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Synthesis and Investigation of Mixed-Ligand Transition Metal Complexes of Alkyl Dithiocarbonate and Benzoylhydrazine or Benzoylhydrazone Derivatives

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ABSTRACT

Mixed-ligand complexes of the types [Ni(Etdtcn)(BH)], [Ni(Budtcn)(BeBH)], and [M(Rdtcn)(salBH)], where M = Co(II), Ni(II), or Cu(II); R = methyl (Me), ethyl (Et), propyl (Prop) or butyl of the dithiocarbonate (Bu); dtcn = dithiocarbonate group; BH = benzoyl-hydrazine anion, BeBH = benzaldehyde benzoylhydrazone anion, and salBH = salicylaldehyde benzoylhydrazone anion have been synthesised. Elemental analyses, molar conductivities, and spectral (IR, UV, and mass) studies have been used to elucidate the structure of the metal complexes. HBH and HBeBH coordinate in the enol form as bidentate ligands forming a square-planar structure around Ni(II). Moreover, the HsalBH ligand

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behaves as tridentate anion with all metal ions and an octahedral structure for these complexes is proposed. The three ligands and some of their complexes were screened against three species of bacteria, namely *B. cereus* (G +ve), *P. aeruginosa* (G −ve), and *S. aureus* (G +ve) and five types of fungi, *A. flavus*, *A. fumigatus var. albus*, *A. niger*, *F. oxysporum* or *C. tropicum*. The HsalBH ligand has shown high activity against bacteria and fungi, probably due to the presence of a hydroxyl group in this ligand.

Key Words: Mixed-ligand complexes; Spectral studies; TG-DTG; Thermogravimetry.

INTRODUCTION

The interest in the study of hydrazones has been growing due to their use in biological systems and analytical chemistry.[1,2] Interest in such studies also has arisen mainly due to structural problems[3] and the tendency of hydrazides to function as antituberculous, antifungal, and antiviral agents in view of their ability to form metal chelates.[4,5] Further, hydrazones can coordinate to transition metals either in the enolic form (I) or in the keto form (II) as shown in Fig. 1.[6,7]

As a part of our program on the synthesis of several ternary complexes,[8–10] the present investigation is concerned with a systematic study of ternary complexes of divalent metal ions with the biological active benzoylhydrazine (HBH), benzaldehyde benzoylhydrazone (HBeBH), or salicylaldehyde benozylhydrazone (HsalBH) and alkyl dithiocarbonate (Fig. 2).

EXPERIMENTAL

All chemicals were of analytical grade. Benzoylhydrazine,[11] benzaldehyde benzoylhydrazone, salicylaldehyde benozylhydrazone,[7] and potassium alkyl dithiocarbonate[12] were prepared according to literature procedures.

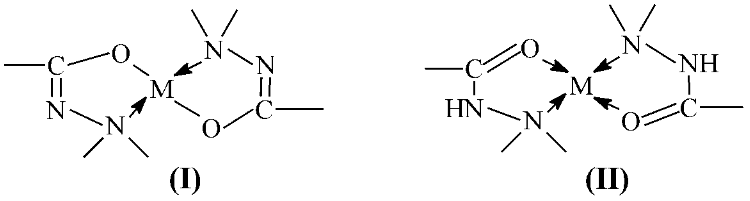
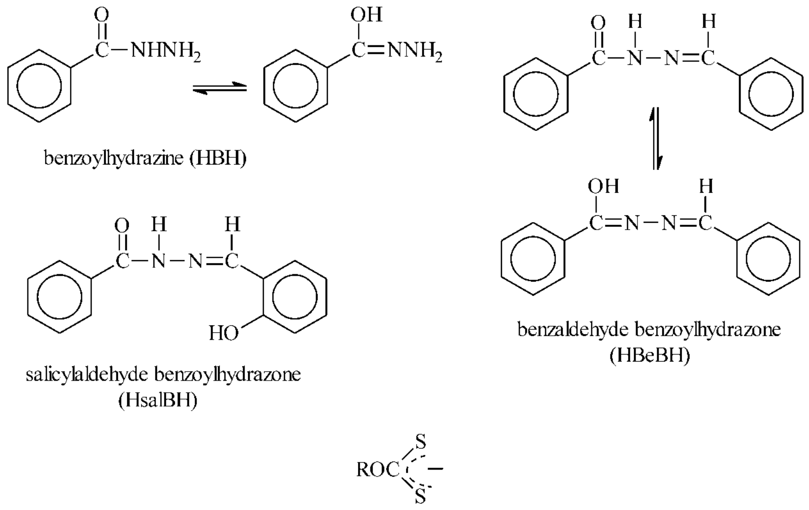


Figure 1. Structures of enol (I) and keto (II) forms of hydrazone complexes.



Rdtcn = methyl dithiocarbonate (Medtcn)
= ethyl dithiocarbonate (Etdtcn)
= propyl dithiocarbonate (Propdtcn)
= butyl dithiocarbonate (Budtcn).

Figure 2. Structures of the ligands.

Synthesis of the Complexes

A quantity of 0.1 mmol of benzoylhydrazine (HBH), benzaldehyde benzoylhydrazone (HBeBH), or salicylaldehyde benzoylhydrazone (HsalBH) was dissolved in 20 mL absolute ethanol and added to 0.1 mmol of the respective metal chloride in 10 mL of aqueous ethanol (70% EtOH). The mixture was stirred for about 0.5 hr and then 0.1 mmol of potassium alkyldithiocarbonate in 10 mL doubly distilled water was added to the mixture with continuous stirring. A precipitate of the ternary complexes separated out, which was filtered, washed with aqueous ethanol (80% ethanol), and dried over P_2O_5.

Physical Measurements

The elemental analysis data were recorded by an Analytischer Funktionstest Vario El Fab-Nr. 11982027 elemental analyser. The infrared spectra were obtained in the solid state (KBr) on a 470 Shimadzu infrared spectrophotometer. Electronic spectra were recorded in DMF as solvent on a Shimadzu UV-2101 PC spectrophotometer. Thermogravimetric analyses were determined using an electrobalance of the type Sartorius 200 MP converted to a thermobalance by addition of a small furnace and sample holder. The temperature was measured using a chromal alumal thermocouple attached to a Soar type ME 550 digital multimeter. The heating rate was adjusted to be 8 °C min^{-1}. Conductance measurements were carried out using a LF Digi. 550 conductance meter. The mass spectra were recorded on a Jeol JMS_{600} mass spectrophotometer.

RESULTS AND DISCUSSION

The analytical data of the complexes (Table 1) indicate that the ternary complexes with metal ions formed according to the following equations:

$$\mathrm{NiCl_2 + HBH + KEtdtcn \longrightarrow [Ni(Etdtcn)(BH)] + KCl + HCl} \quad (1)$$

$$\mathrm{NiCl_2 + HBeBH + KBudtcn \longrightarrow [Ni(Budtcn)(BeBH)] + KCl + HCl} \quad (2)$$

$$\mathrm{MCl_2 + HsalBH + KRdtcn \longrightarrow [M(Rdtcn)(salBH)] + KCl + HCl} \quad (3)$$

where M = Co(II), Ni(II), or Cu(II); R = Me, Et, Prop, or Bu of the dithiocarbonato anion; BH = benzoylhydrazine anion; BeBH = benzaldehyde benzoylhydrazone anion; and salBH = salicylaldhyde benzoylhydrazone anion.

The resulting complexes are coloured solids and have high melting points. All complexes are soluble in DMF and DMSO and are partially soluble in common organic solvents. The molar conductance of 10^{-3} M solutions of the compounds in anhydrous DMF lies in the range 7–10 $\mathrm{ohm^{-1}\,cm^2\,mol^{-1}}$ indicating their behaviour as non-electrolytes.

Attempted preparations of mixed-ligand complexes from the reaction of cobalt(II) chloride or copper(II) chloride with benzoylhydrazine or benzaldehyde benzoylhydrazone and potassium alkyl dithiocarbonate were unsuccessful, where the binary complexes of Co(II) or Cu(II) alkyl dithiocarbonates precipitated. The analytical results of the prepared solids, along with their colours and melting points are listed in Table 1.

IR Spectra

A comparison of the IR spectra (Table 2) of the ligands and their ternary complexes shows the following:

1. The IR spectra of the two ligands HBH and HBeBH are similar, except in the spectrum of HBH where there are two bands at 3400 and 3350 cm^{-1} assigned to $\nu_{as}(\mathrm{NH_2})$ and $\nu_{s}(\mathrm{NH_2})$, respectively. Moreover, bands at 3300–3280, 1665–1640, 1610–1590, and

Table 1. Analytical and physico-chemical data of the complexes.

No.	Compound empirical formula	Formula weight	Colour	Found (calcd. %) C	H	N	S	Dec. p. (°C)	Yield (%)
(1)	[Ni(Etdtcn)(BH)] $C_{10}H_{12}N_2NiO_2S_2$	315.06	Yellow	38.22 (38.12)	3.82 (3.84)	8.82 (8.89)	20.40 (20.35)	240	60
(2)	[Ni(Budtcn)(BeBH)] $C_{19}H_{20}N_2NiO_2S_2$	431.22	Dark green	53.00 (52.92)	4.85 (4.68)	6.45 (6.50)	14.75 (14.87)	232	60
(3)	[Ni(Medtcn)(salBH)] $C_{16}H_{15}N_2NiO_3S_2$	406.15	Green	47.40 (47.32)	3.25 (3.23)	6.93 (6.90)	15.81 (15.79)	210	70
(4)	[Ni(Etdtcn)(salBH)] $C_{17}H_{17}N_2NiO_3S_2$	420.17	Green	48.65 (48.60)	3.64 (3.60)	6.66 (6.67)	15.30 (15.26)	215	75
(5)	[Ni(Propdtcn)(salBH)] $C_{18}H_{19}N_2NiO_3S_2$	434.20	Green	49.75 (49.79)	4.00 (3.95)	6.50 (6.45)	14.80 (14.77)	225	80
(6)	[Ni(Budtcn)(salBH)] $C_{19}H_{21}N_2NiO_3S_2$	448.23	Dark green	50.95 (50.91)	4.74 (4.72)	6.28 (6.25)	14.35 (14.31)	227	75
(7)	[Co(Medtcn)(salBH)] $C_{16}H_{15}CoN_2O_3S_2$	406.37	Dark green	47.34 (47.29)	3.25 (3.22)	6.89 (6.89)	15.81 (15.78)	208	75
(8)	[Co(Etdtcn)(salBH)] $C_{17}H_{17}CoN_2O_3S_2$	420.39	Dark green	48.60 (48.57)	3.64 (3.60)	6.70 (6.66)	15.30 (15.25)	210	80
(9)	[Co(Propdtcn)(salBH)] $C_{18}H_{19}CoN_2O_3S_2$	434.42	Dark green	49.82 (49.77)	4.00 (3.94)	6.40 (6.45)	14.80 (14.76)	215	75
(10)	[Co(Budtcn)(salBH)] $C_{19}H_{21}CoN_2O_3S_2$	448.45	Green	50.95 (50.89)	4.75 (4.72)	6.28 (6.25)	14.35 (14.30)	225	75

(*continued*)

Table 1. Continued.

No.	Compound empirical formula	Formula weight	Colour	Found (calcd. %)				Dec. p. (°C)	Yield (%)
				C	H	N	S		
(11)	[Cu(Medtcn)(salBH)] $C_{16}H_{15}CuN_2O_3S_2$	410.98	Green	46.80 (46.76)	3.25 (3.19)	6.85 (6.82)	15.58 (15.60)	213	80
(12)	[Cu(Etdtcn)(salBH)] $C_{17}H_{17}CuN_2O_3S_2$	425.00	Dark green	48.09 (48.04)	3.60 (3.56)	6.59 (6.59)	15.11 (15.09)	220	78
(13)	[Cu(Propdtcn)(salBH)] $C_{18}H_{19}CuN_2O_3S_2$	439.25	Oily green	49.29 (49.22)	4.00 (3.90)	6.38 (6.38)	14.66 (14.60)	225	75
(14)	[Cu(Budtcn)(salBH)] $C_{19}H_{21}CuN_2O_3S_2$	453.06	Dark green	50.40 (50.37)	4.65 (4.67)	6.21 (6.18)	14.21 (14.15)	227	80

Table 2. Important IR spectral bands of ligands and complexes.

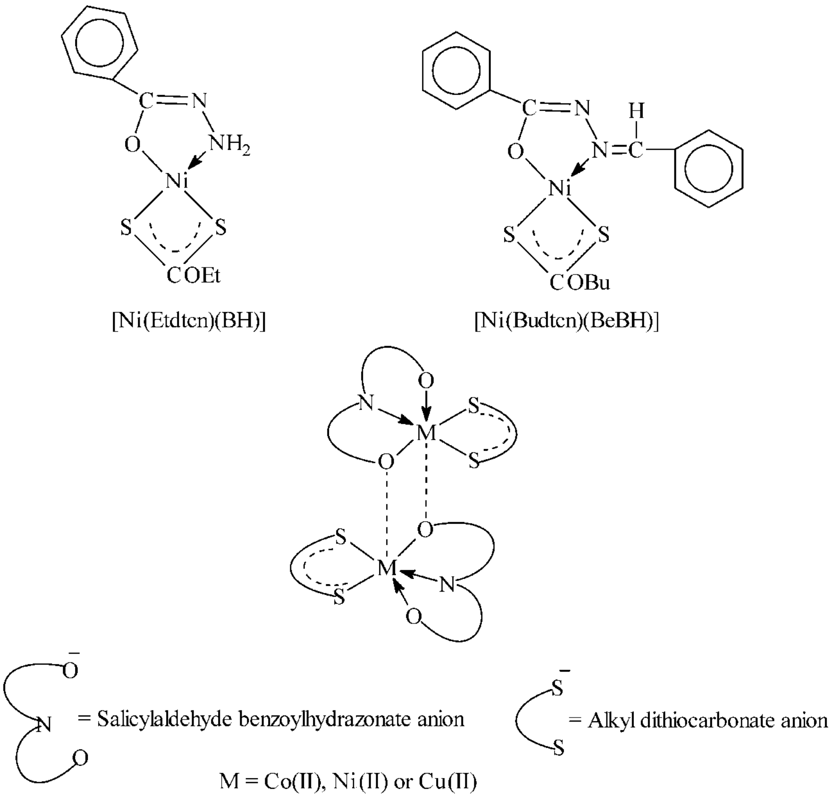
Complex	Hydrazone moiety					Dithiocarbonate moiety					
no.	ν(NH)	ν(C=O)	ν(C=N)	ν(C–O)	ν(N–N)	ν(C–O–C)	ν(C–O)	ν(C–S)	ν(M–O)	ν(M–N)	ν(M–S)
HBH	3,300 m	1,665 s	1,610 s	—	880 m	—	—	—	—	—	—
(1)	3,250 m	—	1,600 s	1,285 m	1,025 m	1,110 m	1,140 m	1,020 s	520 m	430 s	480 m
HBeBH	3,280 m	1,640 s	1,590 s	—	980 m	—	—	—	—	—	—
(2)	—	—	1,580 s	1,280 m	1,020 m	1,120 m	1,140 m	1,030 s	520 m	420 s	490 m
HsalBH	3,430 m	1,660 s	1,605 s	—	980 m	—	—	—	—	—	—
(3)	3,290 m	1,600 s	1,580 s	—	1,010 m	1,090 m	1,140 m	1,020 s	560 w	460 m	495 s
(4)	3,295 m	1,600 s	1,570 s	—	1,020 m	1,105 m	1,150 w	1,020 s	560 m	460 m	495 s
(5)	3,300 m	1,600 s	1,575 s	—	1,015 m	1,110 m	1,150 w	1,025 s	560 m	450 m	490 s
(6)	3,300 m	1,600 s	1,560 s	—	1,025 m	1,120 m	1,145 m	1,020 s	560 m	455 m	500 m
(7)	3,295 m	1,610 s	1,575 s	—	1,030 m	1,110 m	1,140 m	1,030 s	540 w	440 m	495 s
(8)	3,300 m	1,600 s	1,560 s	—	1,025 m	1,110 m	1,145 m	1,025 s	540 m	460 m	510 s
(9)	3,290 m	1,605 s	1,565 s	—	1,020 m	1,115 m	1,140 m	1,030 s	550 w	450 m	490 m
(10)	3,300 m	1,600 s	1,560 s	—	1,030 m	1,120 m	1,145 m	1,030 s	540 m	440 m	495 m
(11)	3,300 m	1,620 s	1,580 s	—	1,020 m	1,110 m	1,140 m	1,030 s	530 m	430 m	490 m
(12)	3,300 m	1,620 s	1,580 s	—	1,020 m	1,110 m	1,145 m	1,020 s	530 m	435 s	495 m
(13)	3,300 m	1,615 s	1,580 s	—	1,025 m	1,105 m	1,130 m	1,025 s	535 m	435 m	510 m
(14)	3,300 m	1,615 s	1,580 s	—	1,025 m	1,110 m	1,130 m	1,025 s	535 m	435 s	505 m

880–980 cm^{-1} were observed in the two ligands and are attributed to ν(NH), ν(C=O), ν(C=N), and ν(N–N), respectively. These facts suggest that the two ligands remained in the keto form in the solid state (Fig. 2). Bonding of HBH and HBeBH to nickel(II) has been suggested by a careful comparison of the infrared spectra of the complexes with those of the free ligands. A few significant bands have been selected to observe the effect of complexation on the ligand vibration in the complexes. The two ligands in the complexes (**1**) and (**2**) chelate with the Ni(II) ion in the enol form. This chelation was supported by the following.

The shift to low frequency of the C=N (~10 cm^{-1}) band and the shift to higher frequency of the ν(N–N) band and its splitting indicated involvement of azomethine nitrogen in coordination.[13] Thus, both the hydrazine and hydrazone behave as bidentate ligands. The first (HBH) bonds through a $-NH_2$ group and C–O in the enol form, and the second ligand (HBeBH) bonds through the azomethine group and C–O in the enol form[14] (Fig. 3). The two complexes showed the absence of C=O and a shift to lower frequency of the –NH band in complex (**1**) and the latter band disappeared in complex (**2**) with the appearance of new bands at 1280 and 1285 cm^{-1}, respectively, assigned to ν(C–O), suggesting enolization of the ligands on complexation,[15] and signifies bonding of the terminal-NH_2 group in complex (**1**).

2. A comparison of IR spectra of HsalBH and its metal complexes shows the following.

(i) Two bands are appearing in the spectrum of the ligand at 3430 and 910 cm^{-1}, which were attributed to ν(OH) and δ(OH), respectively. In the spectra of the complexes (**3**)–(**14**), δ(OH) is absent while it is difficult to trace the disappearance of ν(OH) because it occurs at the same range where ν(NH) is located. This indicates the deprotonation of the hydroxyl group and coordination of the ligand as a mononegative anion. (ii) The band due to ν(NH) remains unaltered compared to the ligand indicating non-participation of –NH in coordination and also that the ligand coordinates in the keto form. (iii) The shift to lower frequency of the two bands ν(C=O) and ν(C=N) by 40–60 and 25–45 cm^{-1}, respectively, may suggest bonding through the carbonyl oxygen and azomethine nitrogen.[16] Coordination of nitrogen to the metal atom would be expected to reduce the electron density in the azomethine links and thus cause a shift in the ν(C=N) band.[17] (iv) The small shift to higher frequency of the ν(N–N) band at ~1025 cm^{-1} and its splitting can be taken as additional evidence for the participation of the azomethine nitrogen in bonding.[13,18]



[Ni(Etdtcn)(BH)]

[Ni(Budtcn)(BeBH)]

= Salicylaldehyde benzoylhydrazonate anion

= Alkyl dithiocarbonate anion

M = Co(II), Ni(II) or Cu(II)

Figure 3. Suggested structures for the complexes.

In conclusion, the HsalBH ligand acts with all metal ions as a mononegative tridentate ligand coordinating via the oxygen of the hydroxyl group, azomethine nitrogen, and carbonyl group in the keto form (Fig. 3).

Moreover, all complexes (**1**)–(**14**) show some bands in the infrared spectra due to the dithiocarbonate moiety and their assignments are as follows: ν(C–O–C), ν(C–O) and ν(C–S) are located in the regions 1090–1120, 1130–1150, and 1020–1030 $\mathrm{cm^{-1}}$, respectively. The presence of only one band at ~1025 $\mathrm{cm^{-1}}$ due to ν(C–S) indicates the bidentate nature of the alkyldithiocarbonate ligands in these complexes.[8–10] Further support for the coordination of the two ligands to the metal ions was provided by the appearance of bands at 520–560, 430–460, and 480–510 $\mathrm{cm^{-1}}$, which are assigned to ν(M–O),[19] ν(M–N),[19] and ν(M–S),[9] respectively.

Electronic Spectra

The electronic spectral data of the complexes under investigation are listed in Table 3. The spectra of the complexes [Ni(Etdtcn)(BH)] and [Ni(Budtcn)(BeBH)] in DMF show two bands in the region 15,120–15,981 and 20,408–20,964 cm^{-1} assignable to $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ transitions, respectively, supporting a square-planar geometry around the Ni(II) ions.[20]

The electronic spectra of [Ni(Rdtcn)(salBH)] show three d–d transition bands at 11,185–12,106, 15,060–16,420, and 24,096–24,331 cm^{-1}. An examination of these bands reveals that these complexes have an octahedral geometry and are assigned to the transitions $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, and $^3A_{2g} \rightarrow {}^3T_{2g}(P)$, respectively.[20–22] Complexes of the type [Co(Rdtcn)(salBH)] display absorption bands in the two regions 15,974–16,129 and 20,790–21,142 cm^{-1}. The positions of the bands indicate that these complexes have an octahedral configuration.[20–22] The assignment of the spectral bands may be given as $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2) and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3), respectively.

The electronic spectra of the Cu(II) complexes show three characteristic bands in the d–d transition region, namely at 11,669–12,346, 17,123–17,530, and 25,445–25,907 cm^{-1}. These bands have been assigned to the transitions $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$, and $^2B_{1g} \rightarrow {}^2E_g$, respectively. On the basis of which a distorted octahedral structure around the Cu(II) is proposed. The broadening of the bands may be attributed to the Jahn–Teller effect.[23,24]

For all complexes (**1**)–(**14**), on the basis of the position and intensity, the two bands at 23,683–33,580 and 38,769–48,077 cm^{-1} are ascribed to charge transfer and intraligand transitions, respectively.

Based on the above spectral studies, the structures in Fig. 3 are suggested for the complexes.

Thermal Analysis

A thermogravimetric analysis of the complexes was made over the temperature range 50–550 °C. The TG and DTG curves of the complex [Ni(Etdtcn)(BH)] (Fig. 4) show three main steps and a number of DTG peaks. The first step occurs at 125 °C corresponding to loss of a C_2H_4 molecule from the ethyl dithiocarbonate group as shown by Eq. (4).

$$[\mathrm{Ni(Etdtcn)(BH)}] \longrightarrow [\mathrm{Ni(HOCS_2)(BH)}] + \mathrm{CH_2{=}CH_2} \quad (4)$$

Elimination of alkenes from alkyl dithiocarbonate was also observed in the literature.[25] The second step contains three DTG peaks at 235,

Table 3. Electronic spectral bands for the complexes in $\nu_{\max}$ cm^{-1} (ε dm^3 mol^{-1} cm^{-1}).

No.	d–d Transition	Charge transfer transition	Intraligand transfer transition
(1)	15,120 (28); 20,408 (100)	24,390 (223)	43,290 (2,670); 46,083 (3,300); 47,847 (3,820)
(2)	15,981 (13); 20,964 (100)	23,683 (280)	44,643 (1,100); 46,512 (1,130); 48,077 (2,270)
(3)	11,919 (52); 15,985 (52); 24,213 (90)	30,769 (1,590)	40,486 (2,068)
(4)	11,820 (52); 16,420 (74); 24,213 (100)	30,769 (1,385)	38,769 (2,001)
(5)	11,185 (17); 15,060 (70); 24,096 (95)	30,769 (1,060)	40,847 (4,083)
(6)	12,106 (21); 16,097 (85); 24,331 (105)	30,864 (1,017)	39,370 (3,088)
(7)	15,974 (165); 20,790 (180)	33,003 (4,716)	43,290 (4,277)
(8)	16,077 (170); 20,790 (195)	33,113 (2,675)	40,841 (5,000)
(9)	16,129 (549); 21,142 (590)	29,155 (1,476)	39,364 (4,716)
(10)	16,103 (532); 21,053 (621)	33,110 (1,580)	40,041 (5,000)
(11)	11,669 (67); 17,123 (67); 25,907 (124)	30,395 (4,729)	42,735 (5,100)
(12)	12,346 (67); 17,241 (78); 25,445 (153)	33,112 (4,612)	40,948 (5,020)
(13)	12,210 (60); 17,420 (62); 25,715 (188)	32,820 (4,720)	41,840 (5,000)
(14)	12,164 (64); 17,530 (70); 25,861 (164)	33,580 (4,640)	41,240 (5,345)

250, and 269 °C. The weight loss in this step corresponds to elimination of benzoylhydrazide anion forming an unstable compound, which decomposes at 350 °C producing NiO as a final product.

For the complex [Ni(Budtcn)(BeBH)], the TG thermograms (Fig. 5) show three steps at 180, 200, and 325 °C (DTG). The weight loss at the first step corresponds to evolution of a $CH_3CH_2CH{=}CH_2$ molecule (calc. 13.6%, found 13.5%). For the second step, the weight loss is about 27.5 and the calculated value 27.88% may correspond to loss of the $[C_7H_6NO^{\bullet}]$

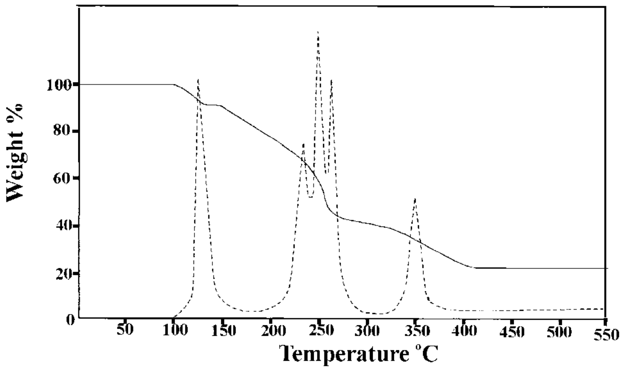


Figure 4. TG (——) and DTG (-----) thermograms of [Ni(Etdtcn)(BH)].

radical. The rupture of the N–N bond during thermal decomposition of hydrazone has been previously reported in the literature.[26] After that, the unstable complex which is formed decomposes at the final step forming NiO as a final product.

The thermal behaviour of complexes of the type [M(Rdtcn)(salBH)] is similar in all compounds (**3**)–(**14**), and the TG thermogram (Fig. 6) of [Ni(Medtcn)(salBH)] is typical. The TG curve of this complex shows three decomposition steps. The first and second decomposition steps occur at 140 and 275 °C, respectively (DTG curve). The total weight loss for these two stages is in agreement with the loss of $[C_7H_7NO]^{\bullet}$ (0.5 salBH) radical (calc. 29.9%, found 30.0%), which may abstract a $H^{\bullet}$ radical to form $[C_7H_8NO]$.

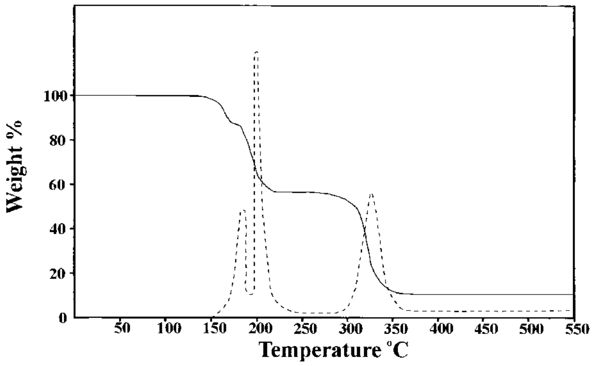


Figure 5. TG (——) and DTG (-----) thermograms of [Ni(Budtcn)(BeBH)].

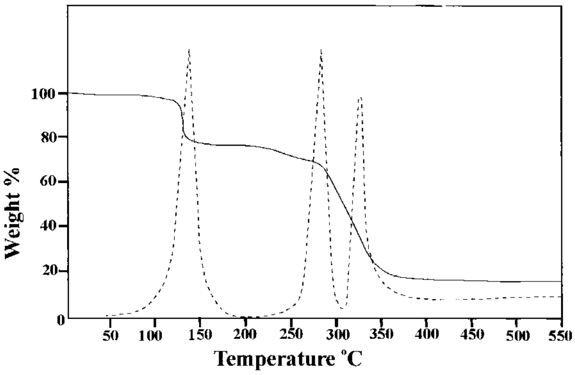


Figure 6. TG (——) and DTG (-----) thermograms of [Ni(Medtcn)(salBH)].

The unstable complex decomposes in the latter step at 325 °C to form NiO as the final product.

The proposed mechanism of thermal decomposition is illustrated by the following equation:

$$[\mathrm{Ni(Medtcn)(salBH)}] \xrightarrow{-0.5\ \mathrm{SalBH}} \underset{\text{unstable complex}}{[\mathrm{Ni(Medtcn)(salBH)}_{0.5}]} \qquad (5)$$

However, expulsion of alkene occurs for alkyl dithiocarbonates, where alkyl = ethyl, propyl, and butyl together with 0.5 molecule of salBH. Elimination of alkenes from alkyl dithiocarbonate was observed in the mass fragmentation patterns of some alkyl dithiocarbonate complexes.[24]

Mass Spectra

The mass spectral behaviour of the complexes [Ni(Etdtcn)(BH)], [Ni(Budtcn)(BeBH)], and [Ni(Budtcn)(salBH)] is reported in the schemes of Figs. 7–9, respectively.

The molecular ion of the two complexes $[\mathrm{Ni(Etdtcn)(BH)}]^+$ and $[\mathrm{Ni(Budtcn)(BeBH)}]^+$ is recorded at $[\mathrm{M}^+] = 314$ and 430, respectively. A step-by-step decomposition process is proposed, based on the results obtained in the schemes of Figs. 7 and 8. From these schemes we conclude that a hydrazone ligand is lost and its peaks are observed at $m/z = 135$ $[\mathrm{HBH}]^+$ and $m/z = 255$ $[\mathrm{HBeBH}]^+$. These ligands lose a nitrogen molecule and in the two cases the peak at $m/z = 105$ $[\mathrm{C_7H_5O^{\bullet}}]^{+[26]}$ results. The second fragment

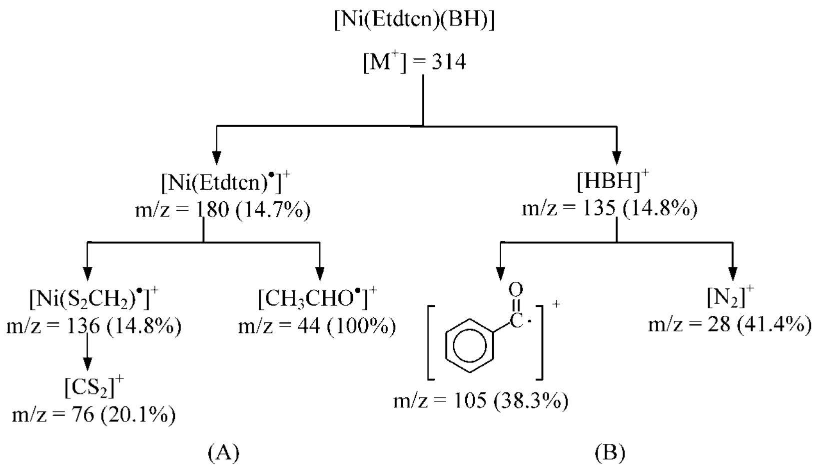


Figure 7. The mass spectral behaviour of [Ni(Etdtcn)(BH)].

represents the metal complexes at $m/z = 180$ [Ni(Etdtcn)$^{\cdot}$]$^{+}$ and $m/z = 205$ [Ni(Budtcn)$^{\cdot}$]$^{+}$, respectively. The aldehyde fragments were detected at $m/z = 44$ [$CH_3CHO^{\cdot}$]$^{+}$ and $m/z = 73$ [$C_4H_8O^{\cdot}$]$^{+}$. Also, in the two cases, there are two peaks at $m/z = 136$ [Ni(S_2CH_2)$^{\cdot}$]$^{+}$ and $m/z = 76$ [$CS_2^{\cdot}$]$^{+}$.

The mass spectral behaviour of some complexes of the type [M(Rdtcn)(salBH)] (Fig. 9) was also investigated. The complexes seem to show the same fragmentation patterns for all the studied complexes. The fragmentation of [Ni(Budtcn)(salBH)] (Fig. 9) is typical. The mass spectral peaks

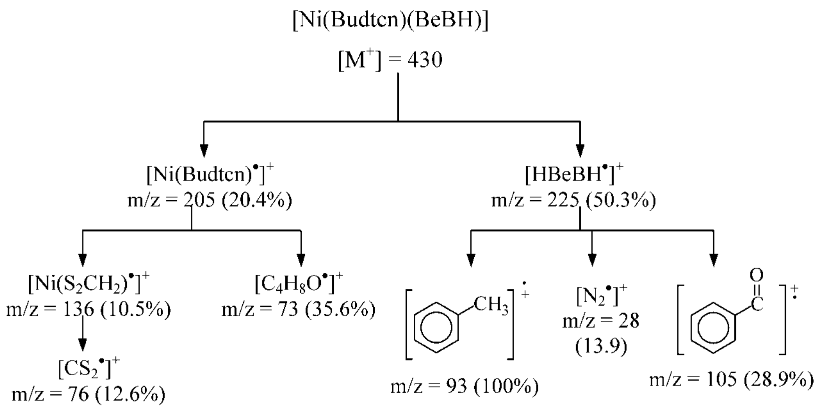


Figure 8. The mass spectral behaviour of [Ni(Budtcn)(BeBH)].

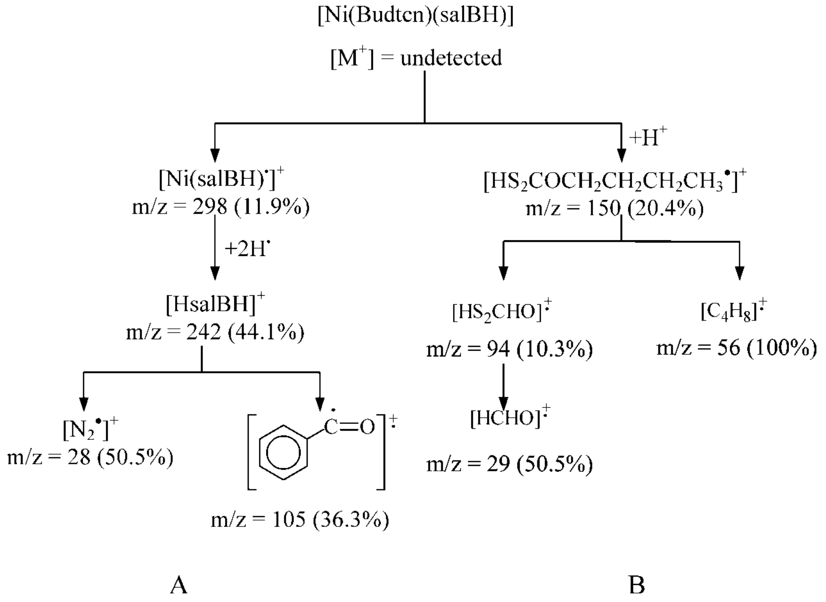


Figure 9. The mass spectral behaviour of [Ni(Budtcn)(salBH)].

of the two fragments $[C_5H_{10}OS_2]^+$ with $m/z = 150$ (20.4%) and $[NiC_{14}H_{11}N_2O_2]^+$ with $m/z = 298$ (11.9%) represent the two parts of the suggested formula. In the scheme A of Fig. 9, the fragments $[C_7H_5O^{\bullet}]^+$ $m/z = 105$ (36.3%) and $[N_2^{\bullet}]^+$ $m/z = 28$ (50.5%) of the HsalBH ligand are detected. Further fragmentation of the dithiocarbonate moiety is depicted in the scheme B of Fig. 9. Fragment $[C_4H_8^{\bullet}]^+$ $m/z = 56$ (100%) represents the alkene molecule of the alkyl dithiocarbonate, in agreement with the thermal decomposition of these complexes. The final fragment ion $m/z = 29$ (50.5%) corresponds to $[CH_2O]^+$.

Microbiological Screening

Benzoylhydrazine, benzaldehyde benzoylhydrazone, salicylaldehyde benzoylhydrazone, some related complexes, and erythromycin (as a reference compound) were tested against a number of bacteria and fungi. The used bacteria were *B. cereus* (G +ve), *P. aeruginosa* (G −ve) and *S. aureus* (G +ve), the tested fungi were *A. flavus*, *A. fumigatus var. albus*, *A. niger*, *F. oxysporum*, and *C. tropicum*. All samples under investigation were prepared in

Table 4. Antibacterial and antifungal activity data[a] of free ligands and some of their complexes.

	Bacteria			Fungi				
Compd. no.	*B. cereus* (G +ve)	*P. aeruginosa* (G −ve)	*S. aureus* (G +ve)	*A. flavus*	*A. fumigatus var. albus*	*A. niger*	*F. oxysporum*	*C. tropicum*
HBH	0	0	0	0	0	0	0	0
HBeBH	0	0	0	0	0	0	0	0
HsalBH	15	17	15	15	26	12	14	20
(1)	13	0	0	0	0	0	0	0
(2)	15	20	0	0	0	0	0	0
(6)	0	0	0	0	15	10	0	0
(8)	0	0	0	0	12	0	0	12
(13)	20	0	0	0	8	10	0	12
Erythro-mycin	0	0	0	0	0	0	0	0

[a] Activity expressed as the diameter (*D*) of the inhibition zone (in mm).

500 μg mL^{-1} concentration in DMF as solvent. The culture media were nutrient agar (NA) media supplemented with 1 g yeast L^{-1}. The biological activity of the ligands and some of their ternary complexes have different activity against bacteria and fungi. The data listed in Table 4 indicates the following:

1. Erythromycin has no effect on all bacteria and fungi.
2. HsalBH is more active against all bacteria and fungi than the HBH and HBeBH ligands and their complexes. This activity maybe due to the OH group of the salicyaldehyde moiety in this compound, which is subjected to deprotonation in the complexes,[27] but it is absent in the other two ligands.
3. The activity of some complexes against *B. cereus* (G +ve bacteria) and *A. fumigatus var. allous*, *A. niger*, and *C. tropicum* maybe due to the combined effect of metal and dithiocarbonato anion toxicity, which interact with trace metals of bacteria and fungi.[11] It is suggested that the neutral mixed-ligand complexes penetrate the cell wall and dissociate into binary complexes as shown below:

$$[\mathrm{Ni(Etdtcn)(BH)}] \longrightarrow \mathrm{Ni(Etdtcn)}^+ + \mathrm{BH}^- \qquad (6)$$

$$[\mathrm{Ni(Budtcn)(BeBH)}] \longrightarrow \mathrm{Ni(Budtcn)}^+ + \mathrm{BeBH}^- \qquad (7)$$

$$[\mathrm{M(Rdtcn)(salBH)}] \longrightarrow \mathrm{M(Rdtcn)}^+ + \mathrm{salBH}^- \qquad (8)$$

Thus, the binary complex ions Ni(Etdtcn)$^+$, Ni(Budtcn)$^+$, and M(Rdtcn)$^+$, act as a toxic agents.[28,29]

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