25]. The 0·11-ppm downfield shift of the acetate resonance (*d* 1·99) compared with that of the ionic acetate (CH_3COONa, *d* 1·88) suggests interaction of the acetate with the metal centres in solution.

4. Conclusions

In this communication, an attempt is made to bring together a dicarbonyl moiety, which provides a backbone for the compartmental ligand, the pharmacologically active indole thiohydrazide and the biologically active zinc ion. The proposed structure of the complex is given in figure 2. By synthesizing these compounds, we are heading towards the designing of synthetic models of sulphur-rich zinc enzymes. Magnetic studies with other transition metal complexes, particularly of copper with this ligand and varying exogenous bridges, may provide some insight into the magnetic environment around the metal ion and the nature of the magnetic exchange interaction between the metal centres. Enhancement of fluorescence behaviour upon complexation can be utilised for analytical applications.

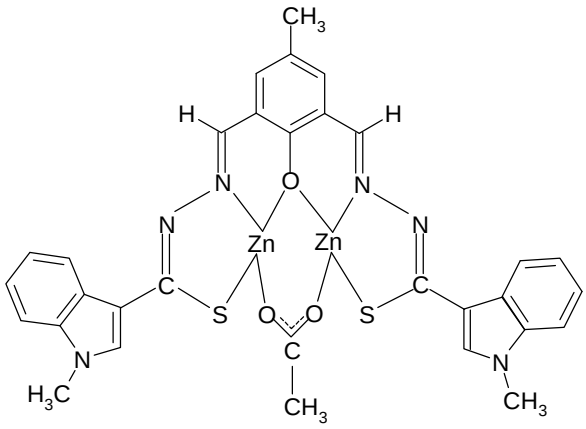

Figure 2. Proposed structure of the complex.

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