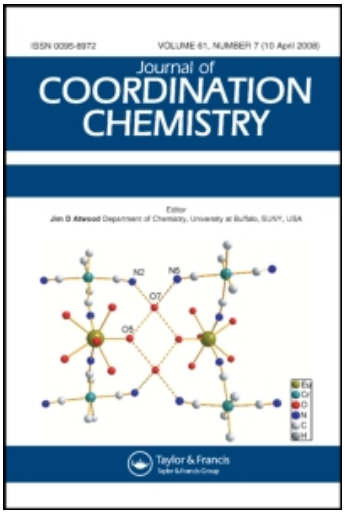

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Synthesis, magnetic and spectral studies of chromium(III), manganese(III), iron(III) and cobalt(III) complexes of thiosemicarbazones derived from benzil α-monoxime and unsubstituted/substituted thiosemicarbazides as biological agents

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Cr(III), Mn(III), Fe(III) and Co(III) complexes of thiosemicarbazones, derived from benzil α-monoxime and thiosemicarbazides ($BMTH_2$), benzil α-monoxime and phenyl thiosemicarbazides ($BMPTH_2$), benzil α-monoxime and 4-bromophenyl thiosemicarbazides ($BMBTH_2$), benzil α-monoxime and 4-chlorophenyl thiosemicarbazides ($BMCTH_2$) and benzil α-monoxime and 4-nitrophenyl thiosemicarbazides ($BMNTH_2$), have been prepared. These complexes have been characterized by elemental analyses, magnetic susceptibilities, molar conductance measurements, electronic, IR, ^1H and ^{13}C NMR spectra (in the case of Co(III) complexes), FAB mass spectra and thermogravimetric analysis to arrive at the geometry of the ligand environment around the metal ion and to elucidate the bonding sites of the ligands with the central metal. The complexes contain two monoprotonic tridentate ligands with NNS donor sites. Coordination to metal ion the oxime nitrogen, imine nitrogen and thione sulfur is confirmed in the complexes by IR spectral studies. The antifungal and antibacterial activities of the ligands and complexes have been screened.

Keywords: Thiosemicarbazones; Mononuclear complexes; Spectral; Biological activity

1. Introduction

Thiosemicarbazones and their metal complexes are of considerable interest because of their potentially beneficial pharmacological properties and wide variation in their modes of bonding and stereochemistry [1–12]. The impetus for developing coordination chemistry of thiosemicarbazone ligands was provided by the carcinostatic potency, antitumour [13], antibacterial [14], antiviral [15], antifungal [16], antimalarial [17], antiamoebic [18] and other biological properties observed for some derivatives. It is

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generally accepted that the pharmacological activity of thiosemicarbazones is related to their ability to form stable complexes with transition metal ions present in trace amounts in living organisms [19, 20]. Thiosemicarbazone ligands derived from benzil α-monoxime, contain both oxime and thione moieties and therefore may lead to interesting structural and functional properties.

2. Experimental

All chemicals and solvents used were of analytical grade. Benzil α-monoxime and substituted thiosemicarbazides were prepared following the methods reported [21, 22]. Thiosemicarbazones were prepared by mixing equimolar amounts of benzil α-monoxime and the desired thiosemicarbazides in EtOH, adding 1% HCl–EtOH and stirring, as described previously [23]. The elemental analyses were obtained from the Microanalytical Laboratory of CDRI, Lucknow, India. Metals and chlorides were determined volumetrically and gravimetrically [21]. Electronic spectra were recorded using chloroform solutions in 1 cm cells with a Perkin-Elmer Lambda 15 UV/Vis spectrophotometer. IR spectra were scanned as KBr pellets on a Perkin-Elmer PC-16F FTIR spectrophotometer in the 4000–350 cm^{-1} region. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX 300 spectrometer using deuterated dimethyl sulfoxide (DMSO-d_6) as the solvent and TMS as internal reference. Magnetic susceptibility measurements were carried out at room temperature by Gouy's balance using $CuSO_4 \cdot 5H_2O$ as a calibrant. Conductivity measurements were made using a Systronic Conductivity Meter with a dip type cell, using approximately 10^{-3} M solution of the complexes in ethanol. Molecular FAB mass spectra were obtained on a JEOL SX 102/DA-6000 mass spectrometer using *m*-nitrobenzyl alcohol as a matrix. The thermogravimetric data were obtained in air at 10°C min^{-1} in the 25–750°C range using a Shimadzu TGA-50 analyzer.

2.1. *Preparation of the complexes*

The complexes were prepared using the following general procedures:

2.1.1. $[M(LH)_2]X \cdot 3H_2O$ (M = Cr, Mn or Fe; X = Cl or OAc). The complexes were prepared by reacting 1 : 2 metal to ligand molar ratios. A magnetically stirred, freshly prepared 0.005 mol methanolic solution (30 cm^3) each of $CrCl_3 \cdot 6H_2O$ (1.33 g), $Mn(OAc)_3 \cdot 2H_2O$ [24] (1.34 g) or $FeCl_3 \cdot 6H_2O$ (1.35 g) was added dropwise to a solution of 0.01 mole each of $BMTH_2$ (2.98 g), $BMPTH_2$ (3.74 g), $BMBPTH_2$ (4.53 g), $BMCPTH_2$ (4.08 g) and $BMNPTH_2$ (4.19 g) in methanol (20 cm^3) over a period of 20 min. The color of the solution changed from green or brown to dark brown. Stirring was continued at 30°C for 6–8 h. The dark brown precipitate was filtered off, washed with ethanol (2×5 cm^3), chilled water (2×5 cm^3) and finally with diethyl ether and dried *in vacuo*.

2.1.2. $[Co(LH)_2]Cl \cdot 3H_2O$. These complexes were prepared by similar procedure. After addition of ligands to $CoCl_2 \cdot 6H_2O$ (1.18 g), H_2O_2 (30%, 0.01 mol) was added slowly, the color of the solution changed to black or brown. Stirring was continued at 35°C for 10 h. The brown or black precipitate was filtered off, washed with ethanol ($2 \times 5\,cm^3$), chilled water ($2 \times 5\,cm^3$) and finally with diethyl ether and dried *in vacuo*.

2.1.3. Purification of $[M(LH)_2]X \cdot 3H_2O$ (M = Cr, Mn, Fe or Co; X = Cl or OAc). The complexes were purified by placing on a column in a minimum of MeOH (1 : 2) (ca $100\,cm^3$). $EtOH/H_2O$ was passed through the column eluting the product. The complexes were efficiently recovered by reducing the volume under *vacuo*. The columns used were 2 cm inner diameter, packed with 10 cm of neutral alumina (Acros).

2.2. *Biological screening*

The Cr(III), Mn(III), Fe(III) and Co(III) complexes together with $BMTH_2$, $BMPTH_2$, $BMBPTH_2$, $BMCPTH_2$ and $BMNPTH_2$ were tested for *in vitro* growth inhibitory activity against various pathogenic fungi and bacteria. Proper temperature, necessary nutrients and growth medium free from other microorganisms were employed for the preparation of the cultures of fungi and bacteria by using aseptic technique [25]. The biological activity of the compounds was evaluated in three replicates.

2.2.1. Antifungal screening. The antifungal activities were evaluated against *Aspergillus niger* and *Fusarium udum* by the agar plate diffusion technique [20]. Cultures of the test fungi were prepared in a potato dextrose agar (PDA) medium and were purified by single spore isolation technique [26]. The thiosemicarbazones and metal complexes were dissolved in 50, 100 and 200 ppm concentrations in MeOH and then mixed with the PDA medium (glucose, starch, agar-agar and H_2O). Untreated aseptic PDA medium served as control. The media were poured into sterilized Petri dishes. After solidification, 5 mm discs of five-day-old fungi were transferred to the center of the plate. The plates were incubated at 27 ± 1°C. The radial growth of fungi was measured at 12 h intervals from 36 h after inoculation. The percentage inhibition was calculated as $100(C - T)/C$, where C and T are the diameters of the fungi colony in the control (an untreated plate) and test plates, respectively.

2.2.2. Antibacterial screening. The antibacterial activities were evaluated against *Escherichia coli* (−) and *Staphylococcus aureus* (+) by the paper disc plate method [27]. The nutrient agar media (peptone, beef extract, NaCl, agar–agar and H_2O) and 5 mm diameter paper discs (Whatman No. 1) were used. The compounds were dissolved in methanol in 100 and 500 ppm concentrations. The filter paper discs were soaked in different solutions of the compounds, dried and then placed in the petri dishes previously seeded with the test organism. The plates were incubated for 24–30 h at 28 ± 2°C. The zone of inhibition thus formed around each disc containing the test compound was measured accurately in mm.

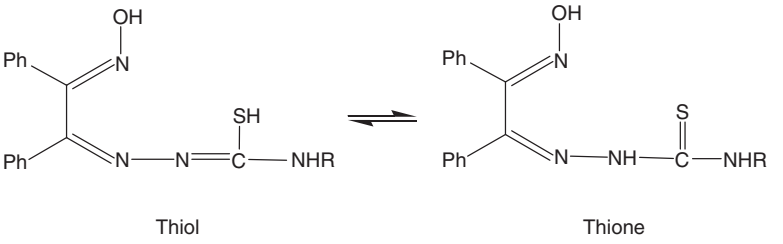

Figure 1. Thiol–thione tautomeric forms of ligand, R = H($BMTH_2$); C_6H_5($BMPTH_2$); 4-BrC_6H_4 ($BMBPTH_2$); 4-ClC_6H_4($BMCPTH_2$); 4-$O_2NC_6H_4$($BMNPTH_2$).

3. Results and discussion

The condensation of benzil α-monoxime with unsubstituted/substituted thiosemicarbazides in the ethanol gives the ligands (figure 1).

The complexes are microcrystalline powders varying from light to dark brown or black and they are all stable to air and moisture. Complexes are soluble in coordinating as well as noncoordinating solvents. Conductance measurements in ethanol indicate the complexes are 1 : 1 electrolytes (table 1).

3.1. *Magnetic moment studies*

Magnetic susceptibility studies were performed on powdered samples of all the complexes at room temperature (table 1). The effective magnetic moment (μ_{eff}) of chromium(III) complexes are 3.92–3.96 μ_B at room temperature, in good agreement with three unpaired electrons [28]. Manganese(III) complexes magnetic moments lie in the range 4.5–4.9 μ_B at room temperature. These values are compatible with a high spin manganese(III) $S_{Mn} = 2$ calculated assuming $g_{Mn} = 2.0$. For all compounds the μ_{eff} values observed are in excellent agreement with the spin-only moment (4.9 μ_B) for a high spin d^4 ($S = 2$) configuration normally observed for manganese(III) complexes [29]. The effective moment, μ_{eff} for iron(III) complexes is 5.2 μ_B at room temperature, a little less than the values expected for high spin (5.9 μ_B). This is attributed to significant antiferromagnetic coupling through the Fe–N coordination bond [30]. Cobalt(III) complexes are diamagnetic which indicate an octahedron around the metal ion producing a strong field [31].

3.2. *Electronic spectra*

The majority of the chromium(III) complexes exhibit d–d transitions typically observed for pseudo-octahedral chromium in the oxidation state +3, two broad bands with maxima at 33,600 and 25,200 cm^{-1}, assigned to charge transfer bands. The visible absorption spectra of $[Cr(LH)_2]Cl \cdot 3H_2O$ show a comparatively weak band in the region 32,260–32,700 and a strong broad absorption band in the region 25,000–25,630 cm^{-1}. These transitions may be assigned to charge transfer and $^4A_{2g} \rightarrow {}^4T_{1g}$ (P) transitions, respectively. These complexes also show a weak band with a maximum at 17,000 cm^{-1}, due to $^4A_{2g} \rightarrow {}^4T_{1g}$ (F), probably overlapped with

Table 1. Elemental analyses and some physical properties of the thiosemicarbazone complexes.

Compound	No.	Mol. Wt. found (Calcd)	Color	Yield (%)	Analysis found (Calcd)% C	H	N	S	Cl/Br	M	Molar conductance (Ω^{-1} cm^2 mol^{-1})	μ_B
$[Cr(BMTH)_2]Cl \cdot 3H_2O$	**1**	736 (736)	Green	60	48.6 (48.9)	4.2 (4.3)	15.1 (15.2)	8.7 (8.7)	4.9 (4.8)	7.1 (7.0)	90	4.01
$[Cr(BMPTH)_2]Cl \cdot 3H_2O$	**2**	886 (887)	Light brown	50	56.9 (56.8)	4.4 (4.5)	12.6 (12.6)	7.3 (7.2)	3.9 (3.9)	5.6 (5.8)	68	3.91
$[Cr(BMBPTH)_2]Cl \cdot 3H_2O$	**3**	1046 (1046)	Brown	50	48.1 (48.2)	3.8 (3.6)	10.9 (10.7)	6.0 (6.1)	3.0/15.2 (3.3)/(15.2)	4.8 (4.9)	90	3.92
$[Cr(BMCPTH)_2]Cl \cdot 3H_2O$	**4**	956 (957)	Light brown	60	52.9 (52.7)	4.2 (4.0)	11.5 (11.7)	6.6 (6.7)	11.2 (11.1)	5.5 (5.4)	84	4.01
$[Cr(BMNPTH)_2]Cl \cdot 3H_2O$	**5**	978 (978)	Greenish brown	50	51.6 (51.6)	3.8 (3.9)	14.2 (14.3)	6.6 (6.5)	3.8 (3.6)	5.5 (5.3)	121	3.98
$[Mn(BMTH)_2](OAc) \cdot 3H_2O$	**6**	816 (816)	Brown	50	47.2 (47.0)	5.1 (5.0)	13.6 (13.7)	7.8 (7.8)	–	6.6 (6.7)	97	4.90
$[Mn(BMPTH)_2](OAc) \cdot 3H_2O$	**7**	966 (968)	Light brown	55	54.6 (54.5)	5.2 (5.1)	11.5 (11.5)	6.8 (6.6)	–	5.7 (5.6)	89	4.51
$[Mn(BMBPTH)_2](OAc) \cdot 3H_2O$	**8**	1126 (1126)	Coffee	45	46.6 (46.9)	4.4 (4.2)	9.8 (9.9)	5.5 (5.6)	–/14.0 –/(14.1)	4.6 (4.8)	111	4.62
$[Mn(BMCPTH)_2](OAc) \cdot 3H_2O$	**9**	1038 (1037)	Light brown	65	50.6 (50.9)	4.5 (4.5)	10.6 (10.8)	6.1 (6.1)	6.8 (6.8)	5.1 (5.2)	126	4.92
$[Mn(BMNPTH)_2](OAc) \cdot 3H_2O$	**10**	1058 (1058)	Dark brown	50	49.8 (49.9)	4.4 (4.4)	13.1 (13.2)	6.1 (6.0)	–	5.0 (5.1)	90	4.83
$[Fe(BMTH)_2]Cl \cdot 3H_2O$	**11**	740 (740)	Light brown	55	48.7 (48.6)	4.5 (4.3)	15.0 (15.1)	8.5 (8.6)	4.6 (4.7)	7.4 (7.5)	89	5.20
$[Fe(BMPTH)_2]Cl \cdot 3H_2O$	**12**	890 (891)	Brown	60	56.4 (56.5)	4.3 (4.5)	12.5 (12.5)	7.0 (7.1)	3.8 (3.9)	6.3 (6.2)	86	5.32
$Fe(BMBPTH)_2]Cl \cdot 3H_2O$	**13**	1050 (1050)	Brown	55	48.1 (48.0)	3.3 (3.6)	10.5 (10.6)	6.2 (6.1)	3.1/15.1 (3.3)/(15.2)	5.5 (5.3)	110	5.26
$Fe(BMCPTH)_2]Cl \cdot 3H_2O$	**14**	962 (961)	Dark brown	70	52.3 (52.4)	3.8 (3.9)	11.6 (11.6)	6.5 (6.6)	11.1 (11.0)	5.6 (5.8)	114	5.33

(*Continued*)

Table 1. Continued.

Compound	No.	Mol. Wt. found (Calcd)	Color	Yield (%)	Analysis found (Calcd)% C	H	N	S	Cl/Br	M	Molar conductance ($\Omega^{-1}cm^2mol^{-1}$)	μ_B
$[Fe(BMNPTH)_2]Cl \cdot 3H_2O$	**15**	982 (982)	Brown	50	51.2 (51.3)	3.6 (3.9)	14.1 (14.2)	6.3 (6.5)	3.8 (3.6)	5.5 (5.6)	112	5.27
$[Co(BMTH)_2]Cl \cdot 3H_2O$	**16**	742 (742)	Black	50	48.5 (48.5)	4.5 (4.3)	15.1 (15.1)	8.5 (8.6)	4.6 (4.7)	7.8 (7.9)	96	Dia.
$[Co(BMPTH)_2]Cl \cdot 3H_2O$	**17**	896 (895)	Brown	50	56.2 (56.3)	4.5 (4.5)	12.2 (12.5)	7.0 (7.1)	3.8 (3.9)	6.3 (6.5)	78	Dia.
$[Co(BMBPTH)_2]Cl \cdot 3H_2O$	**18**	1052 (1053)	Black	50	47.8 (47.9)	3.2 (3.6)	10.3 (10.6)	6.2 (6.0)	3.2/15.2 (3.3)/(15.1)	5.8 (5.6)	81	Dia.
$[Co(BMCPTH)_2]Cl \cdot 3H_2O$	**19**	964 (964)	Dark brown	55	52.1 (52.3)	3.8 (3.9)	11.7 (11.6)	6.8 (6.6)	11.1 (11.0)	6.2 (6.1)	110	Dia.
$[Co(BMNPTH)_2]Cl \cdot 3H_2O$	**20**	986 (985)	Golden brown	60	51.3 (51.2)	3.8 (3.8)	14.1 (14.2)	6.6 (6.5)	3.8 (3.6)	5.8 (5.9)	90	Dia.

$^4A_{2g} \rightarrow {}^4T_{2g}$ (F) of chromium(III) complexes [32]. Electronic spectra in the visible region of the manganese(III) complexes show two regions of absorption near 13,890–13,010 cm^{-1} and 22,220–16,660 cm^{-1}, each associated with high molar absorptivity ($\varepsilon = 1100$–$3950\ dm^3\ mol^{-1}\ cm^{-1}$). Since the thiosemicarbazone ligands are not expected to be chromophoric in this range, these spectral features may be ligand to metal charge transfer, probably originating from $S(\pi) \rightarrow$ Mn(III) electronic transitions. These strong charge transfer bands probably obscure the weak, spin allowed d–d transitions which are normally expected to show up in this region for Mn(III)*bis*(monodentate ligand) complexes [33]. The iron(III) complexes exhibit moderately intense absorbance at 26,280–25,200 cm^{-1}, accompanied by an intense band (Q band) [34] and can be assigned to intraligand transitions. In the 25,000–18,181 cm^{-1} region d–d bands are not found for most iron(III) complexes because of the greater oxidizing power of iron(III). Ligand to metal charge transfer bands often appear in the visible region and obscure the very low intensity d–d bands. For cobalt(III) complexes some assignments indicative of octahedral geometry can be made. The spectra of the cobalt complexes show two bands in the 17,000–18,000 and 24,300–24,700 cm^{-1} ranges, as expected for low spin six-coordinated cobalt(III) complexes [35]. The first band can be assigned to a $^1A_{1g} \rightarrow {}^1T_{1g}$ transition and the other to a $^1A_{1g} \rightarrow {}^1T_{2g}$ transition.

3.3. *IR spectra*

The assignments of the infrared bands useful for establishing the coordination for thiosemicarbazones in their chromium(III), manganese(III), iron(III) and cobalt(III) complexes are compiled in table 2. Although the thiosemicarbazones can exhibit thione $\rightleftharpoons$ thiol tautomerism due to the presence of a thioamide –NH–C=S functionality, the absence of the ν(S–H) band near 2560 cm^{-1} indicates that it exists as the thione form in the solid state [36]. The presence of a band at ca 3360 cm^{-1} is assignable to ν(OH) stretching frequency. A broad band in the region 3160–3295 cm^{-1} arising from overlap of the stretching vibrations of lattice water molecules with ν(N–H) of ligands are observed in almost all of the complexes [37]. It has been further observed that imine nitrogen ν(C=N) in the ligand at ca 1640 cm^{-1} is shifted to lower frequencies by 20–35 cm^{-1} upon metal coordination. In all these complexes the participation of ν(C=N) oxime moiety in complexation has been ascertained by a positive shift of 10–30 cm^{-1} of the ligand band around 1590 cm^{-1} due to ν(C=N) oxime [38, 39]. The strong band at 1050 cm^{-1} in the spectrum of thiosemicarbazones is due to ν(C=S) stretch which is red shifted by ca 30 cm^{-1} in the spectra of metal complexes, pointing to coordination through sulfur [40]. The band around 1000 cm^{-1} in all the free oximes, ν(N–O) shifts to lower frequency by 20–25 cm^{-1} in the spectra of complexes suggesting participation of the oxime oxygen in coordination [41, 42]. The other low frequency bands appearing in 480–500 cm^{-1} and 340–375 cm^{-1} in all these complexes can be attributed to ν(M–N) (azomethine) and ν(M–S), respectively [43, 44]. Thus, the infrared spectra reveal that thiosemicarbazone ligands are neutral tridentate, coordinating through N & N of two azomethine groups and S of thioketo.

Table 2. Important IR spectral bands (cm^{-1}) with assignment.

Complexes	ν(O–H) oxime	ν(N–H)	ν(C=N) imine	ν(C=N) oxime	ν(N–O)	ν(C=S)	ν (M–N)	ν(M–S)
$BMTH_2$	3340s	3240s, 3170s	1590s	1640s	1010s	1050s	–	–
$BMPTH_2$	3380s	3245s, 3165s	1586s	1645s	970s	1060m	–	–
$BMBPTH_2$	3370s	3240m, 3165m	1582s	1650s	990s	1052s	–	–
$BMCPTH_2$	3345s	3250s, 3160s	1590s	1642s	1000s	1055s	–	–
$BMNPTH_2$	3360s	3240m, 3170s	1580s	1643s	1000s	1059s	–	–
1	–	3240m, 3186m	1580m	1620m	890m	1020m	490m	340w
2	–	3290m, 3180m	1560m	1625m	920m	1030m	480m	370m
3	–	3290m, 3185m	1560m	1620m	890m	1026m	485m	375w
4	–	3240w, 3165m	1575m	1615m	940m	1022m	500m	370w
5	–	3245m, 3180w	1560m	1625m	900m	1030m	490m	345w
6	–	3290w, 3185w	1582m	1622m	890m	1025w	490m	360m
7	–	3294w, 3180m	1576m	1630m	890m	1030w	485m	365m
8	–	3295w, 3170m	1572m	1639m	890m	1032m	500m	360m
9	–	3280w, 3185m	1570m	1626m	900m	1022m	495m	363m
10	–	3285w, 3160m	1560m	1628m	900m	1022w	480m	370w
11	–	3295w, 3160w	1582m	1630m	910m	1020w	500w	375w
12	–	3285w, 3170w	1580m	1635m	915m	1020w	500m	350w
13	–	3285w, 3180w	1570m	1620m	885m	1026m	490m	355m
14	–	3270m,3180m	1572m	1628m	889m	1030w	480m	360m
15	–	3245m, 3190w	1565m	1622m	900m	1027m	490m	355w
16	–	3290m, 3180w	1570m	1630m	905m	1030m	485m	370w
17	–	3295m, 3180w	1562m	1635m	890m	1020m	495m	375m
18	–	3280m, 3180w	1576m	1622m	890m	1025m	490m	360w
19	–	3240m, 3170w	1572m	1629m	900m	1026m	490m	350w
20	–	3280m, 3160w	1565m	1621m	910m	1030m	500m	370w

3.4. *^{1}H NMR spectra*

The proton magnetic resonance spectra of ligands and their cobalt(III) complexes recorded in d^6-DMSO are summarized in table 3. Comparing the spectra of these ligands and their complexes leads to the following conclusions:

(a) The signals due to (N–H) protons of thione form of ligand at δ 9.61–9.73, shift downfield for all cobalt(III) complexes indicating coordination via amide form of the ligand.
(b) A signal due to (O–H) proton of oxime moiety of the ligand at δ 10.01–10.13 disappears in the spectra of corresponding metal complexes indicating deprotonation of oxime.
(c) In addition, prominent signals due to phenyl rings at δ 7.23–8.10, NHR at δ 4.90–5.20 and CH at δ 6.21–6.40 can be seen almost at the same position in ligands and complexes.

3.5. *^{13}C NMR spectra*

The ^{13}C NMR spectra of ligands and their corresponding cobalt(III) complexes were recorded in DMSO (table 3). The aromatic carbon signals have been observed in the range δ 127–154 ppm. A considerable shift takes place in the position of thione carbon C=S (ca 178 ppm, ligands) and azomethine carbon C=N (ca 157 ppm, ligands) indicating coordination through thione sulfur and azomethine nitrogen in the cobalt(III) complexes, as compared with their respective ligands $BMTH_2$, $BMPTH_2$,

Table 3. ^{1}H and ^{13}C NMR spectral data (δ, ppm) of thiosemicarbazones and their cobalt(III) complexes.

	^{1}H NMR				^{13}C NMR		
Compounds	–OH (oxime)	–NH (imine)	Phenyl ring	–NHR	>C=S	>C=N	Aromatic ring
$BMTH_2$	10.11s	9.72s	7.71m	4.90s	178.6	157.2	153.6–127.8
$BMPTH_2$	10.01s	9.61s	7.73m	4.91s	179.2	161.2	153.5–129.6
$BMBPTH_2$	10.12s	9.70s	7.23m	5.03s	179.5	160.5	154.2–128.3
$BMCPTH_2$	10.13s	9.72s	7.45m	5.20s	178.2	158.2	153.2–129.8
$BMNPTH_2$	10.11s	9.73s	7.62m	4.93s	179.8	159.3	154.2–127.6
16	–	9.99s	8.02m	4.61s	170.2	151.2	153.8–129.8
17	–	9.89s	7.99m	4.63s	172.3	154.3	153.6–128.7
18	–	9.88s	8.10m	4.75s	171.5	152.5	154.0–129.3
19	–	9.99s	7.89m	4.65s	172.5	154.3	153.5–129.7
20	–	9.87s	7.92m	4.69s	171.8	153.4	154.0–128.8

$BMBPTH_2$, $BMCPTH_2$ and $BMNPTH_2$, lends further support to the proposed coordination in these complexes.

3.6. *Thermal analysis*

A TGA study reveals the presence of chloride and water molecules outside the coordination sphere. In all complexes of chromium(III), manganese(III), iron(III) and cobalt(III) metals with thiosemicarbazones of benzil α-monoxime and unsubstituted or N(4) substituted thiosemicarbazides the thermogram extends up to 110–115°C for elimination of lattice water and thereafter they register a weight loss due to release of chloride ion at 200–215°C. After 450°C these complexes start to decompose and a mass loss of 38–42% up to 480–496°C corresponds to loss of one ligand. At the end of mass loss, 560–570°C, stable metallic oxides of chromium(III), iron(III) and cobalt(III) are found. The manganese compounds give stable oxides at 520°C. The high mass of the residue is attributed to carbonaceous matter. Thus, the decomposition pattern obtained from TGA confirms the proposed formulation of the complexes.

3.7. *FAB mass spectra*

The ligands $BMTH_2$, $BMPTH_2$, $BMBPTH_2$, $BMCPTH_2$ and $BMNPTH_2$ show the molecular ion at $m/z = 298$, 374, 453, 408 and 419, respectively. Other important peaks were due to release of $[M–(RCSNH)]^+$, $[M–(RCSNHOH)]^+$, $[M–(RCSNH_2N_2OH)]^+$, $[M–(RCSNHOHN_3H_2C_2H_2)]^+$. The fragmentation pattern of $BMPTH_2$ is shown in figure 2.

Using a positive accelerating voltage, the molecular ion of the octahedral chromium(III) $[Cr(BMPTH)_2]Cl \cdot 3H_2O$ is observed at $m/z = 736$. The next most intense peak in the positive ion spectra of the complexes results from the loss of one thiosemicarbazone ligand. Other peaks were due to release of $[Ph_2C_2N_2O]$, [PhCNO] and (NH) (figure 3). The manganese complexes behave similarly but their peaks are shifted 3 amu higher by substitution of chromium by manganese. The peaks of iron(III) complexes show shifting from the chromium complexes by 4 amu. The cobalt complexes are shifted to 7 amu higher than the peaks of chromium complexes.

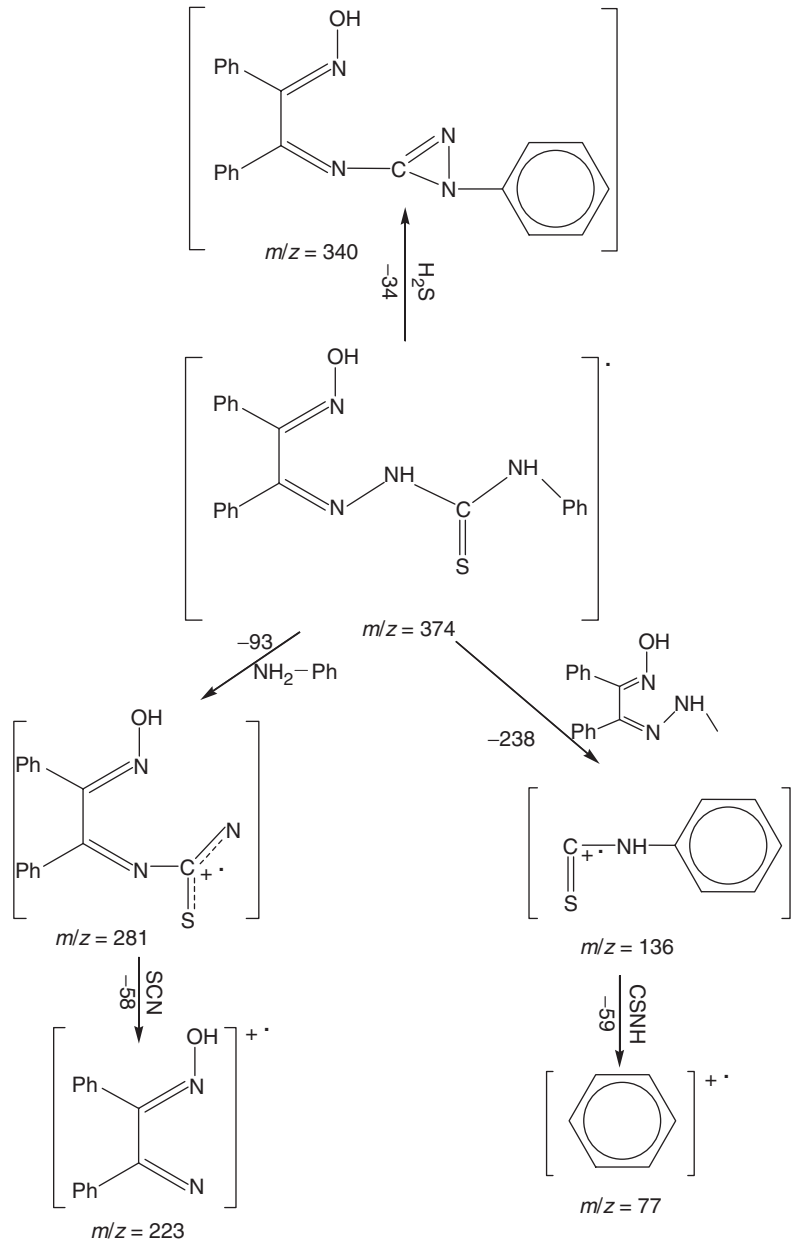

Figure 2. Fragmentation pattern of $BMPTH_2$.

3.8. *Biological activity*

The results of biological screening have been compared with the conventional fungicide ridomil and the conventional bactericide streptomycin, taken as standard in each case. It is evident that although the thiosemicarbazones alone were quite toxic, their activity increased upon complexation (table 4). The concentration plays a vital role in increasing

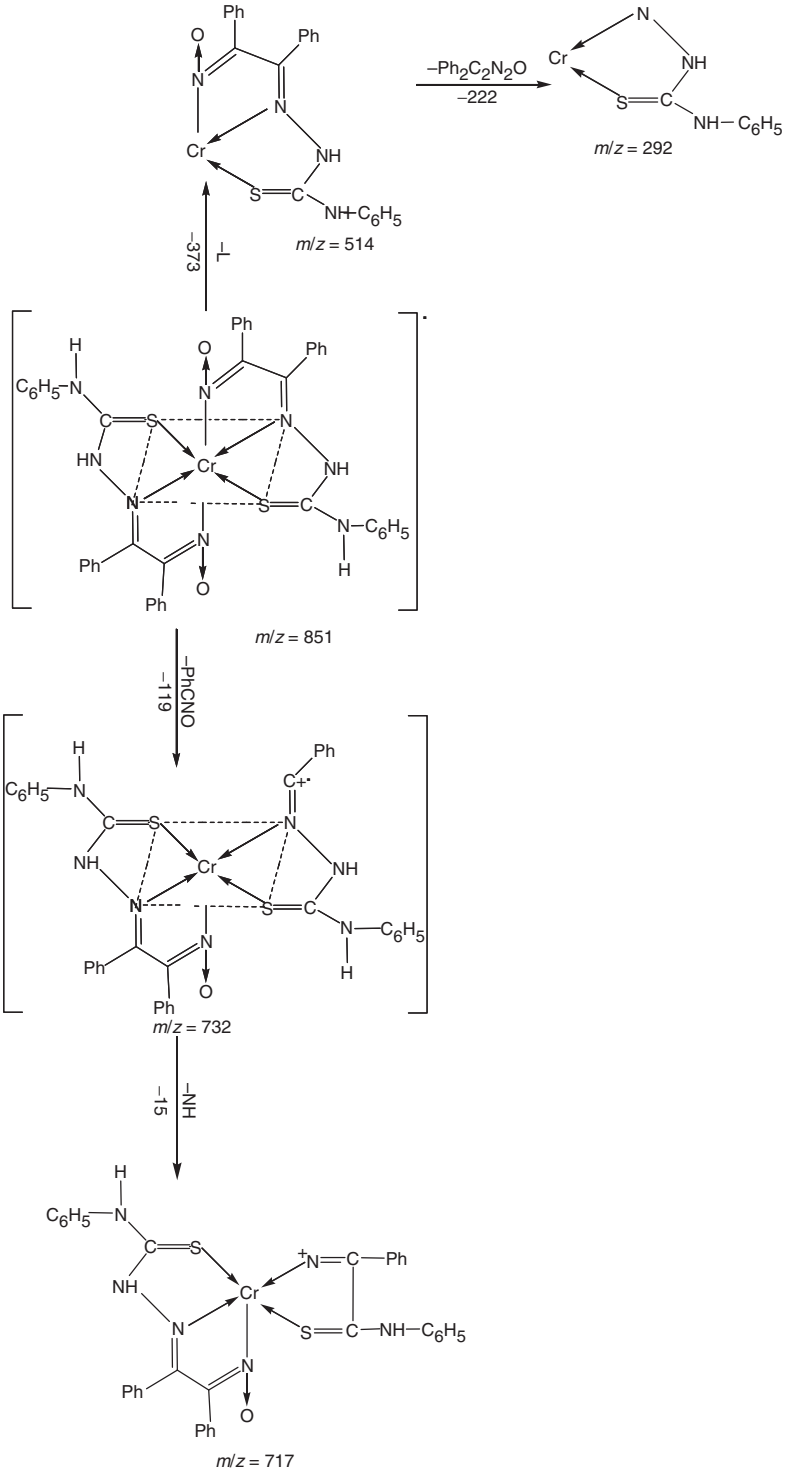

Figure 3. Fragmentation pattern of $[Cr(BMPTH)_2]Cl \cdot 3H_2O$.

Table 4. Antifungal and antibacterial activities of the ligands and its complexes.

	Antifungal activity % inhibition zone ($\mu g\,mL^{-1}$)						Antibacterial activity diameter of inhibition zone (mm)			
	A. niger			*F. udum*			*E coli* (gram −ve)		*S. aureus* (gram +ve)	
Compounds	50 ppm	100 ppm	200 ppm	50 ppm	100 ppm	200 ppm	500 ppm	1000 ppm	500 ppm	1000 ppm
Standard[a]	90	100	100	88	100	100	17	18	15	17
$BMTH_2$	12	16	25	18	21	30	04	06	05	07
$BMPTH_2$	18	21	29	20	25	32	02	03	02	03
$BMBPTH_2$	22	26	31	20	24	33	03	04	06	06
$BMCPTH_2$	24	27	33	24	27	35	03	05	04	06
$BMNPTH_2$	25	28	35	24	26	38	04	05	04	07
1	69	72	79	68	71	78	07	10	08	10
2	72	75	81	68	72	79	06	11	07	11
3	76	81	85	72	76	83	07	10	08	10
4	80	84	88	80	81	86	06	11	07	12
5	81	87	90	80	87	91	07	11	07	12
6	70	78	80	68	76	82	08	12	08	11
7	76	80	84	77	80	85	08	10	07	09
8	79	84	88	77	86	90	07	11	06	10
9	79	81	90	72	78	88	07	12	07	11
10	82	89	93	80	85	89	08	13	09	13
11	67	70	75	68	70	77	05	09	06	10
12	70	73	78	71	73	75	07	10	06	10
13	75	79	83	75	79	88	06	11	07	11
14	78	80	86	80	84	88	07	12	06	10
15	81	84	90	80	86	93	05	11	06	10
16	75	81	90	81	90	92	10	12	10	14
17	78	87	92	80	90	94	13	14	11	12
18	79	89	95	79	91	96	12	13	10	11
19	80	91	96	83	94	97	13	14	10	12
20	82	90	98	80	91	98	12	15	12	14

The result for each concentration is an average of the three replicates.
[a]Redomil for antifungal screening and streptomycin for antibacterial screening.

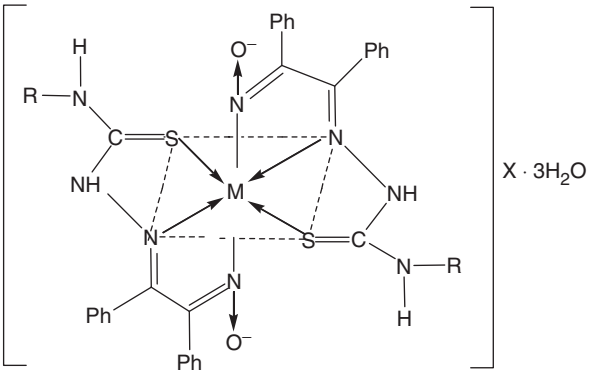

Figure 4. Octahedral structures of the metal complexes, R = H($BMTH_2$); C_6H_5($BMPTH_2$); 4-BrC_6H_4($BMBPTH_2$); 4-ClC_6H_4($BMCPTH_2$); 4-$O_2NC_6H_4$($BMNPTH_2$); M = Cr(III), Mn(III), Fe(III) or Co(III); X = Cl or OAc.

the degree of inhibition. It is clear from the data that thiosemicarbazones show less inhibitory effect for fungal and bacteria than the metal complexes. The Co(III) and Mn(III) complexes show very good activity and Cr(III) and Fe(III) complexes show slightly less activity than Co(III) and Mn(III) complexes. In general metal complexes are more potent than their ligands, hence may serve as vehicles for activation as principal cytotoxic species. These complexes exhibit stronger fungicidal activity than bactericidal activity.

4. Conclusion

Tridentate thiosemicarbazones coordinate to chromium(III), manganese(III), iron(III) and cobalt(III) and give complexes of the type $[M(LH)_2]X \cdot 3H_2O$ (X = Cl or OAc). These compounds are isolated and characterized by various physicochemical data. The structure revealed that NNS donor sets of two ligand fragments form a distorted configuration at the metal ions. Emphasis has been given structural and electronic effects. Based on the above results, the structure of the complexes can be formulated as shown in figure 4.

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