**Synthesis, Spectral Studies of Binuclear Divalent Metal Chelates Derived from Benzofuron-2-carbohydrazide and 1-Chloro-4-isothiocyanatobenzene**

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**Abstract:** The M(II) complex of benzofuron-2-carbohydrazide, 1-chloro-4-isothiocyanatobenzene and nitrophenol (2-nitrophenol, 2,3-dinitropheno, 2,3,4-trinitrophenol) with transition metal ion e.g. Cu(II), Ni(II) and Co(II) were prepared. All the complexes have structure formula \[\text{[Cu}_2\text{C}_5\text{H}_4\text{N}_1\text{Cl}_2\text{O}_{16}\text{S}_2]\], \[\text{[Ni}_2\text{C}_5\text{H}_4\text{N}_1\text{Cl}_2\text{O}_{16}\text{S}_2]\], \[\text{[Co}_2\text{C}_5\text{H}_4\text{N}_1\text{Cl}_2\text{O}_{16}\text{S}_2]\], \[\text{[Cu}_2\text{C}_5\text{H}_3\text{N}_4\text{Cl}_2\text{O}_{24}\text{S}_2]\], \[\text{[Ni}_2\text{C}_5\text{H}_3\text{N}_4\text{Cl}_2\text{O}_{24}\text{S}_2]\] and \[\text{[Co}_2\text{C}_5\text{H}_3\text{N}_4\text{Cl}_2\text{O}_{24}\text{S}_2]\] characterized by the several analytical techniques including elemental analysis (C.H.N.), molar conductance measurements, magnetic measurements, electronic, FAB mass, IR, \(^1\)H NMR and \(^13\)C NMR spectral studies. Based on these studies six coordinated octahedral geometry for all the complexes was proposed.

**Keyword:** Divalent metal complex, Benzofuron-2-carbohydrazide, 1-Chloro-4-isothiocyanatobenzene, Spectroscopic study

**Introduction**

The introduction of S, O and N atom containing group in the organic molecules have often resulted into the important change in the behavior towards metal ions. Organic heterocyclic compounds are one of the important classes of ligand which have shown immense importance in our life. Several heterocyclic compounds are often used as chemotherapeutic agents and drug copolymers. A large number of heterocyclic compounds containing N, S or O as hetero atom in the ring are known to form complexes with transition metal ions. These complexes have shown importance in the field of catalysis, medicine, analytical chemistry and biological activity. The formation and characterization of azomethines complexes was done by Schiff 1, who reported the formation of, 1:2 metal: ligand ratio, copper complexes derived from N-aryl salicyldimine but the first report on the metal complexes of azomethine was much before when Ettling prepared a Cu(II) complex with salicylaldehyde 2 which was a crystalline solid of dark green colour. But the work in this field has gained momentum since the last four decades only. In 1965 Chaston and co-workers 3 reported the preparation of
azonmethine ligand by the condensation of benzoylacetone and 1,2-diaminoethane and its complexes with transition metals. Lindoy and co-workers\textsuperscript{4} reported a number of azomethine complexes of various metals with methyl thioquinoline. A number of publications appeared about the lanthanide ion complexes with azomethines derived from bis-salicylaldehyde and \( o \)-phenylenediamine\textsuperscript{5} and \( p \)-dimethylaminobenzaldehyde and benzidine\textsuperscript{6}. A number of M(II) complexes with azomethine have been reported by various workers\textsuperscript{7-13}. Metal complexes of azomethine ligand derived from pivaloylacetone and 1,2-diaminoethane have also been reported\textsuperscript{14}. Five and six-coordinated Co(II), Ni(II), Cu(II) and Zn(II) complexes of the pentadentate azomethine ligands. \( N,N \)-Bis [(2-hydroxy-5-\( Y \)-phenyl) phenylmethylene-4-azoheptane-1,7-diamine (where \( Y = \text{Chloro or methyl} \)) and \( N-N \)-Bis [5-chloro-2-hydroxyphenyl) phenylmethylene-4-thioheptane-1,7-diamine have been synthesized and characterized by Boge and co-workers\textsuperscript{15}. Azomethine formed in the condensation reactions between unsymmetrical \( \beta \)-diketones and 1,2-diamino ethane and their transition complexes have also been reported in the literature\textsuperscript{16}. The azomethine derived from bis-vanillin and \( o \)-phenylenediamine and their lanthanide complexes have also been reported in the literature\textsuperscript{17}. Tripathy and co-workers prepared azomethines \textit{viz}. bis-salicylaldehyde ethylene diamine and bis-o-hydroxyacetophenone ethylenediamine, and their transition metal complexes\textsuperscript{18}. The aim of the present study is to prepare and characterized divalent bimolecular metal ion complexes derived from benzofuron-2-carbohydrazide and 1-chloro-4-isothiocyanatobenzene.

**Experimental**

The entire chemicals used, were of the analytical grade, benzofuran-2-carbohydrazide, \( p \)-chlorophenyl isothiocyanate, 2, nitrophenol, 2, 3 dinitrophenol, 2, 3, 4, trinitrophenol, procured from s.d.-fine. Metal salts were purchased from Merck.

**Benzofuro- 2-carboxy- [4'-chlorophenyl] thiosemicarbazide**

Benzofuran-2-carbohydrazide (4.58 g, 0.026 mol) was dissolved in ethanol and this solution was added 1-chloro-4-isothiocyanatobenzene (4.41 g, 0.026 mol) in a 1:1 molar ratio containing few drop of concentrated HCl. The solution was refluxed for 3 h. The cream crystalline product which formed was filtered off under vacuum and recrystallized from ethanol (Scheme 1).
Synthesis of the Cu(II), Ni(II) and Co(II) complexes

A solution of divalent metal salt (2.0 mol) in methanol (12 mL) was added to a hot solution (75 °C) of benzofuro- 2-carboxy- [4'-chlorophenyl] thiosemicarbazide ligand (2.0 mol) and nitrophenol (4.0 mol) in ethanol (28 mL) and the reaction mixture was refluxed for 8 h. The solution was concentrated under vacuum. The precipitate was filtered off, washed with methanol and dried under vacuum over anhydrous CaCl$_2$ (68-75% yield) (Scheme 2).

![Scheme 2. Synthesis of divalent bimolecular metal complex](image-url)
Results and Discussion

Mass spectra

The FAB mass spectra of Cu(II), Ni(II) and Co(II) Schiff base complexes have been recorded (Table 1). The molecular ion (M+) peaks obtained from various complexes are as follows: (1) \( m/z = 444.80 \text{C}_{56}\text{H}_{40}\text{N}_{10}\text{Cl}_{2}\text{O}_{16}\text{S}_{2} \) (complex 1), (3) \( m/z = 1360.4 \text{ Ni}_{2}\text{C}_{56}\text{H}_{40}\text{N}_{10}\text{Cl}_{2}\text{O}_{16}\text{S}_{2} \) (complex 2), (4) \( m/z = 1360.88 \text{ Co}_{2}\text{C}_{56}\text{H}_{40}\text{N}_{10}\text{Cl}_{2}\text{O}_{16}\text{S}_{2} \) (complex 3), (5) \( m/z = 1550.09 \text{ Co}_{3}\text{C}_{56}\text{H}_{58}\text{N}_{14}\text{Cl}_{2}\text{O}_{24}\text{S}_{2} \) (complex 4), (6) \( m/z = 1540.3 \text{ Ni}_{2}\text{C}_{56}\text{H}_{36}\text{N}_{14}\text{Cl}_{2}\text{O}_{24}\text{S}_{2} \) (complex 5), (7) \( m/z = 1540.8 \text{ Co}_{2}\text{C}_{56}\text{H}_{36}\text{N}_{14}\text{Cl}_{2}\text{O}_{24}\text{S}_{2} \) (complex 6), (8) \( m/z = 1730.08 \text{ Co}_{3}\text{C}_{56}\text{H}_{32}\text{N}_{18}\text{Cl}_{2}\text{O}_{32}\text{S}_{2} \) (complex 7), (9) \( m/z = 1720.3 \text{ Ni}_{2}\text{C}_{56}\text{H}_{32}\text{N}_{18}\text{Cl}_{2}\text{O}_{32}\text{S}_{2} \) (complex 8), (10) \( m/z = 1720.8 \text{ Co}_{2}\text{C}_{56}\text{H}_{32}\text{N}_{18}\text{Cl}_{2}\text{O}_{32}\text{S}_{2} \) (complex 9). In addition to the peaks due to the molecular ion, the spectra exhibit peaks assignable to various fragments arising from the thermal cleavage of the complexes. The peak intensity gives an idea of the stability of the fragments.

IR spectra

The IR spectral of the Schiff base ligand show a \( \nu(C=N) \) peak at 1610 cm\(^{-1}\) and a medium intensity absorption band at 3180 cm\(^{-1}\) which is attributed to the \( \nu(N-H) \) stretching vibration. The high intensity band at 1613-1632 cm\(^{-1}\) which is attributed to the \( \nu(C=N) \) vibration. The bands present in the range ~3020-3060 cm\(^{-1}\) may be assigned due to \( \nu(C-H) \) stretching vibrations of aromatic moiety\(^{19}\). The various absorption band in the range ~1455-1570 cm\(^{-1}\) may be assigned due to \( \nu(C=C) \) aromatic stretching vibrations of the aromatic ring\(^{20}\). Another strong band at 1690-1735 cm\(^{-1}\) indicate the presence of \( \nu(C=O) \). The absorption of O-O and C-O stretching modes is in the range 900-1000 cm\(^{-1}\). Their strong appearance is an indication of strong mixing with the C-O modes comparison of the calculated peaks and the measured ones in this region shows that the theoretical spectrum is red shifted relative to the experimental data\(^{21}\). The IR spectra of nitrato complexes exhibits bands at 1290-1310 cm\(^{-1}\), 1050-1065 cm\(^{-1}\) and 1435-1450 cm\(^{-1}\) which can be assigned to NO\(_{2}\) symmetric stretching (\( \nu_{1} \)); N-O stretching (\( \nu_{2} \)); NO\(_{2}\) asymmetric stretching (\( \nu_{3} \)) and out of plane rocking, respectively. IR absorption band ~1355–1360 cm\(^{-1}\) assigned the uncoordinated nitro group. The far infrared spectra show bands in the region 420-450 cm\(^{-1}\) corresponding to \( \nu(M-N) \) vibration\(^{22,24}\). The presence of bands in all complexes in the region 420-450 cm\(^{-1}\) originate from (M-N) azomethine vibrational mode and identify coordination of azomethine nitrogen\(^{25}\). The bands present in the region 235-260 cm\(^{-1}\) in all the nitrato complexes are assignable to \( \nu(M-O) \) stretching vibration\(^{22,23}\).

\(^{1}\text{H NMR}\)

A survey of literature reveals that Schiff base have characterized by \(^{1}\text{H NMR}\) and \(^{13}\text{C NMR}\) spectra to ensure ligand structure and purity in \( d_{6}\)-dimethylsulfoxide (DMSO-\( d_{6}\)) solution using Me\(_{4}\)Si (TMS) as internal standard. The \(^{1}\text{H NMR}\) spectra of benzofuro-2-carboxy-[4′-chlorophenyl] thiosemicarbazide was recorded. The \(^{1}\text{H NMR}\) spectra of the ligand shows broad signal at 9.4-12.1 ppm due to the presence of -NH\(^{26}\) and 2.1-2.8 ppm due to the -CH\(_{3}\)- (cyclic)\(^{27}\). The multiplets in the region 6.54-8.76 ppm may be assigned to aromatic proton\(^{28,29}\). \(^{13}\text{C NMR}\) of the Schiff base ligand, the signal appeared in the region 111.6-158.4 are assigned to aromatic carbon. The signal at 172.8-165.6 ppm are due to C=O\(^{27}\).
### Table 1. FAB mass spectral data of the divalent bimolecular Cu(II), Ni(I) and Co(II) metal complexes

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Mol. wt.</th>
<th>Molecular ion peak [M]+</th>
<th>Important peak due to complex fragmentation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}<em>{16}\text{H}</em>{12}\text{N}<em>{5}\text{ClO}</em>{2}\text{S} )</td>
<td>445.8</td>
<td>444.8</td>
<td>92.1, 117.1, 194.2, 219.02, 310.3</td>
</tr>
<tr>
<td>([\text{Cu}<em>2\text{C}</em>{56}\text{H}<em>{40}\text{N}</em>{10}\text{Cl}<em>2\text{O}</em>{16}\text{S}_2])</td>
<td>1371.1</td>
<td>1370.1</td>
<td>92.1, 117.1, 119.2, 138.1, 194.2, 219.02, 276.2, 310.3, 927.34, 1300.2, 1335.6</td>
</tr>
<tr>
<td>([\text{Ni}<em>2\text{C}</em>{56}\text{H}<em>{40}\text{N}</em>{10}\text{Cl}<em>2\text{O}</em>{16}\text{S}_2])</td>
<td>1361.4</td>
<td>1360.4</td>
<td>92.1, 117.1, 119.2, 138.1, 194.2, 219.02, 276.2, 310.3, 922.4, 1290.5, 1325.9</td>
</tr>
<tr>
<td>([\text{Co}<em>2\text{C}</em>{56}\text{H}<em>{40}\text{N}</em>{10}\text{Cl}<em>2\text{O}</em>{16}\text{S}_2])</td>
<td>1361.8</td>
<td>1360.8</td>
<td>92.1, 117.1, 119.2, 138.1, 194.2, 219.02, 276.2, 310.3, 927.2, 1290.9, 1326.4</td>
</tr>
<tr>
<td>([\text{Cu}<em>2\text{C}</em>{56}\text{H}<em>{40}\text{N}</em>{14}\text{Cl}<em>2\text{O}</em>{24}\text{S}_2])</td>
<td>1551.09</td>
<td>1550.09</td>
<td>92.1, 117.1, 119.2, 183.1, 194.2, 219.0, 310.3, 366.0, 1111.3, 1481.0, 1515.6</td>
</tr>
<tr>
<td>([\text{Ni}<em>2\text{C}</em>{56}\text{H}<em>{40}\text{N}</em>{14}\text{Cl}<em>2\text{O}</em>{24}\text{S}_2])</td>
<td>1541.3</td>
<td>1540.3</td>
<td>92.1, 117.1, 119.2, 183.1, 194.2, 219.0, 310.3, 366.0, 1102.4, 1471.5, 1505.9</td>
</tr>
<tr>
<td>([\text{Co}<em>2\text{C}</em>{56}\text{H}<em>{40}\text{N}</em>{14}\text{Cl}<em>2\text{O}</em>{24}\text{S}_2])</td>
<td>1541.8</td>
<td>1540.8</td>
<td>92.1, 117.1, 119.2, 183.1, 194.2, 219.0, 310.3, 366.0, 1102.7, 1471.9, 1506.4</td>
</tr>
<tr>
<td>([\text{Cu}<em>2\text{C}</em>{56}\text{H}<em>{40}\text{N}</em>{18}\text{Cl}<em>2\text{O}</em>{28}\text{S}_2])</td>
<td>1731.08</td>
<td>1730.08</td>
<td>92.1, 117.1, 119.2, 194.2, 219.0, 238.1, 310.3, 456.2, 1287.3, 1661.1, 1695.6</td>
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<tr>
<td>([\text{Ni}<em>2\text{C}</em>{56}\text{H}<em>{40}\text{N}</em>{18}\text{Cl}<em>2\text{O}</em>{28}\text{S}_2])</td>
<td>1721.3</td>
<td>1720.3</td>
<td>92.1, 117.1, 119.2, 194.2, 219.0, 238.1, 310.3, 456.2, 1282.7, 1651.4, 1685.9</td>
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<tr>
<td>([\text{Co}<em>2\text{C}</em>{56}\text{H}<em>{40}\text{N}</em>{18}\text{Cl}<em>2\text{O}</em>{28}\text{S}_2])</td>
<td>1721.8</td>
<td>1720.8</td>
<td>92.1, 117.1, 119.2, 194.2, 219.0, 238.1, 310.3, 456.2, 1282.7, 1651.9, 1685.4</td>
</tr>
</tbody>
</table>

### Table 2. Analytical data of the divalent bimolecular Cu(II), Ni(I) and Co(II) metal complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Mol. mass</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>M (%)</th>
<th>Colour</th>
<th>Yield %</th>
<th>Conductance (\Omega^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}<em>{16}\text{H}</em>{12}\text{N}<em>{5}\text{ClO}</em>{2}\text{S} )</td>
<td>345.80</td>
<td>55.57</td>
<td>3.50</td>
<td>12.15</td>
<td>12.17</td>
<td>Orange</td>
<td>71</td>
<td>72 (\Omega^{-1})</td>
</tr>
<tr>
<td>([\text{Cu}<em>2\text{C}</em>{56}\text{H}<em>{40}\text{N}</em>{10}\text{Cl}<em>2\text{O}</em>{16}\text{S}_2])</td>
<td>1371.10</td>
<td>49.06</td>
<td>2.94</td>
<td>10.22</td>
<td>9.27</td>
<td>Orange</td>
<td>71</td>
<td>72 (\Omega^{-1})</td>
</tr>
<tr>
<td>([\text{Ni}<em>2\text{C}</em>{56}\text{H}<em>{40}\text{N}</em>{10}\text{Cl}<em>2\text{O}</em>{16}\text{S}_2])</td>
<td>1361.40</td>
<td>49.41</td>
<td>2.96</td>
<td>10.29</td>
<td>8.62</td>
<td>Orange</td>
<td>78</td>
<td>90 (\Omega^{-1})</td>
</tr>
<tr>
<td>([\text{Co}<em>2\text{C}</em>{56}\text{H}<em>{40}\text{N}</em>{10}\text{Cl}<em>2\text{O}</em>{16}\text{S}_2])</td>
<td>1361.88</td>
<td>49.39</td>
<td>2.96</td>
<td>10.28</td>
<td>8.65</td>
<td>Light Yellow</td>
<td>75</td>
<td>15 (\Omega^{-1})</td>
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<tr>
<td>([\text{Cu}<em>2\text{C}</em>{56}\text{H}<em>{40}\text{N}</em>{14}\text{Cl}<em>2\text{O}</em>{24}\text{S}_2])</td>
<td>1551.09</td>
<td>43.36</td>
<td>2.34</td>
<td>12.64</td>
<td>8.19</td>
<td>Brown</td>
<td>73</td>
<td>74 (\Omega^{-1})</td>
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<tr>
<td>([\text{Ni}<em>2\text{C}</em>{56}\text{H}<em>{40}\text{N}</em>{14}\text{Cl}<em>2\text{O}</em>{24}\text{S}_2])</td>
<td>1541.39</td>
<td>43.64</td>
<td>2.35</td>
<td>12.72</td>
<td>7.62</td>
<td>Gray</td>
<td>72</td>
<td>11 (\Omega^{-1})</td>
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<td>([\text{Co}<em>2\text{C}</em>{56}\text{H}<em>{40}\text{N}</em>{14}\text{Cl}<em>2\text{O}</em>{24}\text{S}_2])</td>
<td>1541.87</td>
<td>43.62</td>
<td>2.35</td>
<td>12.72</td>
<td>7.64</td>
<td>Light gray</td>
<td>77</td>
<td>16 (\Omega^{-1})</td>
</tr>
<tr>
<td>([\text{Cu}<em>2\text{C}</em>{56}\text{H}<em>{40}\text{N}</em>{18}\text{Cl}<em>2\text{O}</em>{28}\text{S}_2])</td>
<td>1731.08</td>
<td>38.85</td>
<td>1.86</td>
<td>14.56</td>
<td>7.34</td>
<td>Light Yellow</td>
<td>75</td>
<td>79 (\Omega^{-1})</td>
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<tr>
<td>([\text{Ni}<em>2\text{C}</em>{56}\text{H}<em>{40}\text{N}</em>{18}\text{Cl}<em>2\text{O}</em>{28}\text{S}_2])</td>
<td>1721.38</td>
<td>39.07</td>
<td>1.87</td>
<td>14.65</td>
<td>6.82</td>
<td>Reddish</td>
<td>74</td>
<td>12 (\Omega^{-1})</td>
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<td>([\text{Co}<em>2\text{C}</em>{56}\text{H}<em>{40}\text{N}</em>{18}\text{Cl}<em>2\text{O}</em>{28}\text{S}_2])</td>
<td>1721.86</td>
<td>39.06</td>
<td>1.87</td>
<td>14.64</td>
<td>6.85</td>
<td>Light Yellow</td>
<td>76</td>
<td>18 (\Omega^{-1})</td>
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</table>
Magnetic, electronic and electron spin resonance spectral studies

In order to obtain information concerning the stereochemistry of metal ion, the ESR spectrum of this complex is of axial shape with $g_\parallel > g_\perp$ characteristic of complexes with $^3\text{B}_1(\Delta x^2 - \Delta y^2)$ ground state. The average $g$ values were calculated according to the equation $g_{av} = 1/3[g_\parallel + 2g_\perp]$. Complex exhibits $g_\parallel < 2.3$, suggesting covalent characters of the copper–ligand bonding in this complex. The parameter $G=g_\parallel 2.0582, 2.0561$ and 2.0323 respectively, shows the possibility of exchange interaction in the Cu(II) complex. The $G$ values for the complex (G> 4) indicate that there is no direct copper–copper interaction in the solid state. The $g_\parallel A_{20}$ is taken as an indication for the stereochemistry of the copper(II) complexes. Addison has suggested that this ratio may be an empirical indication of the octahedral distortion geometry. The values higher than 148 cm$^2$ are observed for octahedral distorted complexes. The value of $g_\parallel A_{20}$ quotient for the complex under investigation lies higher 148 cm, indicating octahedral geometry around copper in this complex. The magnetic moment value for these complexes was found to be 1.56 B.M. per Cu ion.

The absorption spectral bands of light green Ni(II) complexes exhibit three band in the ranges 945-935, 712-642 and 398-379 nm, respectively shows three spin allowed transitions: $3A_{2g}(F)\rightarrow T_{1g}(F), 3A_{2g}(F)\rightarrow T_{2g}(F), 3A_{2g}(F)\rightarrow 3T_{2g}(P)$ consistent with a typical Ni(II) in an octahedral environment. The magnetic moment values for these complexes were found in the range 3.15-3.17 B.M expected for octahedral nickel complexes.

The electronic spectra of the cobalt(II) complexes gave three bands at 1012-971, 714-645 and 425-388 nm, which could be assigned to the transitions $4T_{1g}(F)\rightarrow 4T_{2g}(F) (v_1), 4T_{1g}(F)\rightarrow 4A_{2g}(F) (v_2)$ and $4T_{1g}(F)\rightarrow 4T_{2g}(P) (v_3)$, respectively, suggesting an octahedral geometry around Co(II) ion. The complexes 5 and 6 show magnetic moment values in the range 2.8-3.1 B.M., which is smaller than the calculated value for two Co(II) ions in octahedral geometries and this may be due to anti-ferromagnetism between the two ion-centers. All complexes give satisfactory elemental analysis results as shown in Table 2.

Synthesis of benzofuro-2-carboxy-[4’-chlorophenyl] thiosemicarbazide

benzofuran-2-carboxylic acid (4.58 g, 0.026 mol) was dissolved in ethanol and this solution was added p-chlorophenyl isothiocyanate (4.41 g, 0.026 mol) in a 1:1 molar ratio containing few drop of concentrated HCl. The solution was refluxed for 3 h. The reaction mixture was cooled to room temperature and the solvent removed under reduced pressure by rotavapour until a solid product was formed and it was washed with cold ethanol and dried under vacuum. Melting point 151 °C and Yield 81%. $^1$H NMR (300 MHz, DMSO-d$_6$) $\delta$= 6.45-7.65 (m, 5H, Ar–H benzofuran), 8.13 (s, Ar-H, Carbonyl Phenyl), 10.15 (s, 1x1H, NH of carbazide). $^{13}$C NMR (300 MHz, DMSO-d$_6$) $\delta$= 166.7 (C=O), 158.4, 150.0, 149.1, 130.5, 129.4, 124.7, 123.7, 121.0, 114.6, 111.6, (Ar–C), UV-Vis (Nujol mul (nm)): $\lambda$ = 370, 420, 480. UV/vis (1x10$^{-4}$ mol, DMSO): $\lambda$ = 360, 390, 445. IR (KBr): $\nu$(N=H) 3245, $\nu$(C=O) 1720, $\nu$(N–N) 1115, $\nu$(C–C) 760, $\nu$(C=C, aromatic) 1540, $\nu$(C–H, aromatic) 3040, $\nu$(NH, hydrazide) 3155 cm$^{-1}$.

Synthesis of the metal complex $[\text{Cu}_2(\text{C}_{56}\text{H}_{40}\text{N}_{10}\text{Cl}_2\text{O}_{105})_2]$ (1)

A solution of divalent metal salt CuCl$_2$2H$_2$O (0.826 g, 4.845 mmol) in methanol (8 mL) was added to a hot solution (75 °C) of benzofuro-2-carboxy-[4’-chlorophenyl] thiosemicarbazide ligand (2.281 g, 5.116 mmol) and 2-nitrophenol (1.410 g, 10.137 mmol) in ethanol (25 mL) and the reaction mixture was refluxed for 7 h. The solution was concentrated under vacuum. The precipitate was filtered off, washed with methanol and dried under vacuum over anhydrous CaCl$_2$ (1.06 g, 71% yield).
Conductance $\Lambda m$: 72 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. UV-Vis (Nujol mul (nm)): $\lambda$=355, 375, 420, 525, 720 and 1155. IR (KBr): $\nu$(N$^2$H) 3272, $\nu$(C=O) 1720, $\nu$(N=N) 1122, $\nu$(C=C, aromatic) 1540, $\nu$(C-H, aromatic) 3040, $\nu$(NH, hydrazide) 3144, $\nu$(M-N) 425.

**Synthesis of the metal complex** $[\text{Ni}_2(\text{C}_5\text{H}_4\text{N}_2\text{Cl}_2\text{O}_6\text{S}_2)]$ (2)

A solution of divalent metal salt NiCl$_2$6H$_2$O (0.988 g, 4.156 mmol) in methanol (12 mL) was added to a hot solution (75 °C) of benzofuro-2-carboxy-[4'-chlorophenyl] thiosemicarbazide ligand (2.281 g, 5.116 mmol) and 2-nitrophenol (1.410g, 10.137 mmol) in ethanol (28 mL), and the reaction mixture was refluxed for 8 h. The solution was concentrated under vacuum. The precipitate was filtered off, washed with methanol and dried under vacuum over anhydrous CaCl$_2$ (1.16 g, 78% yield).

Conductance $\Lambda m$: 09 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. UV-Vis(Nujol mul (nm)): $\lambda$=255, 275, 320, 525, 720 and 1155. IR(KBr): $\nu$(H$_2$O) 3429, $\nu$(N$^2$H) 3272, $\nu$(C=O) 1720, $\nu$(C=C) 770, $\nu$(C=C, aromatic) 1544, $\nu$(C=C, aromatic) 1543, $\nu$(NH, hydrazide) 3150, $\nu$(N=N) 1120, $\nu$(M=N) 422, $\nu$(M-O) 485 cm$^{-1}$.

**Synthesis of the metal complex** $[\text{Co}_2(\text{C}_5\text{H}_4\text{N}_2\text{Cl}_2\text{O}_6\text{S}_2)]$ (3)

A solution of divalent metal salt CoCl$_2$6H$_2$O (0.892 g, 3.749 mmol) in methanol (10 mL) was added to a hot solution (75 °C) of benzofuro-2-carboxy-[4'-chlorophenyl] thiosemicarbazide ligand (2.281 g, 5.116 mmol) and 2-nitrophenol (1.410 g, 10.137 mmol) in ethanol (28 mL), and the reaction mixture was refluxed for 7.5 h. The solution was concentrated under vacuum. The precipitate was filtered off, washed with methanol and dried under vacuum over anhydrous CaCl$_2$ (1.30 g, 75% yield).

Conductance $\Lambda m$: 15 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. UV-Vis(Nujol mul (nm)): $\lambda$=260, 272, 325, 520, 724 and 1150. IR(KBr): $\nu$(H$_2$O) 3340, $\nu$(N$^2$H) 3260, $\nu$(C=O) 1780, $\nu$(N=N) 1123, $\nu$(C=C) 766, $\nu$(C=C, aromatic) 1543, $\nu$(C=C, aromatic) 3033, $\nu$(NH, hydrazide) 3150, $\nu$(M=N) 420, $\nu$(M-O) 500 cm$^{-1}$.

**Synthesis of the metal complex** $[\text{Cu}_2(\text{C}_5\text{H}_6\text{N}_4\text{Cl}_2\text{O}_5\text{S}_2)]$ (4)

A solution of divalent metal salt CuCl$_2$2H$_2$O (0.826 g, 4.845 mmol) in methanol (8 mL) was added to a hot solution (75 °C) of benzofuro-2-carboxy-[4'-chlorophenyl] thiosemicarbazide ligand (2.281 g, 5.116 mmol) and 2, 3-dinitrophenol (1.891 g, 10.270 mmol) in ethanol (25 mL), the reaction mixture was refluxed for 7 h. The precipitate was filtered off, washed with methanol and dried under vacuum over anhydrous CaCl$_2$ (1.37 g, 73% yield).

Conductance $\Lambda m$: 74 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. UV-Vis (Nujol mul (nm)): $\lambda$=260, 280, 320, 450, 700, 1150. IR (KBr): $\nu$(H$_2$O) 3380, $\nu$(N$^2$H) 3260, $\nu$(C=O) 1735, $\nu$(N=N) 1146, $\nu$(M=N) 440, $\nu$(C=C) 755, $\nu$(C=C, aromatic) 1540, $\nu$(C=C, aromatic) 3040, $\nu$(NH, hydrazide) 3145, $\nu$(M-N) 425.

**Synthesis of the metal complex** $[\text{Ni}_2(\text{C}_5\text{H}_6\text{N}_4\text{Cl}_2\text{O}_5\text{S}_2)]$ (5)

A solution of divalent metal salt NiCl$_2$6H$_2$O (0.988 g, 4.156 mmol) in methanol (12 mL) was added to a hot solution (75 °C) of benzofuro-2-carboxy-[4'-chlorophenyl] thiosemicarbazide ligand (2.281 g, 5.116 mmol) and 2, 3-dinitrophenol (1.891 g, 10.270 mmol) in ethanol (30 mL) and the reaction mixture was refluxed for 8 h. The solution was concentrated under vacuum. The precipitate was filtered off, washed with methanol and dried under vacuum over anhydrous CaCl$_2$ (1.06 g, 72% yield).

Conductance $\Lambda m$: 11 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. UV-Vis (Nujol mul (nm)): $\lambda$=255, 275, 320, 525, 720 and 1155. IR (KBr): $\nu$(H$_2$O) 3429, $\nu$(N$^2$H) 3272, $\nu$(C=O) 1732, $\nu$(N=N) 1122, $\nu$(C=C) 754, $\nu$(C=C, aromatic) 1544, $\nu$(C=C, aromatic) 3044, $\nu$(NH, hydrazide) 3144, $\nu$(M-N) 425, $\nu$(M-O) 490 cm$^{-1}$.
Synthesis of the metal complex \([\text{Co}_2(\text{C}_{56}\text{H}_{36}\text{N}_{14}\text{Cl}_2\text{O}_{24}\text{S}_2)]\) (6)

A solution of divalent metal salt CoCl\(_2\)6H\(_2\)O (0.892 g, 3.749 mmol) in methanol (10 mL) was added to a hot solution (75 °C) of benzofuro- 2-carboxy- [4'-chlorophenyl] thiosemicarbazide ligand (2.281 g, 5.116 mmol) and 2, 3-dinitrophenol (1.891 g, 10.270 mmol) in ethanol (28 mL) and the reaction mixture was refluxed for 7.5 h. The precipitate was filtered off, washed with methanol and dried under vacuum over anhydrous CaCl\(_2\) (1.54 g, 77% yield).

Conductance \(\Lambda_m\): 16 Ω\(^{-1}\) cm\(^2\) mol\(^{-1}\). UV-Vis (Nujol mul (nm)): \(\lambda = 255, 280, 330, 451, 680\) and 1140. IR (KBr): \(v(\text{H}_2\text{O}) 3311, v(\text{N}^2\text{H}) 3260, v(\text{C}=\text{O}) 1722, v(\text{N}-\text{N}) 1123, v(\text{C}--\text{C}) 750, v(\text{C}--\text{C}, \text{aromatic}) 1539, v(\text{C}-\text{H}, \text{aromatic}) 3043, v(\text{NH}, \text{hydrazide}) 3140, v(M-N) 470, v(M-O) 510 cm\(^{-1}\).

Synthesis of the metal complex \([\text{Cu}_2(\text{C}_{56}\text{H}_{32}\text{N}_{18}\text{Cl}_2\text{O}_{32}\text{S}_2)]\) (7)

A solution of divalent metal salt CuCl\(_2\)2H\(_2\)O (0.826 g, 4.845 mmol) in methanol (8 mL) was added to a hot solution (75 °C) of benzofuro- 2-carboxy- [4'-chlorophenyl] thiosemicarbazide ligand (2.281 g, 5.116 mmol) and 2, 3, 4-trinitrophenol (2.342 g, 10.211 mmol) in ethanol (25 mL), the reaction mixture was refluxed for 7 h. The precipitate was filtered off, washed with methanol and dried under vacuum over anhydrous CaCl\(_2\) (1.28 g, 75% yield).

Conductance \(\Lambda_m\): 79 Ω\(^{-1}\) cm\(^2\) mol\(^{-1}\). UV-Vis (Nujol mul (nm)): \(\lambda = 260, 331, 467, 652\) and 1061. IR (KBr): \(v(\text{H}_2\text{O}) 3406, v(\text{N}^2\text{H}) 3286, v(\text{C}=\text{O}) 1735, v(\text{N}-\text{N}) 1145, v(\text{C}--\text{C}) 745, v(\text{C}=\text{C}, \text{aromatic}) 1533, v(\text{C}-\text{H}, \text{aromatic}) 3044, v(\text{NH}, \text{hydrazide}) 3145, v(M-N) 455.

Synthesis of the metal complex \([\text{Ni}_2(\text{C}_{56}\text{H}_{32}\text{N}_{18}\text{Cl}_2\text{O}_{32}\text{S}_2])\) (8)

A solution of divalent metal salt NiCl\(_2\)6H\(_2\)O (0.988 g, 4.485 mmol) in methanol (12 mL) was added to a hot solution (75 °C) of benzofuro- 2-carboxy- [4'-chlorophenyl] thiosemicarbazide ligand (2.281 g, 5.116 mmol) and 2, 3, 4-trinitrophenol (2.342 g, 10.211 mmol) in ethanol (30 mL) and the reaction mixture was refluxed for 8 h. The solution was concentrated under vacuum. The precipitate was filtered off, washed with methanol and dried under vacuum over anhydrous CaCl\(_2\) (1.06 g, 74% yield).

Conductance \(\Lambda_m\): 12 Ω\(^{-1}\) cm\(^2\) mol\(^{-1}\). UV-Vis (Nujol mul (nm)): \(\lambda = 255, 275, 320, 525, 720\) and 1155. IR (KBr): \(v(\text{H}_2\text{O}) 3429 (\text{br}), v(\text{N}^2\text{H}) 3272, v(\text{C}=\text{O}) 1690, v(\text{N}-\text{N}) 1132, v(\text{C}--\text{C}) 760, v(\text{C}=\text{C}, \text{aromatic}) 1533, v(\text{C}-\text{H}, \text{aromatic}) 3053, v(\text{NH}, \text{hydrazide}) 3133, v(M-N) 425, v(M-O) 490 cm\(^{-1}\).

Synthesis of the metal complex \([\text{Co}_2(\text{C}_{56}\text{H}_{32}\text{N}_{18}\text{Cl}_2\text{O}_{32}\text{S}_2})\) (9)

A solution of divalent metal salt CoCl\(_2\)6H\(_2\)O (0.892 g, 3.749 mmol) in methanol (10 mL) was added to a hot solution (75 °C) of benzofuro- 2-carboxy- [4'-chlorophenyl] thiosemicarbazide ligand (2.281 g, 5.116 mmol) and 2, 3, 4-trinitrophenol (2.342 g, 10.211 mmol) in ethanol (28 mL), the reaction mixture was refluxed for 7.5 h. The precipitate was filtered off, washed with methanol and dried under vacuum over anhydrous CaCl\(_2\) (1.35 g, 76% yield).

Conductance \(\Lambda_m\): 18 Ω\(^{-1}\) cm\(^2\) mol\(^{-1}\). UV-Vis (Nujol mul (nm)): \(\lambda = 265, 280, 340, 489, 636, 1051. IR (KBr): v(\text{H}_2\text{O}) 3419, v(\text{N}^2\text{H}) 3277, v(\text{C}=\text{O}) 1710, v(\text{N}-\text{N}) 1120, v(\text{C}=\text{C}) 750, v(\text{C}=\text{C}, \text{aromatic}) 1539, v(\text{C}-\text{H}, \text{aromatic}) 3044, v(\text{NH}, \text{hydrazide}) 3144, v(M-N) 460, v(M-O) 525 cm\(^{-1}\).
Conclusion

The analytical data showed the presence of two metal ion molecule and suggested a binuclear structure for the complexes $[M_2(HL)]$. The spectroscopical studies of the metal ion complexes are in the favor of a six coordinate octahedral geometry of the complexes.

References