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Spectrochemical study and effect of high energatic gamma ray on copper (II) complexes

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ABSTRACT

Series of copper (II) complexes of 2- phenylaminoacetyl-N-phenylhydrazine carbthioamide (H_2L) has been prepared and characterized by elemental and analyses, IR, electronic spectra, magnetic moment, molar conductance measurements, thermogravimetric analyses and X-ray diffraction pattern. The IR data before and after γ- irradiation reveal that the ligand behaves as neutral, monobasic bidentate coordination of copper ion via the carbonyl group or enolic oxygen group, NH group and thiol sulphr atom group in complex B_2. The molar conductance data reveal that the chelates are nonelectrolytes. From the electronic spectra and magnetic moment data, the complexes were found to have octahedral and square planar geometrical structures. The thermal behavior of these chelates before and after γ-irradiation induced more thermal stability after radiation. The X-ray diffraction patterns before and after γ- irradiation suffer partial damage after irradiation.

KEYWORDS

Synthesis;
Complexes;
IR;
TGA;
X-ray;
Energatic γ-irradiation.

INTRODUCTION

Complexes of thiosemicarbazide and 1,4-substituted thiosemicarbazide are of interest as models for bioinorganic processes[1-3]. Numerous transition metal complexes of substituted thiosemicarbazides, particularly the 1,4-substituted derivatives have been prepared and characterized and they have been found to possess a wide variety of biological activities against bacteria, fungi and certain type of tumors[4-10]. Acylthiosemicarbazide contains oxygen, sulphur and nitrogen as potential donor atoms and is liable to deprotonated complexes by loss of hydrazinic proton via enolisation/ thioenolisation. Recently, new complexes of Cu(II) and UO_2(VI) with N^1-[4-[4-x-phenylsulfonylbenzoyl]-N-butyl-thiosemicarbazide have been prepared and characterized by analytical and physico-chemical tecniques such as magnetic susceptibility, elemental and thermal analyses, electronic, ESR and IR spectral studies[11]. Among cyclotron produced radioisotopes, palladium-103 offers a unique characteristic of X-ray (20-22KeV) and abundant emission of outer electrons suitable for radio therapy in form of seeds for permanent interstitial in plants[12,13]. Palladium-103 is mainly produced by proton bombardment of rhodium via ^{103}Rh (p,n)^{103}Pd reaction of cyclotron[14]. It has been already shown that Pd thiocarbazone complexes possess interesting anti-proliferative effects on human breast cancer[15,16]. Due to interesting tumor imaging properties of bis-thiosemicarbazones,[^{103}Pd]-di-acetyl-bis(N^4-methylthiosemicarbazones), [^{103}Pd]$ATSM_2$) was prepared according to the analogy of radio copper homologues[17]. Reaction of 3-indole carbonaldehyde with aminothiocarbonyl hydrazines resulted in the formation of 3-indole carboxaldehydethiocarbazones. The synthesized thiosemi carbazones were used as ligands in the formation of $[Pd[TSC]Cl_2]$ complexes with Pd(II) metal ion (H_2L) precursor, $[Pd(DMSO)_2Cl_2]$. The structure of complexes were established by electronic, IR, HNMR, ^{13}CNMR, FABMS and DTA[18].

The analysis of data available in the Cambridge structural data base[19] has demonstrated that the results of the investigations into the structure of metal complexes with HL have been obtained for more than 50 compounds including, for the most part, Ni(II), Fe(III, Co(II), Cu(II), Zn(II), Rh (III) and Cd (II) complexes. The complexes which HL acts as a neutral ligand, X-Ray diffraction data for Pt(II) and Pd(II) complexes have been reported only by Gastadi, Porta and Dorazeo-Gonzalez et al.[20], who described the structures of the $[Pt(HL)_2]SO_4$ and $[Pt\ (HL)_2)](NO_3)_2$ compounds although there are numerous works concerned with different aspects of their synthesis and determination of their properties[21]. Interest in these compounds has been associated primary with the use of thiosemicarbazide and its derivatives as biologically active compound and analytical reagent for the Pt (II) and Pd (II)[22,23].

New complex of Pd (II) Thiosemicarbazide have been synthesis and characterized[24]. New series of UO_2(VI), Ti(IV), Sn(IV), Zr(IV) and Th(IV) complexes were prepared, characterized and were measured, investigated for biological activity[25]. Thus in the present manuscript it is aimed at to study the special and electrical properties copper (II) complexes due to their lack in the literature data and their biological activity.

Abou sekkina etal.investigated γ-pyrolysis of crystalline sodium thiosulphate pentahydrate[26]

EXPERIMENTAL

Materials

Reagent grade chemicals were used without further purification.

Preparation of the ligand

The ligand 2-phenylaminoacetyl-N-phenylhydrazine carbthioamide (H_2L) was prepared by mixing equimolar amount of desired hydrazide (0.01mol) in 10ml of absolute ethanol and phenyl isothiocyanate (0.01mol) in 10 ml of absolute ethanol[27,28]. The reaction mixture was refluxed for 3 hrs. The resulting product was filtered off and crystallized from ethanol.

Preparation of the metal complexes

Copper (II) complexes of the ligand were prepared by adding stoichiometric amount of the copper (II) acetate, bromide and nitrate in absolute ethanol to 2-phenylaminoacetyl-N-phenyl hydrazine carbthioamide (H_2L) in absolute ethanol in a 1:1 molar ratio. The reaction solution was stirred magnetically at 60°C for 5hrs. The resulting solids were filtered off, washed several times with ethanol and dried under vacuum over P_4O_{10}.

Measurements

Elemental analyses (C, H and Cl) was performed by Microanalytical unit of the Cairo Univerisity, Egypt. IR absorption spectra before and after gamma irradiation were recorded using KBr discs and a Perkin-Elmer 1430 recording specrtrophotometer. ^{1}H NMR spectra were recorded in d^6-DMSO using 300 MHz Varian NMR spectrometer. The electronic spectra were carried out as solution (10^{-3}M) in DMF using a Perkin- Elmer Lambada 4B spectrophotometer. The molar conductivity measurements were made in DMF solution (10^{-3}M) using a Tacussel conductometer type CD6N. Magentic susceptibilities were measured at 27°C using a modified Gouy method with Johnson Mattey balance. Thermogravimetric analysis(TGA) before and after gamma radiation were carried out in air using a Schimadzu(Japan) thermal analyzer at a heating rate of 10 °Cmin^{-1} in the temperature range 25-600 using platinum crucibles.X-ray powder diffraction before and after γ-irradiation was measured using a Schimadzu XD-3 diffractometer (Japan) using CuKα radiation and Ni- Filter.Energetic γ-irradiation exposure was undertaken using a γ- Co^{60} unit at atomic energy establishment AEE at El-Naser City Egypt at an accumalated dose of 1 Mega rad in air.

RESULTS AND DISCUSSION

The ligand 2-[phenyl amino acetyl-N-phenyl hydrazine carbothio amide(H_2L) was confirmed by elemental analysis TABLE 1, infrared TABLE 2 and ^{1}HNMR spectroscopy

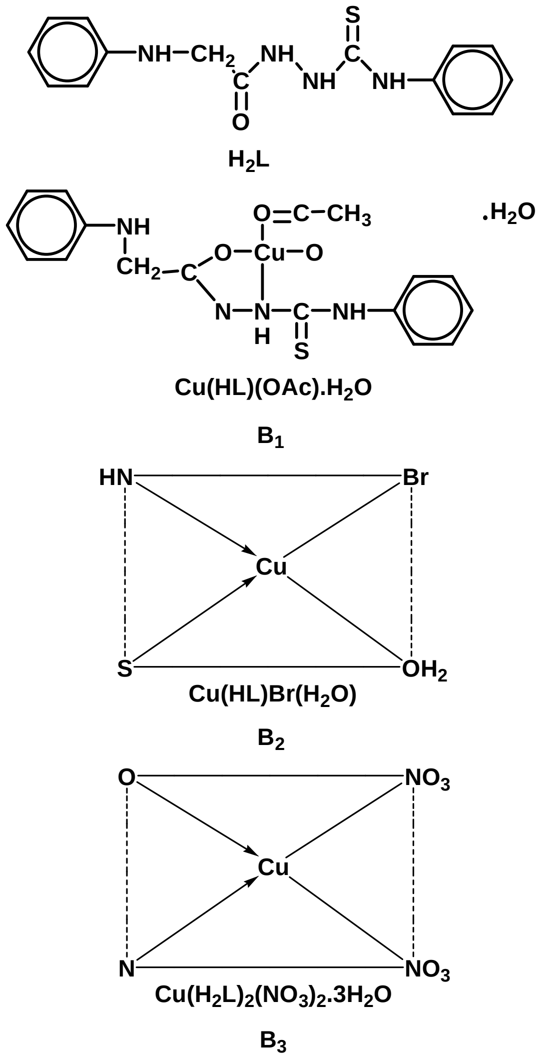
TABLE 1 : Elemental analyses and molar conductivities of the ligand (H_2L) $C_{15}H_{16}N_4OS$ and their copper (II) complexes.

No.	Compound	Colour Yield (%)	Λ_m Mol. Wt.	Found (Calc .) % C	H	^M	μ eff (B.M)
B	H_2 L	Pale brown (75)	300	60.2 (60.1)	5.6 (5.3)	—	—
B_1	$[Cu(HL)(OAc).H_2O]$	Dark green (65)	439	46.6 (46.5)	4.5 (4.5)	19	1.8
B_2	$[Cu(HL)Br.H_2O]$	Green (60)	460	38.7 (38.5)	3.5 (3.6)	28	1.5
B_3	$[Cu(H_2L)_2(NO_3)_2]3H_2O$	Dark green (70)	841	42.6 (42.8)	4.3 (4.5)	20	1.82

Foot notes
B=Before γ-irradiation, A= After γ-irradiation
M=molar conductivity ohm^{-1} cm^2 mol^{-1} in 10^{-3}M DMF solution

^{1}H NMR spectra

The ^{1}H NMR spectrum of the ligand (H_2L) in DMSO –d^6 revealed a chemical shift (δ/ppm) at 9.7 for N(4)H, N(2)H, N(1)H at 10.0, 9.5 ppm, singlet at 3.8 ppm and multiplet at 7.6 ppm are attributed to CH_2 and aromatic protons. The reaction of the ligand H_2L with different salts of Cu(II) acetate, bromide and nitrate produce complexes of the general formulae. $[Cu(HL)(OAc).H_2O]$, $[Cu(HL)Br.H_2O]$ and $[Cu(H_2L)(NO_3)_2]3H_2O$. These air stable complexes are non-hygroscopic, partially soluble in most organic solvents, but freely soluble in DMF and DMSO. Values of molar conductivities in DMF (10^{-3}M) solution (TABLE 1) show that the complexes are non-electrolytes, indicating coordination of the anions to the ligand[29].



Scheme 1 : The chemical structure of lagand and copper (II) complexes

TABLE 2 : Infrared spectral bands (cm^{-1}) of the ligand (H_2L,$C_{15}H_{16}N_4OS$) and their copper (II) complexes.

No.	Compound	ν(N4-H)	ν (N2-H)	ν (N1-H)	ν (C=O)	ν (C=S)	ν (Cu-N)	ν (Cu-O)
B	H_2L	3340(m)	3290(w)	3250(w)	1677(s)	747(s)	-	-
A	H_2L	3448(br)	3295(w)	3290 (w)	1679(s)	748(s)	510(s)	450(m)
B1	$[Cu(HL)(OAc).H_2O]$	3450(w)	3256(w)	-	-	692(m)	515(m)	410(w)
A1	$[Cu(HL)(OAc).H_2O]$	3450(m)	3260(w)	-	-	692(m)	510(w)	405(w)
B2	$[Cu(HL)Br.H_2O]$	3428(br))	3288(m)	3185 (m)	1602(m)	-	504(m)	-
A2	$[Cu(HL)Br.H_2O]$	3433(br)	3289(m)	3184 (m)	1602(m)	-	502(m)	-
B3	$[Cu(H_2L)_2(NO_3)_2]3H_2O$	3436(br)	3292(s)	3203(m)	-1600(s)	755(s)	506(m)	420(w)
A3	$[Cu(H_2L)_2(NO_3)_2]3H_2O$	3445(w)	3292(s)	3205(m)	1600(s)	756(s)	502(m)	410(w)

Foot notes
B=before γ-irradiation
A=after γ-irradiation (1M. Rad.)

The infrared spectra

A study and comparison of the IR spectra before and after γ-irradiation of 2-[phenyl amino acetyl-N-phenyl hydrazine carbothioamide] ligand (H_2L) and copper(II) complexes imply that the ligand is bidentate in nature, with carbonyl oxygen and NH, as two coordinates sites. The IR spectrum of the free ligand shows five bands at 3340, 3290, 3250, 1677 and 747 cm^{-1} assigned to ν(N4-H), ν(N2-H), ν(N1-H), ν(C=O) and ν(C=S) respectivly. As a general trend in common after γ-irradiation higher energy (blue shift). General feature of the bands of ligand (A) after γ-irradiation are observed. As a result of γ-irradiation broadaning of complex (A) after γ-irradiation are observed. Results display that thus complex(A_1) is the most γ-radiation resistant material. Since complex(A_2)undergoes no noticeable radiation damage thus this material is the most stable one. As general feature in common, the bands of N(4)H, N(1)H and some bands disappear as a result of γ-irradiation damage. For complex (A_3) the band of N(4)H weaken by γ-irradiation. This is due to partial damage of material[26].

Electronic absorption spectra

The electronic spectral bands of the copper (II) complexes as well as the spectra of the ligand in solution DMF are shown in TABLE 3. The π - π* transition band is observed at 33000 cm^{-1} for H_2L. Compared to the free ligand, in the copper (II) complexes, this band is shifted to longer wave length (Red shift) which is consistent with an increase in the degree of Pi- cloud conjugation[30]. The electronic spectra of copper (II) complex display one broad band at the 15560 cm^{-1} range due to the $^2B_{2g} \rightarrow {}^2A_{2g}$ transition with a square planar geometry[31], the band at 15950, 15960 cm^{-1}, assigned to charge transfer band.

TABLE 3 : Electronic spectra (cm^{-1}) of the ligand (H_2L) and their Cu (II) complexes.

Compounds	Intraligand and charge transfer		d-d bands
H_2L	33000	-	-
$[Cu(HL)(OAc).H_2O]$	32250	25710	15950
$[Cu(HL)Br.H_2O]$	32020	25310	15560
$[Cu(H_2L)_2(NO_3)_2]3H_2O$	32480	25575	15960

Themogravimetric analyses data

The content of a component in a complex changes with its composition and structure. Thuse, the content of such component can be determined base on the mass losses of these components in thermogravimetric plots of the complex[32,33]. Therefore, the thermogravimetric analysis (TGA,DTA)(50-800) for prepared complexes were recorded to distinguish between the coordinated and hydrated water and to give an insightinto the thermal stabil-

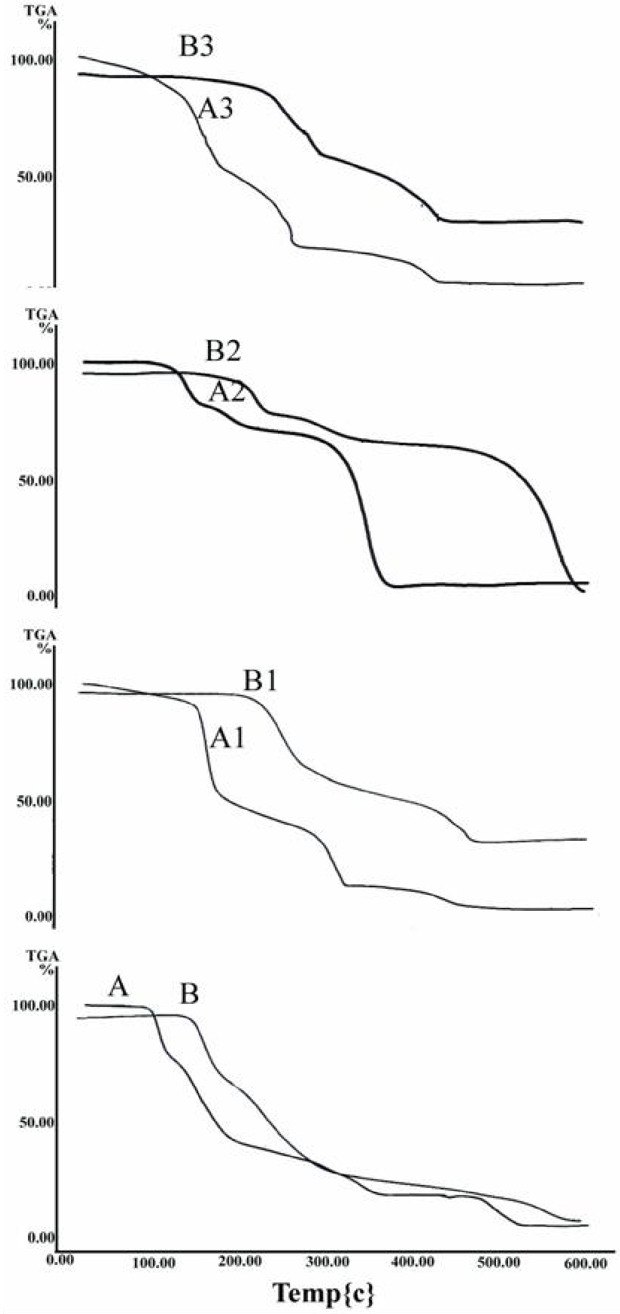


Figure 1 : Thermogrvimetric anlysis of ligand and copper (II) complexs

ity of the studied complexes before and after γ-irradiation.Thermal behaviour of the ligand and copper(II) complexes was investigated by thermogravimetric study before and after γ-irradiation as listed in TABLE 4. Thus Figure 1 shows the TG curves of the ligand and copper(II) complexes before and after γ-irradiation. The correlation between the different decomposition steps of the complexes with the corresponding mass losses are discussed in terms of the proposed formulae of the complexes. The thermogravimetric analysis curve of the ligand before and after irradation reveal that γ-irradiation induced thermal stability to the material. While TG curve of copper (II) complexes before and after irradiation reveal that the complex [Cu(HL)(OAc).H_2O] decomposed in three steps, the first step occurred at 210-350 °C with percentage weight loss of 57.8 % due to a loss of coordinated water molecule, acetate ion and phenyl isothiocyanate moiety. The second and third steps occurred at 350-500 °C with apercentage weight loss of 11%and500-700 °C with a percentage weight loss of 10% respectively due to the decomposition of phenylaminoacetyl but after γ-irradiation tereare thermal stabilization at 500-600 °C show that γ-irradiation induced thermal stability than before γ-irradiation. TABLE 4 shows the material decomposition mass loss also in complexes [Cu(HL)Br(H_2O)] . The TG. Plot of the complex $[Cu(H_2L)_2(NO_3)_2].3H_2O$ the three molecules of water of crystallization liberated at 100-220 °C, γ-irradiation also induced thermal stability than before irradiation as shown in Figure 1.

TABLE 4 : Thermogravimetric analysis (TG) of the ligand (H_2L,$C_{15}H_{16}N_4OS$) and their copper (II) complexes before and after irradiation.

Compounds	TG/°C	Mass loss% Before γ-irradiation	Assignment	TG/°C	Mass loss% After γ-irradiation	Assignment
	Before γ-irradiation	Cal. (F.)		After γ-irradiation	Cal. (F.)	
H_2L	150-350 350-620 620-852	55.7(57.2) 20(22.3)	C_7H_4NS Decomp. Decomp.	150-340 350-600	55.7(57.7) (15.8)	C_7H_4NS Decomp.
[Cu(HL)(OAc).H_2O]	210-350 350-500 500-700	56.5(57.8) (11.0) (10.0)	H_2O+AcO+ C_7H_4NS Decomp. Decomp.	220-300 300-500 500-600	(40) (20)	Thermal stabilization
[Cu(HL)Br.H_2O]	180-220 220-380 400-620	17.4(17.7) 13.2(10.9) (66.9)	HBr H2O+ C_2H_3O Decomp.	200-225 225-320 320-500	17.4(17) 13.2(12)	HBr $H_2O+C_2H_3O$ Thermal stabilization
$[Cu(H_2L)_2(NO_3)_2]3H_2O$	100-220 220-300 300-450 450-700	13.7(11.6) 32.8(35.7) (33.5) (16.3)	$3H_2O+NO_3$ $NO_3+C_2H_5N$ Decomp. Decomp.	180-300 300-420 420-600	46.6(47)	$3H_2O+2NO_3+$ $C_7H_9N_{3+}C_2H_3O$ Decomp. Thermal stabilization

X-ray diffraction patterns

The X-ray differaction patterns of the ligand before and after γ-irradiation show that

(a) The identity of the material is still reserved.
(b) Displacement of longer interplanar spacings.
(c) Some peaks newly appeared.

Figure 2 displays that in complex Cu(HL)(OAc).H_2O new peaks appear and some peaks weaken and displaced to shorter interplanar spacings[26]. Thus these due to partial γ-irradiation damage[13]. While in the complex[Cu(HL)Br (H_2O)] show that the X-ray difraction pattern before and after γ-irradiation appear peaks as in Figure 2. This display high resistance. Also in the complex $[Cu(H_2L)(NO_3)_2.3H_2O]$ show that the X-ray diffraction pattern before and after γ-irradiation appear peaks as in Figure 2. This material show γ-irradiation induced decreased degree of crystallinity. This is a result of partial γ-irradiation damage Figure 2.

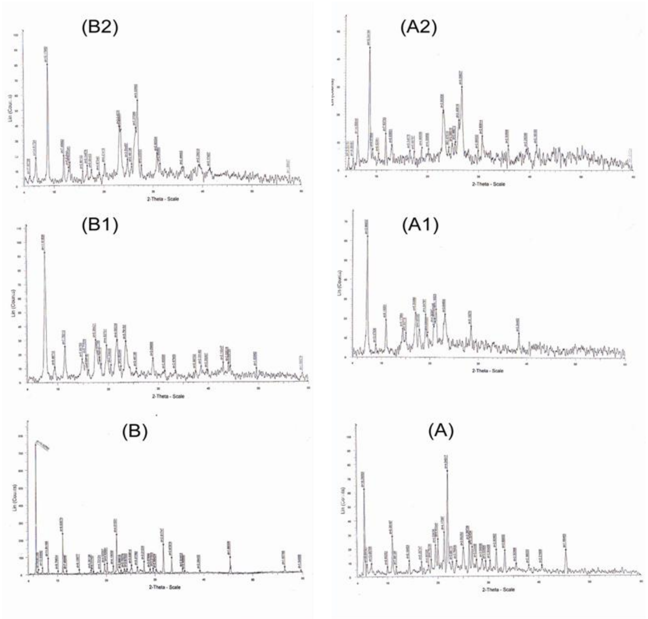


Figure 2 : X-ray diffraction pattern of ligand and copper (II) complexs

CONCLUSION

The molecular structures of the material are evaluated. The interaction with energy γ-irradiation improved thermal stability of material and spectral properties were conculoded the first time.

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