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THERMAL DECOMPOSITION AND MASS SPECTRAL STUDIES OF *TRANS*-[(PSEUDOHALO)(IMIDAZOLE)BIS(DIMETHYLGLYOXIMATO)COBALT(III)] COMPLEXES

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ABSTRACT

The non-electrolytic mixed-ligand complexes, [(pseudohalo)(imidazole)bis(dimethylglyoximato)cobalt(III)], $[Co(DH)_2(X)(Im)]$ (X = SCN, SeCN, N_3; DH = monoanion of dimethylglyoxime; Im = imidazole or its derivatives), are shown to have a *trans* structure on the basis of IR and NMR (^1H and ^{13}C) spectral data. The mass spectra of these complexes and those of dimethylglyoxime (DH_2) and the bis(dimethylglyoximato)nickel(II) complex, $Ni(DH)_2$, have been investigated. Molecular ion peaks are observed for DH_2, $Ni(DH)_2$ and their fragmentation products, but not for the $[Co(DH)_2(X)(Im)]$ complexes. However, in these last complexes, the mass spectral peaks assignable to DH_2, imidazole and their fragmentation products are clearly discernible. The higher intensity peaks for imidazole and its fragmentation products as compared to those for DH_2 and its fragments suggests a relatively much stronger attachment of the dimethylglyoximato chelate ring to the metal centre. Thermal decomposition studies up to 1000°C show that in most cases with increasing temperature, the compounds decompose in a stepwise manner finally forming Co_3O_4 (or Co) as the stable end product. Both mass spectra and thermal decomposition studies are in agreement so far as the binding of imidazole and DH_2 to the central Co(III) are concerned.

INTRODUCTION

The bis(dimethylglyoximato)cobalt(III) complexes, $Co(DH)_2^+$, show many reactions of the Co atom in the corrins [1] and in view of their resemblance to cobalamines are often termed as cobaloximes. They closely simulate the reactions of vitamin B_{12} and are important in vitamin B_{12} model chemistry [2–4]. The X-ray crystal structure of alkylcobaloximes [5] suggests a higher positive charge on Co thus permitting a relatively stronger attachment of a base along the axial direction. The five-membered heterocyclic base imidazole is a fundamental component of nucleic acids, enzymes and proteins and is frequently attached to metal ions. For a closer understanding of the interaction between the cobaloxime and imidazole, both of which are of known biological significance, we have studied the synthesis and other characteristics of a number of imidazole complexes of cobaloximes where the

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sixth coordination position is occupied by anions of differing electronic character [6–9].

This paper deals with the results of thermal decomposition and mass spectral investigations carried on the pseudohalo-cobaloxime complexes containing imidazole as an axial ligand.

EXPERIMENTAL

Synthesis and characterisation of the complexes

All the complexes were synthesised by the interaction of ethanolic solutions of CoX_2 ($X = CNS$, CNSe, N_3), dimethylglyoxime (DH_2) and imidazole (Im) or substituted imidazole in the presence of air [6–9]. All compounds have fairly high melting points, are non-electrolytes in DMF or $MeNO_2$ and are adequately characterised by elemental analyses, and electronic, IR and NMR (^1H and ^{13}C) spectral data.

Mass spectral measurements

The mass spectra of the compounds were recorded in a Varian CH-7 MAT spectrometer operating at an electron energy of 70 eV. The ion source was maintained at 200°C and the emission current was 300 μA.

Thermal measurements

Thermal measurements were carried out using a Netzsch simultaneous thermal analyser (Model 429) fitted with a potentiometric recorder. The equipment records T, TG and DTA simultaneously. The heating rate was 10°C min^{-1}.

RESULTS AND DISCUSSION

The synthesis of these complexes and their characterisation on the basis of electronic, IR and NMR (^1H and ^{13}C) data have been reported by us earlier [6–9]. The IR spectra and thermogravimetric data clearly show the absence of any H_2O molecules either coordinated or present as water of crystallisation. The weak band at 1750 cm^{-1} assigned to the deformation vibration mode, $\delta(O\text{–}H \cdots O)$, of the intramolecular hydrogen bridge suggests a planar configuration of the $Co(DH)_2^+$ moiety. These complexes readily react with $BF_3 \cdot Et_2O$ to form fluoro-boro bridged macrocyclic complexes further confirming the planar structure of $Co(DH)_2^+$ and providing evidence for the *trans* structure of the complexes $[Co(DH)_2(Im)(X)]$ [10]. The $\nu(C{=}N)$ band

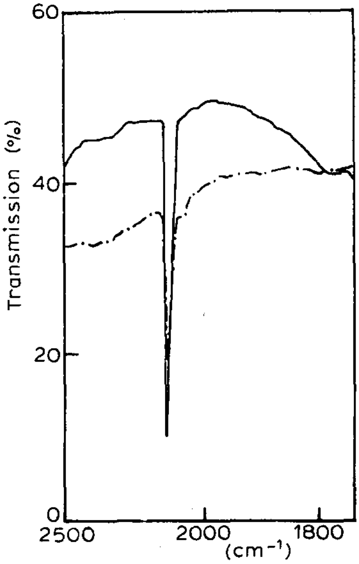


Fig. 1. Partial IR spectra, ν(CN), of [Co(DH)$_2$(SeCN)(1-AlIm)] (———) and [Co(DH)$_2$(SeCN)(1-Vi2-MeIm)] (·–·–·).

of the dioximato chelate ring is obtained at 1560 cm^{-1} and ν(N–O) is seen in two regions, i.e., 1234–1240 and 1088–1100 cm^{-1} indicating the non-equivalent nature of the two N–O bonds [11]. ν(Co–N) (N of imidazole) is seen at 430 cm^{-1} and ν(Co–N) (N of DH$^-$) at 520 cm^{-1}. The IR spectra also reveal that both CNS and CNSe are coordinated through the "soft" S or Se end. Although Co(III) is a typical "hard" acid, it has been rendered "soft" due to coordination to two dimethylglyoximate ions and the imidazole base. The intensity and sharpness of the ν(C≡N) band for the thio- and seleno-cyanato complexes indicate bonding through the S or Se end (Fig. 1) [12]. The azidocomplexes exhibit bands at 650–660 and 2020–2030 cm^{-1} indicating terminal N-bonding of the N_3^- ion [8].

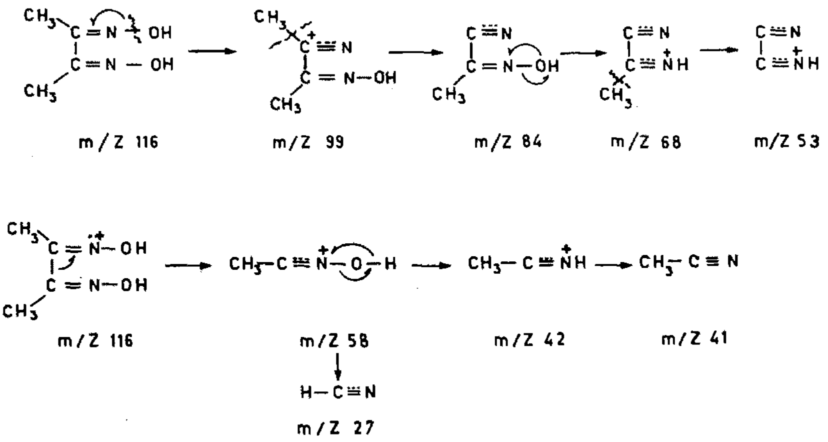
The mass spectra

Dimethylglyoxime

The mass spectra of the uncomplexed dimethylglyoxime are shown in Fig. 2. The molecular ion peak is obtained at *m/z* 116 with a relative intensity of 58.91. The most abundant species has *m/z* 42 with a relative intensity of 100 and this corresponds to the protonated form of acetonitrile, $CH_3–C≡N^+H$. Other prominent peaks are at *m/z* 99, 84, 68 and 58. The fragmentation patterns are shown in Scheme 1.

Bis(dimethylglyoximato)nickel(II), Ni(DH)$_2$

The mass spectra of Ni(DH)$_2$ are shown in Fig. 3. The characteristic



Scheme 1. Fragmentation mechanism for dimethylglyoxime, DH_2.

feature of this spectra is the observation of a isotopic intensity ratio of ^{60}Ni (natural abundance, 68.27%) and ^{58}Ni (natural abundance, 26.095%) in the parent $Ni(DH)_2$ complex and in the metallated fragmentation products. The neutral, bis-chelated parent complex, $Ni(DH)_2$, gives rise to a base peak at *m/z* 288 with an intensity of 100.00. The other prominent peaks corresponding to the fragmentation products are obtained at *m/z* 204, 174, 140, 116, 99, 58 (2 peaks) and 42. The most interesting observation is the appearance

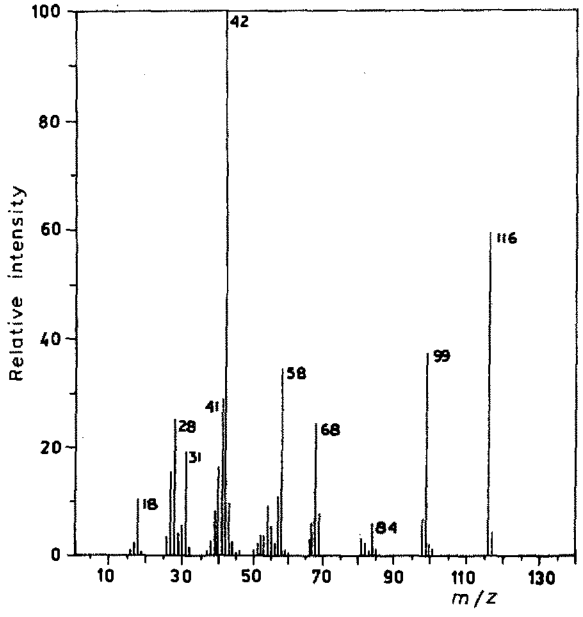
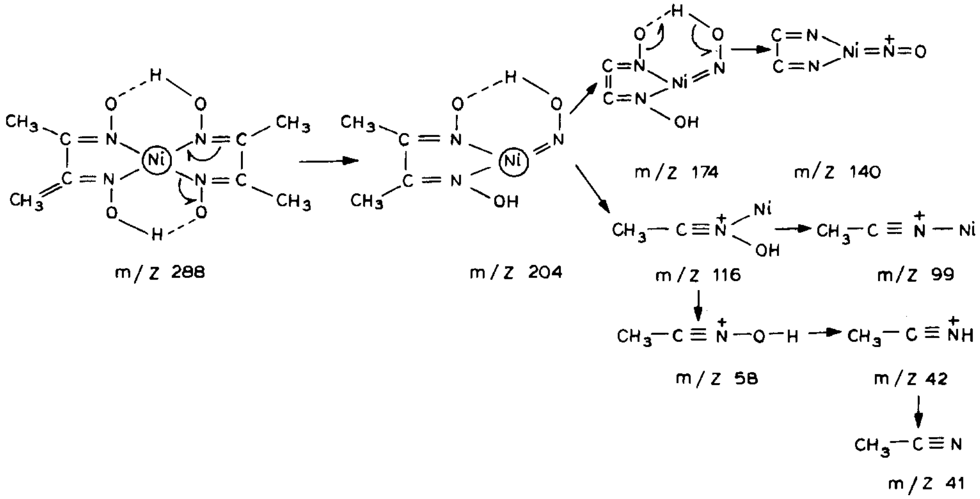


Fig. 2. Mass spectra of dimethylglyoxime, DH_2.

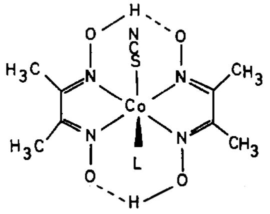


Scheme 2. Fragmentation mechanism for $Ni(DH)_2$.

of two peaks at m/z 58. The peak at m/z 58 (intensity 14.41) and at m/z 60 (intensity 5.29) are in exact isotopic ratio of ^{58}Ni and ^{60}Ni and may be assumed to be due to the Ni ion. The second peak at m/z 58 (intensity 17.10) is the fragmentation product of DH_2, $CH_3\text{-}C{\equiv}N^+\text{-}OH$. The pattern of fragmentation for $Ni(DH)_2$ is shown in Scheme 2.

trans-[Pseudohalo(imidazole)bis(dimethylglyoximato)cobalt(III)] complexes, [Co(DH)$_2$(X)(Im)]

In contrast to our observations in the mass spectra for DH_2 and $Ni(DH)_2$, the $[Co(DH)_2(X)(Im)]$ complexes do not ionise under identical conditions, suggesting greater stability for these complexes. No molecular ion peak is thus obtained. However, the subsequent fragmentation patterns correspond to the molecular ion of DH_2 and imidazole and their fragmentation products. It is of interest to note that the intensity of the peaks corresponding to imidazole or its fragmentation products are much higher as compared to the intensity of peaks corresponding to DH_2 and its fragmentation products. This is as expected since the chelate ligand group DH^- will be involved in



Formula 1

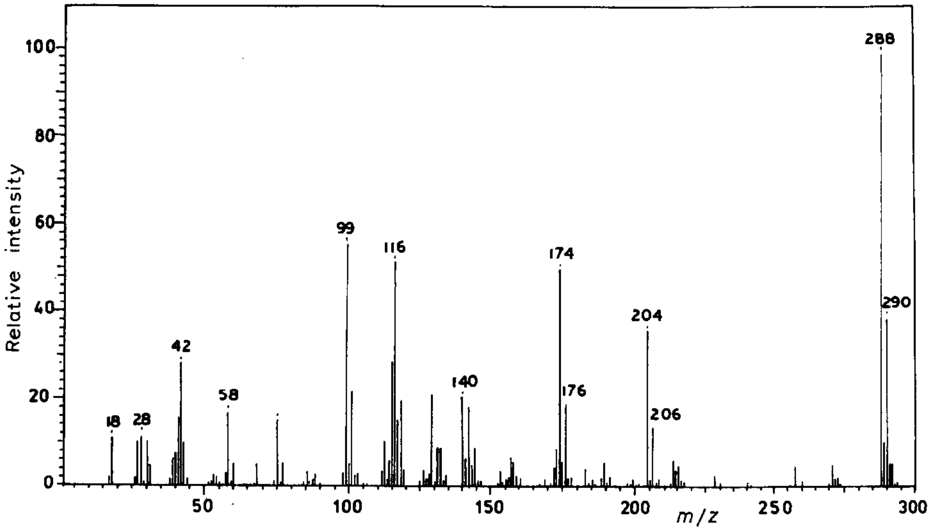


Fig. 3. Mass spectra of bis-(dimethylglyoximato)nickel(II), Ni(DH)$_2$.

stronger interaction with the Co(III) centre as compared to the non-chelating, non-ionic imidazole ligand.

This suggests the extraordinary stability of the Co(DH)$_2^+$ moiety. An examination of the mass spectra reflects the great stability of the aromatic

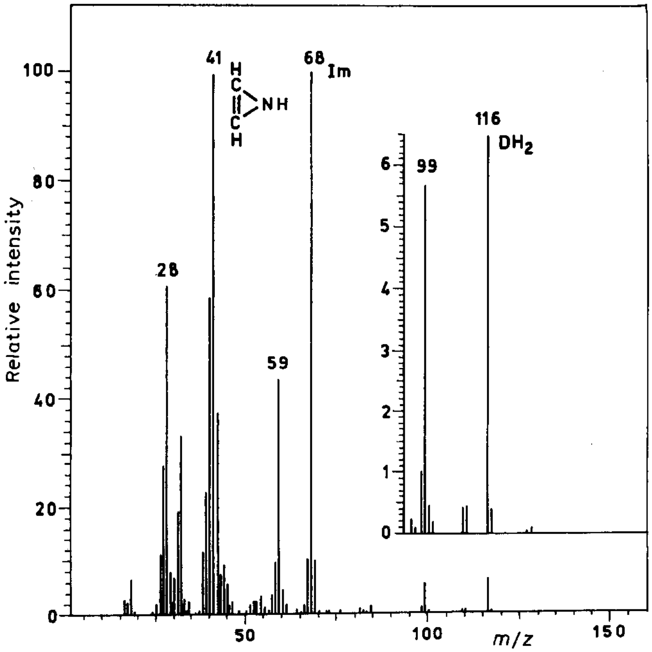


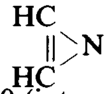
Fig. 4. Mass spectra of [Co(DH)$_2$(SCN)(Im)].

imidazole ring, the base peak corresponding to the imidazole molecular ion (*m/z* 68, intensity 100), and the loss of HCN (*m/z* 27) furnishing the most abundant fragment ion at *m/z* 41 (intensity 99.37) corresponding to the

TABLE 1

Thermal decomposition data of some [Co(DH)$_2$(SCN)(Im)] complexes

Compound	Temperature range (°C)	Weight loss (%)		Species formed	DTA peak
		Obs.	Calc.		
[Co(DH)$_2$-(SCN)(Im)]	240	67.72	67.95	1/2 $Co_2(DH)O_2$	exo
	240–265	75.01	76.28	1/2 $Co_2(DH)$	endo
	265–335	81.00	80.65	1/3 Co_3O_4	endo
	335–1000	no further loss			
[Co(DH)$_2$(SCN)-(1-MeIm)]	260	47.84	45.94	Co(DH)(SCN)	exo
	260–460	60.02	59.46	Co(DH)	exo
	460–530	68.05	69.00	1/2 $Co_2(DH)O_2$	endo
	530–800	80.00	81.53	1/3 Co_3O_4	endo
	800–1000	no further loss			
[Co(DH)$_2$(SCN)-(1-EtIm)]	160	9.18	10.83	$Co(DH)_2(SCN)L_{0.5}$	exo
	160–200	14.19	16.25	$Co(DH)_2(SCN)L_{0.25}$	endo
	200–245	29.23	28.22	$Co(DH)_{1.75}(SCN)$	exo
	245–360	40.49	41.33	$Co(DH)_{1.25}(SCN)$	exo
	360–505	47.59	47.64	Co(DH)(SCN)	exo
	505–580	61.77	60.71	Co(DH)	exo
	580–720	81.00	81.87	1/3 Co_3O_4	endo
	720–1000	no further loss			
[Co(DH)$_2$(SCN)-(1-Vi,2-MeIm)]·H_2O	120	3.52	3.80	[Co(DH)$_2$(SCN)(L)]	endo
	120–180	71.03	71.68	1/2 $Co_2(DH)O_2$	endo
	180–210	74.02	75.05	1/2 $Co_2(DH)$	exo
	210–300	82.58	84.74	1/3 Co_3O_4	endo
	300–1000	no further loss			
[Co(DH)$_2$(SCN)-(4-MeIm)]	240	30.44	32.64	$Co(DH)_{1.5}(SCN)$	exo
	240–260	40.00	39.41	$Co(DH)_{1.25}(SCN)$	exo
	260–420	48.43	45.94	Co(DH)(SCN)	exo
	420–500	60.20	59.46	Co(DH)	exo
	500–640	71.07	69.00	1/2 $Co_2(DH)O_2$	endo
	640–860	80.00	81.30	1/3 Co_3O_4	endo
	860–1000	no further loss			
[Co(DH)$_2$(SCN)-(BzIm)]	230	27.89	25.40	$Co(DH)_2(SCN)$	exo
	230–470	39.85	37.86	$Co(DH)_{1.5}(SCN)$	exo
	470–490	44.50	44.11	$Co(DH)_{1.25}(SCN)$	exo
	490–550	51.92	50.13	Co(DH)(SCN)	exo
	550–820	71.00	71.37	1/2 $Co_2(DH)O_2$	endo
	820–1000	no further loss			

three-membered ring structure,  $\overset{HC}{\underset{HC}{\|}}\!>\!NH$. Further loss of two protons in stages furnishes peaks at *m/z* 40 (intensity 58.38) and *m/z* 39 (22.88). The mass spectra of a $[Co(DH)_2(Im)(X)]$ complex are shown in Fig. 4.

The thermal decomposition studies

The thermogravimetric investigations of some cobaloximes, e.g.,

TABLE 2

Thermal decomposition data of some $[Co(DH)_2(N_3)(Im)]$ complexes

Compound	Temperature range (°C)	Weight loss (%)		Species formed	DTA peak
		Obs.	Calc.		
$[Co(DH)_2(N_3)$-(Im)]	240	66.28	66.65	1/2 $Co_2(DH)O_2$	exo
	240–520	78.71	79.86	1/3 Co_3O_4	endo
	520–630	85.33	85.25	Co	endo
	630–1000	96.00	–	–	–
$[Co(DH)_2(N_3)$-(1-Vilm)]	190	51.74	49.18	$Co(DH)N_3$	exo
	190–280	62.36	62.57	$Co(DH)_{0.5}N_3$	exo
	280–420	68.83	68.69	$Co(DH)_{0.25}N_3$	endo
	420–500	71.80	69.40	1/2 $Co_2(DH)O_2$	exo
	500–560	82.00	81.10	1/3 Co_2O_4	endo
	560–1000	no further loss			
$[Co(DH)_2(N_3)$-(1-AlIm)]	195	66.62	64.00	$Co(DH)_{0.5}N_3$	exo
	195–290	71.55	69.69	1/2 $Co_2(DH)O_2$	exo
	290–440	79.69	81.70	1/3 Co_3O_4	endo
	440–520	85.20	86.58	Co	endo
	520–1000	no further loss			
$[Co(DH)_2(N_3)$-(2-MeIm)]	200	70.66	67.79	1/2 $Co_2(DH)O_2$	exo
	200–440	81.22	80.55	1/3 Co_3O_4	endo
	440–510	86.00	85.73	Co	endo
	510–1000	no further loss			
$[Co(DH)_2(N_3)$-(2-EtIm)]	200	70.08	68.85	1/2 $Co_2(DH)O_2$	exo
	200–380	82.86	81.18	1/3 Co_3O_4	endo
	380–520	87.54	86.20	Co	endo
	520–1000	90.00	–	–	–
$[Co(DH)_2(N_3)$-(2-iPrIm)]	220	49.25	51.00	$Co(DH)N_3$	exo
	220–275	61.96	63.93	$Co(DH)_{0.5}N_3$	exo
	275–480	71.87	69.83	1/2 $Co_2(DH)O_2$	endo
	480–500	81.02	81.85	1/3 Co_3O_4	endo
	500–620	85.40	86.63	Co	endo
	620–1000	no further loss			
$[Co(DH)_2(N_3)$-(Morph)]	180	57.32	55.27	$Co(DH)_{0.75}N_3$	exo
	180–230	65.69	66.21	$Co(DH)_{0.5}N_3$	exo
	230–300	78.62	80.78	1/3 Co_3O_4	endo
	300–430	85.99	85.90	Co	endo
	430–1000	95.00	–	–	–

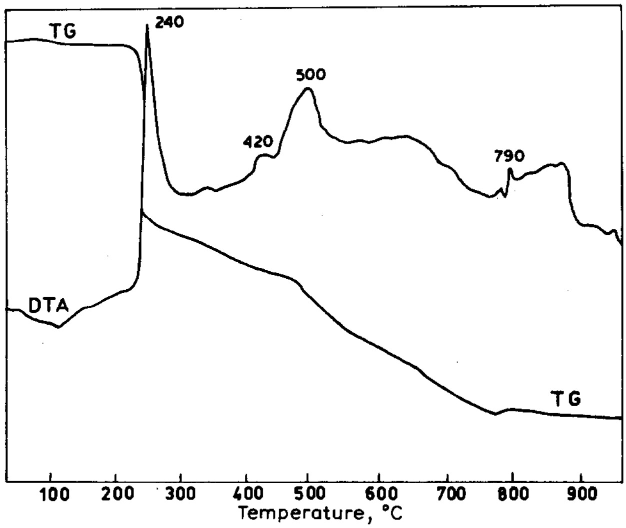


Fig. 5. TG and DTA curves for [Co(DH)$_2$(SCN)(4-MeIm)].

[Co(DH)$_2$L$_2$]X (L = MeCN, cyclohexyl isonitrile, pyridine-*N*-oxide; X = Cl, Br, I, NCS, NO$_2$) have been reported [13,14]. However, such studies with [Co(DH)$_2$(X)(Im)] complexes, particularly when X = SCN, SeCN or N$_3$, have not been made.

The thermal effects causing mass loss in the temperature range 20–250°C for the thioanatocobaloximes (Table 1) and in the temperature range

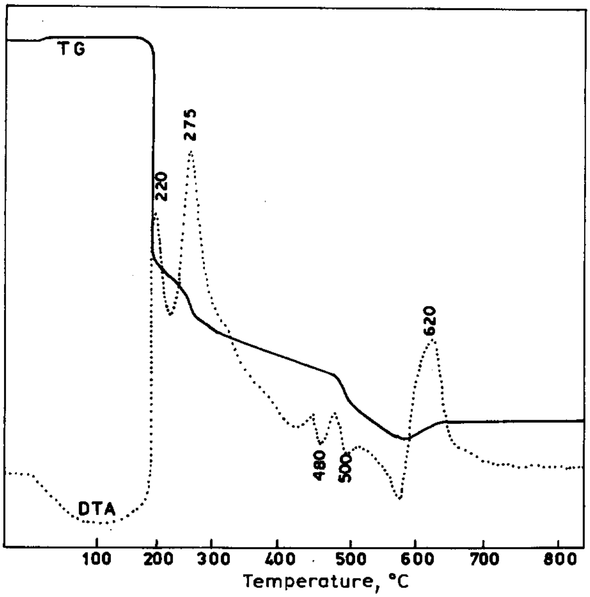


Fig. 6. TG and DTA curves for [Co(DH)$_2$(N$_3$)(2-IPrIm)].

20–180°C for the azido- and selenocyanato-cobaloximes (Table 2) are not observed, showing the absence of lattice water, changes in crystal lattice and state of aggregation, etc. Only one thiocyanato cobaloxime exhibits a weight loss corresponding to the loss of a molecule of water at about 120°C, giving rise to an endothermic peak. For all the complexes, at higher temperatures, a weight loss associated with the loss of imidazole ligand and a part of the dimethylglyoxime ring is observed accompanied by an exothermic reaction, suggesting the decomposition of the entire molecule. This observation indicates the relatively less stable Co–imidazole bonding as compared to the Co–dimethylglyoxime bonding and is in line with the mass spectral observations. At still higher temperatures (~ 600°C) the thiocyanato cobaloximes yield Co_3O_4 as the ultimate end product and the azido complexes yield either Co_3O_4 or metallic cobalt as the final product. The end product, believed to be metallic cobalt for the azido complexes, might have been formed due to the catalytic effect of the azide ion. Further heating up to 1000°C does not indicate any further mass loss due to partial volatilisation in the case of thiocyanato complexes, although this is observed for the azido cobaloxime complexes, similar to the observation made earlier [6] for the chlorocobaloxime complexes. If the initial decomposition temperature is taken as a rough guide, the TG curves indicate the following order of stability for the cobaloxime complexes, $[Co(DH)_2(X)(Im)]$ where X is: $Cl^- > SCN^- > N_3^- > SeCN^-$.

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