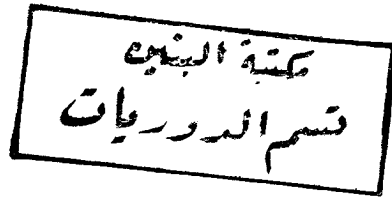


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**SYNTHESIS, SPECTROSCOPIC AND THERMAL PROPERTIES  
OF SOME IONIC POLYMERS AND POLYMERIC  
COMPLEXES DERIVED FROM PHTHALOYL  
BIS (S-METHYLHYDRAZINECARBODITHIOATE).**

By

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*Key Words:* Ionic polymers. Phthaloyl bis (S-methylhydrazinecarbodithioate),  
Polymeric complexes, Thermal analysis of.

**ABSTRACT**

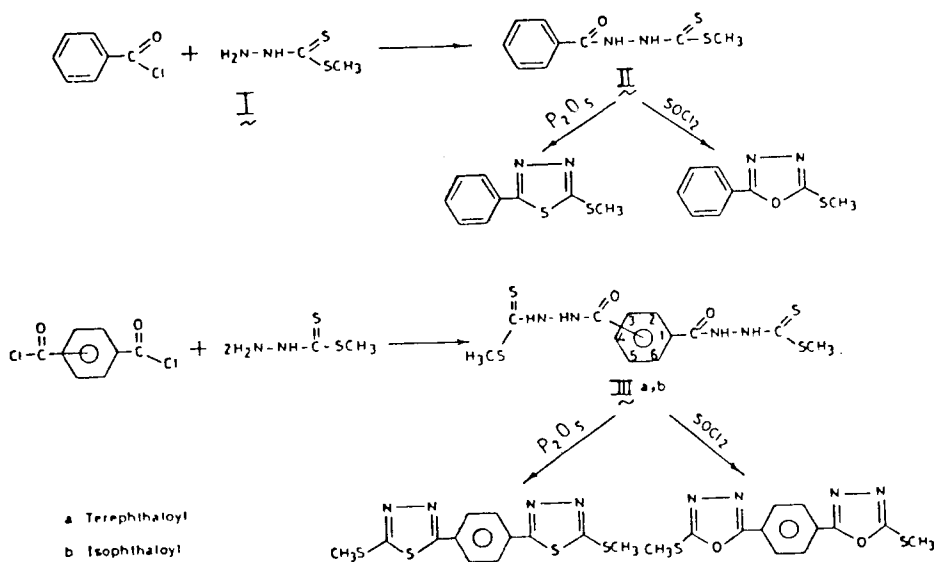
Mono- and bis hydrides derived from the condensation of S-methylhydrazinecarbodithioate with benzoylchloride and tere- and isophthaloyldichloride, respectively, were prepared. Their reactions with secondary (piperazine) and tertiary (N,N,N',N'-tetraethylethyne diamine) diamines forming ionic polymers, and nickel(II) salts forming different polymeric complexes were investigated. Elemental analysis, infrared and electronic spectra have shown that the mono- and bishydrazides behave differently toward the nickel(II) salts. With nickel(II) acetate the monohydrazides behave as bridged dibasic tetradentate molecule forming polymeric nickel(II) complexes while with nickel(II) chloride it behaves as monobasic bidentate ligand. The tere- and isophthaloyl bis-hydrazide behave as bridged dibasic molecule with eight center of coordination in the complexes derived from nickel(II) acetate and four center of coordination in complexes derived from nickel(II) chloride. The thermal properties of the ionic polymers and the polymeric nickel(II) complexes were also investigated.

**INTRODUCTION**

S-methylhydrazinecarbodithioate, I, is a very useful starting material for the synthesis of many complexes (Ali, *et al.*, 1971; Iskander and El-Sayed, 1971) many Schiff bases, (El-Sayed *et al.*, 1972, 1974; El-Toukhy *et al.*, 1982, 1983;

Iskander *et al.*, 1979) many thiosemicarbazones (Klayman *et al.*, 1979, 1984) and thiocarbohydrazone (Kurzer and Wilkinson, 1970). These nitrogen-sulphur containing molecules act as good chelating agents, and have been found to possess a wide range of chemotherapeutic properties (Klayman *et al.*, 1979, 1984; Kurzer and Wilkinson, 1970; Maiti *et al.*, 1988; Mohan *et al.*, 1985). They provide a good potential for development as active agents since they are not found in nature and therefore no organismic resistance can have developed by prior exposure. The activities of these ligands can also be modified by derivatization since small changes to the ligand have been shown, in some instances to markedly alter antiviral (Shipman *et al.*, 1981) or carcinostatic activity (Scovill *et al.*, 1982, 1984). Many chelates of hydrazinecarbodithioate derivatives have been studied as potential antitumor agents (Das and Livingstone, 1976, 1978).

The reaction of **I** with benzoylchloride and phthaloyldichloride afford mono and bis hydrazide of S-methylhydrazinecarbodithioate derivatives **II** and **III**a,b, respectively, the starting materials for many 1,3,4-oxadiazoles and 1,3,4-thiadiazoles, scheme 1, (Mansour *et al.*, 1988). We believe that synthesis of these organic ligands, **II** and **III**, their spectral and thermal behaviour will provide information that will be able to be used to aid in the generalization of both the pharmacological and the synthetic inorganic applications.



SCHEME 1

## EXPERIMENTAL

### Materials

S-methylhydrazinecarbodithioate, I, and its analogue S-methyl-N-methylhydrazinecarbodithioate, were prepared and purified by a literature methods (Iskander and El-Sayed, 1974; *et al.*, 1972). Benzoyl chloride, terephthaloyl dichloride, isophthaloyldichloride and piperazine (Aldrich) and nickel (II) salts (BDH) were used as received. Piperidine, and N,N,N',N'-tetraethylethylenediamine (Aldrich) were dried over 4 Å molecular sieves and distilled under reduced pressure before use.

### Preparation of S-methylbenzoylhydrazinecarbodithioate, II.

Benzoylchloride (0.01 mole) was added slowly to a stirred solution of S-methylhydrazinecarbodithioate (0.01 mole) in dimethylformamide (30 ml). After one hour stirring, the reaction mixture poured into cold water, filtered, and recrystallized from alcohol. White solid, yield 78% m.p. 180-182°C. <sup>1</sup>Hnmr (DMSO-d<sub>6</sub>); δ, 2.43ppm (s, CH<sub>3</sub>, 3H); δ, 7.47-7.8 ppm (m, aromatics, 5H); δ 11.0 ppm (s. NH, 2H) disappeared upon deuteration.

### Preparation of Terephthaloyl bis(S-methylhydrazinecarbodithioate) IIIa

A stirred solution of I (0.02 mole) in DMF (20 ml) was treated with a terephthaloyl dichloride, (0.01 mol.). The reaction mixture was stirred for one hour at room temperature, and poured into ice-water. A white solid was collected, washed and recrystallized from dioxane. White powder, yield 86%, m.p. 250°C, <sup>1</sup>Hnmr (DMSO-d<sub>6</sub>); δ, 2.46 ppm (s, CH<sub>3</sub>, 6H); δ, 7.93 ppm (s, aromatic protons, 4H); δ, 11.1 ppm, δ, 11.53 ppm. (s, NH, 4H) disappeared upon deuteration.

### Preparation of Isophthaloyl bis (S- methylhydrazinecarbodithioate) IIIb

The title compound was prepared as previously described for compound IIIa except using isophthaloyldichloride instead of terephthaloyl dichloride, white powder, yield 65 %, m.p. 219°C <sup>1</sup>Hnmr (DMSO-d<sub>6</sub>); δ, 2.47 ppm (s, CH<sub>3</sub>, 6H); δ, 8.36 ppm (s, C<sub>2</sub>, 1H); δ, 8.07 ppm (d, C<sub>4</sub> and C<sub>6</sub>-2H); δ 7.66 ppm (t, C<sub>5</sub>, 1H) (these last three peaks of aromatic protons show a long-range spin-spin coupling); δ, 11.19 and 11.49 ppm. (s, NH, 4H) disappeared upon deuteration.

### Preparation of terephthaloyl bis (S-methyl-N-methylhydrazinecarbodithioate)

This compound was prepared by the same method described for compound IIIa except using S-methyl-N-methylhydrazinecarbodithioate instead of I. White powder, yield 78% , m.p. = 242°C <sup>1</sup>Hnmr (DMSO-d<sub>6</sub>); δ, 2.46 ppm (s, CH<sub>3</sub>, 6H); δ, 2.93 ppm (s, N-CH<sub>3</sub>, 6H); δ, 7.96 ppm (s, aromatic protons, 4H); δ, 11.2 ppm

(s, NH, 2H) disappeared upon deuteration.

#### **Preparation of the ionic polymer IV, (N N=Piperazine)**

A stirred solution of IIIa (0.01 mole) in methanol (50ml) was treated with a solution of piperazine (0.01 mole), in methanol (20ml) dropwise with constant stirring for 30 min. and the deposited yellow compound was filtered off, washed with ether and then recrystallized from ethanol/ether. Yield 64%, m.p. (decomp 225°C <sup>1</sup>Hnmr (DMSO-d<sub>6</sub>); δ, 2.51 ppm (s-CH<sub>3</sub>, 6H); δ, 2.63-2.97 ppm (m, CH<sub>2</sub>, 8H); δ, 8.11 ppm (s, aromatic protons, 4H).

#### **Preparation of the ionic polymer IV, (N N=TEED)**

This compound was prepared by the same method described for compound IV (N N=Piperazine) except using TEED instead of piperazine. Yellow powder, yield 86%; <sup>1</sup>Hnmr (DMSO-d<sub>6</sub>); δ, 1.18 ppm (t, CH<sub>3</sub>, 12H); δ, 2.57 ppm (s, S-CH<sub>3</sub>, 6H); δ, 2.92 - 2.99 ppm (m, CH<sub>2</sub>, 12H); δ, 8.01 ppm (s, aromatic protons, 4H).

#### **Preparation of bis-piperidine adduct V.**

A stirred solution of IIIa (0.01 mole) in methanol (50 ml) was treated with piperidine (0.02 mole), dropwise with constant stirring at room temperature for 30 min. The solution was reduced to half its volume by rotary evaporator and treated with dry diethyl ether (20 ml). The yellow precipitate was filtered off, washed with ether and dried in vacuum. Yield 80% <sup>1</sup>Hnmr (DMSO-d<sub>6</sub>), δ, 2.55 ppm (s, SCH<sub>3</sub> 6H); δ, 1.62 ppm (s, β, γ -CH<sub>2</sub>, 12H); δ, 4.14 ppm (s, α -CH<sub>2</sub>, 8H); δ, 8.13 ppm (s, aromatic protons, 4H).

#### **Preparation of nickel (II) complexes**

##### **Preparation of polymeric [Ni(II-2H)]<sub>n</sub> complex**

A solution of nickel (II) acetate tetrahydrate (0.01 mol) in ethanol (30 ml) was added to a hot solution of II (0.01 mol) in ethanol (30 ml). The reaction mixture refluxed for 30 min. The brown amorphous precipitate deposited was filtered off, washed several times with hot ethanol and dried in vacuum.

##### **Preparation of [Ni(II-H)<sub>2</sub>] complex**

A clear hot solution of nickel(II) chloride hexahydrate (0.01 mol) in ethanol (20 ml) was added to a hot solution of II (0.02 mol) in ethanol (30 ml). The reaction mixture was refluxed for 2 hour, evaporated to half of its volume and left to cool. The brown complex deposited was filtered off, washed several times with ethanol and dried in vacuum.

##### **Preparation of polymeric [Ni<sub>2</sub>(III-2H) (OAC)<sub>2</sub>]<sub>n</sub> complex**

A hot clear solution of nickel(II) acetate tetrahydrate (0.025 mol) in ethanol (30 ml)

was added to a solution of IIIa or IIIb (0.01 mol) in DMF (30 ml). The reaction mixture was refluxed for one hour and left to cool. The deposited solid was filtered off, washed several times with hot ethanol and dried in vacuum.

Preparation of polymeric  $[\text{Ni}(\text{III-H})]_n$  complexes.

The title complexes were prepared by the same method above except using nickel(II) chloride instead of nickel(II) acetate.

The elemental analysis for all prepared compounds are collected in Table 1.

### Physical Properties

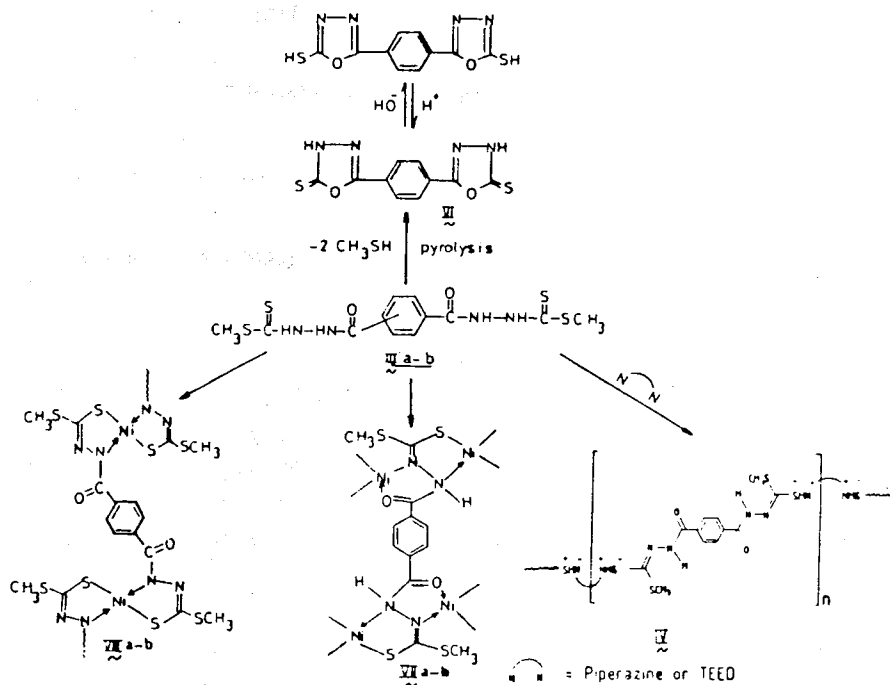
All melting points are uncorrected and were measured with a Kofler-block apparatus. The Nujol mull electronic spectra of the prepared complexes were recorded on a Perkin-Elmer 552 spectrophotometer. Infrared spectra (KBr disks) were obtained with a Pye Unicam SP 2000 spectrophotometer calibrated with the 906.5 or 3026.3  $\text{cm}^{-1}$  absorption of polystyrene.  $^1\text{Hnmr}$  spectra were recorded with a Varian XL-300 MHz spectrometer at Northeastern University, Boston, USA. The magnet temperature was adjusted at 38°C. Tetramethylsilane (TMS) signal ( $\delta = 0$ ) was employed as internal standard. Aldrich DMSO- $d_6$  was used as solvent. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA), were performed by Shimadzu thermal analyzer DT-30, calibrated with both copper sulphate pentahydrate and indium.

## RESULTS AND DISCUSSION

The reaction of S-methylhydrazinecarbodithioate, I, with benzol chloride, terephthaloyl dichloride, and isophthaloyl-dichloride gave S-methylbenzoylhydrazinecarbodithioate, II, terephthloyl bis (S-methylhydrazinecarbodithioate), IIIa, and isophthaloyl bis (S-methylhydrazinecarbodithioate), IIIb, respectively.

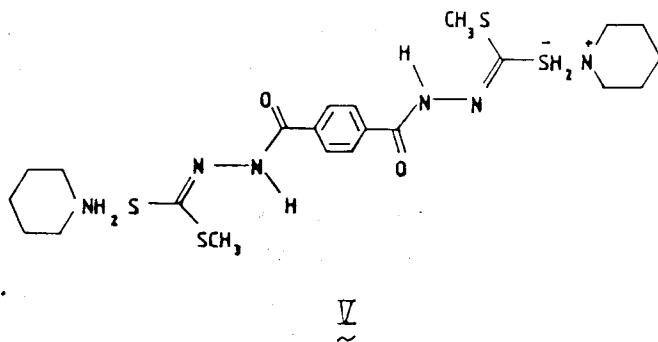
It is well known that the good leaving  $\text{SCH}_3$  group can be replaced from its compounds through nucleophilic substitution reaction with primary or secondary amines. We intended to use this phenomina to polymeric compounds containing thiosemicarbazide moiety (the potential complexing and biologically active molecule) by reaction of III, (which contain two terminal  $\text{SCH}_3$  groups) with piperazine (secondary diamine). The reaction product, instead, was a yellow ionic polymer IV, (adduct formation). The formation of this new types of ionic polymer, IV, Scheme 2, via adduct formation was proved by the reaction of nonprotic tetraalkylated diamines, namely, N,N,N',N'-tetraethylethylenediamine with IIIa in 1:1 molar ratio at room temperature indicating that the reaction of III

Ionic Polymers and Polymeric Complexes



SCHEME 2.

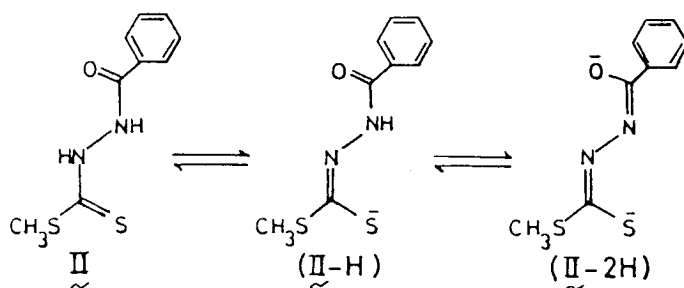
with the diamine is only acid-base reaction without any sign of substitution reaction. These products are sparingly soluble in common organic solvents presumably due to their polymeric nature. The model compound of the polymer IV was prepared by treatment of III with piperidine in 1:2 molar ratio in ethanol and structure V was assigned for the reaction product.



On the other hand, the reaction of N-methyl-S-methyl-hydrazinecarbodithioate with terephthaloyldichloride in 2:1 molar ratio gave the N-methyl analogue of III. Treatment of this product with diamine type bases gave no reaction under any condition, indicating that the thioamide proton, not the amide one, in III is the responsible one for the formation of the polymeric salt.

The reaction of terephthaloyl bis (S-methylhydrazinecarbodithioate), IIIa and the corresponding isophthaloyl bis (S-methylhydrazinecarbodithioate), IIIb with nickel(II) salts afford different types of polymeric nickel(II) chelates depending on the anion of the salt used. On using nickel(II) acetate, the reaction with ligands IIIa or IIIb proceeds instantaneously with the formation of brown nickel(II) chelates of the general formula  $[\text{Ni}_2(\text{III}-2\text{H})(\text{OAc})_2]_n$ , VII, where (III-2H) refer to the dinegative anion ligands. On the other hand, the reaction of IIIa or IIIb with nickel(II) chloride resulted in the formation of reddish brown neutral nickel(II) chelates,  $[\text{Ni}(\text{III}-2\text{H})]_n$ , VIII, irrespective of the metal to ligand molar ratio. The very limited solubilities of the isolated complexes in common organic solvents indicate their polymeric nature and do not permit any solution for physico-chemical studies.

It is of interest to note that the model molecule bezoyl-S-methylhydrazinecarbodithioate, II also, behaves differently toward nickel(II) salts. The reaction of II with nickel(II) acetate in a 1:1 molar ratio gave amorphous chelate of stoichiometry  $[\text{Ni}(\text{II}-2\text{H})]_n$ , where (II-2H) refer to the dibasic ligand. Mononuclear bis ligand nickel(II) chelate  $[\text{Ni}(\text{II}-\text{H})_2]$  was isolated from the reaction of II with nickel(II) chloride. Here, II behaves as monobasic molecule.



All the prepared compounds are quite stable at room temperature and do not show any decomposition after a long period of standing. The compounds do not possess sharp melting points, but appear to decompose above 250°C.



All the isolated nickel(II) chelates prepared either from nickel acetate or nickel chloride are diamagnetic implying an  $^1A_{1g}$  ground state (Lever, 1968). The Nujol mull electronic spectra of these chelates exhibit d-d transitions at ca. 450, 560 and 670 nm, no absorption was observed beyond 750 nm. Both magnetic and spectral data are consistent with a square planar arrangement around the nickel(II) ion (El-Sayed et al., 1974; Lever, 1968). Such an arrangement can be achieved through polymerization and structures VII and VIII, Scheme 2, can be assigned for these chelates.

The infrared spectra of the solid free ligands IIIa, IIIb, and II exhibit  $\nu(\text{N-H})$  absorption bands at ca. 3300 and 3150  $\text{cm}^{-1}$  but neither  $\nu(\text{S-H})$  at ca. 2570  $\text{cm}^{-1}$  nor  $\nu(\text{O-H})$  at ca. 3500  $\text{cm}^{-1}$  are observed (Colthup et al., 1964). The infrared spectra of organic ligands also show a strong absorption band at ca. 1660  $\text{cm}^{-1}$  due to amide  $\nu(\text{C=O})$  beside bands at about 1310 and 860  $\text{cm}^{-1}$  which may be assigned to thioamide  $\nu(\text{C=S})$  vibrations (Maiti et al., 1988; Nakamoto, 1978). Accordingly, in the solid state IIIa, IIIb, and II exist in the keto-thio keto forms. However, in solution the free ligands may form an equilibrium mixture of keto-thio keto  $\rightleftharpoons$  keto-thiol  $\rightleftharpoons$  enol-thio keto  $\rightleftharpoons$  enol-thiol tautomers.

The infrared spectra of nickel(II) complexes VII, suggest that the ligands IIIa and IIIb act as bridged dibasic molecule with eight centers of coordination via the deprotonated thiol sulphur, the amide keto oxygen and the two hydrazinic nitrogen from each side of the molecule. This fact is quite evident from the disappearance of the  $\nu(\text{C=N})$  stretching band at ca. 1600  $\text{cm}^{-1}$  as compared to the parent organic ligands. The complete deprotonation was observed in the infrared spectrum of the model complex  $[\text{Ni}(\text{II}-2\text{H})]_n$  indicating that II behaves as doubly charged ligand coordinating through the mercapto-sulphur, the hydroxo-oxygen and the two hydrazinic nitrogens. The presence of uncoordinated acetate group in VII complexes is confirmed by the appearance of  $\nu_{\text{asym}}(\text{COO})$  and  $\nu_{\text{sym}}(\text{COO})$  bands at ca. 1620 and 1450  $\text{cm}^{-1}$ , respectively (Nakamoto, 1978).

In the far infrared region, the nickel (II) complexes show bands at ca. 420, 390 and 270  $\text{cm}^{-1}$  which are assigned to  $\nu(\text{Ni-O})$ ,  $\nu(\text{Ni-N})$  and  $\nu(\text{Ni-S})$  vibrations, respectively (Nakamoto, 1978; Adams, 1979).

As a matter of fact, the infrared spectra of nickel(II) complexes derived from IIIa, IIIb and II with nickel(II) chloride, show better resolved bands relative to nickel(II) complexes prepared from nickel(II) acetate. This simplifies the interpretation and helps to suggest that the strong band at ca. 1670  $\text{cm}^{-1}$  and the weak sharp band at ca. 3200  $\text{cm}^{-1}$  in the infrared spectra of VIIIa, VIIIb and  $[\text{Ni}(\text{II}-\text{H})_2]$  are due to  $\nu(\text{C=O})$  and  $\nu(\text{N-H})$ , respectively, indicating that the carbonyl oxygen in IIIa, IIIb and II are

not involved in the chelation process. However, the observed positive shift in (C=O) frequencies of nickel(II) complexes may be due to the absence of (C=O...H-N) intra- or intermolecular hydrogen bonding originally presents in the parent organic ligands IIIb, IIIb and II. Another evidence for this conclusion is the fact that the thioamide bands at ca. 1310 and 860  $\text{cm}^{-1}$  in the organic ligands suffered from large negative shift or disappeared. The far infrared spectra of  $[\text{Ni}(\text{IIIa-2H})]_n$ , VIIIa;  $[(\text{Ni}(\text{IIIb-2H}))_n]$  VIIIb, and  $[\text{Ni}(\text{III-H})_2]$  complexes show bands at ca. 400 and 270  $\text{cm}^{-1}$  due to  $\nu(\text{Ni-N})$  and  $\nu(\text{Ni-S})$  vibrations, respectively, but no  $\nu(\text{Ni-O})$  at ca. 420  $\text{cm}^{-1}$  is observed. These results show that the organic ligands IIIa and IIIb in VIIa and VIIb nickel complexes behave as a bridged dibasic ligands with four centers of coordination, while II in  $[\text{Ni}(\text{II-H})_2]$  complex acts as monobasic bidentate ligand chelated to the nickel (II) ion via the deprotonated thiol sulphur and the amide nitrogen.

### Thermal Properties

The observation that compound IIIa is melted at 250°C and solidified after this temperature followed by remelting with decomposition at 290°C stimulate our interest to study the thermogravimetric analysis of IIIa, IIIb, II and their nickel(II) complexes beside the polymeric compounds IV ( $\text{N}\ddot{\text{N}}=\text{Piperazine}$ ). This enabled us to prepare compound VI by pyrolysis of IIIa at 255°C in an oil bath at temperature controlled to within  $\pm 2^\circ\text{C}$ , and characterized it by elemental analysis, infrared and  $^1\text{Hnmr}$  spectra in  $\text{DMSO } d_6$ - which showed lack of  $-\text{SCH}_3$  signal at  $\delta$ , 2.5 ppm. The aromatic protons appeared as one sharp signal at  $\delta$ , 7.9 ppm while the signal of N-H protons located at  $\delta$ , 10.8 ppm disappeared upon deuteration.

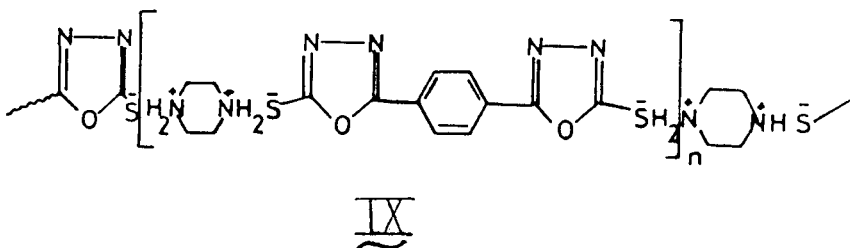
The thermogravimetric analyses, TGA and DTA, were performed with a Shematzo thermogravimetric system using a heating rate of 10-20 degrees C/minute. The atmosphere was flowing air or nitrogen (50 ml/minute) as delivered from a tank of dry air or dry nitrogen with a sample size of 10-15 mg.

The thermogram of some of these compounds are shown in Figures 1 and 2 where the basic features involve loss of  $\text{CH}_3\text{SH}$  and decomposition to inorganic residue especially for the nickel(II) complexes. The temperature ranges for these processes are dependent on such factors as heating rate, sample size and atmosphere and cannot be correlated with thermodynamic stability since they represent kinetic processes (Nikolaev and Logvinenko, 1978). Qualitative assessments of the structure can be made through the comparison of temperatures of the  $\text{CH}_3\text{SH}$  loss from the studied compounds under the same experimental conditions.

The thermal analysis of IIIa and IIIb give an initial mass loss (13.2 % ; 250-300°C) which corresponds with the loss of only one  $\text{CH}_3\text{SH}$  molecule (theo. mass loss,

12.8%) while the TG of IV ( $\widehat{N-N}$ =Piperazine) gives an initial mass loss (19.9%; 225-290°C) which is consistent with theoretical loss of the two  $\text{CH}_3\text{SH}$  molecules together in one step (theor. mass loss, 20.8%). We speculate that the driving force for the simultaneous loss of the two  $\text{CH}_3\text{SH}$  molecules from IV may be due to the formation of the highly conjugated oxadiazole compound IX while in IIIa and IIIb rearrangements of residual parts of IIIa and IIIb take place as the first loss of  $\text{CH}_3\text{SH}$  molecule resulted in the strengthening of the other C-SCH<sub>3</sub> bond energy and delay the evolution of the second  $\text{CH}_3\text{SH}$  molecule, until it is lost simultaneously with decomposition of the rest of the molecules.

Although the ionic polymer IV ( $\widehat{N-N}$ =Piperazine) start to lose its  $\text{CH}_3\text{SH}$  residue before its parent compound IIIa, the thermal product, presumably, polymeric oxadiazole derivative IX shows a high thermal stability relative to any other compound studied in this work (See Figure 1, (A and F)). The ionic nature and the formation of oxadiazole moiety could be suggested as reason for this behaviour.



The nickel(II) complexes VIIa, b and VIIIa, b are thermally degraded to NiO over the temperature range 70-900°C. Observed (73.6, 73.8 and 83.2, 81.4%) and theoretical (75.3 and 82.6%) mass losses, respectively, for VIIa, b and VIIIa, b, are within experimental error ( $\pm 2.0\%$ ). For  $[\text{Ni}(\text{II}-2\text{H})]_n$  and  $[\text{Ni}(\text{II}-\text{H})_2]$  complexes, the total mass loss are, 70.2 and 83.7%, inconsistent with the theoretical mass loss, 71.3 and 85.3%, respectively. The mass loss in the temperature range 70-160°C (14.9, 14.7 and 21.8, 22.7%) are consistent with the simultaneous removal of two -SCH<sub>3</sub> group (theor. 15.8 and 22.3%) for VIIa, b and VIIIa, b, respectively, presumably because each -SCH<sub>3</sub> group is directly attached to chelate ring resulted in lowering of the bond energy of C-SCH<sub>3</sub> grouping. The remaining organic molecules are lost rapidly between 280-900°C.

The infrared spectra of the deposits at various stages showed a significant loss of intensity among the bands due to the organic ligands at 300°C but a clear retention of vibration activity due to Ni-S, Ni-O and Ni-N stretching at 270, 420, 390  $\text{cm}^{-1}$  for VIIb and Ni-S and Ni-N stretching at 270, 400  $\text{cm}^{-1}$  for VIIIb, respectively. At higher

temperatures the products became increasingly contaminated with residual carbon and the spectra were inconclusive. Between 600 and 900°C the residual sulphide is progressively converted to NiO.

The DTA Curve in nitrogen atmosphere for VIIa, Figure 2, consists of an endotherm ( $T = 115^{\circ}\text{C}$ ) followed by a substantial exotherm ( $T = 280^{\circ}\text{C}$ ). The combination of endo- and exotherm is common for complexes of III and suggests that the presence of the metal catalyses the exothermic degradation of the ligand (Raper *et al.*, 1984; Atkinson *et al.*, 1985).

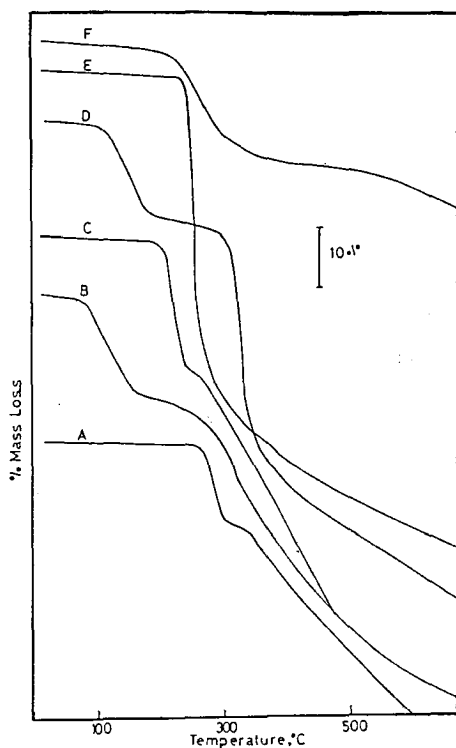


Fig. 1: Thermogravimetric (TG) plots of: A, IIIa; B, VIIa; C, II; D,  $(\text{Ni}(\text{II}-2\text{H}))_n$ ; E,  $(\text{Ni}(\text{II}-\text{H})_2)$ ; F, IV. ( $\widehat{\text{N}}\widehat{\text{N}} = \text{Piperazine}$ ) obtained at a heating rate of  $10^{\circ}\text{C}/\text{min}$ . under air atmosphere.

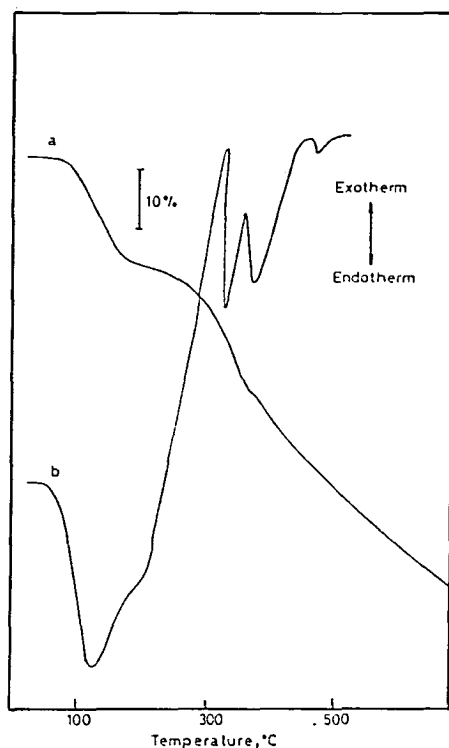


Fig. 2: Thermal analysis of VIIa complex.  
a) TG b) DTA.

Table 1

## Analytical and Thermogravemetric Data

Compound	Elemental Analysis			m.p. (decomp.)	Temp. Range, °C for CH <sub>3</sub> SH Loss	Number of CH <sub>3</sub> SH Loss	Loss for CH <sub>3</sub> SH
	N	S	Ni				
II	12.3 (12.4)	28.5 (28.3)	- -	200	175-190	1	21.6 (21.2)
IIIa	14.6 (14.9)	34.4 (34.2)	- -	320	250-280	1	13.20 (12.8)
IIIb	14.7 (14.9)	34.1 (34.2)	- -	330	240-265	1	13.3 (12.8)
IV <sup>b</sup>	18.1 (18.3)	27.5 (27.8)	- -	520	225-290	2	19.9 (20.8)
IV <sup>c</sup>	16.4 (16.2)	24.3 (24.7)	- -	470	220-300	2	17.4 (18.1)
VIIa	9.0 (9.2)	20.8 (21.1)	20.3 (19.4)	290	70-160	2	14.9 (15.8)
VIIb	8.6 (9.2)	20.6 (21.1)	19.0 (19.4)	280	70-150	2	14.7 (15.8)
VIIIa	12.4 (13.0)	29.2 (29.7)	12.8 (13.7)	310	140-175	2	21.8 (22.3)
VIIIb	12.4 (13.0)	30.3 (29.7)	13.1 (13.7)	305	135-175	2	22.7 (22.3)
(Ni(II-2H)) <sub>n</sub>	9.2 (9.9)	22.4 (22.6)	20.5 (20.6)	330	100-160	1	17.2 (16.6)
(Ni(II-H) <sub>2</sub> )	11.3 (11.0)	24.8 (25.1)	11.2 (11.6)	250	230-250	*	*

\* The [Ni(II-H)<sub>2</sub>] complex loses simultaneously one ligand (II-H) and CH<sub>3</sub>SH molecule from the other ligand (observed mass loss = 51.6 Theor. Mass loss = 53.5 See Figure 1.

a) Calculated values are given in parantheses. b)  $\overline{\text{IV}}$ ,  $\overline{\text{NN}}$  = Piperazine c)  $\overline{\text{IV}}$ ,  $\overline{\text{NN}}$  = TEED.

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تحضير ودراسة الخواص الطيفية والحرارية لبعض البلمرات الأيونية  
والمتراكبات المتبلمرة المشتقة من فثالويل ثنائي  
( كب - ميثيل هيدرازين كاربوداي ثيوات )

أحمد الطوخي - السيد منصور - منال العربي - أحمد قاسم  
ومحمود نصر

يهدف هذا البحث إلى تحضير بعض المركبات أحادية وثنائية الهيدرازيد والمشتقة من  
تكتيف كب - ميثيل هيدرازين كاربوداي ثيوات مع كل من كلوريد البنزويل وثنائي كلوريد  
الفثالويل . وقد تم تفاعل الهيدرازيدات المحضرة مع ثنائي الأمينات الثانوية مثل البيرازين  
والثالثة مثل  $\bar{N}$ ,  $\bar{N}$ ,  $N$ ,  $\bar{N}$  - تترا إيثيل إيثيلين داي أمين لتحضير بعض البلمرات الأيونية  
وكذلك تفاعلها مع أملاح النيكل الثنائي . وقد تم فصل والتعرف على تركيب متراكبات  
متبلمرة مختلفة تعتمد على طبيعة الأنيون لأملاح النيكل تعمل فيها الهيدرازيدات  
الأحادية وثنائية ( عوامل التراكب ) كقنطرة بين أيونات النيكل . هذا وقد نوقشت  
الخواص الحرارية للهيدرازيدات الأحادية وثنائية وبلمرات الأيونية كذلك متراكبات  
النيكل المتبلمرة .