

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- dinitrophenol, 2,3,4- trinitrophenol) with transition metal ion *e.g.* Cu(II), Ni(II) and Co(II) were prepared. All the complex have structure formula [Cu₂(C₅₆H₄₀N₁₀Cl₂O₁₆S₂)], [Ni₂(C₅₆H₄₀N₁₀Cl₂O₁₆S₂)], [Co₂(C₅₆H₄₀N₁₀Cl₂O₁₆S₂)], [Cu₂(C₅₆H₃₆N₁₄Cl₂O₂₄S₂)], [Ni₂(C₅₆H₃₆N₁₄Cl₂O₂₄S₂)], [Co₂(C₅₆H₃₆N₁₄Cl₂O₂₄S₂)], [Cu₂(C₅₆H₃₂N₁₈Cl₂O₃₂S₂)], [Ni₂(C₅₆H₃₂N₁₈Cl₂O₃₂S₂)] and [Co₂(C₅₆H₃₂N₁₈Cl₂O₃₂S₂)] characterized by the several analytical techniques including elemental analysis (C.H.N.), molar conductance measurements, magnetic measurements, electronic, FAB mass, IR, ¹H NMR and ¹³C 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 hetero cyclic 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 Schiff¹, 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 salicyladimine² 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-workers³ reported the preparation of

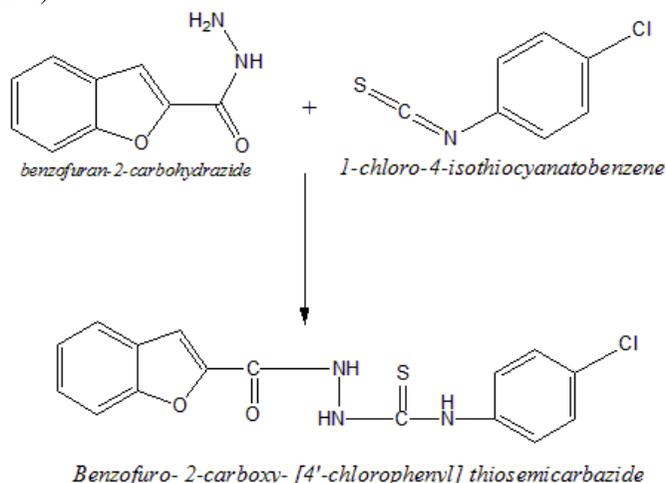
azomethine ligand by the condensation of benzoylacetone and 1,2-diaminoethane and its complexes with transition metals. Lindoy and co-workers⁴ reported a number of azomethine complexes of various metals with methyl thioquinoline. A number of publications appeared about the lanthanide ion complexes with azomethines derived from bis-salicylaldehyde and *o*-phenylenediamine⁵ and *p*-dimethylaminobenzaldehyde and benzidine⁶. A number of M(II) complexes with azomethine have been reported by various workers⁷⁻¹³. Metal complexes of azomethine ligand derived from pivaloylacetone and 1,2-diaminoethane have also been reported¹⁴. 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=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-workers¹⁵. Azomethine formed in the condensation reactions between unsymmetrical β -diketones and 1,2-diamino ethane and their transition complexes have also been reported in the literature¹⁶. The azomethine derived from bis-vanillin and *o*-phenylenediamine and their lanthanide complexes have also been reported in the literature¹⁷. Tripathy and co-workers prepared azomethines *viz.* bis-salicylaldehyde ethylene diamine and bis-*o*-hydroxyacetophenone ethylenediamine, and their transition metal complexes¹⁸. The aim of the present study is to prepare and characterized divalent bimolecular metal ion complexes derived from benzofuran-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

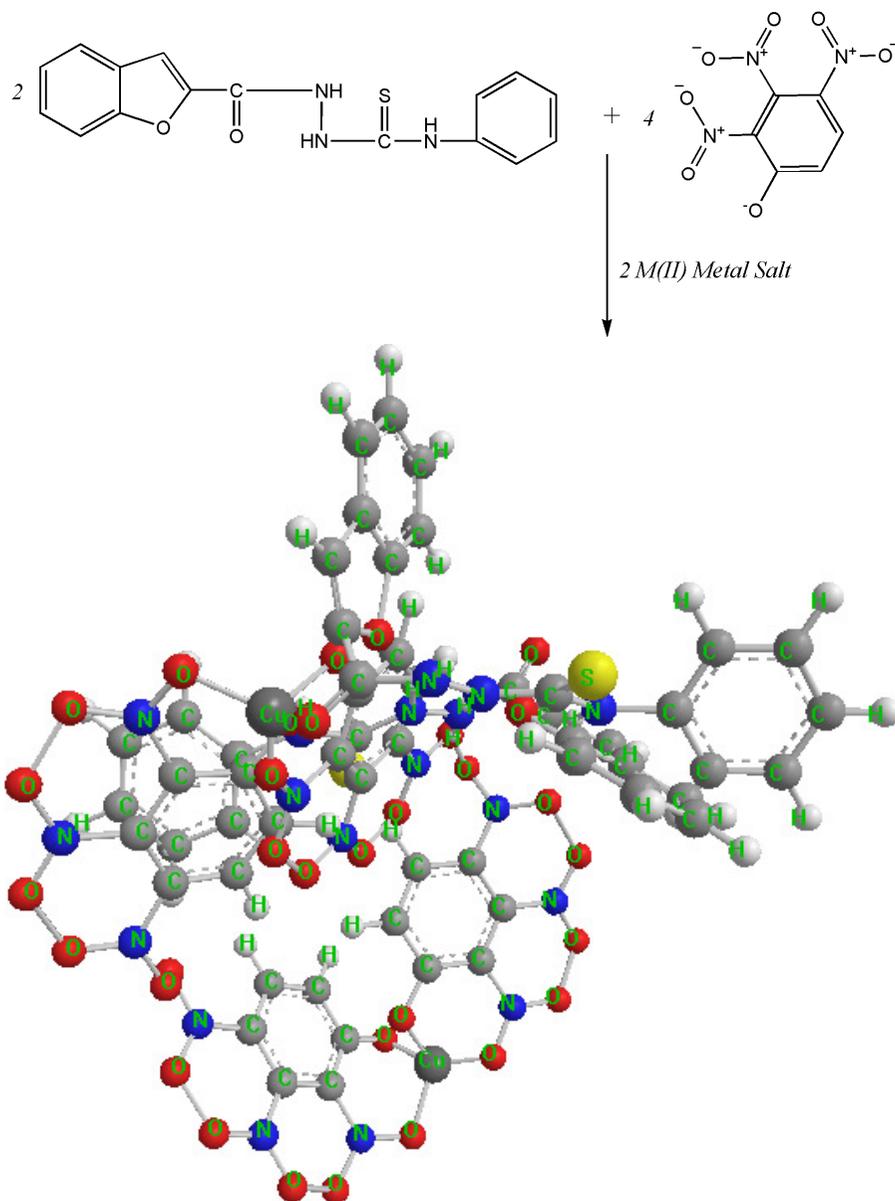
Benzofuran-2-carbohydrazide (4.58 g, 0.026 mol) was dissolved in ethanol and this solution was added 1-chloro-4-isothiocyanatobenzene (4.41 g, 0.026 mol) in a 1:1 molar ratio containing few drop of concentrated HCl. The solution was refluxed for 3 h. The cream crystalline product which formed was filtered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



Scheme 1. Synthesis of ligand

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 CaCl₂ (68-75% yield) (Scheme 2).



Scheme 2. Synthesis of divalent bimolecular metal complex

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) $m/z = 444.80$ $C_{16}H_{12}N_3ClO_2S$, (2) $m/z = 1370.10$ $[Cu_2(C_{56}H_{40}N_{10}Cl_2O_{16}S_2)]$ (complex 1), (3) $m/z = 1360.4$ $[Ni_2(C_{56}H_{40}N_{10}Cl_2O_{16}S_2)]$ (complex 2), (4) $m/z = 1360.88$ $[Co_2(C_{56}H_{40}N_{10}Cl_2O_{16}S_2)]$ (complex 3), (5) $m/z = 1550.09$ $[Cu_2(C_{56}H_{36}N_{14}Cl_2O_{24}S_2)]$ (complex 4), (6) $m/z = 1540.3$ $[Ni_2(C_{56}H_{36}N_{14}Cl_2O_{24}S_2)]$ (complex 5), (7) $m/z = 1540.8$ $[Co_2(C_{56}H_{36}N_{14}Cl_2O_{24}S_2)]$ (complex 6), (8) $m/z = 1730.08$ $[Cu_2(C_{56}H_{32}N_{18}Cl_2O_{32}S_2)]$ (complex 7), (9) $m/z = 1720.3$ $[Ni_2(C_{56}H_{32}N_{18}Cl_2O_{32}S_2)]$ (complex 8), (10) $m/z = 1720.8$ $[Co_2(C_{56}H_{32}N_{18}Cl_2O_{32}S_2)]$ (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 $1613\text{-}1632\text{ cm}^{-1}$ which is attributed to the $\nu(C=N)$ vibration. The bands present in the range $\sim 3020\text{-}3060\text{ cm}^{-1}$ may be assigned due to $\nu(C-H)$ stretching vibrations of aromatic moiety¹⁹. The various absorption band in the range $\sim 1455\text{-}1570\text{ cm}^{-1}$ may be assigned due to $\nu(C=C)$ aromatic stretching vibrations of the aromatic ring²⁰. Another strong band at $1690\text{-}1735\text{ cm}^{-1}$ indicate the presence of $\nu(C=O)$. The absorption of O-O and C-O stretching modes is in the range $900\text{-}1000\text{ cm}^{-1}$. 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 data²¹. The IR spectra of nitrate complexes exhibits bands at $1290\text{-}1310\text{ cm}^{-1}$, $1050\text{-}1065\text{ cm}^{-1}$ and $1435\text{-}1450\text{ cm}^{-1}$ which can be assigned to NO_2 symmetric stretching (ν_1); N-O stretching (ν_2); NO_2 asymmetric stretching (ν_3) and out of plane rocking, respectively. IR absorption band $\sim 1355\text{-}1360\text{ cm}^{-1}$ assigned the uncoordinated nitro group. The far infrared spectra show bands in the region $420\text{-}450\text{ cm}^{-1}$ corresponding to $\nu(M-N)$ vibration²²⁻²⁴. The presence of bands in all complexes in the region $420\text{-}450\text{ cm}^{-1}$ originate from (M-N) azomethine vibrational mode and identify coordination of azomethine nitrogen²⁵. The bands present in the region $235\text{-}260\text{ cm}^{-1}$ in all the nitrate complexes are assignable to $\nu(M-O)$ stretching vibration^{22,23}.

¹H NMR

A survey of literature reveals that Schiff base have characterized by ¹H NMR and ¹³C NMR spectra to ensure ligand structure and purity in d_6 -dimethylsulfoxide (DMSO- d_6) solution using Me_4Si (TMS) as internal standard. The ¹H NMR spectra of benzofuro-2-carboxy-[4'-chlorophenyl] thiosemicarbazide was recorded. The ¹H NMR spectra of the ligand shows broad signal at $9.4\text{-}12.1\text{ ppm}$ due to the presence of $-NH$ ²⁶ and $2.1\text{-}2.8\text{ ppm}$ due to the $-CH_2-$ (cyclic)²⁷. The multiplets in the region $6.54\text{-}8.76\text{ ppm}$ may be assigned to aromatic proton^{28,29}. ¹³C NMR of the Schiff base ligand, the signal appeared in the region $111.6\text{-}158.4$ are assigned to aromatic carbon. The signal at $172.8\text{-}165.6\text{ ppm}$ 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

Complexes	Mol. wt.	Molecular ion peak [M] ⁺	Important peak due to complex fragmentation
C ₁₆ H ₁₂ N ₃ ClO ₂ S	445.8	444.8	92.1, 117.1, 194.2, 219.02, 310.3
[Cu ₂ (C ₅₆ H ₄₀ N ₁₀ Cl ₂ O ₁₆ S ₂)]	1371.1	1370.1	92.1, 117.1, 119.2, 138.1, 194.2, 219.02, 276.2, 310.3, 927.34, 1300.2, 1335.6
[Ni ₂ (C ₅₆ H ₄₀ N ₁₀ Cl ₂ O ₁₆ S ₂)]	1361.4	1360.4	92.1, 117.1, 119.2, 138.1, 194.2, 219.02, 276.2, 310.3, 922.4, 1290.5, 1325.9
[Co ₂ (C ₅₆ H ₄₀ N ₁₀ Cl ₂ O ₁₆ S ₂)]	1361.88	1360.88	92.1, 117.1, 119.2, 138.1, 194.2, 219.02, 276.2, 310.3, 922.7, 1290.9, 1326.4
[Cu ₂ (C ₅₆ H ₃₆ N ₁₄ Cl ₂ O ₂₄ S ₂)]	1551.09	1550.09	92.1, 117.1, 119.2, 183.1, 194.2, 219.0, 310.3, 366.0, 1111.3, 1481.0, 1515.6
[Ni ₂ (C ₅₆ H ₃₆ N ₁₄ Cl ₂ O ₂₄ S ₂)]	1541.3	1540.3	92.1, 117.1, 119.2, 183.1, 194.2, 219.0, 310.3, 366.0, 1102.4, 1471.5, 1505.9
[Co ₂ (C ₅₆ H ₃₆ N ₁₄ Cl ₂ O ₂₄ S ₂)]	1541.8	1540.8	92.1, 117.1, 119.2, 183.1, 194.2, 219.0, 310.3, 366.0, 1102.7, 1471.9, 1506.4
[Cu ₂ (C ₅₆ H ₃₂ N ₁₈ Cl ₂ O ₃₂ S ₂)]	1731.08	1730.08	92.1, 117.1, 119.2, 194.2, 219.0, 238.1, 310.3, 456.2, 1287.3, 1661.1, 1695.6
[Ni ₂ (C ₅₆ H ₃₂ N ₁₈ Cl ₂ O ₃₂ S ₂)]	1721.3	1720.3	92.1, 117.1, 119.2, 194.2, 219.0, 238.1, 310.3, 456.2, 1282.4, 1651.4, 1685.9
[Co ₂ (C ₅₆ H ₃₂ N ₁₈ Cl ₂ O ₃₂ S ₂)]	1721.8	1720.8	92.1, 117.1, 119.2, 194.2, 219.0, 238.1, 310.3, 456.2, 1282.7, 1651.9, 1685.4

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

Complex	Mol. mass	C	H	N	M	Colour	Yield %	Conductance Λ_M
C ₁₆ H ₁₂ N ₃ ClO ₂ S	345.80	55.57(55.55)	3.50(3.48)	12.15(12.17)				
[Cu ₂ (C ₅₆ H ₄₀ N ₁₀ Cl ₂ O ₁₆ S ₂)]	1371.10	49.06 (49.02)	2.94 (2.88)	10.22 (10.02)	9.27(2.32)	Orange	71	72 Ω^{-1}
[Ni ₂ (C ₅₆ H ₄₀ N ₁₀ Cl ₂ O ₁₆ S ₂)]	1361.40	49.41 (49.35)	2.96 (2.85)	10.29 (10.25)	8.62 (8.60)	Orange	78	09 Ω^{-1}
[Co ₂ (C ₅₆ H ₄₀ N ₁₀ Cl ₂ O ₁₆ S ₂)]	1361.88	49.39 (49.35)	2.96 (2.99)	10.28(12.35)	8.65 (8.61)	Light Yellow	75	15 Ω^{-1}
[Cu ₂ (C ₅₆ H ₃₆ N ₁₄ Cl ₂ O ₂₄ S ₂)]	1551.09	43.36 (43.38)	2.34 (2.42)	12.64 (12.94)	8.19 (8.25)	Brown	73	74 Ω^{-1}
[Ni ₂ (C ₅₆ H ₃₆ N ₁₄ Cl ₂ O ₂₄ S ₂)]	1541.39	43.64 (43.66)	2.35 (2.40)	12.72 (12.71)	7.62 (7.66)	Gray	72	11 Ω^{-1}
[Co ₂ (C ₅₆ H ₃₆ N ₁₄ Cl ₂ O ₂₄ S ₂)]	1541.87	43.62 (43.74)	2.35 (2.33)	12.72 (12.86)	7.64 (7.68)	Light gray	77	16 Ω^{-1}
[Cu ₂ (C ₅₆ H ₃₂ N ₁₈ Cl ₂ O ₃₂ S ₂)]	1731.08	38.85 (38.80)	1.86 (1.85)	14.56 (14.58)	7.34 (7.36)	Light Yellow	75	79 Ω^{-1}
[Ni ₂ (C ₅₆ H ₃₂ N ₁₈ Cl ₂ O ₃₂ S ₂)]	1721.38	39.07 (39.00)	1.87 (1.84)	14.65 (14.68)	6.82 (6.85)	Reddish	74	12 Ω^{-1}
[Co ₂ (C ₅₆ H ₃₂ N ₁₈ Cl ₂ O ₃₂ S ₂)]	1721.86	39.06 (39.17)	1.87 (1.82)	14.64 (14.72)	6.85 (6.88)	Light Yellow	76	18 Ω^{-1}

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 ${}^2B_{1(dx^2-y^2)}$ 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 state³⁰. The $g_{\parallel}/A_{\parallel}$ is taken as an indication for the stereochemistry of the copper(II) complexes. Addison³¹ has suggested that this ratio may be an empirical indication of the octahedral distortion geometry. The values higher than 148 cm are observed for octahedral distorted complexes. The value of $g_{\parallel}/A_{\parallel}$ 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 ion³⁰.

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: ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ consistent with a typical Ni(II) in an octahedral environment³². The magnetic moment values for these complexes were found in the range 3.15-3.17 B.M expected³² 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 ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1) ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2) and ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$ (ν_3), respectively, suggesting an octahedral geometry around Co(II) ion³³. 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-carbohydrazide (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%. ¹H NMR (300 MHz, DMSO-*d*₆) δ = 6.45-7.65 (m, 5H, Ar-H benzofuran), 8.13 (s, Ar-H, Carbonyl Phenyl), 10.15 (s, 1x1H, NH of carbazide). ¹³C NMR (300 MHz, DMSO-*d*₆) δ = 166.7 (C=O), 158.4, 150.0, 149.1, 130.5, 129.4, 124.7, 123.3, 121.0, 114.6, 111.6, (Ar-C), UV-Vis (Nujol mul (nm)): λ = 370, 420, 480. UV/vis (1×10^{-4} mol, DMSO): λ = 360, 390, 445. IR (KBr): ν (N²H) 3245, ν (C=O) 1720, ν (N-N) 1115, ν (C-C) 760, ν (C=C, aromatic) 1540, ν (C-H, aromatic) 3040, ν (NH, hydrazide) 3155 cm⁻¹.

Synthesis of the metal complex [Cu₂(C₅₆H₄₀N₁₀Cl₂O₁₆S₂)] (I)

A solution of divalent metal salt CuCl₂·2H₂O (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 CaCl₂ (1.06 g, 71% yield).

Conductance Λ_m : $72 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. UV-Vis (Nujol mul (nm)): $\lambda=355, 375, 420, 525, 720$ and 1155 . IR (KBr): $\nu(\text{N}^2\text{H}) 3272, \nu(\text{C}=\text{O}) 1720, \nu(\text{N}-\text{N}) 1122, \nu(\text{C}-\text{C}) 760, \nu(\text{C}=\text{C}, \text{aromatic}) 1540, \nu(\text{C}-\text{H}, \text{aromatic}) 3040, \nu(\text{NH}, \text{hydrazide}) 3144, \nu(\text{M}-\text{N}) 425,$

Synthesis of the metal complex $[\text{Ni}_2(\text{C}_{56}\text{H}_{40}\text{N}_{10}\text{Cl}_2\text{O}_{16}\text{S}_2)]$ (2)

A solution of divalent metal salt $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (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 (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 (1.16 g, 78% yield).

Conductance Λ_m : $09 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. UV-Vis(Nujol mul (nm)): $\lambda=255, 275, 320, 525, 720$ and 1155 . IR (KBr): $\nu(\text{H}_2\text{O}) 3429, \nu(\text{N}^2\text{H}) 3272, \nu(\text{C}=\text{O}) 1720, \nu(\text{C}-\text{C}) 770, \nu(\text{C}=\text{C}, \text{aromatic}) 1544, \nu(\text{C}-\text{H}, \text{aromatic}) 3030, \nu(\text{NH}, \text{hydrazide}) 3140, \nu(\text{N}-\text{N}) 1120, \nu(\text{M}-\text{N}) 422, \nu(\text{M}-\text{O}) 485 \text{ cm}^{-1}.$

Synthesis of the metal complex $[\text{Co}_2(\text{C}_{56}\text{H}_{40}\text{N}_{10}\text{Cl}_2\text{O}_{16}\text{S}_2)]$ (3)

A solution of divalent metal salt $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (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 Λ_m : $15 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. UV-Vis(Nujol mul (nm)): $\lambda=260, 272, 325, 520, 724$ and 1150 . IR(KBr): $\nu(\text{H}_2\text{O}) 3340, \nu(\text{N}^2\text{H}) 3260, \nu(\text{C}=\text{O}) 1780, \nu(\text{N}-\text{N}) 1123, \nu(\text{C}-\text{C}) 766, \nu(\text{C}=\text{C}, \text{aromatic}) 1543, \nu(\text{C}-\text{H}, \text{aromatic}) 3033, \nu(\text{NH}, \text{hydrazide}) 3150, \nu(\text{M}-\text{N}) 420, \nu(\text{M}-\text{O}) 500 \text{ cm}^{-1}.$

Synthesis of the metal complex $[\text{Cu}_2(\text{C}_{56}\text{H}_{36}\text{N}_{14}\text{Cl}_2\text{O}_{24}\text{S}_2)]$ (4)

A solution of divalent metal salt $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (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 Λ_m : $74 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. UV-Vis (Nujol mul (nm)): $\lambda=260, 280, 320, 450, 700, 1150$. IR (KBr): $\nu(\text{H}_2\text{O}) 3380, \nu(\text{N}^2\text{H}) 3260, \nu(\text{C}=\text{O}) 1735, \nu(\text{N}-\text{N}) 1146, \nu(\text{M}-\text{N}) 440, \nu(\text{C}-\text{C}) 755, \nu(\text{C}=\text{C}, \text{aromatic}) 1540, \nu(\text{C}-\text{H}, \text{aromatic}) 3040, \nu(\text{NH}, \text{hydrazide}) 3145,$

Synthesis of the metal complex $[\text{Ni}_2(\text{C}_{56}\text{H}_{36}\text{N}_{14}\text{Cl}_2\text{O}_{24}\text{S}_2)]$ (5)

A solution of divalent metal salt $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (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 Λ_m : $11 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. UV-Vis (Nujol mul (nm)): $\lambda=255, 275, 320, 525, 720$ and 1155 . IR (KBr): $\nu(\text{H}_2\text{O}) 3429, \nu(\text{N}^2\text{H}) 3272, \nu(\text{C}=\text{O}) 1732, \nu(\text{N}-\text{N}) 1122, \nu(\text{C}-\text{C}) 754, \nu(\text{C}=\text{C}, \text{aromatic}) 1544, \nu(\text{C}-\text{H}, \text{aromatic}) 3044, \nu(\text{NH}, \text{hydrazide}) 3144, \nu(\text{M}-\text{N}) 425, \nu(\text{M}-\text{O}) 490 \text{ cm}^{-1}.$

Synthesis of the metal complex [Co₂(C₅₆H₃₆N₁₄Cl₂O₂₄S₂)] (6)

A solution of divalent metal salt CoCl₂·6H₂O (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 CaCl₂ (1.54 g, 77% yield).

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

Synthesis of the metal complex [Cu₂(C₅₆H₃₂N₁₈Cl₂O₃₂S₂)] (7)

A solution of divalent metal salt CuCl₂·2H₂O (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 CaCl₂ (1.28 g, 75% yield).

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

Synthesis of the metal complex [Ni₂(C₅₆H₃₂N₁₈Cl₂O₃₂S₂)] (8)

A solution of divalent metal salt NiCl₂·6H₂O (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 CaCl₂ (1.06 g, 74% yield).

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

Synthesis of the metal complex [Co₂(C₅₆H₃₂N₁₈Cl₂O₃₂S₂)] (9)

A solution of divalent metal salt CoCl₂·6H₂O (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 CaCl₂ (1.35 g, 76% yield).

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

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