Synthesis and characterization of metal complexes of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Ru(III), Rh(III) and Pd(II) with derivatives of 1,3,4-thiadiazole-2, 5-dithiol as new ligands

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Abstract The synthesis of some new transition metal complexes with 1,3,4-thiadiazole-2, 5-dithiol derivatives (L1 and L2) as new ligands is reported. Each complex was prepared by the reaction of the ligands with the appropriate metal salts (CrCl3, MnCl2·4H2O, FeCl3, CoCl2·6H2O, NiCl2·6H2O, CuCl2·2H2O, RuCl3, RhCl3 and PdCl2). Elemental micro analysis (C.H.N), UV-Visible spectroscopy, 1H NMR, infrared (IR) spectroscopy, atomic absorption, magnetic susceptibility, continuous variation method and molar conductance techniques were used to characterize the structural formulae of these chelate complexes.

1. Introduction

The increasing clinical importance of drug-resistant microbial pathogens has lent additional urgency in microbiological and antifungal research (Hoffer and Grunberg, 1974; Bhatia and Shanbhag, 1984; Palaska et al., 2002). In this regard, thiadiazoles have occupied an important place in drug industry; in particular 1,3,4-thiadiazoles derivatives have been used widely in various fields. Earliest application was in the pharmaceutical area where sulfonamides antibacterial were used as drugs. Some of the later uses are as antitumor and antiinflammatory agents, pesticides, dyes, lubricants and analytical reagents (Vasoya et al., 2005). Interest in 1,3,4-thiadiazole and its derivatives also arises from the fact that they possess also cover a wide spectrum of therapeutic action liking used as anticonvulsant herbicidal (Ores and et al., 1961), pesticidal (Hoggart and Rathghab, 1969, 1975), amoebicidal (Tony and Gen, 1975), CNS depressant (Bourdain et al., 1981), antibacterial (Mody et al., 1982), and antiviral drugs (Teraji and Sakane, 1980, 1981).

Thiosemicarbazone and semicarbazide have aroused considerable interest in the field of chemistry and biology due to their antibacterial, antifungal, antimalarial, antineoplastic and antiviral activities (West et al., 1991, 1993; EI-Sawaf
et al., 1997; Smith, 1997; Pessoa et al., 2001). The biological activities of thiosemicarbazone and semicarbazone are attributed to their ability to form chelates with metals.

Herein, we report the synthesis of new 1,3,4-thiadiazole-2,5-dithiol derivatives as ligands (L₁ and L₂) and their complexes hopefully to look in for their possible antibacterial and antifungal activity. The spectral properties and electrochemical behavior of the new ligands and consequently the new complexes were investigated. The two ligands were also characterized using 1H NMR techniques.

2. Experimental

All chemicals were purchased from Fluka, and B.D.H. Chemicals. IR spectra were recorded on Shimadzu FT-IR-8400 instrument, using KBr disc for the prepared ligands and CsI disc for the metal ion complexes. Elemental analyses were done on a LECO-CHNS-938. The percentages of the transition metals of the prepared complexes were determined using Shimadzu A-A-670, Flame Spectrophotometer. Magnetic measurements were carried out by the Gouy method using Hg[Co(SCN)₄]₄ as calibrant. Molar conductances of the complexes were determined in DMSO at room temperature by using a Jenway model 4070 conductivity meter.

2.1. Preparation of 2-[(5-sulfanyl-1,3,4-thiadiazol-2-yl) hydrazinecarbothioamide (L₁)

A mixture of 1,3,4-thiadiazole-2,5-dithiol (7.5 g, 0.05 mol) and thiosemicarbazide (4.5 g, 0.05 mol) in ethanol (85%) (60 ml) was heated under reflux for 6 h. After cooling, the white precipitate was filtered and recrystallized from absolute ethanol to afford L₁ (8.85 g, 85.5% yield), M.P. 194–196 °C (Scheme 1).

2.2. Preparation of 2-[(5-sulfanyl-1,3,4-thiadiazol-2-yl) hydrazinecarboxamide (L₂)

A mixture of 1,3,4-thiadiazole-2,5-dithiol (7.5 g, 0.05 mol) and semicarbazide (3.75 g, 0.05 mol) in ethanol (85%) (50 ml) was heated under reflux for 1.5 h. After cooling, the solvent was removed by vacuum evaporation. After filtration the precipitate was crystalized from ethanol (30–70 v/v). The molar conductance was 254 T.T. Al-Nahary

2.4. General preparation of complexes of ligand (L₂)

A solution of (1.32 g, 5 mmol) of ligand L₂ dissolved in absolute ethanol (25 ml) was added to (2.5 mmol) of the transition metal salt (CrCl₃, FeCl₃, MnCl₂·4H₂O and CuCl₂·2H₂O) dissolved in hot absolute ethanol (15 ml). The mixture was refluxed for 1.5 h. After cooling, the solvent was removed by vacuum evaporation. After filtration the precipitate was crystalized from DMF. The elemental analysis and physical properties of the resulted complexes are presented in Table 1.

3. Results and discussion

The new synthesized ligands (L₁ and L₂) and their complexes are very stable at room temperature in the solid state. The ligands themselves are soluble in common organic solvents; however, their metal complexes are soluble in DMSO and DMSO. Based on continuous variation results, it is concluded that complexes are conformable with the ratio 1:1 for metal to ligand L₁ whereas the ratio is 1:2 for complexes with ligand L₂.

3.1. Molar conductance

Molar conductance (AM) of 10⁻³ M DMSO solutions of the complexes were determined. The molar conductance values are presented in Tables 1 and 2. The values for Co(II) 3, Ni(II) 5 and Pd(II) 6 complexes indicate that these complexes are 1:1 electrolytes; consequently one chloride ion is present outside the coordination sphere. This in is case confirmed by Fe(III) 1, Rh(III) 4 complexes, the molar conductance (AM) values are too low to account for an ionic complex; therefore, these complex are considered to be neutral. The Cr(III) 7 and Fe(III) 8 complexes behave as 3:1 electrolytes indicating that three anions which are coordinated are replaced by solvent molecules. These complexes are hexa coordinated and their probable geometry may be octahedral. The molar conductance (AM) value for the Mn(II) 9 and Cu(II) 10 complexes corresponds to a 2:1 electrolyte indicating that both the coordinated anions are replaced by solvent molecules. These complexes are hexa coordinated and their probable geometry may be octahedral. The elemental analysis data of the ligands (L₁ and L₂) and their complexes (Tables 1 and 2) are consistent with the calculated results from the empirical formula of each compound.

Scheme 1

metal salt (FeCl₃, RuCl₃, CoCl₂·6H₂O, RhCl₃, NiCl₂·6H₂O and PdCl₂) dissolved in hot absolute ethanol (30 ml). The mixture was refluxed for 1.5 h. After cooling, the solvent was removed by vacuum evaporation. After filtration the precipitate was crystalized using DMF-ethanol (30–70 v/v). The elemental analysis and physical properties of the resulted complexes are presented in Table 1.

2.4. General preparation of complexes of ligand (L₂)

A solution of (1.32 g, 5 mmol) of ligand L₂ dissolved in absolute ethanol (25 ml) was added to (2.5 mmol) of the transition metal salt (CrCl₃, FeCl₃, MnCl₂·4H₂O and CuCl₂·2H₂O) dissolved in hot absolute ethanol (15 ml). The mixture was refluxed for 1.5 h. After cooling, the solvent was removed by vacuum evaporation. After filtration the precipitate was crystalized from DMF. The elemental analysis and physical properties of the resulted complexes are presented in Table 2.

3. Results and discussion

The new synthesized ligands (L₁ and L₂) and their complexes are very stable at room temperature in the solid state. The ligands themselves are soluble in common organic solvents; however, their metal complexes are soluble in DMSO and DMSO. Based on continuous variation results, it is concluded that complexes are conformable with the ratio 1:1 for metal to ligand L₁ whereas the ratio is 1:2 for complexes with ligand L₂.

3.1. Molar conductance

Molar conductance (AM) of 10⁻³ M DMSO solutions of the complexes were determined. The molar conductance values are presented in Tables 1 and 2. The values for Co(II) 3, Ni(II) 5 and Pd(II) 6 complexes indicate that these complexes are 1:1 electrolytes; consequently one chloride ion is present outside the coordination sphere. This in is case confirmed by Fe(III) 1, Rh(III) 4 complexes, the molar conductance (AM) values are too low to account for an ionic complex; therefore, these complex are considered to be neutral. The Cr(III) 7 and Fe(III) 8 complexes behave as 3:1 electrolytes indicating that three anions which are coordinated are replaced by solvent molecules. These complexes are hexa coordinated and their probable geometry may be octahedral. The molar conductance (AM) value for the Mn(II) 9 and Cu(II) 10 complexes corresponds to a 2:1 electrolyte indicating that both the coordinated anions are replaced by solvent molecules. These complexes are hexa coordinated and their probable geometry may be octahedral. The elemental analysis data of the ligands (L₁ and L₂) and their complexes (Tables 1 and 2) are consistent with the calculated results from the empirical formula of each compound.

Scheme 1
Table 1 Analytical data and some physical properties of ligand (L₁) and their complexes.

<table>
<thead>
<tr>
<th>No.</th>
<th>Molecular formula</th>
<th>Colour</th>
<th>M.P. °C (yield %)</th>
<th>( \Delta_{\text{m}}^\circ )</th>
<th>Calc. (found)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C%</td>
<td>H%</td>
</tr>
<tr>
<td>L₁</td>
<td>C₅H₄N₅S₃</td>
<td>White</td>
<td>194–196 (85.5)</td>
<td></td>
<td>17.37 (17.25)</td>
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<tr>
<td>1</td>
<td>[Fe(C₅H₄N₅S₃)Cl]</td>
<td>Pale green</td>
<td>274–276 (74)</td>
<td>22</td>
<td>9.74 (9.69)</td>
</tr>
<tr>
<td>2</td>
<td>[Ru(C₅H₄N₅S₃)Cl]</td>
<td>Brown violet</td>
<td>279–281 (70)</td>
<td>20</td>
<td>8.68 (8.87)</td>
</tr>
<tr>
<td>3</td>
<td>[Co(C₅H₄N₅S₃)Cl]</td>
<td>Green</td>
<td>215–217 (86)</td>
<td>40</td>
<td>10.67 (10.59)</td>
</tr>
<tr>
<td>4</td>
<td>[Rh(C₅H₄N₅S₃)Cl]</td>
<td>Pale brown</td>
<td>294–296 (78)</td>
<td>20</td>
<td>8.64 (8.70)</td>
</tr>
<tr>
<td>5</td>
<td>[Ni(C₅H₄N₅S₃)Cl]</td>
<td>Pale blue</td>
<td>233–235 (85)</td>
<td>38</td>
<td>10.68 (10.57)</td>
</tr>
<tr>
<td>6</td>
<td>[Pd(C₅H₄N₅S₃)Cl]</td>
<td>Brown</td>
<td>272–274 (77)</td>
<td>35</td>
<td>9.36 (9.42)</td>
</tr>
</tbody>
</table>

\* \( \text{OH}^{-1} \text{cm}^{-1} \text{mol}^{-1} \) (in DMSO solvent).

Table 2 Analytical data and some physical properties of ligand (L₂) and their complexes.

<table>
<thead>
<tr>
<th>No.</th>
<th>Molecular formula</th>
<th>Colour</th>
<th>M.P. °C (yield %)</th>
<th>( \Delta_{\text{m}}^\circ )</th>
<th>Calc. (found)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C%</td>
<td>H%</td>
</tr>
<tr>
<td>L₂</td>
<td>C₅H₄N₅S₂O</td>
<td>Pale brown</td>
<td>188–190 (84.53)</td>
<td></td>
<td>18.83 (18.69)</td>
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<tr>
<td>7</td>
<td>[Cr(C₅H₄N₅S₂)Cl]</td>
<td>Green</td>
<td>244–246 (83.86)</td>
<td>95</td>
<td>13.31 (13.45)</td>
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<td>8</td>
<td>[Fe(C₅H₄N₅S₂)Cl]</td>
<td>Dark black</td>
<td>259–261 (75.58)</td>
<td>97</td>
<td>13.22 (13.39)</td>
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<td>9</td>
<td>[Mn(C₅H₄N₅S₂)Cl]</td>
<td>Violet</td>
<td>281–283 (70.63)</td>
<td>80</td>
<td>14.16 (14.23)</td>
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<tr>
<td>10</td>
<td>[Cu(C₅H₄N₅S₂)Cl]</td>
<td>Pale green</td>
<td>288–290 (85)</td>
<td>80</td>
<td>13.93 (13.85)</td>
</tr>
</tbody>
</table>

\* \( \text{OH}^{-1} \text{cm}^{-1} \text{mol}^{-1} \) (in DMSO solvent).

3.2. IR spectra

The infrared spectra technique was used to identify the prepared coordination complexes, specially on comparing with the free ligand spectra so as to locate the position of the donor atoms. Besides identifying the ligands (L₁ and L₂) the infrared spectra were also to determine the position of absorption bands for the different active groups such as (C=N), (C=S), (NH), (C=N–N=C), (M–S), (M–N), (M–O) and (M–Cl). Ligand (L₁), shows four bands at (1620) cm\(^{-1}\), (1531) cm\(^{-1}\), (1256) cm\(^{-1}\), and (723) cm\(^{-1}\), which are attributed to (C=N), (C=S), (SH), (NH) and (NH₂) groups, respectively. Moreover the appearance of the bands located at (1530) cm\(^{-1}\) and (736) cm\(^{-1}\), indicates the formation of (C=N–N=C) and (C–S–C) bands, respectively. For metal complexes of ligand (L₁) the stretching frequencies for the (C=N), (C=S) and (NH) are weakened and shifted to lower frequencies about (5–25) cm\(^{-1}\), while those for the (C=N–N=C), (C–S–C) and (NH₂) become weaker but with no shift (Zalarua et al., 2007); because these groups no coordination with metals ions. New bands are observed indicating coordination as: (M–N) and (M–O); these appear on the regions (430–475) cm\(^{-1}\) and (495–560) cm\(^{-1}\), respectively. This indicates that coordination has occurred through the nitrogen, and oxygen atoms of (C=N), (–NH) and (C=O) groups of the ligand (L₂) (Table 3).

3.3. \(^1\)H NMR spectra

The \(^1\)H NMR spectrum of the ligands (L₁ and L₂) show characteristic signals due to the (–NH₂) protons appearing at 7.62 ppm and 8.96 ppm, respectively. Moreover the appearance of the bands located at 6.95 ppm may be assigned to due to the (–SH) protons for ligands (L₁ and L₂). The bands observed between 9.80 and 11.65 ppm may be assigned to (–NH–NH–) protons for both ligands (L₁ and L₂).
3.4. Magnetic moments

The magnetic moment ($\mu_{\text{eff}}$) values for the complexes with new ligands are given in Table 4. The magnetic moment value for the Fe(III) complex 1 is 6.35 BM indicating a slight ferromagnetic behavior (Prasad and Mathur, 2002), and suggests the high spin state of Fe(III). For the Ru(III) complex 2 is 1.97 BM, indicating the presence of one unpaired electron and suggests low spin state of Ru(III). For the Co(II) complex 3 the $\mu_{\text{eff}}$ value of 3.92 BM corresponds to three unpaired electrons, and may suggests a spin free tetrahedral configuration. The Rh(III) complex 4 is diamagnetic as expected for a d⁶ low spin configuration. The magnetic moment of 0 BM for the Ni(II) 5 and Pd(II) 6 complexes suggests a low spin square planar arrangement. The magnetic moment for the Cr(III) complex 7 is 3.97 BM, indicating the presence of three unpaired electrons. The $\mu_{\text{eff}}$ value for the Fe(III) 8 and Mn(II) 9 complexes are 2.63 BM and 2.60 BM, respectively, indicating the presence of one unpaired electrons and suggests the low spin state of Fe(III) and Mn(II). Higher values of magnetic moment may be due to a large orbital contribution. For the Cu(II) complex 10 the $\mu_{\text{eff}}$ value of 1.96 BM corresponds to one unpaired electron.

3.5. Electronic spectra

The electronic spectra of the ligands and their metal complexes were recorded in DMSO at room temperature. UV spectral data of each ligand and the corresponding complexes are given in Table 4. The bands in the region (275–284) nm attributed to $\pi \rightarrow \pi^*$ transitions show the aromatic nature of part of the ligands specifically. Also shown are bands in the region (360–375) nm due to the $n \rightarrow \pi^*$ transition of the non-bonding electrons present on the sulfur of the (C=S), (C=O) groups and nitrogen of the azomethine (C=N) groups in the ligands. The electronic spectra of Iron (III) complex 1, showed bands at (16,929) cm⁻¹, (23,587) cm⁻¹, (28,794) cm⁻¹ and (33,985) cm⁻¹, which are assignable to $^4A_{2g} \rightarrow ^4T_{2g}(G)$, $^4A_{2g} \rightarrow ^4E_g$, $^4A_{2g} \rightarrow ^4T_{2g}(D)$, and $^4A_{1g} \rightarrow ^4T_{1g}(P)$, transitions, respectively (Sharam and Chowdhary, 1989). The ground state of Ruthenium (III) is $^4T_2g$ and the first excited doublet levels in order of increasing energy are $^2A_{2g}$ and $^2T_{1g}$ which are known to arise from $^4T_{2g}$ $^4E_g$ configuration (Venkatachalam et al., 2005). The electronic spectra of Ruthenium (III) complex 2, showed very weak absorption bands, which may not be useful in assigning geometry; yet the bands at (16,920) cm⁻¹, (20,629) cm⁻¹, (23,587) cm⁻¹, and (24,720) cm⁻¹, may be attributed to $^2T_{2g} \rightarrow ^2T_{1g}$, $^2T_{2g} \rightarrow ^2T_{2g}$, and $^2T_{2g} \rightarrow ^2A_{2g}$, $^2T_{1g}$ transitions, respectively (Venkatachalam et al., 2005). The electronic spectra of Cobalt (II) complexes 3, showed bands at (17,573) cm⁻¹ and (21,890) cm⁻¹ corresponding to transitions, $^4A_{2g}(F) \rightarrow ^4T_{2g}(F)$ and $^4A_{2g}(F) \rightarrow ^4T_{1g}(F)$, respectively, supported the tetrahedral geometry (Sarojini and Ramacha, 1996) around the d⁶ Cobalt(II) ions. Rhodium (III) complexes 4, exhibit electronic spectra with transitions at 18,150 cm⁻¹, 20,498 cm⁻¹, and 26,694 cm⁻¹. These bands resemble to those of reported

<table>
<thead>
<tr>
<th>No.</th>
<th>Compounds</th>
<th>$\mu_{\text{eff}}$ (BM)</th>
<th>$\pi \rightarrow \pi^*$</th>
<th>$n \rightarrow \pi^*$</th>
<th>d-d transitions (cm⁻¹)</th>
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<tbody>
<tr>
<td>L₁</td>
<td>C₅H₅N₅S₂</td>
<td>6.35</td>
<td>360</td>
<td>370</td>
<td>16,929, 23,587, 28,794, 33,985</td>
</tr>
<tr>
<td>1</td>
<td>[Fe(C₅H₅N₅S₂)Cl₃]</td>
<td>1.97</td>
<td>373</td>
<td>365</td>
<td>16,920, 20,629, 24,720</td>
</tr>
<tr>
<td>2</td>
<td>[Ru(C₅H₅N₅S₂)Cl₃]</td>
<td>3.92</td>
<td>367</td>
<td>375</td>
<td>17,573, 21,890</td>
</tr>
<tr>
<td>3</td>
<td>[Co(C₅H₅N₅S₂)Cl₃]</td>
<td>Diamagnetic</td>
<td>369</td>
<td>367</td>
<td>18,150, 20,498, 26,694</td>
</tr>
<tr>
<td>4</td>
<td>[Rh(C₅H₅N₅S₂)Cl₃]</td>
<td>Diamagnetic</td>
<td>367</td>
<td>375</td>
<td>23,549, 27,400</td>
</tr>
<tr>
<td>L₂</td>
<td>C₅H₅N₅S₃</td>
<td>3.96</td>
<td>372</td>
<td>374</td>
<td>17,648, 23,969, 27,605</td>
</tr>
<tr>
<td>7</td>
<td>[Cr(C₅H₅N₅S₃)Cl₂]</td>
<td>2.63</td>
<td>374</td>
<td>367</td>
<td>14,969, 21,280, 28,469</td>
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<td>8</td>
<td>[Fe(C₅H₅N₅S₃)Cl₂]</td>
<td>2.60</td>
<td>372</td>
<td>375</td>
<td>15,220, 21,729, 28,620</td>
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<td>9</td>
<td>[Ni(C₅H₅N₅S₃)Cl₂]</td>
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<td>375</td>
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<td>2.86</td>
<td>374</td>
<td>375</td>
<td>15,373, 21,580</td>
</tr>
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</table>

*BM = Bohr Magneton.*
transitions for other hexacoordinated rhodium complexes (Chandra and Singh, 1988). The ground state for Rhodium (III) ion is $^1A_{1g}$ in octahedral field, although in many instances only $^1A_{1g} \rightarrow ^1T_{1g}$ spin allowed ligand field transitions to be observed. These transitions correspond to $^1A_{1g} \rightarrow ^1T_{2g}$, $^1A_{1g} \rightarrow ^1T_{1g}$, and $^1A_{1g} \rightarrow ^1T_{2g}$, respectively, which agree well with an octahedral geometry (Chandra and Singh, 1988). The electronic spectra of Nickel (II) complexes and Palladium (II) complexes, exhibits bands at (18,288, 23,549) cm$^{-1}$ and (21,890, 27,400) cm$^{-1}$ assignable to $^1A_{1g} \rightarrow ^1A_{2g}$, and $^1A_{1g} \rightarrow ^1B_{1g}$ transitions, respectively, supported the square planar geometry (West et al., 1996; Chandra and Tyagi, 2008). The electronic spectra of the Cr(III) complex exhibits band at 17,648 cm$^{-1}$, 23,969 cm$^{-1}$ and 27,605 cm$^{-1}$ which may be assigned to $^4A_{2g}(F) \rightarrow ^4T_{2g}(F)$, $^4A_{2g}(F) \rightarrow ^4T_{1g}(F)$, and $^4A_{2g}(F) \rightarrow ^4T_{1g}(P)$ transitions, respectively (Thaker et al., 1996). Again the electronic spectrum of Iron (III) complex showed very weak absorption bands, which may not help in assigning geometry, but the bands at (14,969, 15,220) cm$^{-1}$, (21,280, 21,729) cm$^{-1}$, and (28,469, 28,620) cm$^{-1}$, may be attributed to $^6A_{1g} \rightarrow ^4T_{1g}(G)$, $^6A_{1g} \rightarrow ^4E_g$, $^4A_{1g}(G)$ and $^6A_{1g} \rightarrow ^4E_g(D)$ transitions, respectively.

The electronic spectra of the Copper (II) complex showed bands at (15,373) cm$^{-1}$ and (19,580) cm$^{-1}$, assignable to $^2B_{1g} \rightarrow ^2B_{2g}$ and $^2B_{1g} \rightarrow ^2E_g$ transitions, respectively, corresponding to a distorted octahedral geometry around the copper ion (Khan et al., 1997).

4. Conclusion

New compounds, which can be used to prepare many new compounds, have been synthesized. Some of the new derivatives might be important biologically active agents, and their medical research applications should be investigated.

References


Further reading