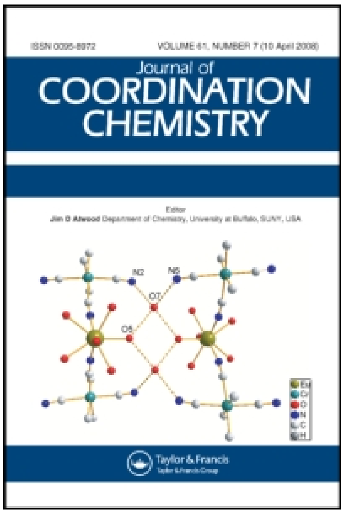

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Synthesis and characterization of a new thiohydrazone ligand, 3-carboxy-2-hydroxybenzaldehydemorpholine N-thiohydrazone and its metal complexes

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The reaction of 3-formylsalicylic acid with morpholine N-thiohydrazide in ethanol leading to the formation of a new thiohydrazone, 3-carboxy-2-hydroxybenzaldehydemorpholine N-thiohydrazone (H_2chbmth) is described. This thiohydrazone ligand remained as the thioketo form in the solid state. However, thioketo- and a small amount of the thiol-tautomeric forms (H_2chbmth and H_3chbmthol, respectively) remain in equilibrium in solution. The reactions of the ligand with different metal salts (in 1 : 1 molar ratio) leading to the synthesis of many new metal complexes have been studied. Depending on pH of the reaction medium and the nature of the metal salt used, the ligand is found to be monobasic tridentate, dibasic tridentate, monobasic bidentate or neutral bidentate giving complexes [Co(H_2chbmth)$_2$]X_2, [X = NO_3 (**11**), $\frac{1}{2}SO_4$ (**13**)]; [Cd(H_2chbmth)(H_2O)$_2$]SO_4 (**21**); [M(Hchbmth)X], [M = Cu(II) and X = Cl (**1**), NO_3 (**2**), CH_3COO (**4**); M = Ni(II) and X = Cl (**6**), NO_3 (**7**); M = Co(II) and X = NO_3 (**12**), CH_3COO (**14**); M = Zn and X = Cl (**17**), CH_3COO (**18**); M = Hg(II) and X = Cl (**23**), CH_3COO (**24**)]; [Ni(H_2chbmthol)(acac)] (**9**); [Co(Hchbmth)Cl] · $2H_2O$ (**10**), [Cu(Hchbmth)H_2O]$\frac{1}{2}SO_4$ (**3**); [Cu(Hchbmthol)]$_2$ (**5**); [M(Hchbmthol)X], [M = Ni(II) and X = H_2O (**8**); M = VO(II) and X = H_2O (**15**); M = Pd(II) and X = H_2O (**16**); M = Zn(II) and X = NH_3 (**19**); M = Cd(II) and X = H_2O (**20**), NH_3 (**22**); M = Hg(II) and X = NH_3 (**25**)]. *In situ* reactions of metal salts with the ligand components (i.e. 3-formylsalicylic acid and morpholine N-thiohydrazide) in ethanol resulted the same complexes. The complexes are characterized by elemental analyses, magnetic susceptibilities, molar conductances, molecular weights and spectroscopic (IR, ESR, ^{1}H NMR and UV-visible) data.

Keywords: Schiff base; Thiohydrazone; Transition metals; Magnetic susceptibility; Electronic spectra; Proton NMR spectra

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1. Introduction

Schiff bases derived from 3-formylsalicylic acid with mono-, di- and polyamines are versatile ligands and their complexes with transition and non-transition metal ions have been studied in recent years [1–12]. However, comparatively little work is available on the metal complexes of hydrazones and thiohydrazones of 3-formylsalicylic acid. We have, therefore, synthesized a new ligand by condensation of 3-formylsalicylic acid with morpholine N-thiohydrazide abbreviated to H_2chbmth (thione-form) and studied its reactions with Cu(II), Ni(II), Co(II), Zn(II), Cd(II), Hg(II), VO(II) and Pd(II) salts and characterized the complexes isolated. It is pertinent to mention here that not much work is available on the thiohydrazone complexes of Zn(II), Cd(II) and Hg(II) although corresponding complexes with hydrazides and thiohydrazide are available [13–19]. It is known that hydrazone ligands have enzyme inhibiting properties [20]. The tuberculosis properties of hydrazides and their derivatives have also been extensively studied [21]. Various hydrazones are known to be less toxic than the parent hydrazides, probably due to the blocking of the free amino group. Although some reports are available on transition metal complexes of thiohydrazides, little investigation has been carried out on complexes of thiohydrazones [22]. In view of this and the potential biological activity of transition metal complexes of thiosemicarbazones, which are structurally very similar to thiohydrazones, we have prepared the titled thiohydrazone (H_2chbmth) and studied its reactions with different metal salts under varied reaction conditions and isolated many new metal complexes of the ligand H_3chbmthol (Ia) which is the 'thiol' form of the thiohydrazone H_2chbmth (I) (see figure 1). Depending on the reaction conditions the ligand is found as a monobasic tridentate, dibasic tridentate, monobasic bidentate or neutral bidentate ligand.

2. Experimental

2.1. *Materials and instruments*

The chemicals used were AR grade. The solvents and chemicals were purified and dried before use by standard procedures. Elemental analyses and ^{1}H NMR spectra were carried out at the Regional Sophisticated Instrumentation Centre, the Central Drug Research Institute, Lucknow and Indian Institute of Chemical Biology, Kolkata, respectively. The electronic spectra (ethanol, DMSO or nujol) were recorded on a Hitachi 200-20 and Shimadzu UV-2401PC spectrophotometers and infrared spectra (KBr, nujol or hexachlorobutadiene; more than one medium was used for some

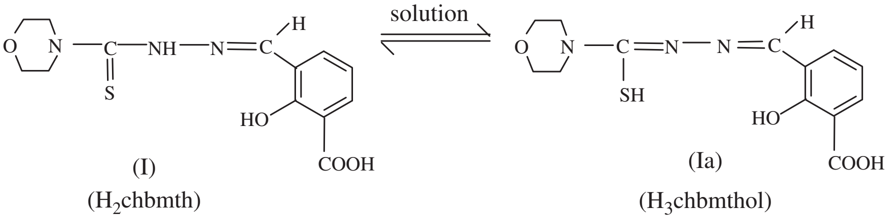


Figure 1. Equilibrium between the thioketo (H_2chbmth) and thiol (H_3chbmthol) form of the ligand.

compounds) on Perkin-Elmer 1330 and L120-000A FTIR spectrophotometers. The molar conductances were measured using an Elico conductivity bridge. The magnetic susceptibility was determined by the Guoy method. Molecular weights were determined by Rast's method and osmometrically.

2.2. *Preparation of the ligand*

To a hot ethanolic solution (20 mL) of morpholine N-thiohydrazide (Hmth) [23] (0.409 g, 0.0025 mol) was added 3-formylsalicylic acid [24] (0.41 g, 0.0025 mol) in 5 mL of dry ethanol. The mixture turned yellow and was refluxed on a water bath for 2 h. The thiohydrazone solution thus obtained, was used for complex formation reactions. Pure isolated H_2chbmth was also used to prepare the metal complexes with equivalent results. Yield 0.542 g (70%).

2.3. *Preparation of the complexes*

(Equimolar quantities of the ligand and metal salts were used in all the preparations.)

2.3.1. [Cu(Hchbmth)Cl] (1). To a solution of H_2chbmth (in 25 mL of ethanol), prepared as described above, $CuCl_2 \cdot 2H_2O$ (0.426 g, 0.0025 mol) in dry ethanol (10 mL) was added, giving a green solution (pH ~ 3) along with some green precipitate. The resulting mixture was heated under reflux for 45 min and the green powdery compound obtained was filtered off, washed with dry ethanol and dried *in vacuo*. Yield: 0.620 g (51%). The compound is soluble in DMSO, Py and DMF, partially soluble in methanol, nitromethane and dichloromethane and insoluble in chloroform, benzene and ether.

2.3.2. [Cu(Hchbmth)NO_3] (2). Similarly, the reaction between the ligand solution and $Cu(NO_3)_2 \cdot 3H_2O$ (0.603 g, 0.0025 mol) in 10 mL dry ethanol gave a dark brown solution (pH ~ 3), from which a greenish-brown powdery compound was isolated. Yield: 0.900 g (65%). The compound is soluble in DMSO, Py and DMF, partially soluble in methanol, nitromethane, dichloromethane and insoluble in ethanol, ether, benzene and chloroform.

2.3.3. [Cu(Hchbmth)H_2O]$\frac{1}{2}SO_4$ (3). This light green solid was isolated by reaction of the ligand solution and $CuSO_4 \cdot 5H_2O$ (0.623 g, 0.0025 mol) (pH ~ 3) in water (5 mL) as described above. Yield: 0.840 g (60%). The compound is soluble in DMSO, Py, DMF and boiling water, partly soluble in methanol, and nitromethane and insoluble in chloroform, dichloromethane, ether and benzene.

2.3.4. [Cu(Hchbmth)CH_3COO] (4). To the ligand solution prepared as described above, $Cu(CH_3COO)_2 \cdot H_2O$ (0.498 g, 0.0025 mol) in 10 mL water and 10 drops of glacial acetic acid was added. The resultant greenish brown solution (pH ~ 6) was heated under reflux for 50 min yielding a yellowish green microcrystalline compound, which was filtered off, washed with dry ethanol and dried *in vacuo*. Yield: 0.900 g (70%). The compound is soluble in DMSO and DMF but insoluble in methanol, ethanol, nitromethane, chloroform and ether.

2.3.5. [Cu(Hchbmthol)]$_2$ (5). This greenish-brown microcrystalline compound **5** was synthesized following the method similar to that used for the complex **1** described above using Cu(acac)$_2$ (0.678 g, 0.0025 mol) in 10 mL dry ethanol (pH of the reaction medium was ~7). Yield: 0.630 g (64%). The compound is soluble in DMSO, Py and DMF but insoluble in methanol, ethanol, nitromethane, dichloromethane and chloroform.

2.3.6. [Ni(Hchbmth)Cl] (6). A dark brown solution (pH ~ 3) was obtained on addition of an ethanolic solution (10 mL) of $NiCl_2 \cdot 6H_2O$ (0.594 g., 0.0025 mol) to the ligand solution. It was refluxed on water bath for 30 min, when a lemon-yellow powder separated out, was filtered, washed with dry ethanol and dried in *vacuo* over anhydrous $CaCl_2$. Yield: 0.750 g (55%). The compound is soluble in DMSO, Py and DMF, partially soluble in methanol and nitromethane, but insoluble in ethanol, chloroform and benzene.

2.3.7. [Ni(Hchbmth)NO$_3$] (7). This yellow-brown microcrystalline compound was obtained following the exact method to that used for complex **6** by using $Ni(NO_3)_2 \cdot 6H_2O$ in place of $NiCl_2 \cdot 6H_2O$. Yield: 0.750 g (50%). The compound is soluble in DMSO, DMF and Py, partially soluble in hot methanol and nitromethane, but insoluble in chloroform, ethanol and dichloromethane.

2.3.8. [Ni(Hchbmthol)H$_2$O] (8). Similarly, the reaction of $Ni(CH_3COO)_2 \cdot 4H_2O$ (0.621 g, 0.0025 mol) in dry ethanol (10 mL) with ligand solution afforded this dark-brown powder. Yield: 0.780 g (60%). The compound is soluble in DMSO, Py and DMF but insoluble in methanol, ethanol, dichloromethane and ether.

2.3.9. [Ni(H$_2$chbmthol)(acac)] (9). Similarly, this yellowish brown compound was obtained by the reaction of Ni(acac)$_2$ (0.640 g, 0.0025 mol) (pH ~ 7) in dry ethanol (20 mL) with ligand solution. Yield: 0.800 g (56%). The compound is soluble in DMSO, Py and DMF methanol, ethanol, dichloromethane and chloroform.

2.3.10. [Co(Hchbmth)Cl]·2H$_2$O (10). To the solution of the Schiff base, prepared as described above, $CoCl_2 \cdot 6H_2O$ (0.594 g, 0.0025 mol) in dry ethanol (10 mL) was added under nitrogen. The resulting bluish brown solution (pH ~ 3) was heated under reflux for 2 h and filtered while hot. The volume of the filtrate was reduced to half and cooled to yield yellowish-brown powder, which was filtered off, washed with dry cold ethanol and dried *in vacuo* over anhydrous $CaCl_2$. Yield: 0.820 g (60%). The compound is soluble in DMSO, DMF and hot ethanol but insoluble in chloroform, dichloromethane and ether.

2.3.11. [Co(H$_2$chbmth)$_2$](NO$_3$)$_2$ (11). Similarly, this yellowish-brown microcrystalline compound was obtained from ligand solution and $Co(NO_3)_2 \cdot 6H_2O$ (0.772 g, 0.0025 mol) in dry ethanol (10 mL) (pH ~ 3). Yield: 0.750 g (50%). The compound is soluble in DMSO, Py, DMF and hot methanol and water but insoluble in dichloromethane, chloroform and nitromethane.

2.3.12. [Co(Hchbmth)NO$_3$] (12). Similarly, $Co(NO_3)_2 \cdot 6H_2O$ (0.727 g, 0.0025 mol) in dry ethanol (10 mL) was added to ligand solution and the resulting reddish brown solution (pH ~ 3) was refluxed for 1 h. To this resulting solution dilute NH_4OH (15%) was added to raise the pH to about 6 and it was further refluxed for 30 min yielding yellowish-brown powder. Yield: 0.700 g (46%). The compound is soluble in DMSO, DMF, and Py but insoluble in methanol, ethanol, chloroform and dichloromethane.

2.3.13. [Co(H_2chbmth)]SO_4 (13). Similarly, treatment of $CoSO_4 \cdot 7H_2O$ (0.702 g, 0.0025 mol) in aqueous ethanol (40 mL) with ligand solution under nitrogen produced a red solution (pH ~ 3), which was refluxed for 2 h and filtered while hot. The filtrate, on concentration and cooling, gave yellowish brown powder. The compound was taken in aqueous ethanol and heated for few minutes, filtered, washed with dry ethanol and dried in *vacuo* over fused $CaCl_2$. Yield: 0.690 g (46%). The compound is soluble in DMSO, Py, DMF and hot water but insoluble in methanol, ethanol and chloroform.

2.3.14. [Co(Hchbmth)(CH_3COO)] (14). A solution of $Co(CH_3COO)_2 \cdot 4H_2O$ (0.622 g, 0.0025 mol) in rectified spirits (30 mL) and a few drops of glacial acetic acid was added to the ligand solution under nitrogen. Within a few minutes a red solution (pH ~ 7) along with some red precipitate was obtained. The mixture was then heated under reflux for 1.5 h. The yellowish-brown powder was filtered off, washed with dry ethanol and dried *in vacuo* over fused $CaCl_2$. Yield: 0.780 g (56%). The compound is soluble in DMSO, partly in DMF but insoluble in methanol, ethanol and chloroform.

2.3.15. [VO(Hchbmthol)H_2O] (15). To a hot methanolic solution (25 mL) of H_2chbmth (0.618 g, 0.0025 mol) was added a methanolic solution (40 mL) of $VOSO_4 \cdot H_2O$ (0.4525 g, 0.0025 mol). The resulting dark brown solution (pH ~ 4) was heated under reflux on a water bath for 3 h. The brown solution, upon concentration and cooling, yielded brown microcrystalline compound. The compound was collected by filtration, washed with methanol and dried *in vacuo*. Yield: 0.528 g (60%). The compound is soluble in DMSO, Py and DMF but insoluble in methanol, ethanol and chloroform.

2.3.16. [Pd(Hchbmthol)H_2O]$5H_2O$ (16). Similarly, this yellow microcrystalline compound was prepared by the reaction of *H_2*chbmth (0.772 g, 0.0025 mol) and Na_2PdCl_4 (0.735 g, 0.0025 mL) in methanol (pH ~ 5). It was collected by filtration and dried *in vacuo*. Yield: 0.781 g (60%). The compound is soluble in DMSO, Py and DMF but insoluble in methanol, ethanol and chloroform.

2.3.17. [Zn(Hchbmth)Cl] (17). To the solution of the ligand prepared as described above, $ZnCl_2$ (0.340 g, 0.0025 mol) in 10 mL dry ethanol was added. The resulting solution (pH ~ 4) was refluxed for 1 h yielding a deep yellow powder, which was filtered off, washed with dry ethanol and dried *in vacuo*. Yield: 0.600 g (54%). The compound is soluble in DMSO and DMF but insoluble in methanol, ethanol and chloroform.

2.3.18. [Zn(Hchbmth)(CH_3COO)] (18). Similarly, the reaction of $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.548 g, 0.0025 mol) in ethanol (10 mL) with ligand solution (pH ~ 6) gave this yellow powdery compound. Yield: 0.750 g (56%). The compound is soluble in DMSO, slightly so in DMF, but insoluble in methanol, ethanol and chloroform.

2.3.19. [Zn(Hchbmthol)NH_3] (19). This greenish yellow compound was obtained when reaction between $ZnCl_2$ (0.340 g, 0.0025 mol) and ligand solution was carried out at pH ~ 9 (15% dilute NH_4OH). Yield: 0.650 g (58%). The compound is insoluble in methanol, ethanol and chloroform but soluble in DMSO, DMF and Py.

2.3.20. [Cd(Hchbmthol)H_2O] (20). This light yellow powdery microcrystalline compound was prepared by the same method used for compound **18** using $Cd(CH_3COO)_2 \cdot 2H_2O$ (0.666 g, 0.0025 mol) (pH ~ 7). Yield: 0.479 g (70%). The compound is soluble in DMSO and DMF but insoluble in methanol, ethanol and chloroform.

2.3.21. [Cd(H_2chbmth)$(H_2O)_2$]SO_4 (21). Similarly, when $CdSO_4 \cdot 2H_2O$ (0.610 g, 0.0025 mol) in minimum water (13 mL) was added to ligand solution a light yellow precipitate was formed. The resulting mixture (pH ~ 4) was heated under reflux for 30 min yielding light yellow powder. It was filtered, washed with dry ethanol and dried *in vacuo*. Yield: 0.900 g (63%). The compound is soluble in DMSO and DMF, partly so in hot water and hot methanol, but insoluble in chloroform, dichloromethane and ether.

2.3.22. [Cd(Hchbmthol)NH_3] (22). This green microcrystalline compound was obtained similarly to compound **20** at pH ~ 9 (15% dilute NH_4OH). Yield: 1.300 g (90%). The compound is soluble in DMSO, slightly so in DMF but insoluble in methanol, ethanol and chloroform.

2.3.23. [Hg(Hchbmth)Cl] (23). Similarly, $HgCl_2$ (0.679 g, 0.0025 mol) in dry ethanol (10 mL) added to the ligand solution gave yellow precipitate. The resulting mixture (pH ~ 4) was refluxed for 30 min yielding yellow powder which was filtered off, washed with dry ethanol and dried *in vacuo*. Yield: 0.900 g (62%). The compound is insoluble in methanol, ethanol and chloroform but soluble in DMSO, Py and DMF.

2.3.24. [Hg(Hchbmth)(CH_3COO)] (24). This yellowish green powder was obtained by the method exactly for compound **23** using $Hg(CH_3COO)_2$ (0.796 g, 0.0025 mol) in dry ethanol (10 mL) with 5–6 drops of glacial acetic acid. Yield: 1.100 g (70%). The compound is insoluble in ethanol, methanol and chloroform but soluble in DMSO, Py and DMF.

2.3.25. [Hg(Hchbmthol)NH_3] (25). Similarly, this green powder was synthesized following the method used for compound **23** at pH ~ 9 (15% dilute NH_4OH). Yield: 0.820 g (56%). The compound is insoluble in methanol, ethanol and chloroform but soluble in DMSO, DMF and Py.

The characterization details are available in table 1.

3. Results and discussion

3.1. *Syntheses*

The reaction between 3-formylsalicylic acid and morpholine N-thiohydrazide in 1 : 1 molar ratio in dry ethanol yielded the thiohydrazone ligand (I)

Table 1. Some characterization data of the complexes.

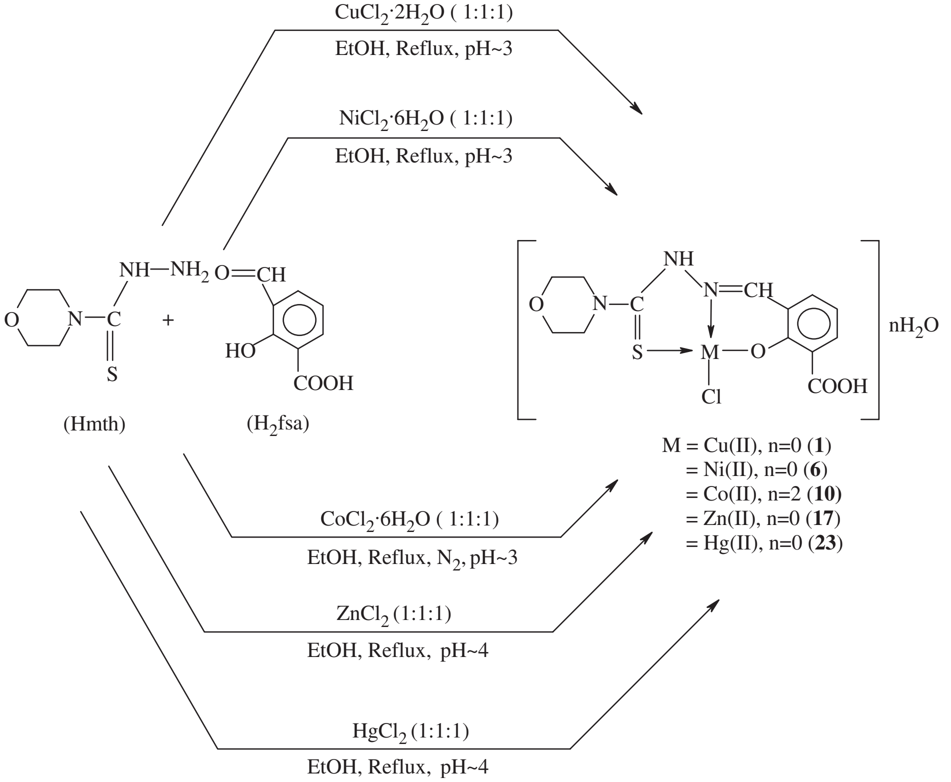
Compound	Colour	Melting Point[d] (°C)	Mol. Wt Found (Calcd)	Analyses Found (Calcd)% C	H	N	M	μ_{eff}[a] (BM)	Λ_M[b] ($\Omega^{-1}cm^2 mol^{-1}$)
H_2chbmth	Yellow	185–187	317 (309.34)	50.52 (50.48)	4.93 (4.89)	13.63 (13.58)	–	–	–
[Cu(Hchbmth)Cl] (**1**)	Green	258–262(d)	415 (407.33)	38.40 (38.32)	3.45 (3.43)	10.38 (10.31)	15.52 (15.60)	1.78	22.17
[Cu(Hchbmth)NO_3] (**2**)	Green brown	251(d)	445 (433.88)	35.99 (35.98)	3.29 (3.22)	12.81 (12.92)	14.72 (14.64)	1.80	5.77
[Cu(Hchbmth)$H_2O]_{\frac{1}{2}}SO_4$ (**3**)	Light green	250–254(d)	450 (437.92)	35.62 (35.65)	3.14 (3.20)	9.52 (9.60)	14.36 (14.51)	1.82	48.17
[Cu(Hchbmth)CH_3COO] (**4**)	Yellowish green	270–272(d)	440 (430.92)	41.87 (41.81)	4.01 (3.95)	9.72 (9.75)	14.80 (14.75)	1.79	3.44
[Cu(Hchbmthol)$]_2$ (**5**)	Greenish brown	240(d)	750 (741.74)	42.15 (42.10)	3.55 (3.50)	11.26 (11.33)	17.35 (17.13)	1.44	7.18
[Ni(Hchbmth)Cl] (**6**)	Yellow	260–264(d)	418 (402.47)	38.64 (38.78)	3.52 (3.48)	10.37 (10.44)	14.53 (14.59)	Dia[c]	12.28
[Ni(Hchbmth)NO_3] (**7**)	Yellowish brown	250–254(d)	443 (407.33)	36.32 (36.38)	3.22 (3.26)	13.66 (13.69)	13.62 (13.69)	Dia	18.36
[Ni(Hchbmthol)H_2O] (**8**)	Dark brown	248–253(d)	390 (384.03)	42.22 (42.28)	3.91 (3.99)	9.92 (9.86)	13.84 (13.78)	Dia	9.89
[Ni(H_2chbmthol)(acac)] (**9**)	Yellowish brown	250–254(d)	480 (466.13)	46.43 (46.38)	4.54 (4.51)	9.10 (9.02)	12.66 (12.60)	Dia	6.12
[Co(Hchbmth)Cl] $\cdot 2H_2O$ (**10**)	Yellowish brown	283(d)	450 (438.75)	35.51 (35.58)	4.15 (4.11)	9.60 (9.58)	13.49 (13.44)	4.23	20.24
[Co(H_2chbmth$)_2](NO_3)_2$ (**11**)	Yellowish brown	270–273(d)	822 (801.62)	38.91 (38.95)	3.67 (3.74)	13.89 (13.98)	7.29 (7.36)	2.48	80.29
[Co(Hchbmth)NO_3] (**12**)	Yellowish brown	250–252(d)	442 (429.27)	36.65 (36.72)	3.19 (3.26)	12.95 (13.05)	13.65 (13.74)	4.65	20.15
[Co(H_2chbmth)]SO_4 (**13**)	Yellow brown	260–267(d)	476 (464.33)	40.31 (40.36)	3.90 (3.88)	10.79 (10.87)	7.65 (7.62)	2.30	48.88
[Co(Hchbmth)CH_3COO] (**14**)	Yellow brown	255–261(d)	435 (426.31)	42.16 (42.26)	4.07 (3.99)	9.78 (9.86)	13.79 (13.83)	4.19	12.32
[VO(Hchbmthol)H_2O] (**15**)	Brown	288(d)	408 (392.28)	39.69 (39.77)	4.30 (4.36)	10.72 (10.70)	13.12 (13.00)	1.82	4.5

(*Continued*)

Table 1. Continued.

Compound	Colour	Melting Point[d] (°C)	Mol. Wt Found (Calcd)	Analyses Found (Calcd)%				μ_{eff}[a] (BM)	Λ_M[b] ($\Omega^{-1}cm^2 mol^{-1}$)
				C	H	N	M		
[Pd(Hchbmthol)H_2O]5H_2O (**16**)	Yellow	292(d)	546 (521.83)	29.79 (29.89)	5.12 (5.17)	8.00 (8.05)	20.51 (20.44)	Dia	5.1
[Zn(Hchbmth)Cl] (**17**)	Deep yellow	260(d)	426 (409.17)	38.20 (38.16)	3.49 (3.42)	10.32 (10.27)	15.85 (15.97)	Dia	3.24
[Zn(Hchbmth)CH_3COO] (**18**)	Yellow	255–258(d)	448 (432.77)	40.67 (41.60)	3.27 (3.23)	9.76 (9.70)	15.02 (15.09)	Dia	3.31
[Zn(Hchbmthol)NH_3] (**19**)	Greenish yellow	250–255(d)	402 (389.74)	40.79 (40.71)	4.02 (4.11)	14.29 (14.38)	16.85 (16.77)	Dia	3.24
[Cd(Hchbmthol)H_2O] (**20**)	Light yellow	245(d)	453 (437.75)	35.63 (35.66)	3.35 (3.43)	9.71 (9.60)	25.76 (25.70)	Dia	6.94
[Cd(H_2chbmth)$(H_2O)_2$]SO_4 (**21**)	Light yellow	230–233(d)	560 (553.84)	28.26 (28.18)	3.51 (3.43)	7.54 (7.59)	20.39 (20.31)	Dia	47.19
[Cd(Hchbmthol)NH_3] (**22**)	Green	232(d)	447 (436.76)	35.82 (35.74)	3.59 (3.66)	9.78 (9.62)	25.66 (25.75)	Dia	4.84
[Hg(Hchbmth)Cl] (**23**)	Yellow	169(d)	558 (544.37)	28.62 (28.67)	2.62 (2.57)	7.84 (7.72)	36.82 36.87	Dia	9.93
[Hg(Hchbmth)CH_3COO] (**24**)	Yellow green	175(d)	580 (567.97)	31.68 (31.76)	2.75 (2.82)	7.50 (7.41)	35.48 (35.40)	Dia	8.24
[Hg(Hchbmthol)NH_3] (**25**)	Green	211(d)	537 (524.94)	29.70 (29.73)	2.98 (3.05)	10.75 (10.67)	38.12 (38.23)	Dia	9.15

[a] Solid state at room temperature.
[b] 10^{-3} M solution in DMSO at room temperature.
[c] Diamagnetic.
[d] Decomposition temperature.



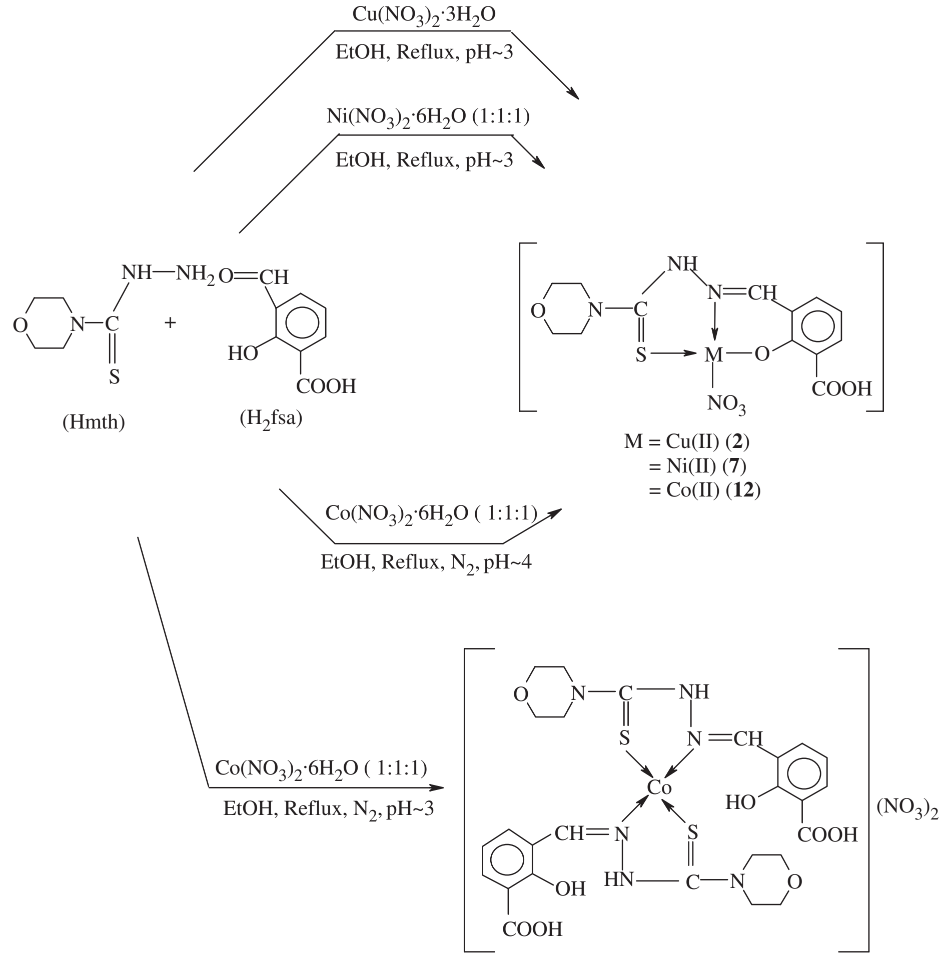
Scheme 1. *In situ* reactions of the ligand components in ethanol with the chlorides of Cu(II), Ni(II), Co(II), Zn(II) and Hg(II) ions in the pH range 3–4 leading to the syntheses of new metal complexes of the ions.

3-carboxy-2-hydroxybenzaldehydemorpholine N-thiohydrazone (figure 1), the formation of which is supported by analytical and spectral data.

The ligand (I) has a proton adjacent to the thione group. The thione group is relatively unstable in the monomeric form and tends to form the more stable C–S bond by enethiolization if there is at least one proton adjacent to thione group [25]. Therefore, the thione (I) and the thiol (Ia) may be in equilibrium in solution (figure 1). Depending on the reaction conditions and the metal salts used, the ligand may be tridentate dibasic or monobasic; bonding through O, N and S atoms with various metal ions. Neutral and bidentate behavior are also observed in certain cases, bonding through thione S and azomethine N (schemes 1–6). All complexes are stable at laboratory conditions and have been characterized by elemental analyses, magnetic susceptibilities, molar conductances (table 1) and spectroscopic (IR, ESR, ^{1}H NMR and UV-Vis) data.

3.2. *Molar conductance*

The molar conductance values (table 1) of complexes **1**, **2** and **4–10**, **12**, **14–20**, **22–25** in DMSO are found in the range 3.24–20.24 $cm^2 Ohm^{-1} mol^{-1}$ suggesting non-electrolytic nature [26]. On the other hand, the values in the range 47.19 to 48.88 $cm^2 ohm^{-1} mol^{-1}$ in DMSO for complexes **3**, **13** and **21** suggest the presence of 1 : 1 electrolyte [26].



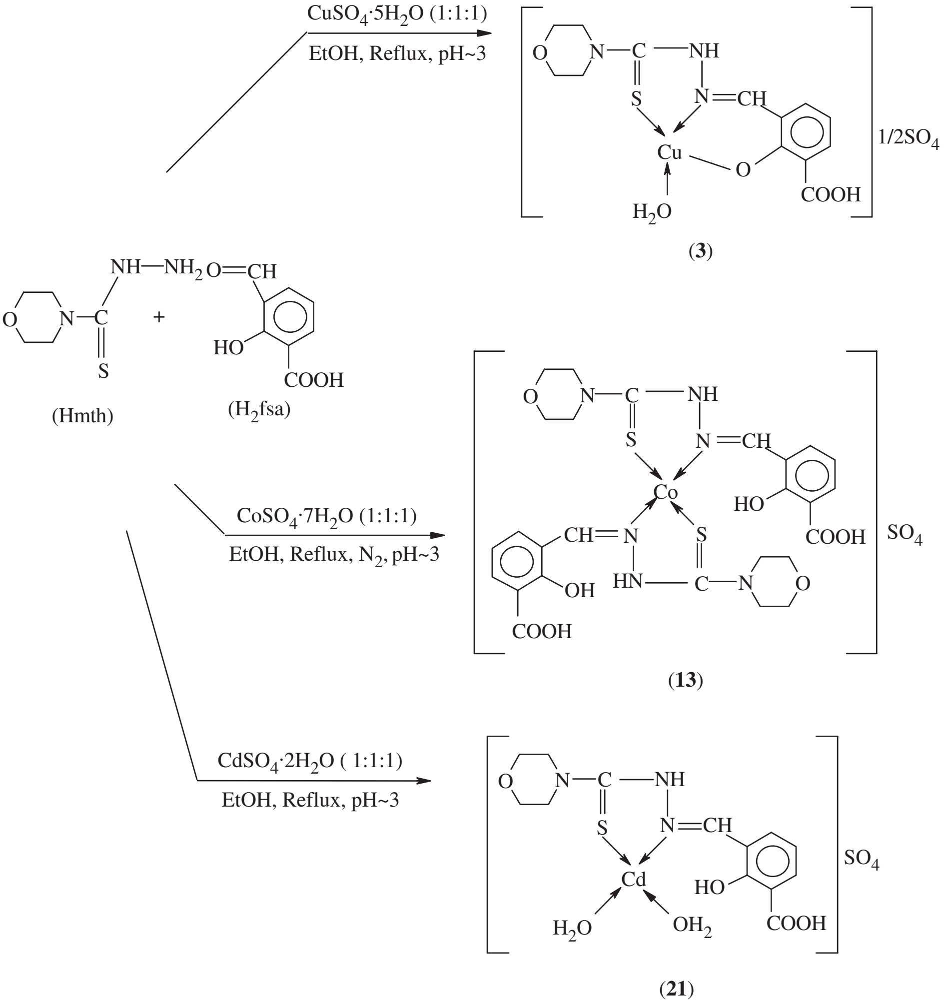
(11)

Scheme 2. *In situ* reactions of the ligand components in ethanol with the notrates of Cu(II), Ni(II) and Co(II) ions in the pH range 3–4 leading to the syntheses of new metal complexes of the ions.

The conductance value of $80.29\,\mathrm{cm^2\,Ohm^{-1}\,mol^{-1}}$ for **11** in DMSO suggests a 1 : 2 electrolyte [26].

3.3. *Magnetic moments, electronic spectra and ESR data*

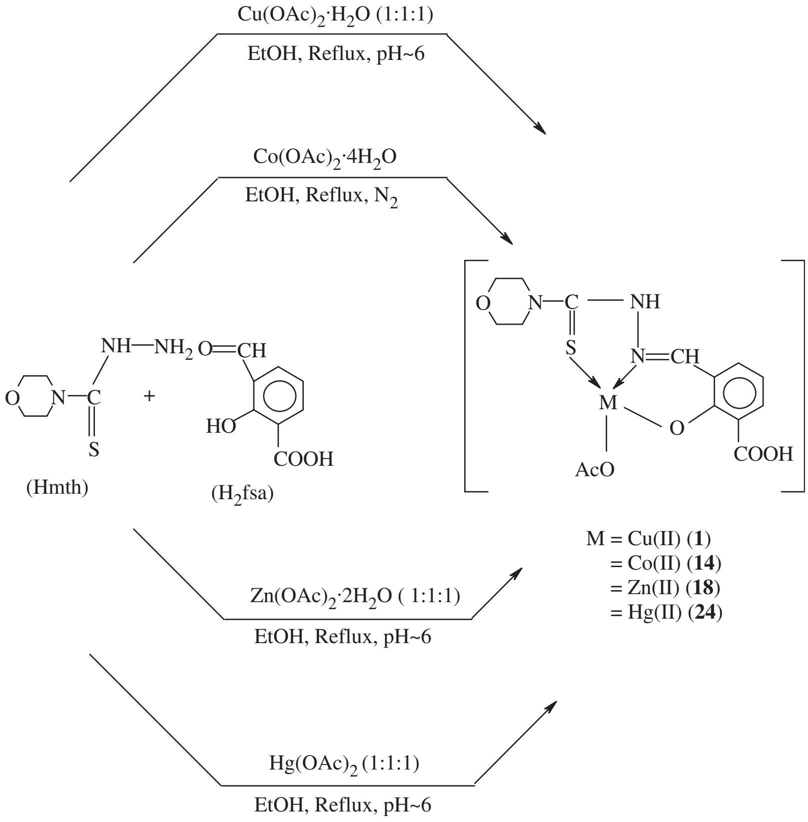
The room temperature magnetic moments of the complexes are reported in table 1, while electronic spectral data in table 2. The observed magnetic moment values for the copper(II) complexes **1–4** are in the range 1.78–1.82 BM. The magnetic moment value for copper(II) complex **5** is 1.44 BM, well below the spin only value *viz.* 1.73 BM expected for an $S=\frac{1}{2}$ system. The low moment of the Cu(II) complex may be ascribed to spin coupling from super exchange through the bridging sulfur (oxygen) atom or metal–metal bonding in the complex [27–29]. The decrease of the magnetic moment with decrease in temperature (table 3) indicates that



Scheme 3. *In situ* reactions of the ligand components in ethanol with the sulphates of Cu(II), Co(II) and Ni(II) ions in pH ~ 3 leading to the syntheses of new metal complexes of the ions.

antiferromagnetic interactions are involved [30]. Unfortunately the cryomagnetic data could not be used to elucidate the structures of the complexes, since the errors involved in the measurements of such low moments were far too large. However, an oxygen-bridged binuclear structure (figure 2) is proposed. The Cu(II) complexes display a broad band in the region 640–600 nm which may be assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ transitions in square planar geometry [31–33], but it is to be noted that electronic spectra of Cu(II) complexes in general are poor indicators of coordination geometries.

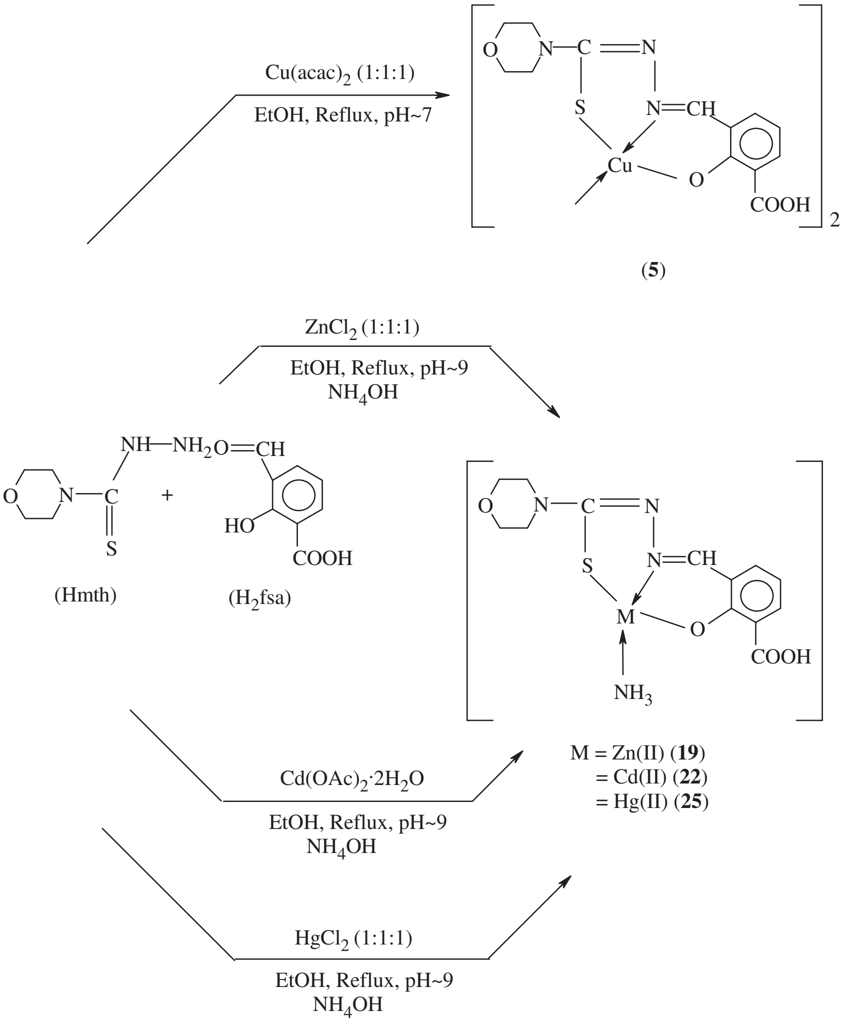
The ESR spectrum of $[Cu(Hchbmthol)]_2$ (**5**) measured in polycrystalline sample at room temperature gives $g_\parallel$ and $g_\perp$ values in the range 2.26 and 2.16 respectively. The $g_\parallel > g_\perp$ is consistent with a primarily $d_{x^2-y^2}$ ground state having elongated tetragonal or square-planar structure [34]. The parameter G, determined as $G = (g_\parallel - 2/g_\perp - 2)$ is less than **4** suggesting considerable interaction in the solid state [35].



Scheme 4. *In situ* reactions of the ligand components in ethanol with the acetates of Cu(II), Co(II), Zn(II) and Hg(II) ions in pH ~ 6 leading to the syntheses of new metal complexes of the ions.

The Ni(II) complexes **6–9** are diamagnetic and display bands in the visible regions 540–520 nm and 420–390 nm. The first band can be assigned to $^1A_{1g} \rightarrow {}^1A_{2g}$ and the 2nd band to $^1A_{1g} \rightarrow {}^1B_{1g}$ transitions in a square-planar geometry [36–38].

The Co(II) complexes **10**, **12** and **14** gave magnetic moment values in the range of 4.19–4.65 BM at room temperature (table 1). The tetrahedral and high spin octahedral Co(II) complexes each possess three unpaired electrons but may be distinguished by the magnitude of the deviation of effective magnetic moment value from the spin only value. The magnetic moments of tetrahedral Co(II) complexes with an orbitally degenerate ground term are higher than the spin only value and occur in the range 4.2–4.7 BM [39, 40]. Octahedral Co(II) complexes have a large contribution from the $^4T_{1g}$ term and have effective magnetic moment values in the range of 4.8–5.6 BM [40]. The Co(II) complexes **10**, **12** and **14** display a broad band in the region 580 nm. This band may be considered as the $^4A_2 \rightarrow {}^4T_1(P)$ transition in the tetrahedral environment of the Co(II) (i.e. ν_3 in Td) [40]. The ν_2 [$^4A_2 \rightarrow {}^4T_1(F)$] of the tetrahedral Co(II) complexes are generally observed in the near infrared, which could not be measured on our instrument.

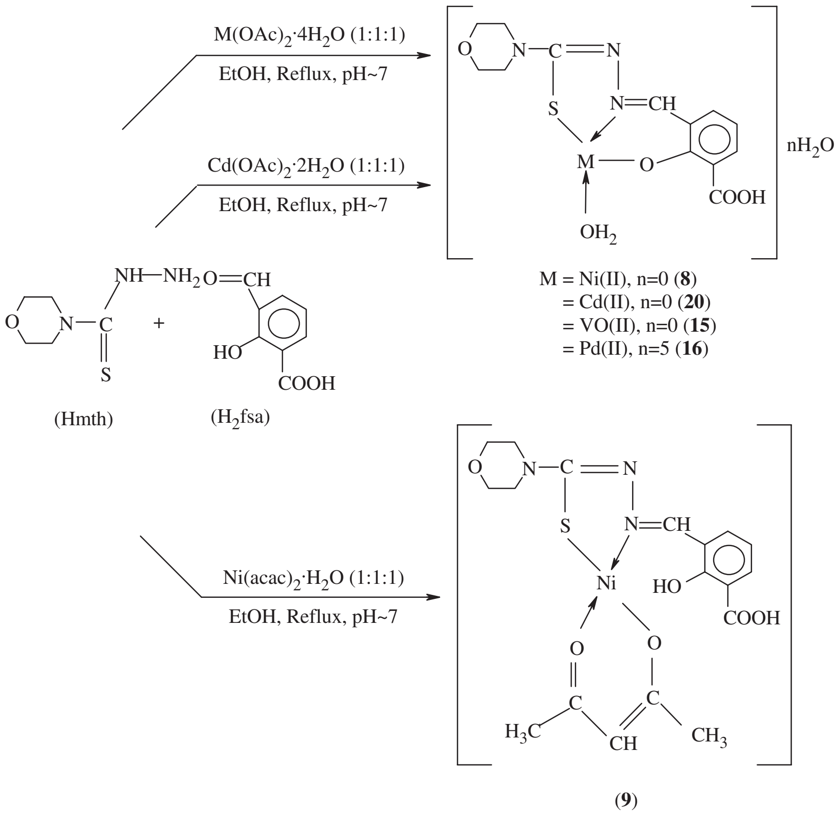


Scheme 5. *In situ* reactions of the ligand components in ethanol with Cu(acac)$_2$ (pH ~ 7), ZnCl$_2$ (pH ~ 9), Cd(OAc)$_2$ (pH ~ 9) and HgCl$_2$ (pH ~ 9) leading to the syntheses of new metal complexes of the ions.

The low spin square-planar Co(II) complexes may be readily distinguished by μ_{eff} in the range 2.1–2.9 BM, arising from one unpaired electron with large orbital contribution [40–44]. The observed magnetic moment values for **11** and **13** are 2.48 and 2.30 BM, respectively, which are in the range of square-planar Co(II) species. Such a square-planar geometry is also confirmed by the electronic spectroscopic data (table 2). The complexes display bands in the visible region 560 and 420 nm assignable to the $^2B_{2g} \rightarrow {}^4E_g(P)$ and $^2B_{2g} \rightarrow {}^4A_{2g}$ transitions [29, 45] (D_{4h} symmetry).

The magnetic moment value for [VO(Hchbmthol)H$_2$O] (**15**) in the solid state is 1.88 BM, consistent with the spin only value for a d^1 case, suggesting no direct vanadium-vanadium interaction.

The electronic spectrum in Nujol mull (**15**) shows a prominent band around 588 nm. In addition, shoulders appear in the spectrum at 769 and 526 nm. The assignment of observed electronic spectral bands for oxovanadium(IV) complexes has been a matter



Scheme 6. *In situ* reactions of the ligand components in ethanol with different metal acetates and $Ni(acac)_2$ in pH ~ 7 leading to the syntheses of new metal complexes of the ions.

of controversy [11]. Most of the discussions are made in terms of C_{4V} and a few in terms of C_{2V} symmetry. In this symmetry three electronic transitions are expected for the d^1 oxovanadium(IV) species [11]. The lowering of the symmetry from C_{4V} to C_{2V} or C_S has the effect of removing the degeneracy in the d-orbitals and thus four transitions are predicted. It has been observed in the present investigation that all the bands are not well resolved into their components. The broad band observed about 588 nm is easily identified, and may be attributed to $^2B_2 \rightarrow {}^2B_1$ in C_{4V} symmetry. The shoulder at about 526 nm may be due to $^2B_2 \rightarrow {}^2A_1$ transition (in C_{4V}). The high intensity of this band may be due to charge transfer or intra-ligand transitions. The low-energy band observed at about 769 nm may be assigned to $^2B_2 \rightarrow {}^2E$ transition. If the present oxo-vanadium(IV) complex is square pyramidal like oxovanadium(IV) complexes of β-diketones, it should readily add a donor ligand to the metal at the vacant axial coordination position and thereby produce a marked shift of the d–d transition bands. The electronic spectrum of **15** shows a slight shift of the d–d bands when measured in DMSO. The steric hindrance of the ligand may present approach of the donor solvent, or the complex may have a trigonal-bipyramidal structure that, unlike the square-pyramidal geometry, hinders complex base interaction [11].

Table 2. Electronic spectral data of the ligand and some complexes with tentative assignments.

Ligand/Complex	Medium	λ_{max} (nm)	Tentative assignments
H_2chbmth	DMSO	260, 310, 370	–
[Cu(Hchbmth)Cl] (**1**)	DMSO	258, 290, 335, 285, 600(br)	$^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$
$[Cu(Hchbmth)NO_3]$ (**2**)	DMSO	258, 280, 335, 380, 650(br)	$^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$
$[Cu(Hchbmth)H_2O]_{\frac{1}{2}}SO_4$ (**3**)	DMSO	260, 290, 336, 386, 600(br)	$^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$
$[Cu(Hchbmth)CH_3COO]$ (**4**)	DMSO	260, 290, 335, 385, 640(br)	$^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$
$[Cu(Hchbmthol)]_2$ (**5**)	DMSO	257, 290, 335, 380, 600(br)	$^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$
[Ni(Hchbmth)Cl] (**6**)	DMSO	258, 288, 390, 540(br)	$^1A_{1g} \rightarrow {}^1B_{1g}$, $^1A_{1g} \rightarrow {}^1A_{2g}$
$[Ni(Hchbmth)NO_3]$ (**7**)	DMSO	258, 288, 400, 520(br)	$^1A_{1g} \rightarrow {}^1B_{1g}$, $^1A_{1g} \rightarrow {}^1A_{2g}$
$[Ni(Hchbmthol)H_2O]$ (**8**)	DMSO	258, 420, 520(br)	$^1A_{1g} \rightarrow {}^1B_{1g}$, $^1A_{1g} \rightarrow {}^1A_{2g}$
$[Ni(H_2chbmthol)(acac)]$ (**9**)	DMSO	258, 390, 520(br)	$^1A_{1g} \rightarrow {}^1B_{1g}$, $^1A_{1g} \rightarrow {}^1A_{2g}$
$[Co(Hchbmth)Cl] \cdot 2H_2O$ (**10**)	DMSO	257, 295, 390, 580(sh)	$^4A_2 \rightarrow {}^4T_1(P)$
$[Co(H_2chbmth)_2](NO_3)_2$ (**11**)	DMSO	260, 300, 420, 560	$^2B_{2g} \rightarrow {}^4A_{2g}$, $^2B_{2g} \rightarrow {}^4E_g$
$[Co(Hchbmth)NO_3]$ (**12**)	DMSO	258, 290, 390, 580(sh)	$^4A_2 \rightarrow {}^4T_1(P)$
$[Co(H_2chbmth)]SO_4$ (**13**)	DMSO	258, 292, 400, 420, 560	$^2B_{2g} \rightarrow {}^4A_{2g}$, $^2B_{2g} \rightarrow {}^4E_g$
$[Co(Hchbmth)CH_3COO]$ (**14**)	DMSO	260, 300, 390, 580(sh)	$^4A_2 \rightarrow {}^4T_1(P)$
$[VO(Hchbmthol)H_2O]$ (**15**)	DMSO	258, 292, 526(sh), 588(br), 769(sh)	$^2B_2 \rightarrow {}^2A_1$, $^2B_2 \rightarrow {}^2B_1$, $^2B_2 \rightarrow {}^2E$
$[Pd(Hchbmthol)H_2O]5H_2O$ (**16**)	DMSO	258, 298, 465	$^1A_{1g} \rightarrow {}^1A_{2g}$
[Zn(Hchbmth)Cl] (**17**)	DMSO	255, 290, 330, 380	–
$[Zn(Hchbmth)CH_3COO]$ (**18**)	DMSO	258, 295, 385	–
$[Cd(Hchbmthol)H_2O]$ (**20**)	DMSO	254, 295, 330, 385, 560	–
$[Cd(H_2chbmth)(H_2O)_2]SO_4$ (**21**)	DMSO	256, 297, 385	–
$[Cd(Hchbmthol)NH_3]$ (**22**)	DMSO	257, 290, 385	–

br = broad, sh = shoulder.

Table 3. Magnetic data for $[Cu(Hchbmthol)]_2$ (**5**) at different temperatures.

Temperature (K)	μ (BM) per Cu atom
293	1.56
273	1.44
213	1.00
193	0.88
153	0.72
133	0.70
113	0.58
93	0.36

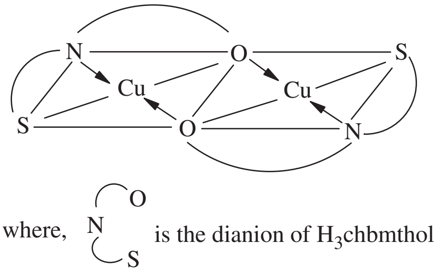


Figure 2. Proposed structure of the dimeric copper complex, [Cu(Hchbmthol)]$_2$ (**5**).

Table 4. ^{1}H NMR spectral data[a] of the ligand and some of the complexes (δ values in ppm).

Compound	–COOH	–OH	–NH	$–C_6H_4$	CH=N	Morpholine ring protons
H_2chbmth	11.90 (s)	10.40 (s)	10.10 (s)	6.88–7.8 (m)	8.56 (s)	3.68–3.91 (m)
[Ni(Hchbmth)Cl] (**6**)	11.82 (s)	–	9.82 (br)	6.66–7.7 (m)	8.32 (s)	3.4–3.8 (m)
[Zn(Hchbmth)Cl] (**17**)	11.88 (s)	–	9.8 (br)	6.5–7.2 (m)	8.28 (s)	3.39–3.88 (m)
[Zn(Hchbmth)NH_3] (**19**)	11.87 (s)	–	–	6.48–7.44 (m)	8.30 (s)	3.39-3.78 (m)

[a]in DMSO-d_6.

The diamagnetic nature of [Pd(Hchbmthol)H_2O]5H_2O **16** suggests square-planar geometry which is supported by the appearance of a band, in the electronic spectrum of the complex, at about 465 nm assignable to the $^1A_{1g} \rightarrow {}^1A_{2g}$ ($d_{xy} \rightarrow d_{x^2-y^2}$) transition in a square planar geometry [6].

Tetrahedral is the preferred structure of Zn(II), Cd(II) and Hg(II) complexes, although five- and six-coordinate complexes are also considered. Based on the analytical data (table 2) for the complexes of Zn(II), Cd(II) and Hg(II) **17** to **23** a tetrahedral structure is tentatively proposed [46, 47]. The free ligand H_2chbmth in DMSO shows absorption bands in the region 266, 310 and 370 nm due to the intra-ligand charge transfer transitions $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$, respectively. Most complexes exhibit some of these bands with slight shifting, indicating coordination of the ligand to the metal.

3.4. *^{1}H NMR spectra*

^{1}H NMR data of the free ligand H_2chbmth and some of the metal complexes in DMSO-d_6 with TMS as internal reference are tabulated in table 4. For H_2chbmth the chemical shift of –NH is found at 10.10 ppm and overlaps with the signal due to the proton of the –OH group. On this basis it is reasonable to assume that both NH and OH groups are involved in the formation of hydrogen bonds, as previously found [48, 49]. However, in the spectrum of [Zn(Hchbmthol)NH_3] (**19**) both –OH and –NH signals disappeared confirming their infrared spectroscopic evidence (see later discussion) that these protons are removed in complexation supporting the dibasic tridentate (NSO donor) nature of the ligand.

The proton on the carbon adjacent to =N is shifted from 8.56 ppm to 8.28–8.32 ppm region in the complexes. This is evidence that the nitrogen of the HC=N– group is coordinated. The multiplets arising from the aromatic and morpholine ring protons between 6.88–7.80 ppm and 3.68–3.91 ppm remain almost unchanged (table 4) in the complexes [50].

In [Ni(Hchbmth)Cl] (**6**) and [Zn(Hchbmth)Cl] (**17**) a broad signal at 9.8 ppm indicates the presence of an NH group suggesting monobasic tridentate nature.

3.5. *Infrared spectra*

Infrared spectra of the ligands and the metal complexes have been recorded in KBr. Important IR data and tentative assignments are given in table 5.

The thiohydrazone ligand (I) shows no band in the region ca 2570 cm^{-1} for ν(SH) group [51]; instead an intense band at 770 cm^{-1} for ν(C=S) is observed suggesting that in the solid state the ligand remains in the thioketo form. However, in solution, both the thioketo (I) and thiolo (Ia) tautomeric forms may remain in equilibrium [42, 53] (figure 1).

The free ligand show bands due to ν(NH) in the region 3200–2900 cm^{-1}. But the ν(OH) band at 3500 cm^{-1} is not observed perhaps due to strong hydrogen bonding, shifting ν(OH) to lower frequency. The bands due to ν(OH/NH) are shifted or disappear in most complexes indicating coordination of the oxygen after deprotonation. The presence of H_2O and NH_3 in **3**, **8**, **10**, **15**, **16**, **19**, **20**, **21**, **22** and **25** and free OH and COOH groups make interpretation very difficult. The C=N stretching vibration of the free ligand occurs [54, 55] at 1630 cm^{-1} but on complexation this band, in almost all the complexes, is shifted to the lower frequency suggesting that the ligand is coordinated to the metal via the azomethine nitrogen [56]. This lowering of the C=N stretch on complexation may be attributed to a lowering of the C=N bond order as a result of the M–N bond formation [57], evident from the appearance of new ν(M–N) bands in the far infrared region.

The free ligand possesses potential thioamide groups and therefore displays characteristic thioamide bands I to IV in the region 1560–770 cm^{-1}. The thioamide bands of the free ligand are located at 1560, 1440, 1305 and 770 cm^{-1} and these are affected appreciably in the metal complexes [58–60]. The thioamide band IV, mainly due to ν(C=S) either disappeared or shifted to lower frequency in most of the metal complexes indicating coordination of sulfur (thione S and/or thiol S after deprotonation) to the metal ion [61–63]; new M–S bands also appear in the far infrared region.

Table 5. Some important infrared bands of the ligand and some of the complexes with their tentative assignments

	Frequencies (cm^{-1})				
Complex	C=S/C–S	C=N	M–N + M–O	M–S	M–Cl
H_2chbmth	770	1630	–	–	–
[Cu(H_2chbmthol)Cl] (**1**)	756	1603	448, 412, 396	337	276
[Co(H_2chbmthol)Cl]2H_2O (**10**)	766	1605	452, 415, 382	292, 340	248
[Co(H_3chbmthol)]SO_4 (**13**)	762	1596	445, 398, 388	342, 300	–
[Zn(H_2chbmthol)CH_3COO] (**18**)	750	1590	448, 430, 390	350, 332	–
[Cd(Hchbmthol)H_2O] (**20**)	750	1605	452, 430, 386	345	–
[Cd(Hchbmthol)NH_3] (**22**)	752	1601	450, 425, 390	355	–
[Hg(Hchbmthol)NH_3] (**25**)	755	1600	458, 416, 395	362	–

In complexes **1** to **4**, **6**, **7**, **10**, **12**, **14**, **17**, **18**, **23** and **24** the thioamide band ν(C=S) shifted to lower frequency by 10–20 cm^{-1} and the ν(OH) band disappeared, suggesting coordination through the thioketo sulfur and phenolic oxygen via deprotonation. The ν(C=N) stretching mode is lowered by about 30 cm^{-1}. Thus in these complexes the ligand is monobasic tridentate, bonding through thioketo sulfur, azomethine nitrogen and phenolic oxygen. In complexes **5**, **8**, **15**, **16**, **19**, **20**, **22** and **25** both the phenolic OH and thioamide band IV disappeared, and a new band due to ν(C–S) is observed around 740–700 cm^{-1} suggesting coordination through thiol sulfur and phenolic oxygen. The ν(C=N) stretching mode is also lowered by about 30 cm^{-1}. Thus in these complexes the ligand is dibasic tridentate bonding through O, N and S. In complexes **3**, **8**, **10**, **15**, **16**, **20** and **21** the presence of water makes the interpretation very difficult.

The phenolic ν(C–O) frequency occurs at ca 1530 cm^{-1} in the infrared spectra of mononuclear complexes of salicylaldehyde Schiff bases [64, 65], whereas, the spectra of bi- and tri-nuclear phenolic oxo-bridged complexes have ν(C–O) within the range 1545–1550 cm^{-1} [66]. The C–O stretching frequency for **5** occurs at 1555 cm^{-1} indicating that bridging occurs through phenolic oxygen atoms after deprotonation. The coordination of NH_3 in complexes **19** and **22** are indicated by bands at 3300–3100, 1585, 1250 and 870 cm^{-1} assignable to $\nu(NH_3)$, $\delta_d(NH_3)$, $\delta_s(NH_3)$ and $\rho_r(NH_3)$, respectively [67–69]. The complexes **4**, **14**, **18** and **24** show bands in the region 1640–1610 and 1320–1310 cm^{-1} which may tentatively be assigned to coordinated acetate [70]. However, the presence of $\nu_{C=N}$ and thioamide band III make the interpretation difficult. Complexes **8**, **10**, **20** and **21** show broad bands in the region 3600–3240 cm^{-1}, which are assignable to OH stretching vibrations from water.

Complex **11** shows bands at 1380 and 860 cm^{-1} demonstrating the presence of nitrate [71]; the band at 860 cm^{-1} may be mixed with the thioamide band (IV) ν(C=S) [62]. Therefore, this assignment is tentative. Complex **21** shows bands in the region 1100, 990–970 and 600 cm^{-1} due to the presence of SO_4^{2-} [72].

All complexes show broad medium bands in the region 3620–2980 cm^{-1}, assignable to free carboxyl [73, 74]. This assignment is tentative for **3**, **8**, **10**, **19**, **20**–**22** and **25** because the presence of H_2O or NH_3 molecule makes interpretation difficult.

The bands at 1210–1200 [ν(CO)], 1250–1240 [ν(CN)] and 1105 and 920–895 cm^{-1} (out of plane and inplane deformation) of the morpholine ring moiety are not affected appreciably in the metal complexes, indicating that the morpholine ring oxygen and nitrogen are not involved in coordination [75, 76].

All complexes display a number of bands in the far infrared region 460–410, 400–380, 360–320 and 300–230 cm^{-1} which are tentatively assigned to M–O, M–N, M–S and M–Cl stretching vibrations [30, 77, 78].

4. Conclusion

A new thiohydrazone ligand, 3-carboxy-2-hydroxybenzaldehydemorpholine N-thiohydrazone (H_2chbmth) has been synthesized and characterized. In solution the 'thione' form of the ligand (H_2chbmth) remains in equilibrium with its 'thiol' form (H_3chbmthol). Depending on the reactions conditions the ligand is monobasic tridentate, dibasic tridentate, monobasic bidentate or neutral bidentate. [Cu(Hchbmthol)]$_2$ (**5**) shows antiferromagnetic interactions between the two copper(II) centers.

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