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Synthesis, characterization and thermal studies of 1-substituted- 3-formamidinothiocarbamides Complexes

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Abstract

Organic compounds of thiocarbamides have been reported to have noteworthy, industrial and analytical applications. The complexes of some Co(II), Ni(II), Cu(II), Mn(II), Cd(II) and Zn(II) with 1-substituted 3-formamidino thiocarbamides have been isolated in ethanol. These complexes have been characterized with the help of diffuse reflectance and infrared spectra magnetic moment and thermogravimetric analysis (TGA). Thermogravimetric studies indicate two-stage decomposition. Kinetic parameters were obtained for each stage of thermal degradation of the complexes using Freeman-Carroll and Sharp-Wentworth methods. Comparable values of parameters indicate common decomposition reaction mode in all chelates.

Keywords: Thiocarbamide, diffuse reflectance, magnetic moment, TGA.

1. Introduction

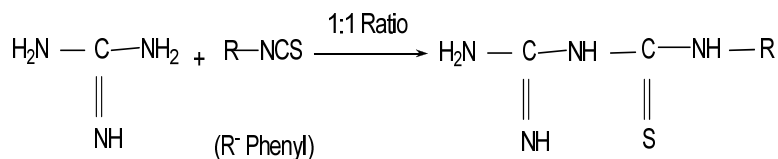
The synthesis of complexes is a field of active research. Further they have been found to be potential coordinating centers, yielding complexes of great thermal stability. Many of these complexes show thermal stability much higher than that of the organic substrate, employed as ligands in the synthesis of metal complexes. These complexes offer academic interest and at the same time provide materials of desired and superior qualities which promises a variety of applications such as they act as catalysts ^[1, 2]. energy devises, dyes, etc. In this contest, the present work describes the synthesis and characterization of some Co(II), Cd(II) and Zn(II) 1-substituted 3-formamidino thiocarbamides complexes. TGA data have been analysed by both Freeman-Carroll and Sharp-Wentworth methods and various kinetics and thermodynamic parameters have also been evaluated ^[3, 4].

2. Material and methods

Nickel (II) acetate tetrahydrate, Cobalt (II) acetate tetrahydrate, Manganese (II) acetate tetrahydrate, Copper (II) acetate monohydrate zinc (II) acetate dihydrate and cadmium (II) chloride monohydrate were obtained from E. Merck. DMF and ethanol were used after distillation. The metal content in each chelate was further confirmed by oxide method ^[5]. Sulfur was estimated as BaSO₄ by gravimetric method ^[6]. Elemental microanalysis was performed on a (C.H.N) analyzer from Heraeus (Vario EL). IR spectra of the compounds were recorded on Shimadzu-FTIR: Affinity 1 spectrophotometer in the region 400-4000cm⁻¹ and diffuse reflectance spectra were recorded on photoacoustic spectrophotometer using BaSO₄ as calibrant. The magnetic susceptibility was measured at room temperature by the Gouy method using Hg[Co(NCS)₄] as the calibrant. TG analyses were carried out on Perkin-Elmer TGS-2 thermobalance at 10 °C/min heating rate.

2.1 Synthesis of ligand

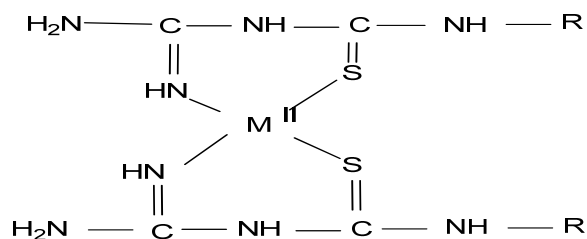
The chosen chelate, 1-substituted-3-formamidino thiocarbamide (PFTC) is rich in electron due to the existence of nitrogen and a sulphur atom is synthesized by following method. The synthesized ligand showed the expected elemental composition and infrared spectra.



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2.2 Synthesis of Complex

The synthesis of the complexes is carried out by refluxing 1-substituted-3-formamidino thiocarbamide (PFTC) with Ni(II), Co(II), Mn(II), Cu(II), Zn(II) and Cd(II) metal ions.



3. Results and discussion

All the complexes are amorphous powders, insoluble in water and common organic polar and non-polar solvents. Elemental data confirms the assigned stoichiometries and shows that all the chelates have the general formula ML_2 .

The diffuse reflectance spectra of Ni(II) complex with PFTC displays three bands suggested octahedral geometries. The first lower energy bands at 10882 cm^{-1} can be assigned to ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, the second band at 13605 cm^{-1} region can be assigned to ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and higher energy medium broad band in 23342 cm^{-1} region can be assigned to ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transition for octahedral Ni(II) complexes. The magnetic moment value of the Ni(II) complex at room temperature is 2.38 B.M., which is higher than spin only

value. This may be due to either orbital contribution of ${}^3A_{2g}$ ground term to magnetic moment or some mixing of ${}^3T_{2g}$ and ${}^3A_{2g}$ term and spin-orbit coupling in ${}^3T_{1g}$ term [7]. The Co(II) complex exhibits three d-d bands at 8800, 17730 and 23310 cm^{-1} due to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions respectively, in the conformity with octahedral stereochemistry around Co(II) ion. The magnetic moment of Co(II) complex (5.30 B. M.) is also indicative of a high spin octahedral structure [8]. Mn(II) complex exhibited broad bands in the range 17241, 23809 and 27027 cm^{-1} due to ${}^6A_{1g} \rightarrow {}^4T_{1g}(4G)$, ${}^6A_{1g} \rightarrow {}^4T_{2g}(4G)$ and ${}^6A_{1g} \rightarrow {}^4E_g$ transitions suggesting octahedral geometry. The magnetic moment value of Mn(II) is 5.67 B.M. slightly less than, generally observed for spin free d^5 system. This lower value of magnetic moment may be due to the spin exchange in the solid complexes or may be aerial oxidation of Mn(II) to Mn(III) during synthesis [9]. The electronic spectra of Cu(II) complex consists of two bands at 25253 cm^{-1} and 18051 cm^{-1} . These were assigned to ${}^2B_{1g} \rightarrow {}^2E_g$ and ${}^2B_{1g} \rightarrow {}^2A_{1g}$ respectively. The spectra pattern suggested a square planar geometry around the copper (II) ion [10]. The magnetic moment value 1.64 B.M. lies below the spin only value. The lower value of magnetic moment at room temperature is consistent with square planar geometry around the metal ion [11]. The Zn(II) and Cd(II) complexes are found to be diamagnetic as expected for d^{10} ion system and may have tetrahedral geometry [12].

Table 1: Magnetic moments and assignments of diffuse reflectance spectra of complexes

S.N.	Compound	μ_{eff} (B.M.)	Absorption band(cm^{-1})	Assignments
1.	[Ni(PFTC) ₂ (H ₂ O) ₂].H ₂ O	2.38	10882	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
			13605	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$
			23342	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$
2.	[Co(PFTC) ₂ (H ₂ O) ₂].H ₂ O	5.30	8800	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$
			17730	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
			23310	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
3.	[Mn(PFTC) ₂ (H ₂ O) ₂].H ₂ O	5.67	17241	${}^6A_{1g} \rightarrow {}^4T_{1g}(4G)$
			23809	${}^6A_{1g} \rightarrow {}^4T_{2g}(4G)$
			27027	${}^6A_{1g} \rightarrow {}^4E_g$
4.	[Cu(PFTC) ₂]	1.64	18051	${}^2B_{1g} \rightarrow {}^2A_{1g}$
			25253	${}^2B_{1g} \rightarrow {}^2E_g$
5.	[Cd(PFTC) ₂]	Diamagnetic	----	----
6.	[Zn(PFTC) ₂]	Diamagnetic	----	----

The thermal stability and the decomposition temperatures can be ascertained and can also understand the modes of decomposition of the complexes, nature of the phase changes during the programmed heating and purity of the complexes can also be checked.

Thermogram of PFTC and its metal complexes are shown in Fig.1 (a) and (b). The perusal of thermograms indicates that the complexes decomposed in gradual manner. The TG curve of Ni(II), Co(II) and Mn(II) complexes show slight sharp weight losses in the range 80-110 °C corresponding to one lattice water molecule [13]. Ni(II) complex loses weight [% wt loss: obs (cal): 4.10 (4.54)], Co(II) complex loses weight [% wt loss: obs (cal): 4.50 (4.64)] and Mn(II) complex loses weight [% wt loss: obs (cal): 4.45 (4.31)] corresponding to one lattice water molecule each. After dehydration of lattice water molecule, these complexes lose their weight [% wt loss: obs (calc.): 7.63 (7.55)], [% wt loss:

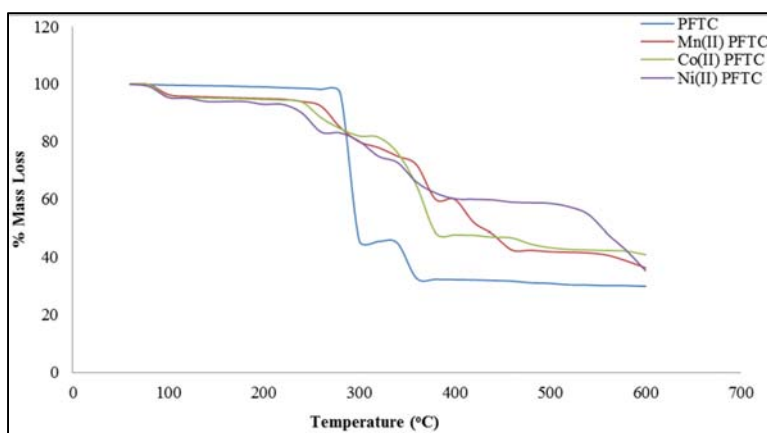
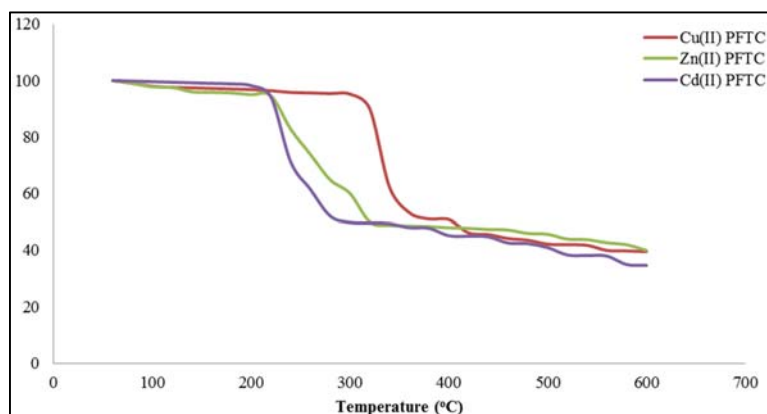
obs (calc.): 8.13 (8.15)] and [% wt loss: obs (calc.): 7.51 (7.47)] respectively at around 180-300 °C corresponding to two co-ordinated water molecules [14] for Ni(II), Co(II) and Mn(II) complexes respectively. Complexes of Cu(II), Zn(II) and Cd(II) do not show any lattice as well as coordinated water molecule. Weight loses continuously up to 600 °C indicating the decomposition of free part of complexes.[15] Above 600 °C TG curves attains a constant level corresponding to formation of metal oxides as NiO, Co₃O₄, MnO₄, CuO, ZnO and CdO.

The different differential methods of Freeman-Carroll and Sharp-Wentworth were applied for evaluating the thermodynamic and kinetic parameters and the values obtained are compared shown as in Table 2. The relative thermal stability on the basis of half decomposition temperature is in the order as Mn(II) > Cd(II) > Zn(II) > Co(II) > Ni(II) > Cu(II) > PFTC.

Table 2: Thermal and kinetic parameters of PFTC and its complexes

S.N.	Compound	DH (°C)	Activation Energy (kJmol ⁻¹)		-ΔS (JK ⁻¹ mol ⁻¹)	ΔF (kJmol ⁻¹)	Z (S ⁻¹)	-S* (Kcal)	Order of reaction (n)
			FC	SW					
1.	PFTC	100	35.13	32.87	---	---	---	---	---
2.	[Ni(PFTC) ₂ (H ₂ O) ₂].H ₂ O	220	31.70	30.32	313.04	121.57	68.34	48.95	0.50
3.	[Co(PFTC) ₂ (H ₂ O) ₂].H ₂ O	260	30.23	29.50	309.53	123.57	65.57	53.35	0.55
4.	[Mn(PFTC) ₂ (H ₂ O) ₂].H ₂ O	360	30.26	34.90	306.63	126.61	70.79	48.63	0.50
5.	[Cu(PFTC) ₂]	180	32.69	32.27	312.06	131.83	63.69	41.15	0.54
6.	[Cd(PFTC) ₂]	320	36.44	28.85	310.91	132.91	64.89	58.65	0.52
7.	[Zn(PFTC) ₂]	330	31.19	35.45	300.15	134.15	71.81	44.15	0.58

FC = Freeman-Carroll, SW = Sharp-Wentworth, DH = Half Decomposition temperature.

**Fig 1(a):** Thermogravimetric analysis of PFTC, Mn(II)PFTC, Co(II)PFTC, Ni(II)PFTC**Fig 1(b):** Thermogravimetric analysis of Cu(II)PFTC, Zn(II)PFTC, Cd(II)PFTC

4. Conclusions

The TGA study confirmed the presence of lattice as well as coordinated water molecule(s) in metal complexes. The thermogram of ligand and metal complexes showed that all the complexes comparatively more stable than their respective ligand. It also showed that all the complexes did not melt easily but undergo decomposition at high temperature to give final product as metal oxide. Thus on the basis of spectral and TGA studies, the Ni(II), Co(II) and Mn(II) complexes were suggested to possess octahedral structures, Cu(II) complex shows square planer and Zn(II) and Cd(II) complexes show tetrahedral structures.

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