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Mixed Ligand Copper(II) Complexes of Pyrrolidinedithiocarbamate and Diamines

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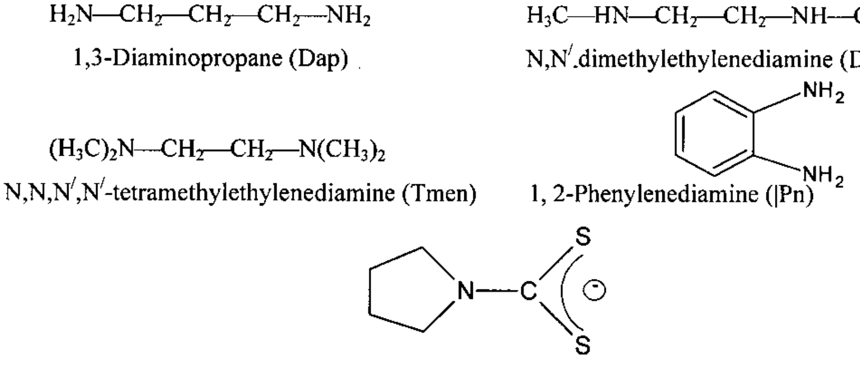
Summary: Copper(II) complexes of pyrrolidinedithiocarbamate (PDTC) and diamines having the general formula, [Cu(diamine)(PDTC)]Cl, [Cu(diamine)Cl_2][Cu(PDTC)Cl] or [Cu_2(diamine)$(PDTC)_2Cl_2$] (diamine = 1,3-diaminopropane, N,N′-dimethylethylenediamine, N,N,N′,N′-tetramethylethylenediamine and 1,2-phenylenediamine) have been prepared and characterized by IR spectroscopy and thermal analysis. The results of thermal analysis are consistent with the proposed composition of the complexes. The IR data suggest that coordination of the pyrrolidinedithiocarbamate (PDTC) takes place through the two sulfur atoms in a symmetrical bidentate fashion.

Introduction

Metal complexes of dithiocarbamates have been widely investigated because of their medicinal, industrial and analytical applications [1-9]. Dithiocarbamates such as diethyldithiocarbamate and pyrrolidinedithiocarbamate (PDTC) display cytotoxic properties and they have been used to fight against metal poisoning [1, 9-16]. Dithiocarbamate complexes 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 of cisplatin [17-22]. Copper(II) complexation with PDTC is also important for PDTC induced apoptosis in several cancer cells [2]. Due to their strong complex formation ability, they are also used as chelating agents for the extraction of trace metals [3]. They can act as molecular precursors in the synthesis of novel metal sulfide nanomaterials [23, 24]. Because of the large number of applications of metal dithiocarbamates, several dithiocarbamate complexes of nickel(II), copper(II), zinc(II), palladium(II), platinum(II) and gold(III) have been reported in the literature [17-23, 25-30]. This paper presents the preparation and thermal characterization of four new mixed ligand copper(II) complexes of pyrrolidinedithiocarbamate and diamines. The structures of ligands used in this study are given in scheme 1.

Results and Discussion

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^-



Scheme 1: Structures of ligands and their abbreviations.

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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 [30]. The v(N–CSS) band defines a carbon-nitrogen bond order intermediate between a single bond (v = 1350–1250 cm^{-1}) and a double bond (v = 1690–1640 cm^{-1}) [31,32]. Table-1 shows that the v(N–CSS) mode of PDTC is shifted to higher frequency upon coordination consistent with 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 Pd^{2+} ; $[Pd(PDTC)_2]$ = 1500 cm^{-1}, $[Pd(PDTC)Cl]_n$ = 1548 cm^{-1}, $NMe_4[Pd(PDTC)Cl_2]$ = 1533 cm^{-1} [25]. The band around 1000 cm^{-1} belong to the v(-CSS) (partial double bond) stretching is indicative of dithiocarbamate acting as a bidentate ligand [33, 34]. The v(N-H) stretch of Dap and Dmen is observed around 3235 cm^{-1}, while that of Pn at 3424 cm^{-1} showing their coordination to the metal center. The methylene C–H bands are observed at 2925 cm^{-1}. The Tmen complex showed the C–H stretching band of methyl groups at 2962 cm^{-1}.

Thermal Studies

The proposed stoichiometry of the synthesized complexes has been established by studying their thermal behavior. The results of analysis shown in Figs. 1-4 indicate a good correlation between the calculated and found weight loss values for the proposed complexes.

Table-1: Melting point and IR spectral data (cm^{-1}) of the investigated complexes.

Compound	M.p (°C)	IR bands v(N–CSS)	v(–CSS)
PDTC	-	1410	995
[Cu(Dap)(PDTC)]Cl	340 (decomp)	1500	1004
[Cu(Dmen)(PDTC)]Cl	320 (decomp)	1499	1004
$[Cu(Tmen)Cl_2][Cu(PDTC)Cl]$	310	1503	1000
$[Cu_2(Pn)(PDTC)_2Cl_2]$	259-261	1499	1038

The decomposition of expected [Cu(Dap)(PDTC)]Cl complex starts at 120 °C and occurs in two steps as shown in Fig. 1. At the first stage, PDTC ligand is released corresponding to the weight loss of about 42-44 % (calculated weight loss 46 %). The next weight loss of 26-28 %, which is due to removal of diamine (Dap) takes place in the 280–370 °C temperature range (calculated value 23.2 %). The residual mass of 30.0 % corresponds to the percentage of CuCl (31.0 %). These observations are consistent with the proposed formula of the complex, *i.e.*, [Cu(Dap)(PDTC)]Cl.

Thermal degradation of expected [Cu(Dmen)(PDTC)]Cl complex illustrated in Fig. 2 shows that the complex is stable upto 210 °C. The

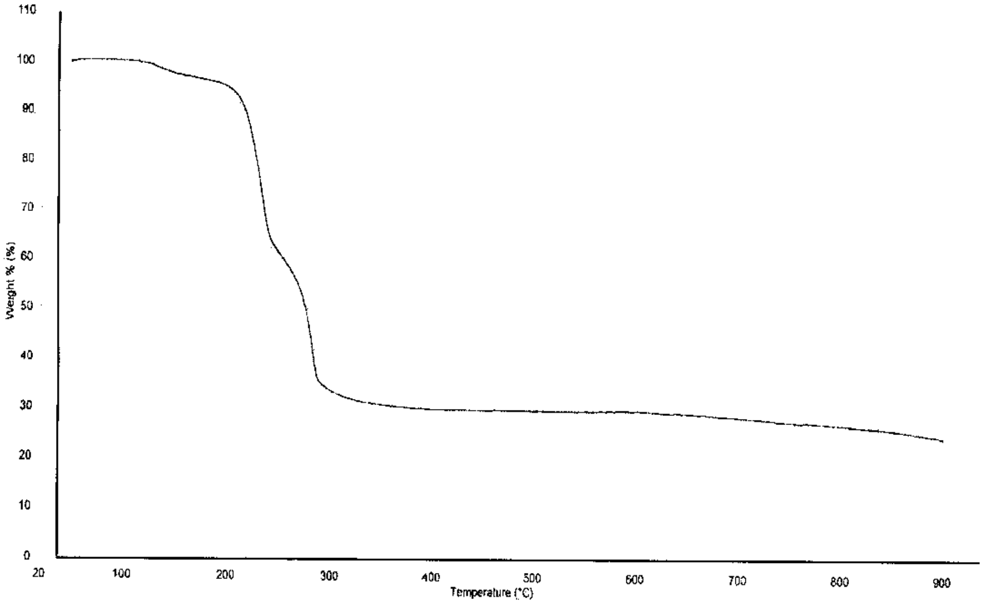

Fig. 1: TGA Curve of [Cu(Dap)(PDTC)]Cl.

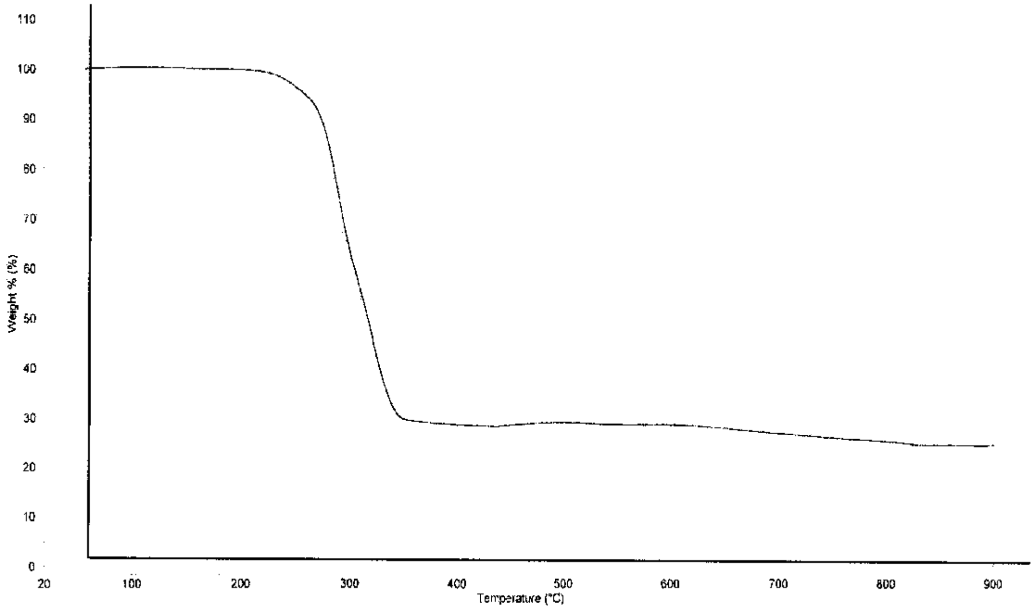

Fig. 2: TGA Curve of $[Cu(Dmen)(PDTC)]Cl$.

TGA curve describes a sharp decrease in weight of 70.2 % associated with the release of both PDTC and diamine ligands against a calculated weight loss of 70.2 % (43.8 % for PDTC and 26.4 % for Dmen). The two individual steps for the release of PDTC and Dmen could not be identified separately. However, the combined weight loss agrees to the proposed composition. The residual mass of 29.0 % is also consistent with the predicted value for CuCl (29.8 %).

The decomposition behavior of expected $[Cu(Tmen)(PDTC)]Cl$ complex is shown in Fig. 3. The decomposition starts at 180 °C and occurs in two well-defined steps. For the proposed composition, the weight loss corresponding to the release of PDTC is 40.5 % and that of Tmen is 32.1 %. However, Fig. 3 describes the weight losses of ~25 % and ~31 % in two steps, which do not correspond to the proposed formula. These weight losses agree well with the composition, $[Cu(Tmen)Cl_2][Cu(PDTC)Cl]$, the calculated values for which are, 23.4 % for Tmen and 29.5 % for PDTC. These results suggest that the proposed formula of the resulting complex is probably $[Cu(Tmen)]Cl_2][Cu(PDTC)Cl]$. Due to its different nature compared to the Cu-PDTC complexes described above, the removal of diamine takes place first. Table-1 shows that although it melts at 310 °C, the other two complexes did not melt but decompose above 300 °C.

Thermal behavior of the mixed ligand complex of 1,2-phenylenediamine also does not correspond to the formula $[Cu(Pn)(PDTC)]Cl$. The calculated weight losses for the proposed composition are 41.4 % and 31 % for PDTC and diamine, respectively. However, the thermogram (Fig. 4) shows that the first weight loss due to removal of PDTC ligands is about 46-47 % at 290 °C. The next weight loss of *ca.* 21 % (calculated value 18.1 %) taking place in the range of 290−760 °C is due to removal of phenylenediamine. This decomposition pattern suggests that the most probable formula of the complex is $[Cu_2(Pn)(PDTC)_2Cl_2]$, for which the percentage values are; 49 % for PDTC and 18.1 % for Pn.

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 [26, 37]. Similarly, in the present study, formation of no such intermediate corresponding to weight loss of 15-20 % (Figs. 1-4) has been detected. This might be because of the closed ring of pyrrolidine instead of two alky groups attached to nitrogen atom.

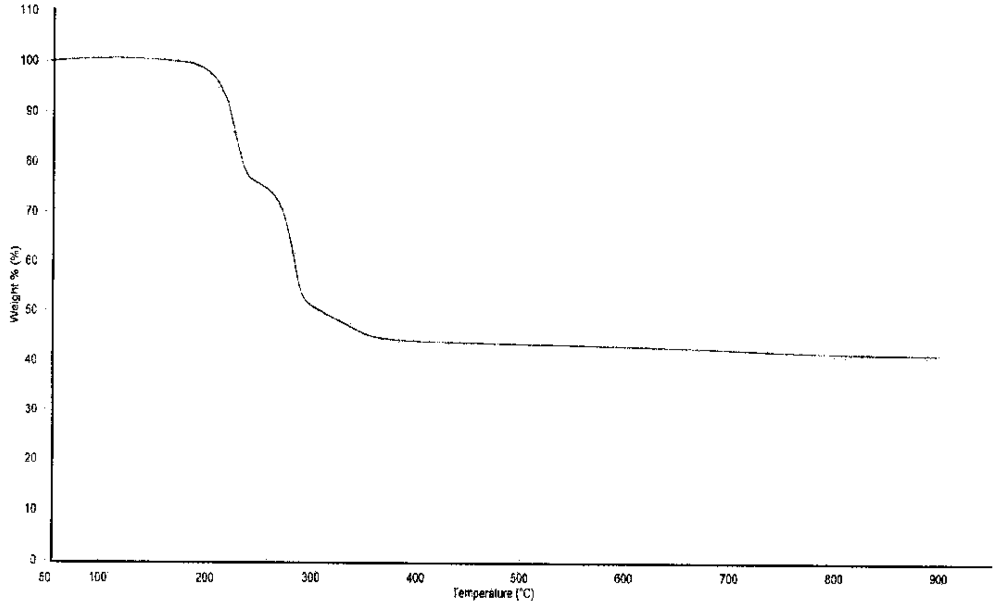

Fig. 3: TGA Curve of [Cu(Tmen)Cl_2][Cu(PDTC)Cl].

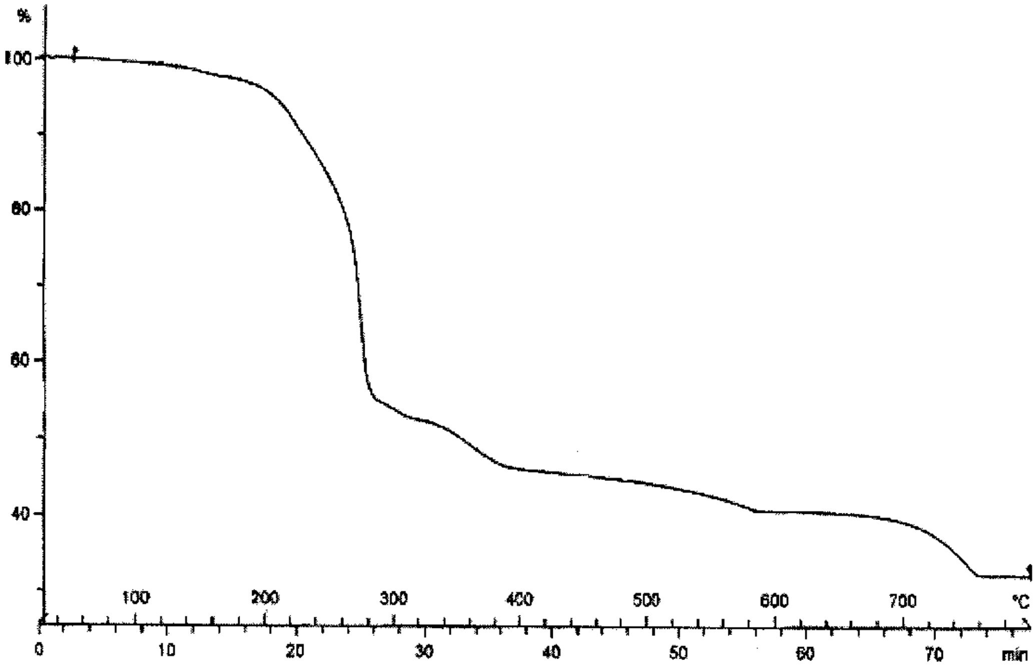

Fig. 4: TGA Curve of [Cu_2(Pn)$(PDTC)_2Cl_2$].

We could not separate any of the compounds in the crystalline form; therefore, x-ray analysis could not be carried out. The complexes are only partially soluble in DMSO, therefore their exact molar conductivity values could not be determined. However, the conductance measurements of partially miscible solutions of the complexes showed that these solutions are conducting and hence the complexes should be ionic in nature. The present study shows that pyrrolidine dithiocarbamate and diamines react with copper(II) to form the mixed ligand complexes in which the PDTC binds as a symmetrically bidentate ligand in the solid state.

Experimental

Chemicals

Ammonium pyrrolidinedithiocarbamate is a product of Sigma Chemical Company. $CuCl_2.2H_2O$, N,N,N′,N′-tetramethylethylenediamine (Tmen) and 1,2-phenylenediamine (Pn) were obtained from Merck, Germany. N,N′-dimethylethylenediamine (Dmen) and 1,3-diaminopropane (Dap) were purchased from Acros Organics, Belgium.

Instrumentation

IR spectra were recorded on the Bio-Rad Elmer 16 FPC FT-IR spectrophotometer using KBr pellets. Thermal analysis was carried out on Mettler Toledo 851e TGA/SDTA analyzer. The conditions were: heating rate 20 °C/ min in argon environment (40 mL/min.).

Synthesis of Complexes

The mixed ligand complexes, $[Cu(diamine)(PDTC)]^+$ were prepared by the reaction of $CuCl_2.2H_2O$ (0.17 g, 1.0 mmol) in methanol with one equivalent of diamines in water, followed by addition of one mmolar solution of PDTC in methanol (1,2-phenylenediamine was dissolved in methanol and water was added to the mixture after its addition). After stirring for half an hour, the brown precipitates were filtered and air-dried.

Acknowledgement

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