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SPECTRAL AND THERMAL STUDIES OF SOME NOVEL BIVALENT METAL CHELATES OF DICHLOROBENZOYLHYDRAZINES

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ABSTRACT

A series of twelve novel chelate complexes of the general type, $[M(Cl_2Bh)_3]Cl_2$, where $M = Mn$, Co, Ni and $Bh = -C_6H_3CONHNH_2$, was synthesized. Their spectra (IR and electronic) and their magnetic susceptibility measurements suggested a distorted octahedral structure in the solid state.

Thermal investigations of the complexes using TG/DTG were carried out in a nitrogen atmosphere to determine their mode of decomposition. The thermal stability of the ligand is the determining factor in the thermal stabilities of the complexes, which follow the series 3,4-Cl_2Bh > 2,4-Cl_2Bh > 2,5-Cl_2Bh ⩾ 3,5-Cl_2Bh.

INTRODUCTION

With the knowledge of the significant applications of the benzoylhydrazines and their coordination compounds to analytical chemistry [1], coordination chemistry and pharmacology [2–5], a research project [6–8] started several years ago. In this, a number of monohalogen-benzoylhydrazines and their complexes with Co(II) and Ni(II) ions were synthesized and studied spectroscopically. As a continuation of our previous work we report here a series of twelve novel chelate complexes of the general type, $[M(x,y\text{-}Cl_2Bh)_3]Cl_2$, where M = Mn(II), Co(II) or Ni(II), x, y = 2,4-, 2,5-, 3,4- or 3,5- and $Bh = -C_6H_3CONHNH_2$. In order to study the structure and bonding of the dichlorobenzoylhydrazines, we describe the spectral data (IR and electronic), the conductivity and magnetic susceptibility measurements and the behaviour of the above-mentioned complexes in solutions of organic solvents. In particular, we focus our attention on the thermal behaviour of the compounds in question by applying the TG/DTG technique in a nitrogen atmosphere. A literature survey revealed that thermal studies on

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transition metal benzoylhydrazine complexes are limited to two papers [9,10]. In ref. 9 the thermal stabilities of hydrated unsubstituted benzoylhydrazine complexes are reported, while in ref. 10 the researchers found that the compounds decomposed exothermally.

EXPERIMENTAL

Preparation

The dichlorobenzoylhydrazines and their complexes were prepared by known methods [6–8].

Physical methods

IR spectra, in Nujol mulls and KBr matrix, were recorded in the 4000–200 cm^{-1} range on a Perkin–Elmer 1430 spectrophotometer calibrated against polysterene film. Electronic absorption spectra were recorded in the region 200–800 nm at ca. 25 °C in different solvents using a Perkin–Elmer model 200 spectrophotometer. The magnetic susceptibility measurements were performed at ambient temperature on an Alpha Scientific Inc. system employing the Faraday method with $Hg[Co(SCN)_4]$ as calibrant. The conductivity measurements were carried out with a WTW conductivity bridge for freshly prepared 10^{-3} M solutions in water at 25 °C.

Thermogravimetric analyses (TG/DTG) were done on a DuPont Instruments Series 99 thermal analyser with combined apparatus DuPont Instruments Series 951 thermogravimetric analyser. The measurements were performed in a dynamic atmosphere of nitrogen at a flow rate of 60 ml min^{-1} up to 800 °C. The heating rate was 10 °C min^{-1} and the sample weight was about 10 mg.

RESULTS AND DISCUSSION

The formulae of the ligands and the complexes obtained together with analytical data and some physical properties are reported in Tables 1 and 2. The complexes possess 1:3 metal to ligand stoichiometry in all cases. Substitution reactions of halogen and conductivity measurements suggest an ionic character of the complexes. The molar conductivity of the complexes confirms $2^+:1^-$ electrolytes.

The magnetic moment values (Table 2), corrected for diamagnetism using Pascal constants, show paramagnetic compounds with distorted octahedral symmetry.

TABLE 1

Melting point and analytical data of dichlorobenzoylhydrazines

Ligand	Melting point (°C)	N found (calc.) (%)	C found (calc.) (%)	H found (calc.) (%)	Cl found (calc.) (%)
2,4-$Cl_2C_6H_3CONHNH_2$	164–165	13.9 (13.9)	41.2 (41.0)	2.8 (3.0)	34.7 (34.6)
2,5-$Cl_2C_6H_3CONHNH_2$	173–175	13.9 (13.9)	41.1 (41.0)	2.8 (3.0)	34.3 (34.6)
3,4-$Cl_2C_6H_3CONHNH_2$	155–156	13.9 (13.9)	41.0 (41.0)	3.0 (3.0)	34.4 (34.6)
3,5-$Cl_2C_6H_3CONHNH_2$	195–197	14.0 (13.9)	41.0 (41.0)	2.8 (3.0)	34.5 (34.6)

IR spectra

To establish the coordination of the ligands, the IR spectra of the complexes were recorded and, for comparison, the spectra of the uncoordinated ligands. These results are reported in Table 3 and suggest that the ligands act as bidentates with the carbonyl oxygen and the nitrogen of the amine group at the coordination sites [11,12], forming five-membered chelate rings.

On the basis of IR data and the results of conductivity and magnetic susceptibility measurements, a possible octahedral structure of the complexes is proposed (Fig. 1).

The real symmetry is, however, distorted octahedral probably as a result of the inequality of the M–O and M–N bonds.

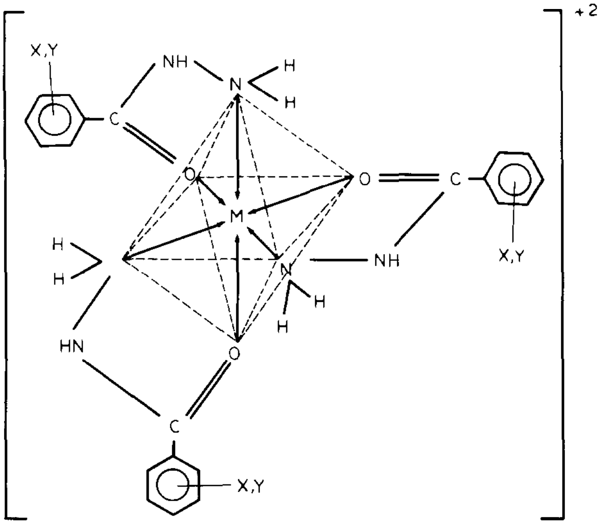


Fig. 1. Schematic diagram of the proposed octahedral structure of the dichlorobenzoylhydrazine complexes studied.

TABLE 2

Melting point, solid state magnetic and analytical data of some dichlorobenzoylhydrazine complexes with divalent metals

Compound	Melting point (°C)	μ_{eff} μ_B	N found (calc.) (%)	C found (calc.) (%)	H found (calc.) (%)	M found (calc.) (%)	C found (calc.) (%)
$[Mn(2,4\text{-}Cl_2Bh)_3]Cl_2$	232–235	6.2	10.7 (11.2)	33.1 (33.6)	2.4 (2.4)	7.5 (7.8)	9.0 (9.4)
$[Mn(2,5\text{-}Cl_2Bh)_3]Cl_2$	268–270	5.8	10.9 (11.2)	33.1 (33.6)	2.6 (2.4)	7.5 (7.8)	9.1 (9.4)
$[Mn(3,4\text{-}Cl_2Bh)_3]Cl_2$	257–259	5.5	10.9 (11.2)	33.4 (33.6)	2.3 (2.4)	7.6 (7.8)	9.0 (9.4)
$[Mn(3,5\text{-}Cl_2Bh)_3]Cl_2$	229–232	5.7	11.0 (11.2)	33.3 (33.6)	2.1 (2.4)	7.5 (7.8)	9.1 (9.4)
$[Co(2,4\text{-}Cl_2Bh)_3]Cl_2$	210–212	5.2	11.3 (11.3)	33.7 (33.8)	2.4 (2.4)	7.6 (7.9)	9.2 (9.5)
$[Co(2,5\text{-}Cl_2Bh)_3]Cl_2$	206–209	5.2	11.5 (11.3)	34.1 (33.8)	2.6 (2.4)	7.7 (7.9)	9.3 (9.5)
$[Co(3,4\text{-}Cl_2Bh)_3]Cl_2$	295–297	5.2	10.7 (11.3)	33.5 (33.8)	2.6 (2.4)	7.8 (7.9)	9.4 (9.5)
$[Co(3,5\text{-}Cl_2Bh)_3]Cl_2$	301–303	5.1	11.0 (11.3)	33.4 (33.8)	2.1 (2.4)	7.6 (7.9)	9.2 (9.5)
$[Ni(2,4\text{-}Cl_2Bh)_3]Cl_2$	298–300	3.1	11.1 (11.3)	33.6 (33.8)	2.5 (2.4)	7.5 (7.9)	9.4 (9.5)
$[Ni(2,5\text{-}Cl_2Bh)_3]Cl_2$	264–266	2.8	11.4 (11.3)	33.7 (33.8)	2.5 (2.4)	7.6 (7.9)	9.3 (9.5)
$[Ni(3,4\text{-}Cl_2Bh)_3]Cl_2$	332–333	3.3	10.8 (11.3)	33.5 (33.8)	2.7 (2.4)	7.8 (7.9)	9.5 (9.5)
$[Ni(3,5\text{-}Cl_2Bh)_3]Cl_2$	311–312	2.9	10.9 (11.3)	33.5 (33.8)	2.4 (2.4)	7.5 (7.9)	9.6 (9.5)

TABLE 3

Most important IR bands (cm^{-1}) of free dichlorobenzoylhydrazines and their complexes with Mn(II), Co(II) and Ni(II)

	Ligand 3,4-Cl_2Bh	$[M(3,4\text{-}Cl_2Bh)_3]Cl_2$			Ligand 2,4-Cl_2Bh	$[M(2,4\text{-}Cl_2Bh)_3]Cl_2$		Ligand 3,5-Cl_2Bh	$[M(3,5\text{-}Cl_2Bh)_3]Cl_2$		Ligand 2,5-Cl_2Bh	$[M(2,5\text{-}Cl_2Bh)_3]Cl_2$		
		Mn(II)	Co(II)	Ni(II)		Co(II)	Ni(II)		Co(II)	Ni(II)		Mn(II)	Co(II)	Ni(II)
ν(NH)	3290 s [d]	3230 s	3300 br	3310 m	3320 s	3250 br	3250 br	3345 m	3240 br	3230 br		3290 m	3270 s	3258 s
$\nu_{as}(NH_2)$	3220 br	3180 br	3130 br	3140 br	3275 s	3090 br	3080 br	3290 s	3180 br	3170 br	3298 vs	3210 m	3220 br	3210 br
$\nu_s(NH_2)$	3060 br 3030 br		2880 w	2950 w	3220 s	2990 s	2985 s	3098 m 3085 m	3060 m		3180 m	3170 m	3285 s	3085 s
"Amide I" [a]	1660 s	1658 vs	1650 vs	1650 vs	1665 vs	1655 vs	1655 vs	1657 vs	1650 vs	1655 vs	1665 vs	1648 vs	1658 vs	1658 vs
$\delta(NH_2)$, δ(NNX)	1608 vs	1590 vs	1612 vs	1612 vs	1635 vs	1612vs	1610 vs	1630 s	1612 s 1598 s	1618 vs	1612 vs	1600 vs	1610 vs	1610 vs
"Amide II" [b]	1575 s	1555 vs	1562 s	1565 vs	1598 vs	1560 s	1560 s	1578 vs	1570 vs	1575 vs	1560 m	1550 m	1554 s	1555 s
$\omega(NH_2)$, δ(HNC)	1470 s	1345 vs	1344 vs	1345 vs	1472 vs	1350 vs	1350 vs	1438 m	1342 vs	1340 s	1462 vs	1320 m	1335 vs	1332 s
"Amide III" [c]	1350 vs	1190 vs	1202 s	1210 vs	1380 m	1210 vs	1218 vs	1338 s	1204 vs	1212 s	1382 s	1205 s	1208 s	1212 s
$\rho(NH_2)$	830 vs	780 s	782 s	788 s	838 vs	795 vs	797 vs	870 vs	802 vs	805 vs	880 vs	818 m	820 vs	820 s
ν(MN), ν(MO), δ(MNN)	675 vs 550 m	560 vs	582 vs	592 s	652 vs	582 s	580 s	675 vs 642 m	552 vs	562 m	642 vs	595 m	590 s	600 vs
ν(MO), ν(MN), δ(CCO)	450 m	457 w	462 m	467 m	436 m	482 m	486 m	470 s	485 vs	489 m	468 s	485 m	490 m	496 m

[a] "Amide I" = ν(C=O), ν(CN), ν(CC), δ(NCO), δ(CCO).

[b] "Amide II" = ν(C=O), ν(CN), ν(CC), δ(NCO), δ(CCO).

[c] "Amide III" = ν(C=O), δ(HNC), δ(HNN).

[d] vs = Very strong, s = strong, m = medium, w = weak, br = broad.

Electronic spectra

The distorted octahedral geometry of the complexes studied is further supported by their absorption spectra. These exhibit the ligand field bands expected for octahedral and pseudo-octahedral structures [13]. The Mn(II) complexes are white, which means the absence of *d–d* transitions. The Ni(II) complexes are light blue in the solid state as well as in solution. The ethanolic solution absorption spectra of the dichlorobenzoylhydrazine Ni(II) complexes show three regions of absorption all of weak intensity ($\varepsilon \sim 11$ $\text{mol}^{-1}\ \text{dm}^3\ \text{cm}^{-1}$). The first ($\bar{\nu}_1 \sim 1020$ nm) is attributed to the transition, ${}^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$, while the second ($\bar{\nu}_2 \sim 600$ nm) is assigned to the transition, ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$. In the third region ($\bar{\nu}_3 \sim 400$ nm) a unique band appears corresponding to the transition, ${}^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$.

The Co(II) complexes studied are pink solids, while in solution their colour depends on the "acceptor number" (AN) of the solvent according to Gutman et al., [14]. In solvents with AN greater than 20 (water, ethanol or chloroform) they have the characteristic pink colour of Co(II) octahedral complexes. The electronic absorption spectra in the aforementioned solvents show the "red" spectrum, characterized by a broad band with a maximum at ~ 1200 nm, which should be assigned to the ${}^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$ excitation. A second broad band at ~ 520 nm (Fig. 2a) is attributed to the ${}^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$ transition. The shoulder at approximately 450 nm is the beginning of a strong charge-transfer band. When the "acceptor number" (AN) of the solvents is less than 20 (acetonitrile, acetone, dimethyl sulphoxide, dioxan or tetrahydrofuran) the Co(II) complexes studied have the characteristic blue colour of the Co(II) tetrahedral compounds. In addition, when these solvents are employed in electronic absorption spectra a new envelope at about 580–695 nm appears (Fig. 2b) which characterizes the "blue" spectrum indicative of the tetrahedral structure.

Consequently the change in colour should be assigned to the change in structure. It has been established that in solvents with AN below 20 the halogen coordination is enhanced and in substantial concentrations of halide

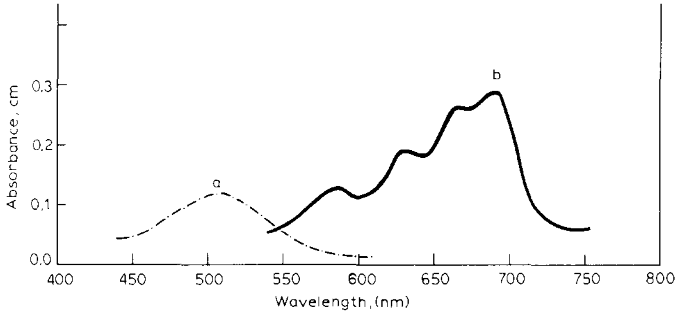


Fig. 2. Electronic absorption spectra of $[Co(3,4\text{-}Cl_2Bh)_3]Cl_2$ in: (a) 5×10^{-3} M ethanolic solution (-·-) and (b) 1.25×10^{-3} M acetonitrile solution (———).

ions the tetrahedral structure predominates. It has also been confirmed that the octahedral and the tetrahedral structures in such solvents exist in equilibrium. Equilibrium constants for analogous Co(II) complexes have been determined in a previous paper [8].

Thermal analyses

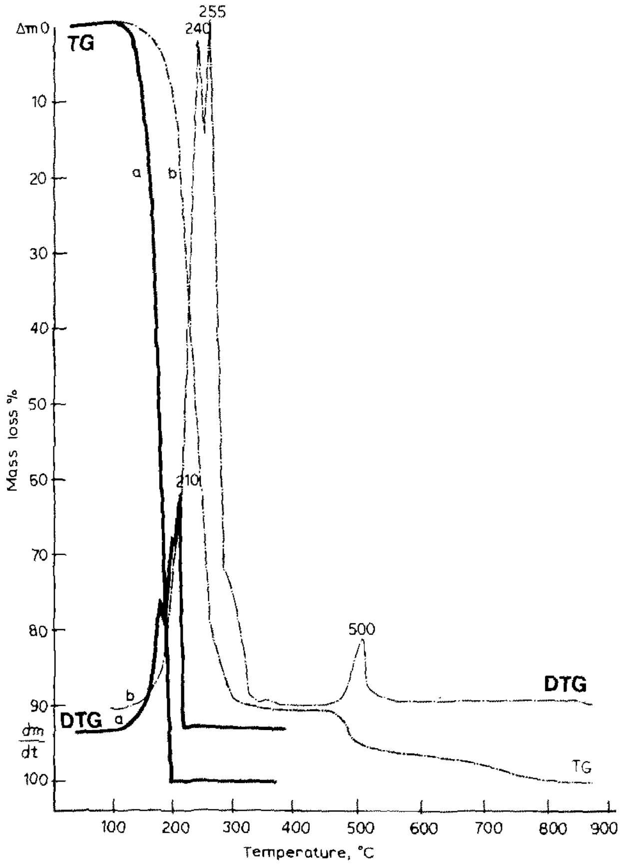
Thermogravimetric studies (TG/DTG) over the temperature range 50–800 °C for both the ligands and the corresponding complexes, were carried out in nitrogen to determine their stability and mode of decomposition. The thermal analysis curves of representative compounds are depicted in Figs. 3–10. The free ligands are found to be volatile in the range 100–250 °C ($DTG_{max} = 220$ °C) (Fig. 3a) with total mass loss, with the exception of the 3,5-Cl_2Bh ligand (Fig. 3b) which decomposes at 120–300 °C ($DTG_{max} = 240$, 255 °C) losing 88% of its weight. This is attributed to the evolution of the moiety $\{Cl_2C_6H_3CO\}$ (calculated 84.8%), while a second decomposition occurs at 300–580 °C ($DTG_{max} = 500$ °C) leading to an empty crucible.

The decomposition processes of the complexes include various thermal effects. The temperature ranges and percentage mass losses of the decompositions, the temperatures of the greatest rate of decomposition (DTG_{max}) and the theoretical percentage mass losses are presented in Tables 4–6.

The dichlorobenzoylhydrazine derivatives decompose at 160–300 °C with a rapid mass loss (55.2% found) corresponding to the elimination of two ligands (55.33% calculated.). The DTG curves of some complexes, e.g. $[Mn(2,5\text{-}Cl_2Bh)_3]Cl_2$ (Fig. 4), however, show two distinct consecutive steps for this decomposition, each one corresponding to the evolution of one ligand molecule.

The second stage (300–380 °C, $DTG_{max} = 330$ °C) corresponds to the evolved moiety $\{Cl_2C_6H_3CO\}$, after breaking of the metal–oxygen and carbon–nitrogen bonds, which means that the coordination bond M–O is weaker than the corresponding M–N. The third stage (480–650 °C) depends on the metal and corresponds to the evolution of the chlorine molecule. The residues above 700 °C were metallic Mn or Co plus a remaining portion of the ligand and, in the case of nickel complexes, metallic Ni or a mixture of metallic Ni with $NiCl_2$ owing to partial sublimation of the latter [15]. Moreover, the thermolysis curve of $NiCl_2$ at 599–800 °C ($DTG_{max} = 760$ °C) gave 84% mass loss.

As a conclusion we can state that the thermal stability of the ligand is an important determining factor in the thermal stabilities of the complexes which follow the order 3,4-Cl_2Bh > 2,4-Cl_2Bh > 2,5-$Cl_2Bh \geq$ 3,5-Cl_2Bh. The thermal stabilities based on the initial decomposition temperatures of the investigated complexes with the same ligand depend on the nature of the metal and increase in the order Ni > Co $\geq$ Mn.



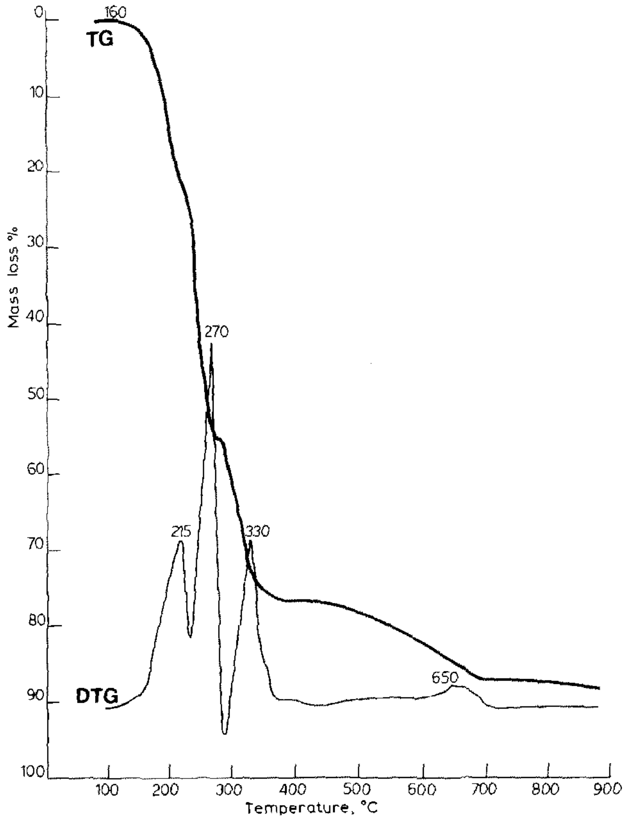


Fig. 3. Thermal curves in nitrogen for the dichlorobenzoylhydrazines: (a) $2,5\text{-}Cl_2Bh$ (———); (b) $3,5\text{-}Cl_2Bh$ (·–·–·).

Fig. 4. Thermal curves for $[Mn(2,5\text{-}Cl_2Bh)_3]Cl_2$ in nitrogen.

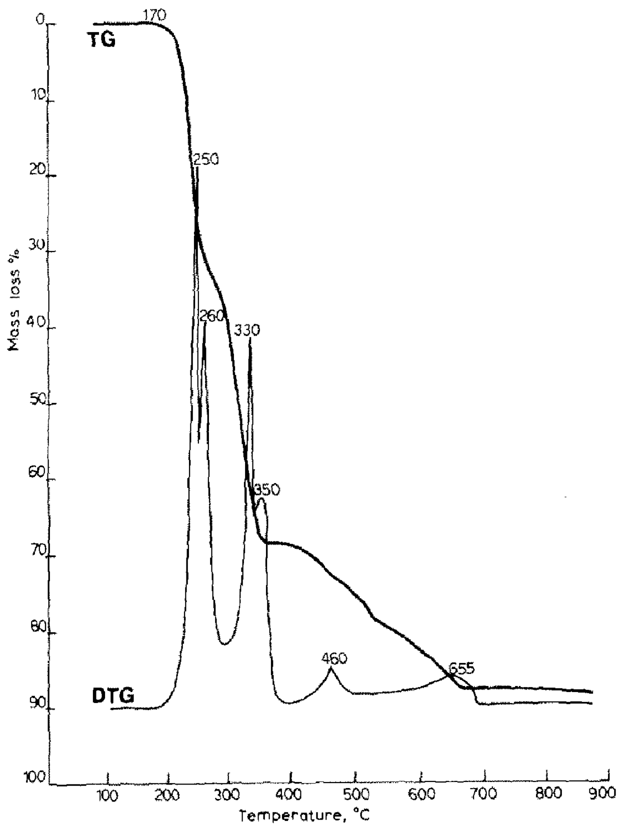


Fig. 5. Thermal curves for [Mn(3,4-Cl_2Bh$)_3$]Cl_2 in nitrogen.

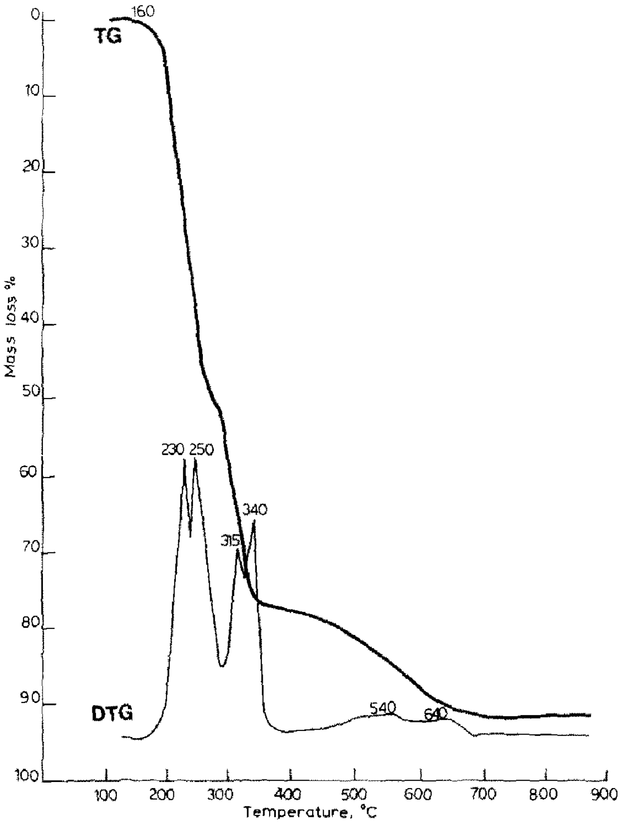


Fig. 6. Thermal curves for [Co(2,4-Cl_2Bh$)_3$]Cl_2 in nitrogen.

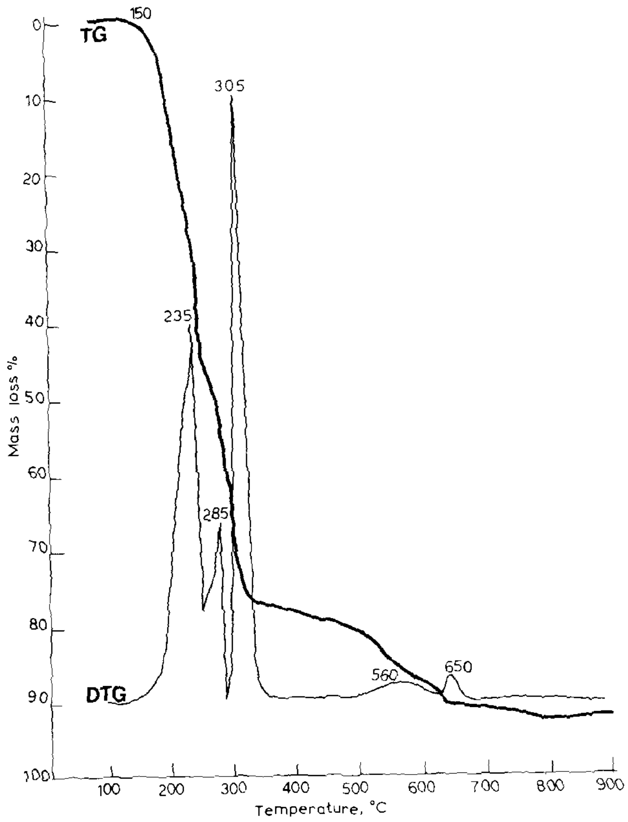


Fig. 7. Thermal curves for $[Co(2,5\text{-}Cl_2Bh)_3]Cl_2$ in nitrogen.

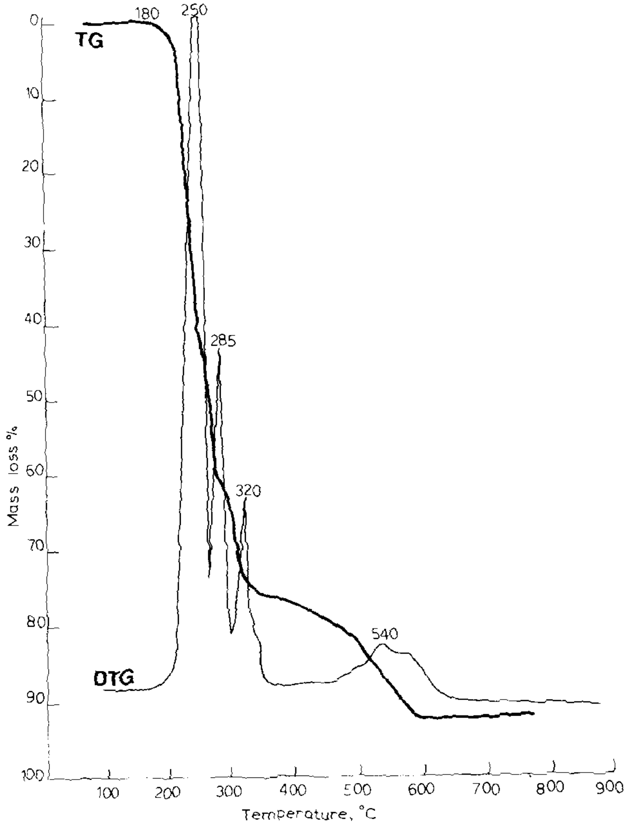


Fig. 8. Thermal curves for $[Ni(2,4\text{-}Cl_2Bh)_3]Cl_2$ in nitrogen.

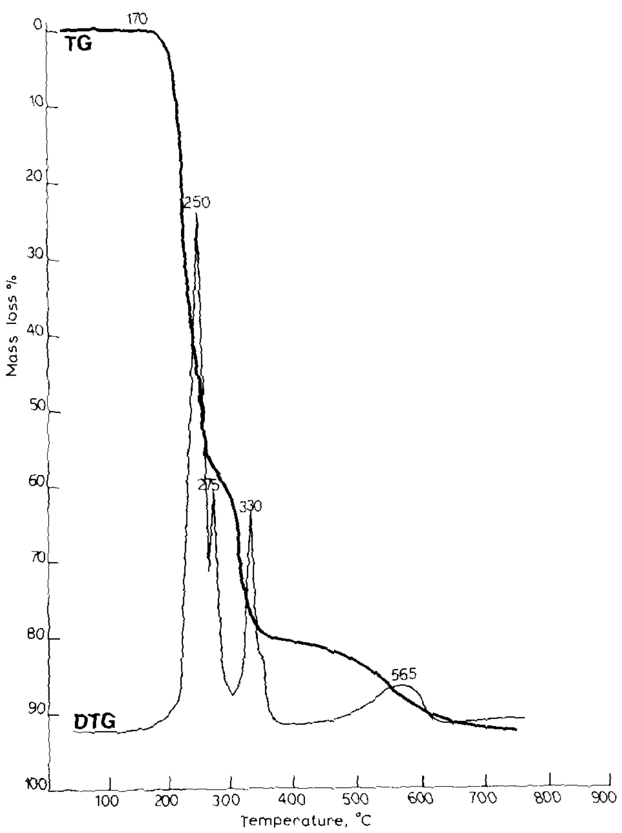


Fig. 9. Thermal curves for [Ni(2,5-Cl$_2$Bh)$_3$]Cl$_2$ in nitrogen.

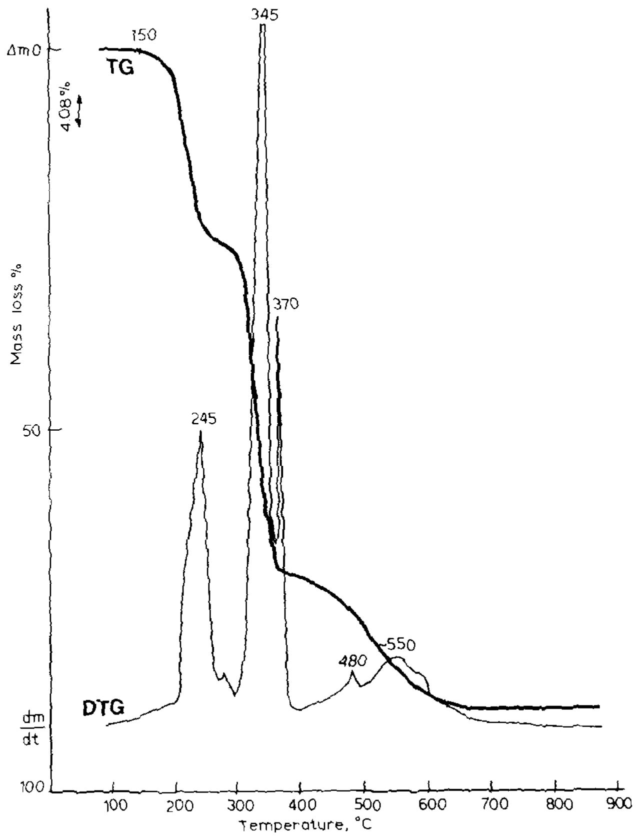


Fig. 10. Thermal curves for [Ni(3,5-Cl$_2$Bh)$_3$]Cl$_2$ in nitrogen

TABLE 4

Thermoanalytical results (TG/DTG) of some 2,4-dichlorobenzoylhydrazine complexes in nitrogen atmosphere

Complex	Stage	Temperature range (° C)	DTG_{max} (° C)	Mass loss (%)	Evolved moiety formula	Mass calcd. (%)
$[Mn(2,4\text{-}Cl_2Bh)_3]Cl_2$	1	120–260	200, 235	40.0	1.5 $Cl_2C_6H_3CONHNH_2$	41.49
	2	260–370	300, 330	29.0	1 $Cl_2C_6H_3CONHNH_2$	27.66
	3	370–650	630, br [a]	10.0	Cl_2	9.58
	Residue	> 650	–	21.0	Mn + unknown	7.42 + –
$[Co(2,4\text{-}Cl_2Bh)_3]Cl_2$	1	160–290	230, 250	54.0	2 $Cl_2C_6H_3CONHNH_2$	55.02
	2	290–370	315, 340	23.6	$Cl_2C_6H_3CO$	23.35
		370–480	–	4.4	$NHNH_2$	4.16
	3	480–690	540–br, 640 br	9.9	Cl_2	9.53
	Residue	> 690	–	8.0	Co	7.92
$[Ni(2,4\text{-}Cl_2Bh)_3]Cl_2$	1	180–265	250	50.0	1 $Cl_2C_6H_3CONHNH_2$ + $Cl_2C_6H_3CO$	50.88
	2	265–370	285, 320	27.0	1 $Cl_2C_6H_3CONHNH_2$	27.52
		370–480	–	4.5	$NHNH_2$	4.16
	3	480–620	540	10.5	Cl_2	9.53
	Residue	> 620	–	7.9	Ni	7.88

[a] br = Broad.

TABLE 5

Thermanalytical results (TG/DTG) of some 2,5-dichlorobenzoylhydrazine complexes in nitrogen atmosphere

Complex	Stage	Temperature range (° C)	DTG_{max} (° C)	Mass loss (%)	Evolved moiety formula	Mass calcd. (%)
$[Mn(2,5\text{-}Cl_2Bh)_3]Cl_2$	1	165–290	215, 270	55.2	$2\ Cl_2C_6H_3CONHNH_2$	55.33
	1a	165–235	215	27.6	$Cl_2C_6H_3CONHNH_2$	27.66
	1b	235–290	270	27.7	$Cl_2C_6H_3CONHNH_2$	27.66
	2	290–380	380	21.2	$Cl_2C_6H_3CO$	23.48
		380–560	–	4.0	$NHNH_2$	4.18
	3	560–760	650 br [a]	7.6	Cl_2	9.58
	Residue	> 760	–	12.0	Mn + unknown	7.42 + –
$[Co(2,5\text{-}Cl_2Bh)_3]Cl_2$	1	150–285	235	55.5	$2\ Cl_2C_6H_3CONHNH_2$	55.33
	2	285–360	305	22.3	$Cl_2C_6H_3CO$	23.35
		360–500	–	4.0	$NHNH_2$	4.16
	3	500–690	560 br, 650	10.2	Cl_2	9.53
	Residue	> 690	–	8.0	Co	7.92
$[Ni(2,5\text{-}Cl_2Bh)_3]Cl_2$	1a	170–265	250	56.0	$2\ Cl_2C_6H_3CONHNH_2$	55.04
	1b	265–300	275	4.0	CO	3.75
	2	300–380	330	18.4	$Cl_2C_6H_3$	19.60
		380–490	–	4.6	$NHNH_2$	4.16
	3	490–700	565	9.5	Cl_2	9.53
	Residue	> 700	–	7.5	Ni	7.88

[a] br = Broad.

TABLE 6

Thermoanalytical results (TG/DTG) of some dichlorobenzoylhydrazine complexes in nitrogen atmosphere

Complex	Stage	Temperature range (° C)	DTG_{max} (° C)	Mass loss (%)	Evolved moiety formula	Mass calcd. (%)
$[Mn(3,4\text{-}Cl_2Bh)_3Cl_2$	1a	170–250	250	28.0	1 $Cl_2C_6H_3CONHNH_2$	27.66
	1b	250–300	260	12.0	$\frac{1}{2}$ $Cl_2C_6H_3CONHNH_2$	13.83
	2	300–390	330, 350	28.4	1 $Cl_2C_6H_3CONHNH_2$	27.66
		390–530	460	10.0	Decomp. of ligand	–
	3	530–750	655 br [a]	9.6	Cl_2	9.58
	Residue	> 750	–	12.0	$MnCl_2$, Mn	17.00, 7.42
$[Co(3,4\text{-}Cl_2Bh)_3]Cl_2$	1	180–280	250	27.7	1 $Cl_2C_6H_3CONHNH_2$	27.51
	2	280–380	315, 370	35.1	1 $Cl_2C_6H_3CONHNH_2$ + unknown	27.51 + –
		380–480	–	4.4	$NHNH_2$	4.16
	3	480–700	520, 570	17.5	Cl_2 + unknown	9.53 + –
	Residue	> 700	–	14.3	Co	7.92
$[Ni(3,5\text{-}Cl_2Bh)_3]Cl_2$	1	150–300	245	27.6	1 $Cl_2C_6H_3CONHNH_2$	27.52
	2	300–400	345, 370	42.4	$1\frac{1}{2}$ $Cl_2C_6H_3CONHNH_2$	41.28
		400–500	480	6.0	$NHNH_2$	4.16
	3	500–650	550 br	11.0	Cl_2	9.53
	Residue	> 700	–	11.5	$NiCl_2$, Ni	17.41, 7.88

[a] br = Broad.

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