STUDIES ON THE COORDINATION COMPOUNDS OF THIAZOLIDIN-4-ONE DERIVED FROM SALICYLALDEHYDE-O-HYDROXYPHENYLUREA

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ABSTRACT

An equimolar mixture of salicylaldehyde and o-hydroxyphenylurea upon refluxing in MeOH forms the Schiff base (1). The latter upon reacting with HSCH$_2$COOH in dry C$_6$H$_6$ undergoes cycloaddition reaction and forms the corresponding thiazolidin-4-one, LH$_2$ (2). A MeOH solution of 2 reacts with Cu (II), Co (II), Ni (II), MoO$_2$ (VI) and Zr (OH)$_2$ (IV) ions and forms the monomeric, non-electrolyte coordination compounds, [Cu(OAc)(LH$_2$)] (3), [M(OAc)(LH$_2$)(MeOH)$_2$] (4) (here M = Co, Ni), [MoO$_2$(acac)(LH$_2$)(MeOH)] (5) and [Zr(OH)$_2$(LH$_2$)] (6). A THF solution of a bidentate ON or NN donor ligand (AA) like ethanolamine (ea), o-aminophenol (oap), ethylenediamine (en), o-phenylenediamine (phen), 2,2'-bipyridyl (bipy) and 1,10-phenanthroline (ophen) reacts with a THF solution of (6) and forms the heterochelate, [Zr(OH)$_3$(LH$_2$)(AA)] (7). The coordination compounds have been characterized on the basis of elemental analyses, molecular weight, molar conductance, spectral (IR, reflectance, NMR) studies and magnetic susceptibility measurements. (2) behaves as a monobasic tridentate ON donor ligand in these coordination compounds. A square-planar structure for (3), an octahedral structure for (4) (M = Co, Ni) and (6), and an eight-coordinate structure for (5) and (7) are suggested.

Key words: Thiazolidin-4-one, Coordination compounds, Spectral studies, Magnetic susceptibility, Heterochelates.

INTRODUCTION

Thiazolidin-4-ones belong to an important group of heterocyclic compounds with carbonyl group at fourth position$^{1,2}$. They show broad spectra of biological activities due to their ready accessibility and diverse chemical reactivity$^3$. They are involved in variety of applications such as, antimicrobial, antibacterial, anticonvulsant, antifungal, anti-HIV,
antiproliferative, anti-inflammatory, antithyroid etc. Many drugs possess modified pharmacological properties in the form of the metal complexes. These facts prompted us to explore the coordination behavior of thiazolidin-4-one derived from the Schiff base (I) towards Cu (II), Co (II), Ni (II), MoO₂ (VI) and Zr (OH)₂ (IV) ions.

**EXPERIMENTAL**

**Materials**

Ethylenediamine (Sarabhai); copper (II) acetate monohydrate (IDPL); cobalt (II) acetate tetrahydrate, o-aminophenol, hexadecaqua octahydroxotetrazirconium (IV) chloride (BDH); nickel acetate tetrahydrate (Fluka); ethanolamine, o-phenylenediamine, 2,2'-bipyridyl, 1,10-phenanthroline (Aldrich); ammonium molybdate tetrahydrate, NaHCO₃, MeOH, HSCH₂COOH, dry C₆H₆, THF, pet. ether (Ranbaxy) were used as supplied for the syntheses. Bis (acetylacetonato)dioxomolybdenum (VI) and hexadecaqua octahydroxotetra-zirconium (IV) acetate were prepared by adopting the published procedures.

**Analyses and physical measurements**

The metal contents of the complexes were estimated as per reported methods. The C, H and N contents of LH₃ and its coordination compounds were estimated by CHN Eager analyzer model-300. The S contents was estimated gravimetrically as BaSO₄. The molecular weights were determined by the Rast method using diphenyl as the solvent. The molar conductivity measurements were carried out in DMF with the help of a Toshniwal conductivity bridge (CL01-02A) and a dip type cell calibrated with KCl solution. The IR spectra were recorded in KBr pellets (4000-400 cm⁻¹) on a Beckman-20 spectrophotometer. The reflectance spectra were recorded on a Beckmann DU spectrophotometer attached with a reflectance arrangement. The ¹H NMR spectra of (I) and (3) (when M = Zn) were recorded on Bruker Avance II 400 NMR spectrometer. Magnetic susceptibility measurements were carried out at room temperature with a Gouy balance using mercury (II) tetraisothiocyanatocobaltate (II) (χ₆ = 16.44 × 10⁻⁶ cgs unit).

**Synthesis of o–hydroxyphenylurea (ohypu)**

o-Aminophenol (10.9 g, 0.1 mol) was dissolved in 20 mL of 1 : 1 HCl. To this solution, urea (24.0 g, 0.4 mol) in small quantity with constant stirring, distilled water (30 mL), HCl (1 mL) and glacial acetic acid (1 mL) were added. The brown solution obtained was refluxed on a water bath for 2 h. The light-brown compound separated on cooling was suction filtered, washed with distilled water and recrystallised from 50% EtOH and dried in vacuo. m.p. = 154°C, Yield = 90%; Anal. [C₇H₆N₂O₂; Found (calcd.) % C = 55.38 (55.26);
H = 5.32 (5.26); N = 18.23 (18.42); IR bands: \( \nu(N-H) \) (3050 cm\(^{-1}\)), \( \nu(C=O) \) (carbonyl) (1655 cm\(^{-1}\)), \( \delta(NH_2) \) (1630 cm\(^{-1}\)) and \( \nu(C-O) \phi \) (1520 cm\(^{-1}\)).

**Synthesis of (1)**

An EtOH solution (50 mL) of \( o \)-hydroxyphenylurea (15.2 g, 0.1 mol) and salicylaldehyde (12.2 g, 0.1 mol) were refluxed on a water bath for 1 h. The excess of solvent was evaporated and the mixture was allowed to stand at room temperature. The brown compound separated out, was suction filtered, washed with and recrystallized from EtOH. The compound was dried as mentioned above. m.p. = 162\(^{\circ}\)C, Yield = 70%; Anal. \([C_{14}H_{12}N_{2}O_{3}; \text{found (calcd)} \% C = 65.58 (65.62); H = 4.75 (4.69); N = 10.88 (10.94)]\); IR bands: \( \nu(N-H) \) (2950 cm\(^{-1}\)), \( \nu(C=O) \) (carbonyl) (1665 cm\(^{-1}\)), \( \nu(C=N) \) (azomethine) (1620 cm\(^{-1}\)) and \( \nu(C-O) \phi \) (1526 cm\(^{-1}\)).

**Synthesis of (2)**

A dry \( C_6H_6 \) solution of (1) (2.56 g, 10 mmol) and HSCH\(_2\)COOH (0.92 g, 10 mmol) were refluxed for 12 h on a water bath. The mixture was cooled to room temperature and then washed with 10% NaHCO\(_3\) solution. \( C_6H_6 \) layer was separated using a separating funnel. The partial evaporation of \( C_6H_6 \) layer gave a solid product, which was filtered, washed with and recrystallized from pet. ether. The compound was dried as mentioned above. Yield = 15%. [Anal: \( C_{16}H_{14}N_{2}O_{4}S \) found (calcd) \% C = 58.67 (58.18); H = 4.36 (4.24); N = 8.35 (8.48), S = 9.57 (9.70)]; IR bands (KBr): \( \nu(O-H) \) (intramolecular H-bonding) (2870 cm\(^{-1}\)), \( \nu(C=O) \) (thiazolidinone ring) (1710 cm\(^{-1}\)), \( \nu(C=O) \) (amide) (1665 cm\(^{-1}\)), \( \nu(C=N) \) (thiazolidinone ring) (1575 cm\(^{-1}\)), \( \nu(C-O) \) (phenolic) (1528 cm\(^{-1}\)) and \( \nu(C-S) \) (thiazolidinone ring) (832 cm\(^{-1}\)).

**Syntheses of (3-6)**

A MeOH solution (30-50 mL) of the appropriate metal salt (5 mmol) was added to a MeOH solution (50 mL) of (2) (1.65 g, 5 mmol) and the mixture was then refluxed for 3-4 h. The solid products formed were suction filtered, washed repeatedly with MeOH and were then dried as mentioned above. Yield = 50-65%.

**Syntheses of (7)**

A THF solution (~20 mL) of appropriate AA (2 mmol) was added to a THF solution of 6 (0.94 g, 2 mmol). The mixture was refluxed on a water bath for 1 h. The excess of the solvent was evaporated and the separated compound was suction filtered. It was washed with and recrystallized from THF and dried as mentioned above. Yield = 70-85%.
RESULTS AND DISCUSSION

The cycloaddition reaction of the Schiff base (1) with HSCH₂COOH in dry C₆H₆ results in the formation of LH₃ (2). The reaction of a MeOH solution of (2) with appropriate metal salts in 1 : 1 molar ratio on refluxing produces respective stable coordination compounds (3-6). The reaction of (6) with AA (where AA = ON or NN donor ligands) in THF results in the formation of its respective heterochelates (7). The compounds, (4) (M = Co, Ni) and (5) do not lose weight on heating at 120°C for hours, indicating that MeOH molecule(s) are not lost but are coordinated to metal ion. The coordination compounds and heterochelates are monomers in diphenyl. They are insoluble in H₂O, MeOH, EtOH and soluble in DMSO and DMF. Their molar conductance measurements (Λₑ = 3.3-9.6 mho cm² mol⁻¹) (Table 1) indicate their non-electrolytic nature. The heterochelates are more stable than the precursor (6).

Table 1: Analytical, molar conductance and molecular weight of compounds

<table>
<thead>
<tr>
<th>Compd.</th>
<th>Mol. formula</th>
<th>Λₑ (mho cm² mol⁻¹)</th>
<th>Mol. wt.</th>
<th>Found (calcd.) %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>obs. (calcd.)</td>
<td>M</td>
</tr>
<tr>
<td>1</td>
<td>C₁₄H₁₂N₂O₃</td>
<td>256ₐ (256)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>C₁₆H₁₄N₂O₄S</td>
<td>330ₐ (330)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>3</td>
<td>CuC₁₈H₁₆N₂O₆S</td>
<td>467.4 (451.5)</td>
<td>13.94</td>
<td>47.65</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>CoC₂₀H₂₄N₂O₈S</td>
<td>523.6 (510.9)</td>
<td>11.64</td>
<td>46.83</td>
</tr>
<tr>
<td>(M = Co)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>NiC₂₀H₃₄N₂O₈S</td>
<td>522.6 (510.7)</td>
<td>11.37</td>
<td>46.87</td>
</tr>
<tr>
<td>(M = Ni)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>MoC₂₂H₂₄N₂O₈S</td>
<td>565.6 (587.9)</td>
<td>16.37</td>
<td>44.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>ZrC₁₈H₁₆N₂O₇S</td>
<td>495.5 (471.2)</td>
<td>19.18</td>
<td>40.93</td>
</tr>
<tr>
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</table>

Cont…
The IR spectra of the compounds (1-7) were recorded in KBr and the important peaks are presented in Table 2. The Schiff base (1) exhibits the $\nu$(C=O) (carbonyl), $\nu$(C=N) (azomethine) and $\nu$(C–O) $\phi$ stretches at 1665, 1620 and 1528 cm$^{-1}$, respectively. The disappearance of the $\nu$(C=N) (azomethine) stretch (1620 cm$^{-1}$) of (1) and the appearance of a new band at 1575 cm$^{-1}$ due to the $\nu$(C–N) (thiazolidinone ring) stretch$^{21}$ in (2) suggests the formation of the corresponding thiazolidin-4-one. The formation of (2) is further supported by the appearance of a new band at 832 cm$^{-1}$ due to the $\nu$(C–S) (thiazolidinone ring) stretch$^{22}$. Both these bands remain unchanged in the coordination compounds indicating the non-involvement of both N and S atoms of thiazolidin-4-one moiety towards the coordination. The $\nu$(C=O) (thiazolidinone ring) stretch$^{23}$ of (2) occurring at 1710 cm$^{-1}$ undergoes a negative shift by 26-38 cm$^{-1}$ in (3-7) indicating the coordination through carbonyl O atom of thiazolidin-4-one moiety. (2) occurs in the keto form as evident by the presence of a strong band at 1665 cm$^{-1}$ due to the $\nu$(C=O) (amide) stretch$^{24}$. This band remains almost at the same energy in (3-7), which rules out the involvement of keto O atom towards coordination. The strong band occurring at 2870 cm$^{-1}$ in (2) due to the intramolecular H-bonded OH group of the phenolic moiety disappears in (3-7) indicating the breakdown of H-bonding and the...
subsequent deprotonation of OH group followed by the involvement of phenolic O atom towards coordination\textsuperscript{25}. The $\nu$(C–O) (phenolic) stretch of (2) occurring at 1528 cm$^{-1}$, undergoes a positive shift by $\leq 10$ cm$^{-1}$ in (3-7) supports the involvement of phenolic O atom towards coordination\textsuperscript{26}. The magnitude of the above shift of the $\nu$(C–O) (phenolic) stretch supports the monomeric structures of (3-7) as suggested by molecular weight measurements. Free acetate ion exhibits $\nu_{as}$(OAc) and $\nu_s$(OAc) stretches at 1560 cm$^{-1}$ and 1416 cm$^{-1}$, respectively\textsuperscript{27}. On complexation, the former band undergoes a positive shift and the latter to a negative shift.

Table 2: IR, reflectance spectral data (cm$^{-1}$) and magnetic moments of the coordination compounds

<table>
<thead>
<tr>
<th>Compd.</th>
<th>$\nu$(C=O) (thiazolidine)</th>
<th>$\nu$(C–O) $\Phi$</th>
<th>$\nu_{as}$(OAc)</th>
<th>$\nu_s$(OAc)</th>
<th>$\nu$(C–O) (MeOH)</th>
<th>$\nu_{\text{max}}$</th>
<th>Mag. Moment (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1710</td>
<td>1528</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>3</td>
<td>1680</td>
<td>1537</td>
<td>1570</td>
<td>1345</td>
<td>–</td>
<td>17300</td>
<td>1.82</td>
</tr>
<tr>
<td>4 (M = Co)</td>
<td>1676</td>
<td>1535</td>
<td>1572</td>
<td>1352</td>
<td>966</td>
<td>8650, 17340, 19500</td>
<td>4.78</td>
</tr>
<tr>
<td>4 (M = Ni)</td>
<td>1680</td>
<td>1536</td>
<td>1564</td>
<td>1340</td>
<td>972</td>
<td>8670, 15860, 24500</td>
<td>3.32</td>
</tr>
<tr>
<td>5</td>
<td>1672</td>
<td>1532</td>
<td>–</td>
<td>–</td>
<td>970</td>
<td>–</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>6</td>
<td>1675</td>
<td>1534</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>7 (AA = ea)</td>
<td>1678</td>
<td>1537</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>7 (AA= oap)</td>
<td>1674</td>
<td>1537</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>7 (AA = en)</td>
<td>1684</td>
<td>1536</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>7 (AA= ophen)</td>
<td>1680</td>
<td>1534</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>7 (AA = bipy)</td>
<td>1677</td>
<td>1538</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>7 (AA = phen)</td>
<td>1679</td>
<td>1535</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Diamagnetic</td>
</tr>
</tbody>
</table>
The appearance of two new bands at 1564-1572 cm\(^{-1}\) \([\nu_{as}(OAc)]\) and 1340-1352 cm\(^{-1}\) \([\nu_{s}(OAc)]\) stretches indicates the presence of the coordinated acetato group in (3) and (4). The energy difference (\(\Delta\nu = 220-225\) cm\(^{-1}\)) between these stretches is > 210 cm\(^{-1}\) which indicates the monodentate nature of the acetato moiety. The presence of a broad band between 3345-3435 cm\(^{-1}\) due to the \(\nu(O-H)\) (MeOH) stretch and the decrease of the \(\nu(C-O)\) (MeOH) stretch\(^{27}\) from 1034 cm\(^{-1}\) to lower energy by 62-68 cm\(^{-1}\), respectively in (4) \((M = Co, Ni)\) and (5) indicates the presence of coordinated MeOH molecule(s). The appearance of bands at 945 and 914 cm\(^{-1}\) due to the \(\nu(C-O)\) (alcoholic/phenolic) stretches of ethanolamine and \(\phi(OH)\) (MeOH) occurring at 1230 and 1520 cm\(^{-1}\), respectively, shift to 1205 cm\(^{-1}\) and 1550 cm\(^{-1}\) in respective heterochelate conforming the participation of alcoholic/phenolic O atom towards coordination\(^{31,32}\). The \(\nu(C=N)\) (ring) stretch of 2,2’-dipyridyl and 1,10-phenanthroline occurring at 1585 and 1590 cm\(^{-1}\), respectively undergoes higher shift (~25 cm\(^{-1}\)) in (7), indicating the coordination of their ring N atoms to the respective metal ion\(^{31,32}\).

**Reflectance spectra**

The reflectance spectrum of (3) exhibits an asymmetric broad band at 17300 cm\(^{-1}\) due to the \(2B_{1g} \rightarrow 2A_{1g}, 2B_{2g}\) and \(2E_g\) transitions suggesting a square-planar geometry\(^{33}\). The absence of a band in the range 8000-10000 cm\(^{-1}\) precludes the presence of an octahedral structure\(^{34}\). (4) \((M = Co)\) exhibits three bands at 8650, 17340 and 19500 cm\(^{-1}\) due to the \(4T_{1g}(F) \rightarrow 4T_{2g}(P)(\nu_1), 4T_{1g}(F) \rightarrow 4A_{2g}(F)(\nu_2), 4T_{1g}(F) \rightarrow 4T_{1g}(P)(\nu_3)\) transitions, respectively in an octahedral symmetry\(^{35}\). The \(\nu_3/\nu_1\) value in the present compound is 2.25 and it lies in the usual range (2.0-2.8) reported for majority of octahedral Co (II) compounds\(^{35}\). The spectral parameters are: \(Dq = 978.69\) cm\(^{-1}\), \(B = 799.1\), \(\beta = 0.82\), \(\beta^0 = 18.0\)% and CFSE = –93.7 kJ mol\(^{-1}\). The reduction of Racah parameter from the free ion value (971 cm\(^{-1}\)) to 799.1 cm\(^{-1}\) and the % covalence value (18.0) in (4) \((M = Co)\) are indicative of the presence of covalent nature in the present case\(^{35}\). The appearance of three bands at 8980, 16410 and 24500 cm\(^{-1}\) in (4) \((M = Ni)\) is due to the \(3A_{2g}(F) \rightarrow 3T_{2g}(F)(\nu_1), 3A_{2g}(F) \rightarrow 3T_{1g}(P)(\nu_2)\) and \(3A_{2g}(F) \rightarrow 3T_{1g}(F)(\nu_3)\)
transitions, respectively in an octahedral symmetry\(^3^5\). The \(\nu_2/\nu_1\) value in the present compound is 1.8, which occurs in the usual range (1.6-1.82) reported for the majority of octahedral Ni (II) compounds\(^3^6\). The spectral parameters are: \(Dq = 898\) cm\(^{-1}\), \(B = 811.74\), \(\beta = 0.79\) and \(\beta^0 = 21.0\%\), CFSE = \(-128.91\) kJmol\(^{-1}\). The reduction of Racah parameter from the free ion value (1030 cm\(^{-1}\)) to 811.74 cm\(^{-1}\) and the % covalence value (21.0) in (4) (M = Ni) are indicative of the presence of covalent nature in the present case\(^3^6\). The 10\(Dq\) value (9786 cm\(^{-1}\)) of Co (II) compound is greater than the corresponding Ni (II) compound, (8980 cm\(^{-1}\)). This is in line with the spectrochemical series of metal ions for a given ligand, given stoichiometry and a given stereochemistry\(^3^6\): Ni (II) < Co (II). The \(\beta^0\) values of (4) (M = Ni) is comparable to the corresponding Co (II) compound : 21% ~ 18%. This is in line with the nephelauxetic metal ion series in terms of \(B\) and \(\beta^0\) for a given ligand, given stoichiometry and a given stereochemistry\(^3^6\). The higher negative CFSE value in the Co (II) coordination compound in comparison to that of the corresponding Ni (II) coordination compound is as expected.

\(^1^H\) NMR spectra

The \(^1^H\) NMR spectra of (1), (2), (6) and (7) (where AA = ea and oap) have been recorded in DMSO-d\(_6\). The chemical shifts (\(\delta\)) are expressed in ppm from TMS\(^3^7\). (1) exhibits signals at \(\delta\) 6.82-8.00 ppm due to aromatic protons\(^3^2\), \(\delta\) 7.32 ppm due to azomethine proton\(^2^7\), a broad signal at \(\delta\) 10.91 ppm due to –OH protons\(^3^2\) and a signal at \(\delta\) 11.7 ppm due to –NH proton\(^3^2\). (2), (6) and (7) exhibit signal at \(\delta\) 3.83, \(\delta\) 3.3, \(\delta\) 3.04 ppm (AA = ea) and at \(\delta\) 3.02 ppm, (AA = oap) ppm respectively due to the > CH\(_2\) protons of thiazolidin-4-one moiety\(^3^8\). The presence of the signal at \(\delta\) 5.89, \(\delta\) 5.82, \(\delta\) 5.78 ppm (AA = ea) and \(\delta\) 5.73 ppm (AA = oap) ppm is due to the proton of –CHNS moiety \(^3^8\). The appearance of –NH proton in the spectra of (2), (6) and (7) (where AA = ea and oap) at \(\delta\) 11.54, \(\delta\) 11.08, \(\delta\) 11.2 ppm and 11.05 ppm, respectively suggests the presence of keto form of the thiazolidin-4-one in these compounds\(^3^2\). The signals at \(\delta\) 10.72, \(\delta\) 10.83, \(\delta\) 10.81 ppm (AA = ea) and \(\delta\) 10.78 (AA = oap) ppm in (2), (6) and (7), respectively are due to the presence of the phenolic –OH protons in (2), (6) and (7) (when) \(^2^7\). The presence of multiplet in the range 6.48-7.45 ppm is due to the aromatic protons in (2), (6) and (7)\(^3^2\). The appearance of the signals at \(\delta\) 2.3 ppm and \(\delta\) 1.8 ppm in (7) (AA = ea) are due to the –OH and –NH\(_2\) protons, respectively, and it indicates the neutral bidentate ON donor nature of the ethanolamine in the heterochelate. (7) (AA = oap) exhibits signal at \(\delta\) 7.3 ppm due to –NH\(_2\) group\(^3^9\) of coordinated o-aminophenol.

Magnetic susceptibility measurements

The Cu (II) ion belongs to the \(S = \frac{1}{2}\) system and since its spin-orbit coupling constant is negative\(^4^0\), the magnetically dilute Cu (II) complexes are expected to exhibit magnetic moments higher than the spin-only value (1.73 B.M.) due to the presence of orbital
contribution. The magnetic moment of (3) is 1.82 B.M., which lies in the usual range (1.75-2.20) reported for the magnetically dilute Cu (II) compounds. The magnetic moment of (4) (M = Co) is 4.78 B.M., which is consistent with high-spin octahedral structure. The magnetic moment of (4) (M = Ni) is 3.32 B.M., which suggests six-coordinate structure. The coordination compounds of MoO$_2$ (VI) and Zr (OH)$_2$ (IV) ions are diamagnetic as expected.

**Proposed structures of the compounds**
CONCLUSION

On the basis of analytical data, conductance measurements, molecular weight, spectral, magnetic susceptibility measurements, We propose a square-planar structure for (3), an octahedral structure for (4) (M = Co, Ni) and (6), and an eight-coordinate structure for (5) and (7).

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REFERENCES


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