

The thermal behaviour of ternary Co(II), Ni(II) and Cu(II) complexes with phthalate ion and 1,10-phenanthroline or 2,2'-dipyridylamine

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Abstract

The synthesis, spectroscopic and structural characteristics, as well as the thermal behaviour, of a series of Co(II), Ni(II) and Cu(II) complexes with the phthalate ion and 1,10-phenanthroline or 2,2'-dipyridylamine are presented. Thermal stability increases in the order $\text{Cu} < \text{Ni} < \text{Co}$ for the 1,10-phenanthroline complexes, and $\text{Ni} < \text{Cu} < \text{Co}$ for the 2,2'-dipyridylamine complexes. The relationship between the thermal properties of the complexes and their crystal structures, their polymeric nature, and the presence or absence of water of crystallization is discussed.

INTRODUCTION

The factors affecting the thermal stability of transition metal complexes in the solid state are not well understood. There are many examples in which the following order of thermal stability was established [1–5]: $\text{Mn} > \text{Fe} > \text{Co} > \text{Ni} > \text{Cu} < \text{Zn}$ (order (1)). This is the reverse of the Irving–Williams series [6], i.e. the stability order of the complexes in aqueous solution. In accordance with a suggestion made by D'Ascenzo and coworkers, such behaviour can be explained by a decrease of the intermolecular forces in the solid state with increasing strength of the intramolecular metal–ligand bonds [1,3]. However, in several cases, exceptions to the above series [7,8], or even an inverse trend of thermal stability, have been observed [9].

Previous studies were generally performed on compounds which are not well characterized in the crystallographic sense. This paper reports the synthesis and thermal decomposition of six ternary transition metal complexes with phthalate ion (pht) and 1,10-phenanthroline (phen) or 2,2'-di-

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pyridylamine (dipy). Three of the complexes were obtained only as monocrystals and their crystal structures have been published elsewhere [10]. The complex $[\text{Cu}(\text{H}_2\text{O})(\text{phen})(\text{pht})] \cdot 0.7\text{H}_2\text{O}$ has been previously studied in some detail, either as an anhydrous [11–13] or as a hydrated compound [14]. Its crystal structure is also published [15]. The fact that crystal structures are known for four of the described compounds could provide more insight into the factors determining their thermal stability.

EXPERIMENTAL

Preparation of the complexes

The 2,2'-dipyridylamine used was of purum quality, while the other reagents were of p.a. grade. After mixing diluted solutions of $\text{M}(\text{NO}_3)_3$ (in H_2O) and the amine ligand (in EtOH), an aqueous solution of Na_2pht was added dropwise with stirring. The instantly formed precipitate was filtered after standing overnight, rinsed with water, EtOH and ether, and air dried. In all cases, equimolar (typically 0.01 mol) quantities of reagents were used, giving yields of about 90%.

The metal content was determined by dry combustion of the samples followed by weighing of the residual metal oxide (as MO). The percentage contents of C, H and N were determined by standard microanalysis.

Apparatus

The IR spectra were recorded as Nujol mulls ($4000\text{--}500\text{ cm}^{-1}$ range) on a Perkin-Elmer FTIR 1600 spectrophotometer.

The diffuse reflectance spectra were obtained on a Beckman 5240 UV spectrophotometer in the $750\text{--}350\text{ nm}$ range.

X-ray powder diffraction analysis was carried out on a Philips PW 1710 diffractometer using $\text{Cu K}\alpha$ (graphite monochromated) radiation.

The thermal analysis studies were performed on a Perkin-Elmer model TGS-2 thermobalance using 5–10 mg samples. The heating rate was 5°C min^{-1} in a dry nitrogen ($60\text{ cm}^3\text{ min}^{-1}$) or dry oxygen ($30\text{ cm}^3\text{ min}^{-1}$) atmosphere.

RESULTS AND DISCUSSION

Stoichiometry and structure

The formulae of the complexes, together with their colour, and analytical and spectral data are listed in Table 1. Because the crystal structures of complexes 1, 2, 3 and 5 are known [10,15], it was possible to compare peak

TABLE 1

Analytical data (calculated values in parentheses), some characteristic IR vibrations and positions of maxima in diffuse reflectance spectra

No.	Complex and abbreviation	Colour	Analytical data			$\bar{\nu}_{\text{as}}(\text{COO})$ (cm^{-1})	$\bar{\nu}_{\text{s}}(\text{COO})$ (cm^{-1})	$\Delta\bar{\nu}^{\text{a}}$ (cm^{-1})	$\lambda_{\text{max}}^{\text{b}}$ (nm)
			M (%)	C (%)	H (%)				
1	[Co(pht)(H ₂ O) ₃ (phen)]·H ₂ O CoPhen	Pink	12.74 (12.40)	50.79 (50.54)	4.43 (4.24)	6.32 (5.89)	1409	150	490 (525) ^c
2	[Ni(pht)(H ₂ O) ₃ (phen)]·H ₂ O NiPhen	Light blue	12.33 (12.36)	50.60 (50.56)	4.03 (4.24)	6.32 (5.89)	1409	150	610
3	[Cu(pht)(H ₂ O)(phen)]·0.7H ₂ O CuPhen	Blue	14.82 (14.49)	54.37 (54.78)	3.72 (3.54)	6.65 (6.39)	1613	211	613
4	[Co(pht)(dipy)] CoDipy	Pink	14.32 (14.95)	54.39 (54.84)	3.68 (3.32)	10.99 (10.66)	1553	135	498 542
5	[Ni(pht)(H ₂ O) ₃ (dipy)]·2H ₂ O NiDipy	Light blue	12.53 (12.13)	44.91 (44.66)	4.79 (4.79)	9.50 (8.68)	1393	152	606
6	[Cu(pht)(dipy)] CuDipy	Green	15.72 (15.93)	54.48 (54.20)	3.37 (3.29)	10.60 (10.53)	1404	165	769

^a Where necessary, $\Delta\bar{\nu}$ was calculated as a mean value.^b The maxima listed are the [⁴T_{1g}(F) → ⁴T_{1g}(P)] transition for high-spin Co(II) and the [³A_{2g} → ³T_{1g}(F)] transition for octahedral Ni(II) complexes.^c Shoulder.

positions in the X-ray powder diffraction patterns with the values calculated from cell constants. In all cases, identical structures were confirmed.

Because one of the aims of this study is to relate the thermal properties of these complexes to their molecular structures, the discussion will start with a brief description of the structures.

The complexes CoPhen and NiPhen (for abbreviations see Table 1) are isostructural; the structure of NiDipy is very similar [10]. The central atoms are in a distorted octahedral environment with three H₂O molecules in the meridian position. The remaining three sites are occupied by two N atoms of the diamine ligand and by an O atom of the pht ion. All three compounds consist of discrete molecules. Phthalate ions act as unidentate ligands with only one –COO[–] group coordinated to the metal. The second –COO[–] group, together with coordinated and uncoordinated H₂O molecules, forms an extended system of hydrogen bonding. In the Cuphen complex, Cu has square-pyramidal geometry with an H₂O molecule in the apical position [15]. Phthalate ion is coordinated in a bis-unidentate manner and plays a bridging role.

Both CoDipy and CuDipy are slightly disordered (broad diffraction maxima). This fact and their insolubility in common polar and non-polar solvents suggest that these compounds are polymeric in nature. Although some similarities between their diffractograms are observed, they are not isostructural.

The electronic spectra of the Co and Ni complexes (Table 1) are in accordance with a (distorted) octahedral geometry of the metal site. The spectra of the Cu complexes consist of a broad asymmetric band characteristic for the Cu²⁺ (d⁹) ion.

IR spectra confirm the coordination of diamine ligands and the presence (or absence) of water of hydration. It is worth examining the position of the –COO[–] vibrations in the IR spectra in some detail (Table 1). It is clear that $\Delta\bar{\nu}$ ($\bar{\nu}_{\text{as}} - \bar{\nu}_{\text{s}}$) for the Cu complexes is greater than $\Delta\bar{\nu}$ for the Co and Ni complexes. Also, if the data in Table 1 are compared with the data for “purely ionic” Na₂pht ($\Delta\bar{\nu} = 157 \text{ cm}^{-1}$), it is seen that there is no support for unidentate coordination of –COO[–] groups in the Co and Ni complexes [16]. Both these conclusions are to be expected for transition-metal–pht complexes [17]. Although it is obvious that IR spectroscopy is not a very good tool for predicting the nature of the coordination of the pht ions, the low value of $\Delta\bar{\nu}$ for CoDipy might suggest that the –COO[–] groups play a chelating role [16].

Thermal decomposition

The TG curves recorded in N₂ and O₂ atmospheres are given in Figs. 1 and 2, respectively.

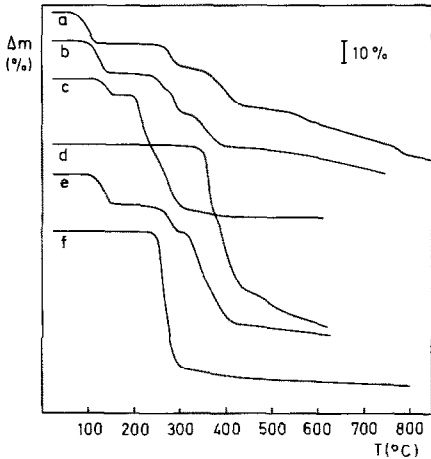


Fig. 1. TG curves of (a) CoPhen, (b) NiPhen, (c) CuPhen, (d) CoDipy, (e) NiDipy, and (f) CuDipy in N_2 .

In both the N_2 and O_2 atmosphere, the dehydration processes are very similar, but the initial and final temperatures are slightly lower under O_2 . All hydrated complexes lose water in a single step and it was not possible to distinguish between coordinated and lattice water molecules.

Only CuPhen can be obtained as an anhydrous compound. In the other complexes, between 4.3% (CoPhen) and 27.4% (NiDipy) of the total H_2O

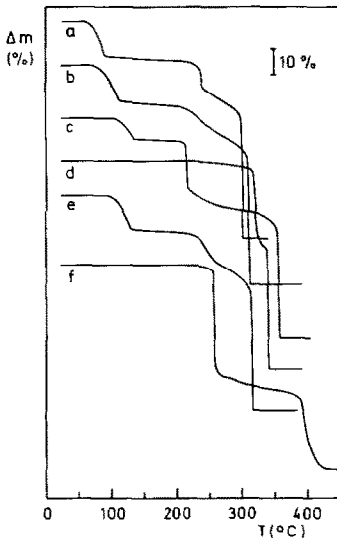


Fig. 2. TG curves of (a) CoPhen, (b) NiPhen, (c) CuPhen, (d) CoDipy, (e) NiDipy, and (f) CuDipy in O_2 .

content remains. These water molecules are eliminated in the subsequent almost horizontal step; further decomposition begins before the compounds are completely dehydrated.

The initial dehydration temperature for phen complexes increases in the order $\text{CoPhen} < \text{NiPhen} < \text{CuPhen}$.

The type of atmosphere has a great influence on the further decomposition of the compounds. In N_2 , the decomposition takes place in two or more unidentified steps (Fig. 1) and the residue does not reach constant mass up to 850°C .

In O_2 atmosphere, after an initial period, the Co and Ni complexes burn with vertical mass loss. The Cu complexes decompose in two steps (Fig. 2, curves c and f). This suggests a specific role of the Cu(II) ion in the examined systems.

The first step in the decomposition of the Cu(II) complexes corresponds either to the removal of the phthalic anhydride from CuPhen (mass loss found, 37.5%; calculated for $1.7\text{H}_2\text{O} + \text{phthalic anhydride}$, 39.94%) or to the removal of the dipy ligand from CuDipy (mass loss found, 41.2%; calculated for dipy, 42.92%). Both possibilities were found previously during study of the analogous mixed Cu(II) complexes with dicarboxylate ions and heterocyclic polyamines [12]. The differences are explained by the different π -acceptor abilities of the polyamine ligands [12]. In the complexes containing a strong π -acceptor (such as phen), the Cu–N bond is stronger than the Cu–O bond and the dicarboxylato ligand is removed first. If diamine ligands are weak π -acceptors (such as dipy), the order of elimination is reversed.

In all cases, oxides of the MO type were confirmed as residues in the O_2 atmosphere. An exception is CuPhen, where Cu_2O is in better agreement with the experimental data (found, 16.5%; calculated, 15.31% for Cu_2O and 18.14% for CuO).

Thermal stability

The initial decomposition temperatures (T_d) of (partially) dehydrated or anhydrous complexes are shown in Fig. 3. It should be noted that an incipient decomposition of CuDipy begins some 80°C below the temperatures indicated in the figure. In the range $214\text{--}292^\circ\text{C}$ (under O_2) and $248\text{--}324^\circ\text{C}$ (under N_2), this compound loses 2.0% of its mass in a nearly horizontal section of the TG curve. The reason for this behaviour is unknown (the presence of a small amount of impurities may be a reason) and the higher values are chosen as the “true” decomposition temperatures.

With the exception of the CuPhen complex, the decomposition temperatures are higher in N_2 atmosphere. However, a comparison of some literature data [1,2,18], as well as the data presented here, does not allow a

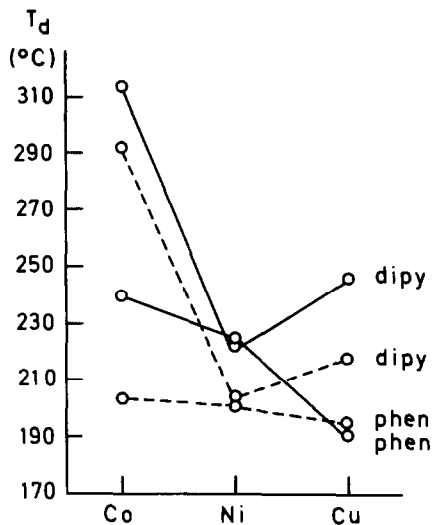


Fig. 3. The initial decomposition temperature of the complexes in N_2 (—) and O_2 (---). The curves for phen and dipy complexes are denoted by diamine ligand.

definite conclusion concerning the influence of the gas atmosphere on T_d to be reached. It seems that the nature of the central ion and of the ligands play the dominant role.

From the data in Fig. 3, it is clear that the T_d of the phen complexes follow order (1), while the T_d of the dipy complexes do not.

The existence of numerous exceptions shows that order (1) is of limited validity. This is because order (1) was originally established [1] by employing thermodynamic parameters obtained in aqueous solution, thus neglecting factors related to the crystalline and molecular structures of solid compounds.

The polymeric character is a factor that is expected to increase the thermal stability of the complexes [12]. And indeed, CoDipy and CuDipy, which are most probably polymeric complexes (see above), are more stable than NiDipy which consists of discrete molecules; they also exhibit the highest T_d values of the compounds studied here (Fig. 3). However, polymeric CuPhen has the lowest T_d value.

In addition, it should be noted that among the studied complexes, only CoDipy and CuDipy do not contain water of crystallization. Accordingly, they are the only compounds that do not undergo the chemical and structural changes associated with the process of dehydration. Therefore, the intermediate solid products formed on dehydration of the complexes (either partial or complete) were studied in detail.

The intermediate products were obtained by heating the complexes for 3 h at temperatures determined from the TG curves; the products were then characterized by IR and X-ray powder diffraction. Dehydration is also

accompanied by a colour change: CoPhen turns orange, CuPhen a lighter blue, and the nickel complexes become light green. The IR spectra show, in most cases, the presence of small amounts of water, in agreement with the TG data already discussed. There are no significant shifts of the -COO^- vibrations, but some widening of the bands is observed indicating that new carboxylate O atoms have coordinated to the central ion [19]. Powder patterns of the intermediate products consist either of several broad maxima (CuPhen) or of only one intense peak (all the other compounds).

The data indicate that dehydration involves not only the breaking of the M-OH_2 bonds but also the formation of new M-OOC bonds as replacements in the metal-ion coordination sphere. It is possible that changes in the coordination geometry occur in the process. Dehydration introduces large disturbances in the structure, and the intermediates are very disordered. Because they are comparatively rich in energy, owing to their disordered structure, the intermediates should have lower T_d values than the complexes that do not initially contain water of crystallization.

It is obvious that the intermediates differ markedly from the starting compounds, but it would be very difficult to characterize them more completely. Therefore, firm grounds for a discussion concerning the influence of the structure of the complexes on their thermal stability are apparently lacking. Nevertheless, it is reasonable to expect that the structural transformations accompanying dehydration should depend on the original structure of the complex and that the structure of the intermediate should in some manner be a reflection of the structure of the parent complex. This is supported by the fact that NiPhen and NiDipy, two species of very similar structure [10], have very close T_d values in both gaseous media, although Phen and Dipy differ in their π -accepting abilities. Extending this reasoning, it is seen that for the isostructural complexes CoPhen and NiPhen, stability increases in the order $\text{CoPhen} > \text{NiPhen}$; the only factor that causes the stability difference here is the influence of the central ion. Thus, comparison of the thermal properties of isostructural metal complexes can yield insight into the relative stability of the complexes. However, it is highly unlikely that isostructural complexes with the same ligand could be obtained for a series of transition metal ions. A more promising way is to obtain pairs of isostructural complexes (such as $\text{M}^1\text{L}^1 + \text{M}^2\text{L}^1$; $\text{M}^2\text{L}^2 + \text{M}^3\text{L}^2$; ...; $\text{M}^n\text{L}^n + \text{M}^{n+1}\text{L}^n$, where $\text{M}^1\text{-M}^{n+1}$ and $\text{L}^1\text{-L}^n$ are different metals and ligands, respectively), and to study and compare their thermal properties.

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