

## THERMAL AND SPECTROSCOPIC CHARACTERIZATION OF Co(III) AND Ni(II) DIPHENYLCARBAZONATE COMPLEXES

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### ABSTRACT

Co(III) and Ni(II) diphenylcarbazonate complexes (ligand: 3 oxo-1,5-diphenylformazan,  $\text{PhN}=\text{NCONHNHPh}$ ; abbreviation,  $\text{H}_2\text{DCO}$ ) were synthesized as solid phases by extraction from dilute solutions.

Chemical and thermogravimetric analysis, together with IR and electronic absorption spectra of the ligand and the two complexes were carried out. IR vibrational bands revealed that both complexes are ketonic in nature, where Co(III) and Ni(II) ions are hexacoordinated as deduced from their electronic absorption bands characteristic of an octahedral configuration. Results of thermogravimetric analysis were in agreement with the general molecular formulae  $\text{Co}(\text{HDCO})_3$  and  $\text{Ni}(\text{HDCO})_2 \cdot 2\text{H}_2\text{DCO}$  proposed by chemical analysis. The TG and DTG curves of the Co(III) complex showed four thermal dissociation steps ending with a volatilization process at  $> 392^\circ\text{C}$ . The TG and DTG curves of the Ni(II) complex showed five thermal steps with a final step at  $> 545^\circ\text{C}$ . On the basis of the initial decomposition temperatures, the thermal stability of the compounds studied was found to follow the order  $\text{H}_2\text{DCO} \approx \text{Co}(\text{HDCO})_3 > \text{Ni}(\text{HDCO})_2 \cdot 2\text{H}_2\text{DCO}$

### INTRODUCTION

Information on the reactions of a considerable number of transition metal ions with diphenylcarbazone in solution is available in the literature [1–3], where determination of equilibrium, extraction, dissociation and stability constants of such complexes have been performed. In addition, the general molecular formula of the complexes was proved to be  $\text{M}(\text{HDCO})_n$  according to the valence of the cation, with the exception that Hg(I) and Hg(II) seemed to form more than one complex. Among the series of cations studied [1–3], the chemical composition of cobalt and nickel complexes was given as  $\text{M}(\text{HDCO})_2$  ( $\text{M} = \text{Co(II)}$  and  $\text{Ni(II)}$ ) (experiments were performed under nitrogen atmosphere in the case of the easily oxidizable Co(II) ions). Previous work [4,5] on an analogous cobalt dithizonate complex (ligand,  $\text{PhN}=\text{NCSNHNHPh}$ ; abbreviation  $\text{H}_2\text{Dz}$ ) revealed uncertainty concerning its chemical composition, which was partially resolved [6] giving support to the formula  $\text{Co}(\text{HDz})_3$ . Further valuable information on structural chemical

formulae of solid  $M(\text{HDCO})_n$  complexes could be achieved by using other experimental techniques such as thermal analysis, which is not usually applicable to the study of complexes in solution. Much work dealing with the thermal behaviour of coordination compounds has been published [7,8], owing to the continuously increasing interest in their properties. However, available results on the preparation and characterization of solid cobalt and nickel diphenylcarbazone complexes are apparently lacking in the literature. In view of the previous results reported on such complexes in solution, in order to try to characterize the complexes, we have prepared them in the solid state.

## EXPERIMENTAL

Benzene (thiophene and methylthiophene free), sodium perchlorate-perchloric acid buffer solutions and diphenylcarbazone ( $\text{H}_2\text{DCO}$ ) were purified according to the methods described in the literature [9–11]. The two starting salts  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  were obtained from BDH. Under normal atmosphere, complexes were prepared by shaking, for 10 min, 1 l of  $2 \times 10^{-4}$  M solution of purified ligand ( $\text{H}_2\text{DCO}$ ) with 1 l of  $10^{-4}$  M aqueous solution of the corresponding metal salt buffered at  $\text{pH} \approx 4$  and  $\text{pH} \approx 5$  for cobalt and nickel reaction media, respectively. The organic layer was separated and the bulk of the solvent distilled off under mild reduced pressure at  $40^\circ\text{C}$ . The residual complexes were washed several times with benzene to remove unreacted ligand.

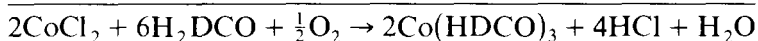
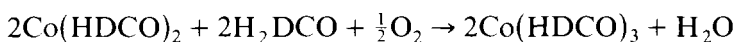
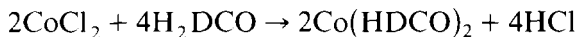
IR spectra were recorded using a Perkin–Elmer 577 spectrophotometer (KBr-disc method). The electronic spectrum of the solid Co complex was recorded against MgO as a reference using an automatic Carl Zeiss DMR 21 spectrophotometer. A recording Shimadzu 240 spectrophotometer was used in measuring the electronic spectra of the Ni complex and the ligand in solution. TG and DTG curves were measured using a Netzsch apparatus at a heating rate of  $5^\circ\text{C min}^{-1}$  in static air. The ligand, Co and Ni complexes were subjected to microchemical analysis (Table 1).

TABLE 1  
Results of microanalysis of the compounds studied

Compound	C (%)		N (%)		H (%)		Metal (%)	
	Found	Theor.	Found	Theor.	Found	Theor.	Found	Theor.
$\text{H}_2\text{DCO}$	65.16	65.26	23.07	23.42	4.97	4.63	–	–
$\text{Co}(\text{HDCO})_3$	60.80	60.31	21.34	21.64	4.76	4.28	7.30	7.59
$\text{Ni}(\text{HDCO})_2 \cdot 2\text{H}_2\text{DCO}$	62.56	61.37	20.47	22.02	5.57	4.56	5.40	5.77

## RESULTS AND DISCUSSION

Based on the results of the microchemical analysis (Table 1), the general molecular formulae of the complexes can be given as  $\text{Co}(\text{HDCO})_3$  and  $\text{Ni}(\text{HDCO})_2 \cdot 2\text{H}_2\text{DCO}$ . The  $\text{Co}(\text{II})$  ion (starting valency) was oxidized to  $\text{Co}(\text{III})$  ion, which normally shows a particular affinity for nitrogen donors. The formation of  $\text{Co}(\text{HDCO})_3$  may take place via the following reactions



It seems, under the present experimental conditions, that the formation of  $\text{Co}(\text{HDCO})_3$  as an end product is thermodynamically more favourable and stable than that of  $\text{Co}(\text{HDCO})_2$ . However, it is well known that  $\text{Co}(\text{III})$  in many of its complexes, such as with ammonia and ethylenediamine, can be obtained by drawing a vigorous stream of air for several hours through  $\text{Co}(\text{II})$  solutions containing the corresponding ligand [12].

*IR spectra*

A comparison of the IR spectra of  $\text{Co}(\text{HDCO})_3$  and  $\text{Ni}(\text{HDCO})_2 \cdot 2\text{H}_2\text{DCO}$  complexes with that of the ligand  $\text{H}_2\text{DCO}$  (Fig. 1), reveals that  $\text{Co}(\text{III})$  and  $\text{Ni}(\text{II})$  complexes are ketonic in nature. This conclusion is based on the assignment of the frequencies of most interest with regard to structure which are described below.

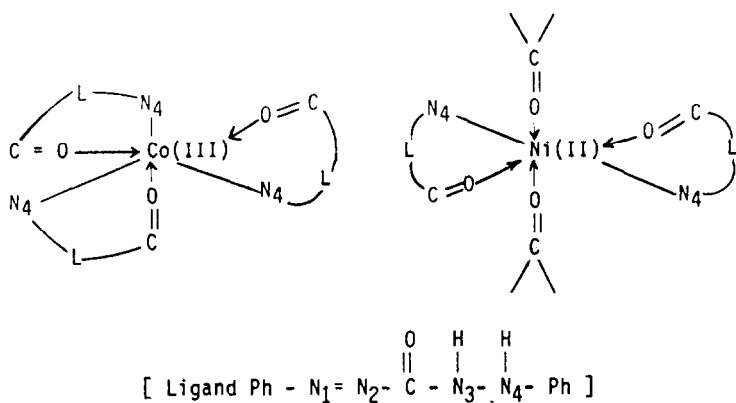
(a) The bands arising in the  $1700 \text{ cm}^{-1}$  ( $\text{Co}(\text{III})$  complex) and  $1705 \text{ cm}^{-1}$  ( $\text{Ni}(\text{II})$  complex) range can be assigned to  $\nu(\text{>C=O})$  stretching vibration. This feature enables us to suppose that the two complexes are in the ketonic form. It is observed, however, that this band is more intense in the  $\text{Co}(\text{III})$  complex than in the  $\text{Ni}(\text{II})$  complex which may be a result of the presence of the  $\text{>C=O}$  group in the *cis* position around the  $\text{Co}(\text{III})$  ion and in the *trans* position around the  $\text{Ni}(\text{II})$  ion. Moreover, the intensities of these two bands of the complexes are somewhat weaker than that of the pure ligand as a result of the  $\text{>C=O}$  group sharing in coordination (Fig. 1).

(b) The absence of  $\nu(\text{C=N})$  stretching vibration at  $1590 \text{ cm}^{-1}$  supports the ketonic structure.

(c) The presence of  $\nu(\text{NHCO})$  stretching vibrations at  $3190$  and at  $1645\text{--}1670 \text{ cm}^{-1}$  (very weak shoulder) show that complexation has taken place through the carbonyl group.

(d) The appearance of some very weak bands in the lower frequency range ( $< 520 \text{ cm}^{-1}$ ) may be related to metal–oxygen and metal–nitrogen bonds.

According to the results obtained from the chemical analysis and the IR spectra we suggest the following molecular structural formulae



### Electronic spectra

Figure 2 shows the electronic absorption spectra of the ligand together with those of the two complexes. It is known that the majority of Co(III)

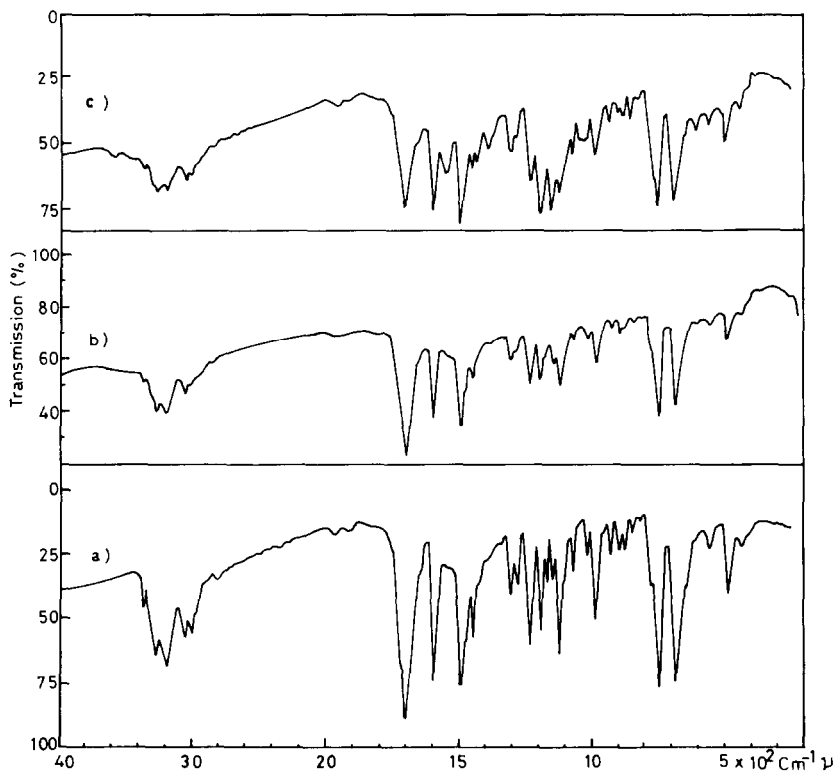


Fig. 1. IR vibrational spectra of: (a) diphenylcarbazone; (b) cobalt(III) diphenylcarbazonate; (c) Ni(II) diphenylcarbazonate.

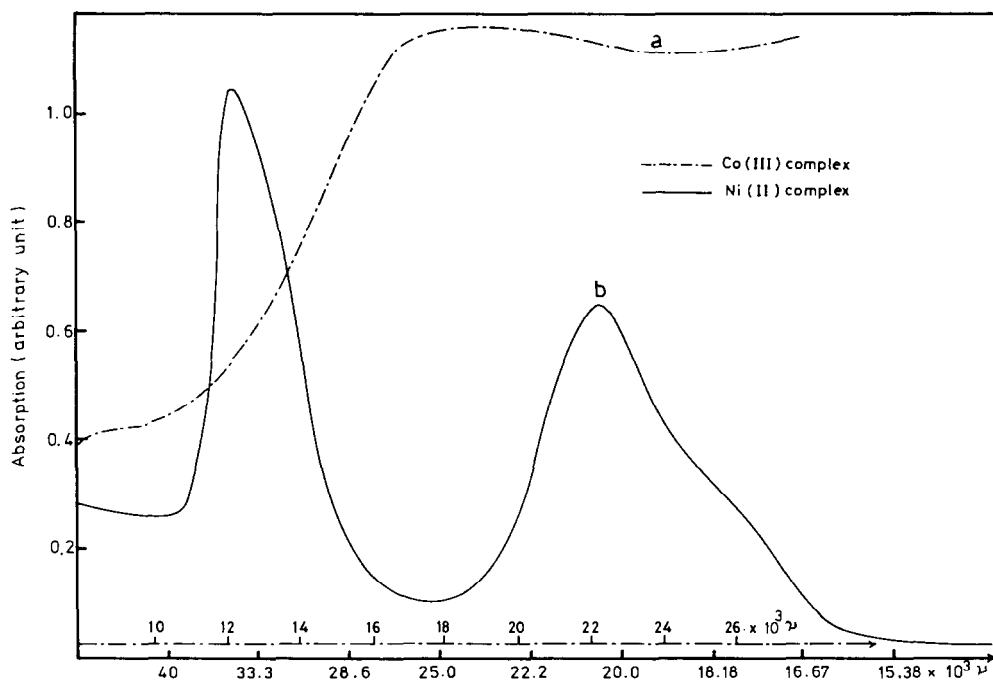


Fig. 2. Electronic absorption spectra of: (a) solid cobalt(III) diphenylcarbazonate; (b) dilute solution of Ni(II) diphenylcarbazonate in benzene.

complexes do not contain any unpaired spins, and hence, the absorption spectra of an octahedrally coordinated Co(III) should show two strong bands corresponding to the transitions,  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  and  ${}^1A_{1g} \rightarrow {}^1T_{2g}$  (low and high frequency band, respectively). In addition, some weak singlet-triplet bands could occur. Based on theoretical consideration, a decrease in symmetry from  $O_h$  to  $D_{4h}$  or  $C_{2v}$  (*trans* or *cis* configuration, respectively) would lead to a splitting or a broadness of the absorption maxima as a result of the splitting of the excited states. The measured absorption spectrum of the Co(III) complex (Fig. 2, curve 2) shows two bands: a low frequency band as a shoulder at  $14200\text{ cm}^{-1}$  and a high frequency broad band centred at  $19200\text{ cm}^{-1}$ , together with a very weak spin-forbidden band at  $\sim 9000\text{ cm}^{-1}$ . This spectrum is in fair agreement with the assumption that the  $\text{Co}(\text{HDCO})_3$  complex is in the *cis* configuration as estimated from the IR spectrum and resembles, at the same time, the spectra of many known Co(III) complexes [13]. The spectrum of the Ni(II) complex (Fig. 2, curve 3) shows, generally, the feature that is normally found for octahedrally coordinated Ni(II), although the true environment will be of lower symmetry than  $O_h$ . The observed bands at  $17540$  and  $20610\text{ cm}^{-1}$  may be assigned to the transitions,  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$  and  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ , respectively.

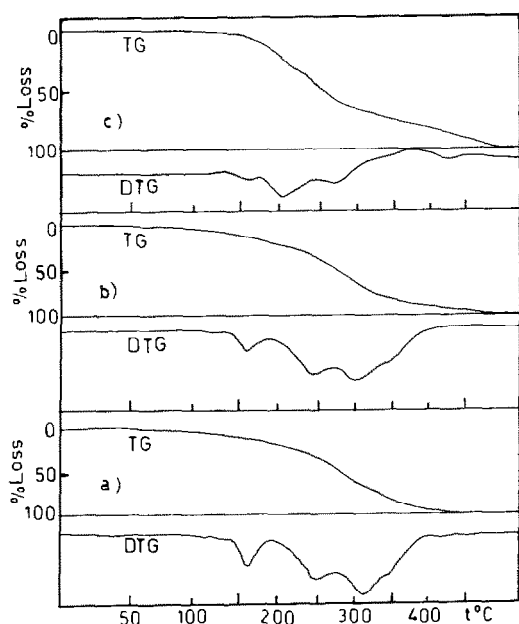
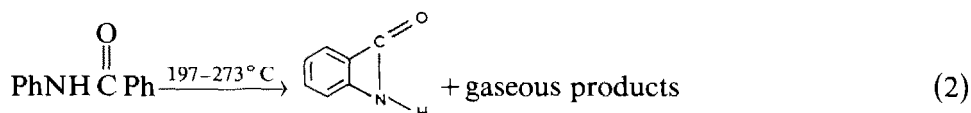


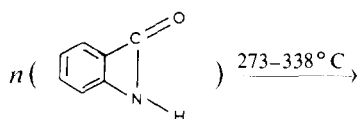
Fig. 3. TG and DTG curves of: (a) diphenylcarbazone; (b) cobalt(III) diphenylcarbazonate and Ni(II) diphenylcarbazonate.

### Thermal analysis

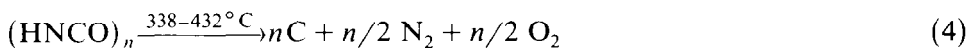
An examination of the TG curves (Fig. 3) of the free solid diphenylcarbazone ligand and the Co(III) and Ni(II) complexes indicate that the ligand and the Co(III) complex are stable up to  $\sim 135^{\circ}\text{C}$ , whereas the Ni(II) complex is stable up to  $\sim 130^{\circ}\text{C}$ . Moreover, the mass losses observed beyond these temperatures are not separated by a period of constant mass, indicating that the intermediate products formed are not stable over a definite temperature range. However, the TG curves do show a number of discontinuities at different temperatures owing to the formation of the thermodynamically unstable and non-isolable intermediate species. Accordingly, the sequence of thermal decomposition reactions and their corresponding defined steps as deduced from the TG and DTG curves, respectively (Fig. 3, Table 2) are presented below

(a) Ligand (abbreviation,  $\text{H}_2\text{DCO}$ )

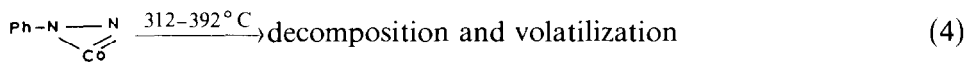
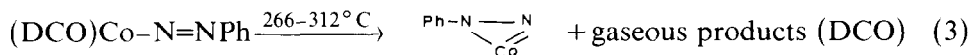
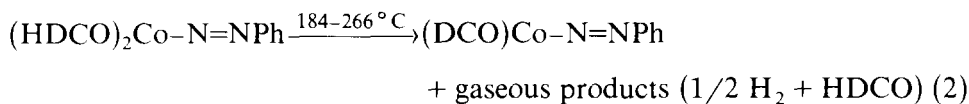
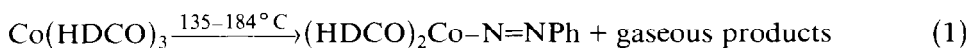




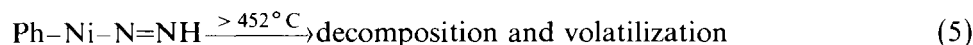
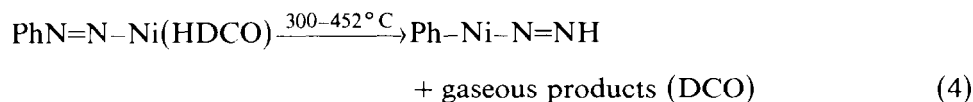
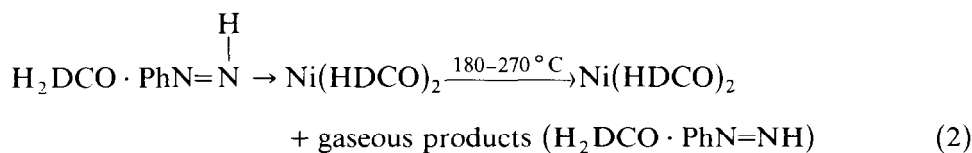
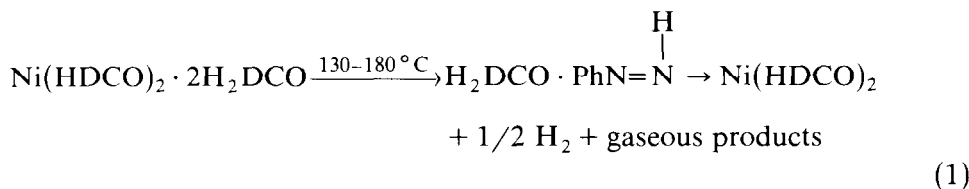
(HNCO)<sub>n</sub> as polymer + gaseous products (3)



(b) Co(III) complex



(c) Ni(II) complex



It appears from the above results of thermal studies that the diphenyl-carbazone ligand (chelate type) is a non-volatile ligand since it undergoes





decomposition (Fig. 3a). Therefore one can expect, that for metal ion–diphenylcarbazonate complexes, the thermal decomposition may occur predominantly by the cleavage of some bonds of the chelate ring and not normally by the cleavage of metal ion–donor atom bonds. This is analogous to previously reported thermal observations of complexes with non-volatile ligands, such as oxime complexes [8]. Actually, the thermal results obtained for Co(III) and Ni(II) diphenylcarbazonates show that both types of bond cleavage occur. However, a difference between the starting temperatures of the first decomposition reactions of the Co(III) and Ni(II) complexes ( $\sim 135$  and  $\sim 130^\circ\text{C}$ , respectively, Fig. 3) is observed, which can be attributed to the presence of some less strongly bonded ligands to Ni(II) than to Co(III). This assumption agrees fairly well with the suggested structural formulae of both complexes, where Ni(II) adds two weakly-bonded ligands to complete its octahedral configuration. However, further decomposition of the two complexes at higher temperatures reveals the formation of different intermediates, thus representing a cleavage of bonds with different strengths within the bonded ligands, which are probably not equivalent in energy. Therefore, a prediction of the stepwise course of the thermal decomposition reaction of the Co(III) and Ni(II) complexes is not possible.

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