

IR and Thermal Studies on Nickel(II) Complexation with Pyrrolidine dithiocarbamate in the Presence of Other Competing Ligands

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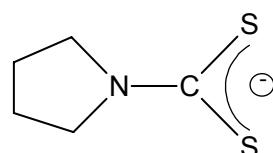
Summary: Nickel(II) complexes of pyrrolidinedithiocarbamate (PDTC) having the general formula, $[Ni(PDTC)_2]$, $[Ni(PDTC)Cl]_n$, $K[Ni(PDTC)(CN)_2]$ and $[Ni(PDTC)(Cys)]$ (Cys = cysteine) have been prepared and characterized by IR spectroscopy and Thermal analysis (TGA and DTA). The results of thermal analysis are consistent with the proposed composition of the complexes. It has been observed that the ligands I, SCN⁻ and thiolates (except cysteine) are replaced on addition of PDTC leading to the formation of $[Ni(PDTC)Cl]_n$. The IR data suggest that coordination of the pyrrolidinedithiocarbamate (PDTC) takes place through the two sulfur atoms in a symmetrical bidentate fashion. Single crystal analysis of the expected $[Ni(PDTC)_2]$ crystals showed that the product was NiS, rather than a PDTC complex.

Keywords: Nickel(II) Complexes; Pyrrolidinedithiocarbamate; Cyanide; Thiolates; Thermal analysis.

Introduction

The dithiocarbamate moiety has received much attention in recent years due to its ability to act as a bidentate ligand [1-3]. Dithiocarbamates such as diethyldithiocarbamate and pyrrolidinedithiocarbamate display cytotoxic properties and they have been used to fight against metal poisoning [4-11]. Due to their ability to form thermodynamically stable complexes, they are also used as chelating agents for the extraction of trace metals [12]. Metal complexes of dithiocarbamates present a wide range of applications in agriculture, medicines, industry and, in analytical and organic chemistry [11-17]. The use of dithiocarbamate complexes in the rubber vulcanization process is an example of their commercial importance [17,18]. ZnS, a technologically important material as phosphor and as a white pigment, can be prepared from the Zn(II)-diethyldithiocarbamate complex [19]. Dithiocarbamates from nickel group that is of platinum(II) and palladium(II), as well as of isoelectronic gold(III) showed remarkable antitumor properties and in some cases their cytotoxic activity was greater than cisplatin [2,20-24]. Dithiocarbamates coordinate platinum (of cisplatin) through two sulfur atoms preventing, or at least limiting the reaction with other sulfur-containing renal proteins [20,25]. However, nickel(II) complexes of dithiocarbamates are less studied [26] as compared to those of palladium(II) and platinum(II). A number of Ni(II)-dithiocarbamate complexes have been reported [27]. Considering the

diverse applications of dithiocarbamates and their complexes, we attempted to prepare a series of nickel(II) complexes of pyrrolidinedithiocarbamate (PDTC) containing a number of auxiliary ligands, which include, Cl⁻, I⁻, SCN⁻, CN⁻, diamines and thiolates, and characterized them by IR spectroscopy and thermal analysis. But it is interesting to note that except CN⁻ and cysteine, the rest of the competing ligands were replaced on addition of PDTC. Thus only 4 of the 9 complexes could be isolated ($[Ni(PDTC)_2]$, $[Ni(PDTC)Cl]_n$, $[Ni(PDTC)(CN)_2]$ and $[Ni(PDTC)(Cys)]$). So far, there are no known reports of mixed ligand nickel(II) complexes containing both PDTC and thiolate or amine ligands. The main purpose of this study is to highlight the strong binding of PDTC in preference to halides, thiolates and diamines using thermal analysis. We have already reported the complexation of pyrrolidinedithiocarbamate with copper(II) in the presence of Cl⁻, I⁻, SCN⁻, CN⁻, and ethylenediamine [28]. The structure of Pyrrolidinedithiocarbamate (PDTC) is given below.



Pyrrolidinedithiocarbamate (PDTC)

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Results and Discussion

IR Studies

The most significant bands recorded in the FT-IR spectra of the ligand and the complexes are reported in Table-1. For dithiocarbamate compounds, three main regions are of interest: the 1580–1450 cm⁻¹ region, which is primarily associated with the stretching vibration of C-N group of the N-CSS moiety; the 1060–940 cm⁻¹ region associated with v(-CSS) vibrations; and the 420–250 cm⁻¹ region, which is associated with v(M-S) vibrations [29]. The v(N-CSS) band defines a carbon-nitrogen bond order intermediate between a single bond ($\nu = 1350\text{--}1250\text{ cm}^{-1}$) and a double bond ($\nu = 1690\text{--}1640\text{ cm}^{-1}$) [30–32]. On passing from pyrrolidinedithiocarbamate to the complexes, the v(N-CSS) mode is shifted to higher energies, showing an increase of the carbon-nitrogen double bond character. The v(N-CSS) value of these complexes is comparable to the pyrrolidinedithiocarbamate (PDTC) complexes of Pd²⁺; [Pd(PDTC)₂] = 1500 cm⁻¹, [Pd(PDTC)Cl]_n = 1548 cm⁻¹, NMe₄[Pd(PDTC)Cl₂] = 1533 cm⁻¹ [3]. The band around 1000 cm⁻¹ belonging to the v(-CSS) (partial double bond) stretching is indicative of dithiocarbamate acting as a bidentate ligand [33,34].

Table-1: Melting point and IR spectral data (cm⁻¹) of Ni⁺²-PDTC Complexes.

Compound	M.p (°C)	IR bands	
		v(N-CSS)	v(-CSS)
PDTC	-	1410	995
[Ni(PDTC) ₂]	316 (decomp)	1510	1003
[Ni(PDTC)Cl] _n	310 (decomp)	1508	1002
K[Ni(PDTC)(CN) ₂]	324 (decomp)	1500	1002
[Ni(PDTC)(Cys)]	(did not melt until 330)	1508	1001

For [Ni(PDTC)(CN)₂] the v(CN) vibration is observed at 2170 cm⁻¹, which for [Ni(CN)₄]⁻² appears at 2128 cm⁻¹ [34]. This suggests that there is a greater donation of electron density to Ni⁺², when CN⁻ is trans to a CN⁻ rather than a PDTC ligand (*i.e.*, CN⁻ is a strong sigma donor as compared with PDTC). As a result, the extent of back bonding is greater in [Ni(CN)₄]⁻² than in [Ni(PDTC)(CN)₂] and consequently, the v(CN) for [Ni(PDTC)(CN)₂]⁻ is higher. In [Ni(PDTC)(Cys)], v(C=O) vibrations are observed at 1624 and 1586 cm⁻¹, while the peaks due to N-H stretching were not detected.

In the IR spectra of [Ni(PDTC)X₂]⁻ type complexes (X = SCN⁻, Mercaptoacetate, Mercaptopropanoate and Mercaptosuccinate) the bands due to SCN⁻ and C=O groups of thiolates were not observed, although for a copper complex, [Cu(PDTC)(SCN)₂]⁻ a sharp peak for SCN⁻ stretch was observed at 2110 cm⁻¹ [28]. The spectrum of I

product was similar to that of [Ni(PDTC)₂]. This observation suggests that I⁻, SCN⁻ or thiolate ligands are replaced by PDTC forming some more stable complex. Similarly, the v(N-H) stretching vibration of diamines were not detected in the IR spectra of expected [Ni(PDTC)(diamines)]⁺ indicating the absence of diamines in these complexes. On the other hand, for a similar copper complex, [Cu(PDTC)(en)₂]⁺ peaks due to N-H vibrations were clearly observed at 3299 and 3233 cm⁻¹ [28].

Thermal Studies

The proposed stoichiometry of the synthesized complexes has been established by studying their thermal behavior. The results of analysis indicate a good correlation between the calculated and found weight (wt) loss values for the proposed complexes. The decomposition behavior of a complex with Ni⁺²:PDTC ratio of 1:1 is shown in Fig. 1. Three possible species, which may be formed during the reaction are; NH₄[Ni(PDTC)Cl₂], [Ni(PDTC)Cl]_n and [Ni(PDTC)₂]. In case of NH₄[Ni(PDTC)Cl₂], the combined weight loss due to PDTC and Cl⁻ ligands, is 73.9 %, while for [Ni(PDTC)Cl]_n it is 75.6 %. However, for NH₄[Ni(PDTC)Cl₂] an additional wt loss of 6 % should be observed for the removal of NH₃ [28] and so the residual mass should be 20 %. The absence of N-H vibration due to NH₄⁺ in the IR spectrum of the complex also rules out the formation of NH₄[Ni(PDTC)Cl₂]. For [Ni(PDTC)₂], the weight loss corresponding to the release of PDTC is 83.3 % and residual mass is 16.7 %. The thermogram shown in Fig. 1 describes a sharp decrease in wt of 72 % suggesting the formation of an intermediate species, which releases some group slowly until 750 °C with a total wt loss of 84 %. A similar behavior has been observed for the product of the reaction Ni⁺² and PDTC mixed in the ratio of 1:2. It was also observed that in the preparation of intended 1:1 complex only about half of the nickel(II) ions were utilized in the reaction. These unused ions yielded the same of product when further one equivalent of PDTC was added to the filtrate of above mixture. These observations suggest that the proposed formula of the complex is [Ni(PDTC)₂], whether the molar ratio of Ni⁺² and PDTC is 1:1 or 1:2. Previous thermal studies of metal-dithiocarbamates suggest that the decomposition of these complexes proceeds through the formation of metal-thiocyanate intermediates [35,36]. However, complexes of cyclic dithiocarbamates such as PDTC were observed to undergo decomposition without the formation of thiocyanate intermediate [37]. Similarly, in the present study, formation of no such intermediate

corresponding to weight loss of 50.2 % (Fig. 1) has been detected. This might be because of the closed ring of pyrrolidine instead of two alkyl groups attached to nitrogen atoms.

Thermal degradation of $K[Ni(PDTC)(CN)_2]$ is illustrated in Fig. 2. The TGA curve shows a sharp decrease in weight of 68 %, associated with an endothermic transition at 365 °C. This weight loss

indicates a simultaneous release of both ligands against a calculated value of 67.0 % (49.4% for PDTC and 17.6% for 2CN). The decomposition after 500°C occurs slowly and indicates the release of potassium (which has a melting point of 63.8 °C and boiling point of 774 °C) or K-Ni alloy. Because of the loss of Ni, the actual residual mass corresponding to the percentage of nickel (20 %), could not be obtained.

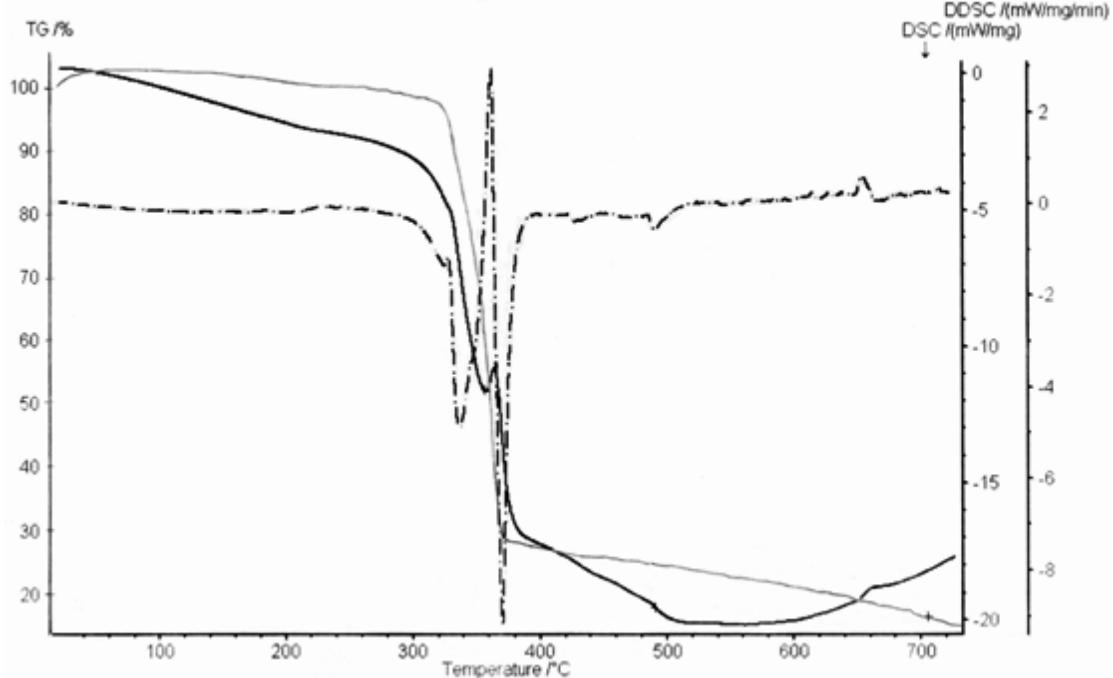


Fig. 1: Thermogram of $[Ni(PDTC)_2]$.

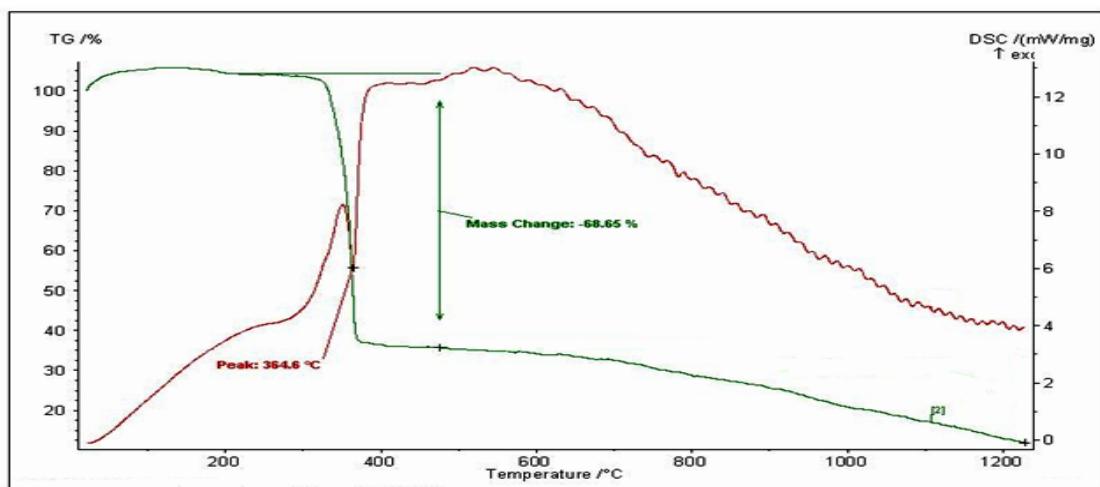


Fig. 2: Thermogram of $K[Ni(PDTC)(CN)_2]$.

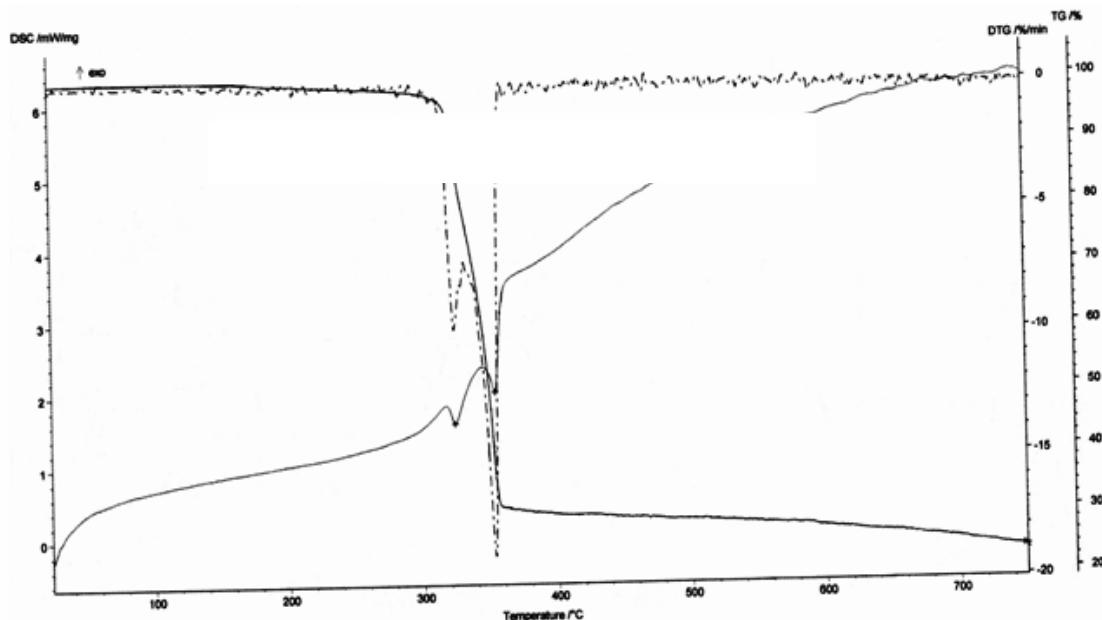


Fig. 3: Thermogram of expected $K[Ni(PDTC)(SCN)_2]$ (Actual product seems as $[Ni(PDTC)(Cl)]_n$).

The thermal behavior of $[Ni(PDTC)X_2]$ -type complexes ($X = I^-$, SCN^-) does not correspond to the proposed formula. The decomposition pattern of expected $K[Ni(PDTC)(SCN)_2]$ is illustrated in Fig. 3. The calculated wt loss due to removal of PDTC and X^- for the expected iodide product is 80.4 %, while for thiocyanato complex it is 73.9 %. However, in both complexes a wt loss of ca. 70 % was observed in the first step at 360 °C corresponding to an endothermic transition. A similar wt loss suggests that the same product is obtained in both cases. The next wt loss of 7 % at 750 °C gives a residual mass of 23 %, but the sample is still undergoing decomposition. This residual mass is intermediate between those observed for $[Ni(PDTC)Cl]_n$ (24.4 %) and for $[Ni(PDTC)_2]$ (16.7 %). These results suggest that the proposed formula of the resulting complex is probably $[Ni(PDTC)Cl]_n$ but it contains some impurity of $[Ni(PDTC)_2]$.

The decomposition of the mixed ligand complex $[Ni(PDTC)(Cys)]$ starts at 200 °C and occurs in two steps (Fig. 4). In the first step both ligands (PDTC and Cys) are released with a weight loss of ca. 73 % (calculated value 81.95 %) at 380 °C describing the formation of an intermediate species. The next weight loss of 8.2 % starting at 680 °C gives a residual mass of 18.8 %, which corresponds to the percentage of nickel (18.05 %).

The results of thermal analysis of $[Ni(PDTC)X_2]$ and $[Ni(PDTC)(diamines)]^+$ type

complexes (X^- = Mercaptoacetate, Mercapto-propanoate and Mercaptosuccinate, and diamine = ethylenediamine, N,N' -dimethylethylenediamine, 1,3-diaminopropane) indicate that these complexes were not formed. Instead, the decomposition pattern suggests the formation of a similar complex in all cases. Thermogravimetric curves for three representative complexes are shown in Figs. 5 and 6. The total wt loss is ca. 74 % and the residual mass is 26 % for all three complexes although the calculated values are different. These values correspond to the formula of the $[Ni(PDTC)Cl]_n$ for which the residual mass is 24.4 %.

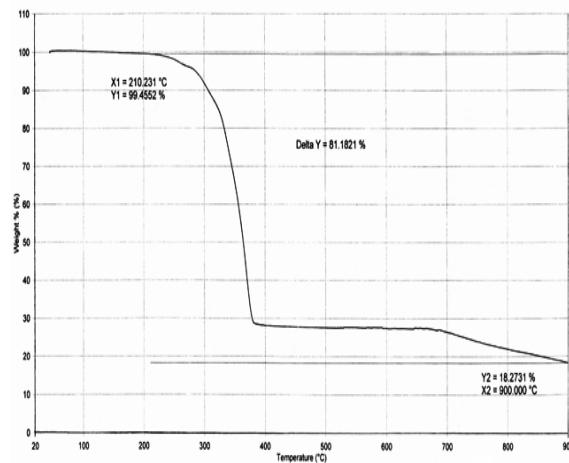


Fig. 4: Thermogram of $[Ni(PDTC)(Cys)]$.

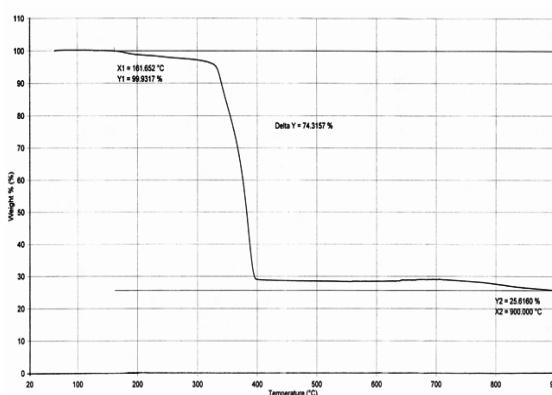
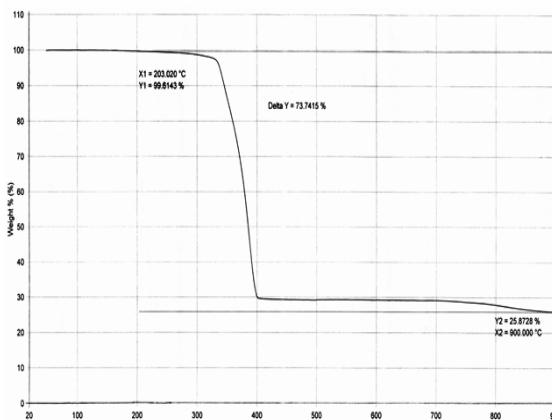
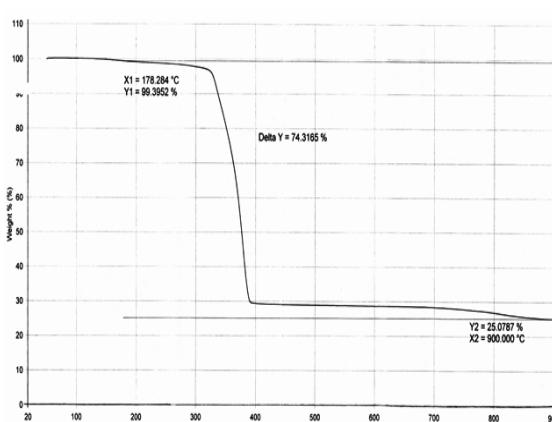


Fig. 5 Thermogram of expected $[\text{Ni}(\text{PDTC})(\text{L})]\text{Cl}$ (Actual product seems as $[\text{Ni}(\text{PDTC})(\text{Cl})]_n$, L = 1,3-diaminopropane).



(a)



(b)

Fig. 6: Thermogram of expected $[\text{Ni}(\text{PDTC})(\text{SR})_2]$, RS⁻=(a) Mercaptoacetate (b)Mercapto-succinate (Actual product in both cases seems as $[\text{Ni}(\text{PDTC})(\text{Cl})]_n$)

X-ray studies

The single crystal x-ray analysis of the light green crystals obtained in the filtrate of $[\text{Ni}(\text{PDTC})_2]$ solution shows that the resulting compound has the same unit cell and space group as NiS. So, along with a Ni-PDTC complex, NiS is also formed during the reaction. Thus the study provides important information regarding the preparation of metal sulfide materials from dithiocarbamate complexes. Preparation of metal sulfides from the corresponding complexes, e.g., ZnS from Zn(II)-diethyldithiocarbamate complex has already been reported [19]. We could not get rest of the compounds in the crystalline form; therefore, x-ray analysis could not be carried out. However, we were able to prepare a crystalline compound from the reaction of Zinc(II) with PDTC in the presence of mercaptosuccinate. The x-ray analysis of the resulting compound showed that it was a bis complex $[\text{Zn}(\text{PDTC})_2]$ existing in the dimeric form rather than a mixed thiolate complex. This result suggested that the thiolate ligand was displaced [39]. Thus the replacement of other ligands from Ni^{+2} in the presence of PDTC as observed in the present study is also possible.

Experimental

Chemicals

Ammonium Pyrrolidinedithiocarbamate is a product of Sigma Chemical Company and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ was obtained from BDH Chemical Co., England. NaI, KSCN and ethylenediamine were obtained from Merck, Germany. N,N'-dimethylethylenediamine, 1,3-diaminopropane and thiolates were purchased from Acros Organics, Belgium.

Instrumentation

IR was obtained on the Bio-Rad Elmer 16 FPC FT-IR spectrophotometer in the frequency range of 4500–450 cm^{-1} using KBr pellets. Thermal analysis was carried out on Mettler Toledo 851e TGA/SDTA analyzer. The conditions were: heating rate 10°C/min in argon environment (40 mL/min.).

Synthesis of complexes

$[\text{Ni}(\text{PDTC})_2]$ was prepared by the reaction of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.24 g, 1.00 mmol) in methanol with 1 or 2 mmoles (0.164 g or 0.328 g) of Amm. Pyrrolidinedithiocarbamate (PDTC) in methanol. The addition of PDTC in the green-colored metal ion

solution resulted in the formation of yellowish green precipitates immediately. After stirring for half an hour, the precipitates were filtered and dried. The filtrate of the solution yielded light green crystals.

The mixed ligand complexes, $[\text{Ni}(\text{PDTC})(\text{CN})_2]^-$ and $[\text{Ni}(\text{PDTC})(\text{Cys})]$ were prepared by mixing 1 mmolar Ni^{+2} solution in methanol with two equivalents of KCN or one equivalent of cysteine in water respectively, followed by addition of one mmolar solution of PDTC in methanol. As a result grassy green precipitates were obtained.

For the preparation of $[\text{Ni}(\text{PDTC})\text{X}_2]^-$ and $[\text{Ni}(\text{PDTC})\text{L}]^+$ type complexes ($\text{X} = \text{I}^-$, SCN^- , Mercaptoacetate, Mercaptopropanoate and Mercaptosuccinate; and $\text{L} = \text{ethylenediamine}$, $\text{N,N}'\text{-dimethylethylenediamine}$ and $1,3\text{-diaminopropane}$), one equivalent of X^- or L ligands (for I^- , SCN^- , 2 equivalents) were added first followed by the addition of PDTC. All the reactions resulted in the similar green product.

Conclusion

The present study shows that PDTC has a strong kinetic preference for nickel(II) and in the presence of PDTC, other ligands, which include; I^- , SCN^- and thiolates (non-chelating) are dissociated from Ni^{+2} forming a more stable complex, $[\text{Ni}(\text{PDTC})\text{Cl}]_n$. However, sulfur-containing chelating ligands such as cysteine do not undergo replacement but form a mixed-ligand complex. In the absence of a competing ligand the bis complex $[\text{Ni}(\text{PDTC})_2]$ is formed favorably. Thus the study highlights the importance of thermal analysis in identifying the actual species formed during the reaction and provides useful information about the nature of Ni-S bonding in Ni-PDTC complexes.

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