Research Article

Physico-Chemical Studies on the Coordination Compounds of Thiazolidin-4-One

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A dry benzene solution of the Schiff base, N-(2-hydroxyphenyl)-3-carboxy-2-hydroxybenzylimine upon reacting with mercaptoacetic acid undergoes cyclization and forms N-(2-hydroxyphenyl)-C-(3-carboxy-2-hydroxyphenyl)thiazolidin-4-one, LH3 (I). A MeOH solution of I reacts with MnII, CuII, ZnII, FeIII and MoOVI ions and forms the monomeric coordination compounds, [Mn(LH)(MeOH)] (II), [Cu(LH)(MeOH)] (III), [Zn(LH)(MeOH)] (IV), [FeCl(LH)(MeOH)]2 (V), and [MoO2(LH)(MeOH)] (VI). The coordination compounds have been characterized on the basis of elemental analyses, molar conductance, molecular weight, spectral (IR, reflectance, ESR) studies, and magnetic susceptibility measurements. I behaves as a dibasic tridentate OOS donor ligand in these compounds. The compounds are nonelectrolytes (ΛM = 6.2–13.8 mho cm2 mol−1) in DMF. A square-planar structure for III; a tetrahedral structure for IV and an octahedral structure for II, V, and VI are suggested.

1. Introduction

Heterocyclic compounds of Schiff bases possessing thiazolidin-4-one skeleton (having carbonyl group at 4th position) are known for their versatile pharmacological and industrial importance [1]. They have been studied extensively because of their ready accessibility, diversified chemical reactivity, and broad spectrum of biological activities [2].

In recent years, thiazolidin-4-ones have been investigated most extensively. The presence of a thiazolidine ring in penicillin and related derivatives was the first recognition of its occurrence in nature [3]. Thiazolidine-4-one represents a prevalent scaffold in drug discovery [4]. Literature surveys show that thiazolidine-4-ones have many interesting activity profiles, namely COX-1 inhibitors [5], inhibitors of the bacterial enzyme MurB, which was a precursor acting during the biosynthesis of peptidoglycan [6], nonnucleoside inhibitors of HIV-RT [7] and antihistaminic agents [8]. Thiazolidinones are also known to exhibit antibacterial, anticonvulsant, antifungal, amoebicidal, antioxidant, and anticancer [9–12] activities.

A perusal of the literature reveals that much has been reported on the syntheses and characterization [13, 14] of a variety of thiazolidin-4-ones, but little is known about their coordination compounds [15–17].

Metal ions play a key role in the actions of drugs. They are involved in specific interactions with antibiotics, proteins, membrane components, nucleic acids, and other biomolecules [18, 19]. Many drugs possess modified pharmacological properties in the form of the metal complexes. Transition metal ions possess an important role in the design of metal-based drugs and such complexes are more effective against infectious diseases compared to the uncomplexed drugs [20, 21]. Metals complexes of Cu(II) has proved to be beneficial in diseases such as tuberculosis, gastric ulcers,
rheumatoid arthritis, and cancers [22]. The complexes of Fe(III) and Mn(II) also have excellent medicinal values [23].

Hence these facts prompted us to explore the coordination behavior of a newly synthesized thiazolidin-4-one with transition metal ions.

In this paper, we describe the syntheses and characterization of \(N\)-(2-hydroxyphenyl)-\(C\)-(3\'-carboxy-2\'-hydroxyphenyl) thiazolidin-4-one, \(\text{LH}_3\) \(I\) and its coordination compounds with \(\text{Mn}^{II}\), \(\text{Cu}^{II}\), \(\text{Zn}^{II}\), \(\text{Fe}^{III}\), and \(\text{MoO}_2^{VI}\) ions. The structure of Schiff base and thiazolidin-4-one, \(\text{LH}_3\) \(I\) is shown in Figure 1.

2. Experimental

2.1. Materials. 2-Aminophenol [Loba-Chemie (Mumbai)], mercaptoacetic acid, dry benzene, sodium bicarbonate, ammonium molybdate(VI) tetrahydrate, acetyl acetone [Ranbaxy], manganese(II) acetate tetrahydrate, iron(III) chloride (anhydrous) [Sarabhai], copper(II) acetate monohydrate, and zinc(II) acetate dihydrate [s d fine-chem Limited] were used as received for the syntheses. 3-Aldehydro-2-hydroxybenzoic acid and bis(acetylacetonato) dioxomolybdenum(VI) were synthesized by following the reported procedure [24].

2.2. Analyses and Physical Measurements. The organic skeleton of the respective coordination compounds was decomposed by the slow heating of ~0.1 g of the latter, with conc. \(\text{HNO}_3\). The residue was dissolved in minimum amount of conc. \(\text{HCl}\) and the corresponding metal ions were estimated as follows: the \(\text{Mn}(II)\) and \(\text{Zn}(II)\) contents of the respective coordination compounds were estimated by complexometric titration method against standardized EDTA solution using eriochrome black-T as the indicator. The \(\text{Cu}(II)\) contents was estimated iodometrically against a standard solution of sodium thiosulphate to the starch end point. The \(\text{Fe}(III)\) ions were reduced to \(\text{Fe}(II)\) ions with aqueous \(\text{SnCl}_2\) and then estimated iodometrically against a standard solution of \(\text{KI}\) using value of \(60 \times 10^{-6}\) cgs units for \(\text{Cu}(II)\) ions, zero for \(\text{Mn}(II)\), and \(\text{Fe}(III)\) ions.

The ESR spectrum of \(\text{III}\) was recorded at liquid \(\text{N}_2\) temperature in polycrystalline solids on a Varian V4502-12 X-band ESR spectrophotometer with 100 KHz modulation using diphenylpicrylhydrazide as a \(g\)-marker and monitoring the frequency with frequency meter.

2.3. Synthesis of the Schiff Base. The Schiff base was prepared as per the reported procedure [27].

2.4. Synthesis of \(\text{I}\). A dry benzene solution of the Schiff base (2.57 g, 10 mmol) and mercaptoacetic acid (0.92 g, 10 mmol) were refluxed for 12 h on a water bath. The mixture was cooled to room temperature and then was washed with 10% sodium bicarbonate solution. The benzene layer was separated using a separating funnel. The partial evaporation of the benzene layer gave a solid product, which was filtered, washed with, and recrystallized from petroleum ether. Yield = 25%. Anal: \(\text{I}; \text{C}_{16}\text{H}_{13}\text{NO}_5\text{S}\) (obsd: C, 57.80%; H, 3.75%; N, 4.10%; S, 9.50%. calc.: C, 58.01%; H, 3.93%; N, 4.23%; S, 9.67%); IR bands (KBr): 2860 cm\(^{-1}\) [\(\nu\text{(C-O)}\) (intramolecular H-bonding)], 1700 cm\(^{-1}\) [\(\nu\text{(C=O)}\) (thiazolidinone ring)], 1670 cm\(^{-1}\) [\(\nu\text{(C=O)}\) (carboxylic)], 1575 cm\(^{-1}\) [\(\nu\text{(C=O)}\) (phenolic)], and 835 cm\(^{-1}\) [\(\nu\text{(C=S)}\) (thiazolidinone ring)].

2.5. Syntheses of Coordination Compounds of \(\text{I}\). A MeOH solution (30–50 mL) of the appropriate metal salt (10 mmol) was added to a MeOH solution (50 mL) of \(\text{I}\) (3.31 g, 10 mmol) and the mixture was then refluxed for 3-4 h. The solid products formed were suction filtered, washed with, and recrystallized from MeOH, and were then dried as mentioned above. Yield = 50–80%.
3. Results and Discussion

A dry benzene solution of the Schiff base (obtained by the nucleophilic addition reaction between 3-aldehydo-2-hydroxybenzoic acid and 2-aminophenol followed by the elimination of one water molecule) reacts with mercaptoacetic acid and forms $N$-(2-hydroxyphenyl)-C-(3′-carboxy-2′-hydroxyphenyl)thiazolidin-4-one, LH$_3$ (I). The reaction of I with appropriate metal salt in $IH_2$O, partially soluble in $H_2$O, partially soluble in $MeOH$, EtOH, and completely soluble in DMSO and DMF. Their molar conductance measurements ($\Lambda_m$ = 6.2 – 13.8 mho cm$^2$ mol$^{-1}$) in DMF indicate their nonelectrolytic nature. The analytical data of I and its coordination compounds are presented in Table 1.

3.1. Infrared Spectral Studies. The infrared spectra of the Schiff base ($N$-(2-hydroxyphenyl)-C-(3′-carboxy-2′-hydroxy benzylideneimine), LH$_3$ (I) ($N$-(2-hydroxyphenyl)-C-(3′-carboxy-2′-hydroxyphenyl)thiazoli-din-4-one), and the coordination compounds of I were recorded in KBr and the prominent peaks (in cm$^{-1}$) are shown in Table 2. The Schiff base exhibits the $\nu(C=N)$(azomethine) stretch at 1630 cm$^{-1}$. This band disappears in I and a new band appears at 1575 cm$^{-1}$ due to the $\nu(C=O)$(thiazolidinone ring) stretch [28] indicating the conversion of the Schiff base into I. The formation of I is further supported by the appearance of a new band at 835 cm$^{-1}$ due to the $\nu(C=S)$(thiazolidinone ring) stretch [29], and it shows a negative shift by 15–35 cm$^{-1}$ in the coordination compounds indicating the involvement of the S atom of the thiazolidinone moiety towards coordination [30]. I shows the $\nu(C=O)$(thiazolidinone ring) stretch [31] at 1700 cm$^{-1}$. This band remains unchanged in the coordination compounds indicating the noninvolvement of O atom towards the coordination. I exhibits a strong band at 2860 cm$^{-1}$ due to the intramolecular H-bonded [32, 33] OH group of phenolic and/or carboxylic acid moieties. This band disappears in the coordination compounds indicating the break down of H-bonding and subsequent deprotonation of the OH group followed by the involvement of phenolic and carboxylic acid O atoms towards coordination. The presence of a broad band at ~3400 cm$^{-1}$ due to $\nu(O=H)$(MeOH) and the decrease of $\nu(C=O)$(MeOH) stretch from 1034 cm$^{-1}$ to lower energy by 40–64 cm$^{-1}$ in the coordination compounds of I indicate the involvement of the O atom of MeOH towards coordination [34]. The appearance of two new bands between 1558–1575 cm$^{-1}$, $\nu_{as}$(COO) and 1333–1360 cm$^{-1}$, $\nu_{s}$(COO) stretches indicate the presence of the coordinated carboxylate group in the coordination compounds. The energy difference
(Δν = 212 – 225 cm\(^{-1}\)) between these stretches is $>210$ cm\(^{-1}\) which indicates the monodentate nature of the carboxylate moiety [35]. The ν(C–O)\(^g\) stretch [34] of I occurs at 1525 cm\(^{-1}\). This band shifts to higher energy by 5–10 cm\(^{-1}\) in the coordination compounds indicating the involvement of phenolic O atom of either 3-aldehydo-2-hydroxybenzoic acid or 2-aminophenol moieties towards coordination. On the basis of steric grounds, we suggest the noninvolvement of phenolic (2-aminophenol moiety) O atom towards coordination. The absence of a band between 820–860 cm\(^{-1}\) of phenolic (2-aminophenol moiety) O atom precludes the presence of an oligomeric chain with $\text{MoO}_2\text{VI}$ compound. This absence of a band between 820–860 cm\(^{-1}\) in V precludes the presence of the (Fe–O–Fe) bridged structure [36]. The presence of a peak at 357 cm\(^{-1}\) in V confirms the presence of Fe–Cl linkage [37] in the compound. VI exhibits the ν\(_s\)(O=Mo=O) and ν\(_{as}\)(O=Mo=O) stretches at 946 and 910 cm\(^{-1}\), respectively [38]. These bands occur in the usual ranges: ν\(_s\)(O=Mo=O) stretch, 892–964 cm\(^{-1}\) and ν\(_{as}\)(O=Mo=O) stretch, 842–928 cm\(^{-1}\), reported for the majority of MoO\(_2\)\(^{VI}\) compounds [38]. The presence of two bands due to ν\(_s\)(O=Mo=O) stretch is indicative of a cis-MoO\(_2\) configuration as the compound with trans-MoO\(_2\) structure shows only ν\(_{as}\)(O=Mo=O) stretch since the ν\(_s\)(O=Mo=O) stretch is IR inactive [39]. The absence of a band at $\sim775$ cm\(^{-1}\) in the MoO\(_2\)\(^{VI}\) compound indicates the absence of an oligomeric chain with $\cdots\text{Mo}--\cdots\text{Mo}--\cdots\text{Mo}--\cdots$ interaction [40]. The new nonligand bands in the present coordination compounds in the low frequency region are assigned to the ν(M-O)(550–570 cm\(^{-1}\)) and the ν(M-S)(345–370 cm\(^{-1}\)) and these bands [41] are in the expected order of increasing energy: ν(M-S) < ν(M-O). On the basis of analytical data (Table 1), valence requirements, and the infrared spectral studies, it is proposed that I behaves as a dibasic tridentate OOS donor ligand in the coordination compounds.

3.2. Reflectance Spectral Studies. II exhibits three bands at 17450, 22320, and 25300 cm\(^{-1}\) due to $^6A\_1g \rightarrow ^4T\_1g(G)$, $^6A\_1g \rightarrow ^4T\_2g(G)$, and $^6A\_1g \rightarrow ^4A\_1g(G)$ transitions, respectively, in an octahedral environment [42]. The presence of an asymmetric broad band at 17230 cm\(^{-1}\) due to the $^2B\_1g \rightarrow ^2A\_1g$, $^2B\_2g$, and $^2E\_g$ transitions in III suggests a square-planar arrangement of I around Cu\(^{II}\) ion [43]. The absence of a band in the range 8000–10000 cm\(^{-1}\) precludes the presence of a tetrahedral structure [44]. V exhibits three bands at 12700, 16100, and 24900 cm\(^{-1}\) due to $^6A\_1g \rightarrow ^4T\_1g(G)$, $^6A\_1g \rightarrow ^4T\_2g(G)$, and $^6A\_1g \rightarrow ^4A\_1g(G)$ transitions, respectively, in an octahedral environment [45].

3.3. Magnetic Measurements. The room temperature magnetic moments of the coordination compounds of I are presented in Table 2. The magnetic moments of II, III, and V are 5.90, 2.02, and 5.95 B.M., respectively. These values are indicative of magnetically dilute high-spin octahedral coordination compounds of Mn\(^{II}\) and Fe\(^{III}\) ions [46]. The IV and VI are diamagnetic as expected.

3.4. ESR Studies. The ESR spectra of III shows well resolved four hyperfine lines with no super hyperfine lines. The various ESR spectral parameters obtained are as follows: $g|| = 2.26$, $g_\perp = 2.09$, $A|| = 1.916 \times 10^{-2}$ cm\(^{-1}\), $A_\perp = 0.467 \times 10^{-2}$ cm\(^{-1}\), $G = 2.93$, $\alpha_{Cu}^2 = 0.87$, $\langle \alpha' \rangle^2 = 0.19$, $\kappa = 0.55$, and $P_d = 1.86 \times 10^{-3}$ cm\(^{-1}\). The observed order of A and $g$ values ($A|| > A_\perp$; $g|| > g_\perp > 2.0023$) indicate that the complex possesses a square planar structure [47] and the ground state [48, 49] of Cu(II) is predominantly $d_{x^2-y^2}$ ($^2B\_3g$ as the ground state). Here $g||$ and $g_\perp$ values denote the effective g-values when the externally applied DC field is parallel ($B\_\parallel$) and perpendicular ($B\_\perp$) to the symmetry axis of the crystalline field around the paramagnetic centre, respectively. The value of geometric parameter (G), a measure of the exchange interaction, is 2.93, and this value lies within the range [50] 2.1–3.8, consistent with the ground state [47] $d_{x^2-y^2}$. Further the value of $g||/A||$ for the complex is 117.95 cm which lies in the range (90–140) cm as reported for square planar Cu(II) complexes [26]. For ionic environments, $g||$ is normally $\geq 2.3$ and is $< 2.3$ for covalent environments.
The $g_{\parallel}$ value (2.26) indicates that the metal-ligand bonding in the compound is covalent. The G value (2.93) is less than 4.0, hence the ligand forming the Cu$^{II}$ compound is regarded as a strong field ligand. The in-plane covalence parameter ($\alpha_{Cu}^2$) has been calculated using the relation: $\alpha_{Cu}^2 = (g_{\parallel} - 2.002) + 3/7(g_{\perp} - 2.002) - (A_{||}/0.036) + 0.04$, where $\alpha$ is related to the overlap integral (S) according to the relation [51]: $\alpha^2 - 2 \alpha \alpha' S + (\alpha')^2 = 1$. The values of $\alpha_{Cu}^2$ (0.87) and $(\alpha')^2$ (0.19) indicate its covalent nature. The smaller the value of $\alpha_{Cu}^2$, the more covalent is the bonding; $\alpha_{Cu}^2 = 1$ indicates completely ionic bonding, while $\alpha_{Cu}^2 = 0.5$ indicates completely covalent bonding [26]. The larger the value of $(\alpha')^2$, the more covalent is the bonding; $(\alpha')^2 = 0$ suggests a complete ionic bonding [26]. The symbol $\kappa P_d$ represents the Fermi contact contribution (A) to the coupling, where $P_d$ is the dipolar contribution. The value of $P_d$ and $\kappa$ have been calculated using the relation [48, 49]: $P_d = -(A_{||} - A_{\perp})/0.78$ and $\kappa = -0.48 - (A_{||}/P_d)$. The positive value of $\kappa$ suggests that $A_{||}$ should be greater than $A_{\perp}$, and it has also been observed by us. The lower value of $P_d$ in comparison to that of the free ion value ($3.5 \times 10^{-2}$ cm$^{-1}$) indicates the presence of covalent character between the metal-ligand bonding. The absence of any band $\sim 1500$ G due to the $\Delta M_s = \pm 2$ transition rules out the presence of M–M interaction.

4. Conclusion

Thus, on the basis of analytical, molecular weight, spectral, and magnetic studies, we suggest a square-planar structure, III for [Cu(LH)(MeOH)], a tetrahedral structure, IV for [Zn(LH)(MeOH)] and an octahedral structure, II for [Mn(LH)(MeOH)$_3$], V for [FeCl(LH)(MeOH)$_2$], and VI for [MoO$_2$(LH)(MeOH)] as shown in Figure 2.

References


[2] S. M. Kudari and S. E. Badiger, "Synthesis of new series of 1,8-bis (2-arylimino thiazolidin-4-one-3-yl) octanes and related


