SYNTHESIS, CHARACTERIZATION AND THERMAL STUDIES OF MIXED LIGAND COMPLEXES OF Hg(II) THIOSEMICARBAZONES WITH 2-AMINOTHIAZOLE

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حضر عدد من المترابكات مختلطة الليجندات للزئبق الثنائي مع الثيوسيميكاربازونات (- أستيل بيريدين ثايوسيميكاربازون ، - أمينو اسيتوفينون ثايوسيميكاربازون ، - فيورالدهيد ثايوسيميكاربازون) وكذلك مع - أمينوثيازول. درست المترابكات باستخدام أطياف المنطقة المرئية وال فوق بنفسجية والمنطقة تحت الحمراء. كما درس السلوك الحراري لهذه المترابكات وأظهرت منحنيات التحلل الوزني الحراري عددا من مراحل التفكك يدل على أن التحلل الحراري للمركبات السابقة ليس بسيطا. و تم حساب الثوابت الحركية لخطوات التحلل المختلفة.

Several Hg(II) mixed ligand complexes of thiosemicarbazones (2-acetylpyridine-, 4-aminoacetophenone- and 2-furaldehyde thiosemicarbazones) with 2-aminothiazole have been prepared. Structural investigations of the complexes have been made based on elemental analyses, spectral (UV-Vis, IR) studies and conductivity measurements. The I.R. spectra indicated the bidentate (neutral) behaviour of the ligands. The thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analyses (DTA) have been used to study the thermal decomposition and kinetic parameters of the complexes using the Coats-Redfern and Horowitz-Metzger equations.

INTRODUCTION

Thiosemicarbazones and their metal complexes have been a subject of interest in numerous studies because of their chemical and biological activities^{1&2}. They have a wide range of beneficial medicinal properties^{3&4} that are often attributed to their chelating ability with metal ions⁵. Really, an important number of thiosemicarbazones being NNS tridentate donors and possess carcinostatic efficacy⁶, and substantial *in-vivo* activity against various human tumors^{7&8}. However, structural variations in some thiosemicarbazones with regard to their chelating ability may destroy or reduce their medicinal values⁹.

Hg(II) complexes of benzophenone, acetophenone and salicylaldehyde thiosemicarbazones containing the neutral or anionic form of these ligands were prepared and fully characterized¹⁰.

The present work gives an insight about the preparation, spectral characterization and thermal studies of Hg(II) mixed ligand complexes of thiosemicarbazones (2-acetyl-

pyridine-, 4-aminoacetophenone- and 2-furaldehyde-thiosemicarbazones) (HPTSC, HTASC and HFTSC respectively) with 2-aminothiazole (AZ) (Fig. 1). The kinetic and thermodynamic parameters for some thermal decomposition steps have been studied.

EXPERIMENTAL

All chemicals used were of analytical reagent grade (Merck or BDH).

Preparation of thiosemicarbazone ligands

The thiosemicarbazone ligands used in this study were prepared according to published procedures¹¹ as follows:

2-Acetylpyridine thiosemicarbazone (HPTSC), 4-aminoacetophenone thiosemicarbazone (HATSC) and 2-furaldehyde thiosemicarbazone (HFTSC) were prepared by mixing an ethanolic solution (20 ml) of 2-acetylpyridine, 4-aminoacetophenone or 2-furaldehyde (2 mmol) with 20 ml of an ethanolic solution of thiosemicarbazide (2 mmol). The mixture was stirred for 5 min. and

Fig. 1: The structures of the studied thiosemicarbazones and 2-aminothiazole.

then heated on a water bath for 10 min. whereupon the ligands precipitated immediately. The separated compounds were filtered, washed with ethanol and finally dried over anhydrous calcium chloride. The proposed chemical structure of the prepared thiosemicarbazone ligands are in good agreement with the stoichiometric concluded from their analytical data (Table 1) and confirmed from the IR spectral data (Table 2).

Preparation of Hg(II) mixed ligand complexes

The Hg(II) mixed ligand complexes of thiosemicarbazones with 2-aminothiazole were prepared by mixing a hot ethanolic solution (20 ml) of the respective thiosemicarbazones (HPTSC or HATSC or HFTSC) (2 mmol) with an ethanolic solution (10 ml) of 2-aminothiazole (2 mmol). To this solution was added with constant stirring a hot ethanolic solution (20 ml) of $HgCl_2$ (1 mmol). The mixture was heated under reflux for 30 min, cooled and left overnight, microcrystalline products were separated thoroughly washed with ethanol and dried in air.

Analysis and physical measurements

CHNS analyses were preformed using Elementar-Analyses system GmbH Vario El analyzer at the Microanalytical unit of Assiut University. Infrared spectra were recorded on a 470 Shimadzu infrared spectrophotometer as KBr disks at room temperature. The electronic spectra were measured in DMF solutions on a Perkin Elmer, Lambda 35 UV/VIS

spectrophotometer. Electrical conductivity of 10^{-4} M solution of the complexes were measured at room temperature on a Jenway 4330 conductivity meter. Thermogravimetric (TG) and differential thermal analyses (DTA) of the solid complexes were done using a DTG-60H thermogravimetric analyser (Shimadzu). TG/DTA measurements were run under dynamic air at a heating rate $10^\circ C\ min^{-1}$ and between ambient temperature $750^\circ C$.

RESULTS AND DISCUSSION

The isolated complexes are stable in air, insoluble in water and common organic solvents, but completely soluble in DMF and DMSO.

The reaction of Hg(II) chloride with the thiosemicarbazone and 2-aminothiazole ligands is illustrated in equation (1).

(where HTSC= thiosemicarbazone and AZ= 2-aminothiazole)

Table 1 includes the physical and elemental analyses of the thiosemicarbazones and their corresponding complexes.

Molar conductance

Molar conductance measurements of 10^{-4} M solutions of the complexes in DMF are in the range $139.2\text{--}156.4\ \Omega^{-1}\ cm^2\ mol^{-1}$ for all complexes indicating their neutral electrolytic nature of the complexes¹².

Table 1: Physical properties and elemental analysis of the thiosemicarbazones and Hg(II) mixed ligand complexes.

Thiosemicarbazones and complex	M.F (M. Wt)	Colour	m.p./°C (Decomp)	Found / (Calc.)			
				C%	H%	N%	S%
HPTSC	C ₈ H ₁₀ N ₄ S (194.18)	Light Brown	139	49.62 (49.44)	5.12 (5.15)	28.51 (28.84)	16.67 (16.48)
HATSC	C ₉ H ₁₂ N ₄ S (208.18)	Light Brown	141	51.54 (51.88)	5.72 (5.76)	26.78 (26.90)	15.19 (15.37)
HFTSC	C ₆ H ₇ N ₃ OS (169.15)	Light Brown	132	42.11 (42.57)	4.23 (4.14)	24.97 (24.83)	19.13 (18.92)
[Hg(HPTSC) ₂ (AZ) ₂]Cl ₂	C ₂₂ H ₂₈ Cl ₂ HgN ₁₂ S ₄ (860.23)	Yellow	261	30.80 (30.91)	2.56 (2.71)	19.53 (19.31)	14.90 (14.76)
[Hg(HATSC) ₂ (AZ) ₂]Cl ₂	C ₂₄ H ₂₃ Cl ₂ HgN ₁₂ S ₄ (888.24)	Yellow	275	32.42 (31.73)	3.60 (3.52)	18.91 (18.46)	14.41 (14.23)
[Hg(HFTSC) ₂ (AZ) ₂]Cl ₂	C ₁₈ H ₂₂ Cl ₂ HgN ₁₀ S ₄ (810.19)	Yellow	252	26.67 (27.11)	2.72 (2.84)	17.28 (17.36)	15.80 (15.93)

Table 2: IR spectral data (cm⁻¹) of free thiosemicarbazones and Hg(II) mixed ligand complexes.

Complex	ν (NH/ NH ₂)	ν (C=N)	ν (C=S)	ν (C-S)	ν (M-N)
Free thiosemicarbazones, 2-aminothiazole	3220-3450 m 3230-3440 m	1600 s 1580 s	830 s -	- 690 s	-
[Hg(HPTSC) ₂ (AZ) ₂]Cl ₂	3110-3420 m	1590 s	820 s	690 s	450 s
[Hg(HATSC) ₂ (AZ) ₂]Cl ₂	3220-3440 m	1585 s	790 s	690 s	440 s
[Hg(HFTSC) ₂ (AZ) ₂]Cl ₂	3250-3400 m	1580 m	785 m	695 s	455 s

s= strong

m = medium

IR Spectra

The most characteristic bands of the free ligands and complexes are summarized in Table 2. A representative example for their spectra is given in Figure 2.

The coordination sites of the ligands under investigation with Hg(II) ions were elucidated using IR spectra. The data obtained suggest that the thiosemicarbazone ligands bind to the metal ions in a bidentate fashion and coordinate through the C=N and C=S groups. This was suggested because of the shift of ν (C=N) and ν (C=S) of the complexes to a lower frequency by 10-20 and 10-45 cm⁻¹, respectively, compared to the thiosemicarbazones¹³⁻²⁰. The complexes exhibit an additional band in the region 1350-1380 cm⁻¹ which can be assigned to ν (C-N) and gives a positive shift if compared with that of the free 2-aminothiazole (1322 cm⁻¹)²¹. This is an evidence in favour of bonding through amino nitrogen of the 2-aminothiazole due to polarization of the π - π

electrons after coordination from the thiazole ring towards the nitrogen atom of the amino group. This will increase the double-bond character of C-N in the C-NH₂ group, thus giving rise to the positive shift²¹. A band at 695 cm⁻¹ (ν C-S) of the complexes occurs at almost the same frequency as that of free 2-aminothiazole (690 cm⁻¹), which may rule out the possibility of coordination through the ring sulphur²¹. Having concluded that the site of binding in 2-aminothiazole is exocyclic nitrogen one may ask why the site is amino nitrogen and not the nitrogen or sulfur of the ring. One possible reason for this might be that the lone pair electrons on the nitrogen of the amino group are more exposed whereas those present on the ring nitrogen or sulphur are sterically hindered by the presence of the amino group at the 2-position, thus favouring the coordination through the exocyclic nitrogen²¹. Observation of a band in the region 3220-3450 cm⁻¹ indicates the existence of

Fig. 2: IR spectrum of $[\text{Hg}(\text{HPTSC})_2(\text{AZ})_2]\text{Cl}_2$.

$\nu(\text{NH})/(\text{NH}_2)$ of the thiosemicarbazones and 2-aminothiazole ligands²²⁻³² compared with that of the complexes ($3110\text{--}3340\text{ cm}^{-1}$). This coordination is confirmed by the presence of a new band at $430\text{--}455\text{ cm}^{-1}$ which is assigned to the stretching frequency of metal-nitrogen $\nu(\text{M--N})$ for all the complexes³³⁻³⁵.

Electronic spectra

The electronic spectra of these complexes, recorded in DMF solution, show a great similarity and exhibit two main broad bands centered at $37, 468\text{--}32, 751$ and $29, 421\text{--}25, 629\text{ cm}^{-1}$, which can be ascribed to $\pi\text{--}\pi^*$ and intraligand charge transfer transitions, respectively³⁶⁻⁴¹. The electronic spectral bands of the complexes are summarized in Table 3.

Thermal studies

a- Thermal behaviour

The thermal behaviour of the $\text{Hg}(\text{II})$ complexes under investigation was studied in dynamic air using thermogravimetric analysis (TGA), derivative thermogravimetry (DTG) and differential thermal analysis (DTA). The thermal decomposition of the complexes was recorded from ambient temperature to 750°C

(Table 4). The results showed that the complexes generally decomposed in several thermal events, i.e., three or five decomposition steps. The first step for all complexes represents a dehydration step which correlates well with the theoretical values corresponding to the elimination of 2HCl molecules present. The end products of the decomposition were identified from the TG traces to be HgO .

The thermal decomposition of $[\text{Hg}(\text{HATSC})_2(\text{AZ})_2]\text{Cl}_2$ is depicted in Figure 3, as a typical example for the decomposition of these compounds. The decomposition of $[\text{Hg}(\text{HATSC})_2(\text{AZ})_2]\text{Cl}_2$ proceeds in three steps in the temperature ranges $140\text{--}277$, $278\text{--}409$ and $410\text{--}682^\circ\text{C}$. The complex is stable up to 140°C , then started to decompose at a temperature above this limit. The observed mass loss of the first step agreed with the loss of 2HCl molecules (calc. 8.2% , found 8.4%) due to deprotonation of thiosemicarbazone ligand (DTG peak at 248°C), for which an endotherm appears in the DTA curve at 241°C (equation 2).

Table 3: Electronic spectral data (cm^{-1}) of Hg(II) mixed ligand complexes.

Complex	$\nu_{\text{max}}(\text{cm}^{-1})$	Assignment
[Hg(HPTSC) ₂ (AZ) ₂] Cl_2	25,778	IL-charge transfer
	33,958	$\pi - \pi^*$ transition
[Hg(HATSC) ₂ (AZ) ₂] Cl_2	29,421	IL-charge transfer
	37,468	$\pi - \pi^*$ transition
[Hg(HFTSC) ₂ (AZ) ₂] Cl_2	25,629	IL-charge transfer
	32,751	$\pi - \pi^*$ transition

Table 4: Thermal decomposition data of Hg(II) mixed ligand complexes in dynamic air.

Complex	Step	TG/DTG			Mass loss (%)
		$T_i/^\circ\text{C}$	$T_m/^\circ\text{C}$	$T_f/^\circ\text{C}$	
[Hg(HPTSC) ₂ (AZ) ₂] Cl_2	1 st	118	251	274	9.1
	2 nd	276	314	425	11.4
	3 rd	426	660	750	44.7
[Hg(HATSC) ₂ (AZ) ₂] Cl_2	1 st	140	248	277	8.4
	2 nd	287	308	409	12.2
	3 rd	410	587	683	47.9
[Hg(HFTSC) ₂ (AZ) ₂] Cl_2	1 st	124	268	281	8.7
	2 nd	286	334	475	13.3
	3 rd	476	671	750	39.1

Fig. 3: TG, DTG and DTA thermograms of [Hg(HATSC)₂(AZ)₂] Cl_2 .

The second mass loss corresponds to the expulsion of one AZ molecule (calc. 11.3%, found 12.2%) (DTG peak at 308°C). This step is marked on the DTA curve by an exothermic effect at 339°C. The third mass loss (47.9%) is indicated on the DTG curve as two peaks at 587 and 634°C, with an exothermic effect at 579°C and an endothermic effect at 654°C in the DTA trace. The third mass loss represents the decomposition of 2(ATSC) and AZ molecules (calc. 46.9%, found 47.9%). The mass loss at 682°C indicates that the left stable residue is HgO (calc. 31.6%, found 31.5%) (equations 3, 4).

b- Kinetic analysis

Nonisothermal kinetic analyses for the thermal decomposition of the complexes were carried out by the application of two different procedures, namely the Coats-Redfern⁴² and Howowitz-Metzger⁴³ equations. The kinetic parameters were evaluated only for clear-cut and nonoverlapping stages. The thermal data and kinetic parameters of the thermal decomposition of the complexes are included in Table 5. The activation energies in general are relatively low, indicating the low thermal stability of the complexes.

According to Cordes⁴⁴, Shannon⁴⁵ and Aly *et al.*⁴⁶, the frequency factor Z is related to the freedom degree of the activated complex and may vary between 10^5 s^{-1} and 10^{18} s^{-1} . Small values are often associated with a rigid activated complex, without degree of freedom, while high values may be correlated with a flexible activated complex. The Z values for the the first decomposition step of the complexes $[\text{Hg}(\text{HPTSC})_2(\text{AZ})_2]\text{Cl}_2$ and $[\text{Hg}(\text{HATSC})_2(\text{AZ})_2]\text{Cl}_2$ are 10^4 s^{-1} and 10^8 s^{-1} , respectively (Coats-Redfern equation). This means that the latter complex has more freedom or less rigidity than the first one.

Based on the above results of elemental analysis, I.R. & electronic spectra, molar conductance and thermal analyses, the structures of Hg(II) mixed ligand complexes are proposed and given in Figure 4.

Fig. 4: Suggested structure of Hg(II) mixed ligand complexes.

Table 5: Kinetic parameters for the thermal decomposition of Hg(II) mixed ligand complexes using non- mechanistic equations in dynamic air.

Compound	Step	Coats-Redfern equation				Horowitz-Metzger equation			
		n	r	E	Z	n	r	E	Z
[Hg(HPTSC) ₂ (AZ) ₂] Cl ₂	1 st	0.00	0.9989	107.1	2.01 x 10 ⁶	0.00	0.9987	103.1	2.26 x 10 ⁶
		0.33	0.9997	145.2	1.12 x 10 ⁸	0.33	0.9975	135.1	2.23 x 10 ⁸
		0.50	0.9998	187.1	3.63 x 10 ¹⁰	0.50	0.9998	196.9	2.85 x 10 ¹⁰
		0.66	0.9999	211.1	3.71 x 10 ¹¹	0.66	0.9943	213.9	1.68 x 10 ¹²
		1.00	<u>1</u>	246.2	3.52 x 10 ¹³	1.00	<u>0.9999</u>	244.1	4.68 x 10 ¹⁴
		2.00	0.9988	281.7	1.32 x 10 ¹⁸	2.00	0.9972	278.8	5.19 x 10 ¹⁸
[Hg(HATSC) ₂ (AZ) ₂] Cl ₂	1 st	0.00	0.9948	106.0	1.30 x 10 ⁸	0.00	0.9949	105.3	2.36 x 10 ⁸
		0.33	0.9967	121.3	6.16 x 10 ⁹	0.33	0.9964	118.8	1.53 x 10 ¹⁰
		0.50	0.9998	156.4	2.52 x 10 ¹³	0.50	0.9990	158.3	4.32 x 10 ¹⁴
		0.66	<u>0.9999</u>	163.6	1.65 x 10 ¹⁴	0.66	<u>0.9999</u>	166.7	1.16 x 10 ¹⁵
		1.00	0.9992	184.2	9.35 x 10 ¹⁵	1.00	0.9992	180.4	9.84 x 10 ¹⁶
		2.00	0.9997	242.5	3.90 x 10 ¹⁹	2.00	0.9997	237.9	1.39 x 10 ¹⁹
[Hg(HFTSC) ₂ (AZ) ₂] Cl ₂	1 st	0.00	0.9988	101.4	2.34 x 10 ⁷	0.00	0.9991	100.3	3.64 x 10 ⁷
		0.33	0.9989	111.7	4.12 x 10 ⁸	0.33	0.9988	114.3	4.35 x 10 ⁹
		0.50	0.9997	149.3	3.75 x 10 ¹¹	0.50	0.9992	151.8	2.31 x 10 ¹²
		0.66	<u>1</u>	164.8	2.17 x 10 ¹⁴	0.66	<u>0.9999</u>	161.2	1.69 x 10 ¹⁵
		1.00	0.9993	179.4	6.54 x 10 ¹⁷	1.00	0.9997	181.6	4.44 x 10 ¹⁸
		2.00	<u>1</u>	233.6	1.92 x 10 ¹⁹	2.00	<u>0.9999</u>	234.9	3.689 x 10 ¹⁹

E in kJ mol⁻¹; Z in s⁻¹ underlined *r* in all tables represent the best fit values of n, E and Z.

n = order of the decomposition reaction

r = correlation coefficient

E = activation energy of decomposition

Z = preexponential factor

REFERENCES

- 1- A. Mohsen, M. E. Omar, I. M. Labouta, M. G. Kasem and J. Boudais, J. Pharm. Sci., 72, 1226 (1983).
- 2- M. J. M. Campbell, Coord. Chem. Rev., 15, 279 (1975).
- 3- S. Padye and G. B. Kauffmann, *ibid.*, 63, 127 (1985).
- 4- D. X. West, S. B. Padye and P. B. Sonawane, Struct. Bond., 76, 1 (1991).
- 5- D. L. Klayman, J. F. Bartosecich, T. S. Grinffin C. J. Mason and J. P. Scoveill, J. Med. Chem., 22, 885 (1979).
- 6- E. J. Blanz and F. A. French, Cancer Res., 28, 2419 (1968).
- 7- M. C. Miller, C. N. Stineman, J. R. Vance, D.X. West and I. M. Hall, Anticancer Res., 18, 4131 (1998).
- 8- M. C. Miller, C. N. Stineman, J. R. Vance, D. X. West and I. M. Hall, Appl. Organomet. Chem., 13, 9 (1999).
- 9- J. P. Scovill, D. L. Klayman, C. Lambros, G. E. Childs, W. Antholing and D. H. Petering, J. Med. Chem., 27, 87 (1984).
- 10- A. A. El-Asmy, O. A. El-Gammal and H. S. Saleh, Spectrochim. Acta, Part A, 71, 39 (2008).
- 11- A. I. Matesanz, J. M. Perez, P. Navarro, J. M. Moreno, E. Colacio and P. Souza, J. Inorg. Biochem., 76, 29 (1999).
- 12- W. J. Geary, Coord. Chem. Rev., 7, 81 (1971).
- 13- M. Mohan, P. Sharma and M. Kumar, Inorg. Chim. Acta., 125, 9 (1986).
- 14- S. Chandra and L. K. Gupta, Spectrochim. Acta., Part A, 61, 269 (2005).
- 15- E. Jouad, G. Larcher, M. Allain, A. Riou, G. M. Bouet, M. A. Khan and X. D. Thanh, J. Inorg. Biochem., 86, 565 (2001).
- 16- M. J. M. Campbell, Coord. Chem. Rev., 15, 279 (1975).
- 17- V. S. Maliyeckal, R. P. Kurup and M. Nethaji, Polyhedron, 26, 3097 (2007).
- 18- S. Halder, R. J. Butcher and S. Bhattacharya, *ibid.*, 26, 2741 (2007).

- 19- S. Chandra and A. Kumar, *Spectrochim. Acta.*, Part A, 67, 697 (2007).
- 20- S. V. Kolotilov, O. Cadot, S. Golhen, O. Shvets, V. G. Ilyin, V. V. Pavlishchuk and L. Ouahab, *Inorg. Chim. Acta.*, 360, 1883 (2007).
- 21- P. P. Singh and A. K. Srivastava, *Aust. J. Chem.*, 27, 509 (1974).
- 22- S. Chandra and A. Kumar, *Spectrochim. Acta.*, Part A, 66, 1347 (2007).
- 23- E. B. Seena and M. R. P. Kurup, *Polyhedron*, 26, 829 (2007).
- 24- P. F. Rapheal, E. Manoj, M. R. P. Kurup and E. Suresh, *ibid.*, 26, 607 (2007).
- 25- V. Philip, V. Suni, M. R. P. Kurup and M. Nethaji, *ibid.*, 25, 1931 (2006).
- 26- M. Joseph, A. Sreekanth, V. Suni and M. R. P. Kurup, *Spectrochim. Acta.*, Part A, 64, 637 (2006).
- 27- V. Philip, V. Suni, M. R. P. Kurup and M. Nethaji, *ibid.*, Part A, 64, 171 (2006).
- 28- D. Mishra, S. Naskar, M. G. B. Drew and S. K. Chattopadhyay, *Inorg. Chim. Acta.*, 359, 585 (2006).
- 29- M. Joseph, M. Kuriakose, M. R. P. Kurup, E. Suresh, A. Kishore and S. G. Bhat, *Polyhedron*, 25, 61 (2006).
- 30- S. Chandra and U. Kumar, *Spectrochim. Acta.*, Part A, 62, 940 (2005).
- 31- S. Chandra and L. K. Gupta, *ibid.*, Part A, 62, 1089 (2005).
- 32- S. Chandra and L. K. Gupta, *ibid.*, Part A, 61, 2549 (2005).
- 33- E. Bermejo, R. Carballo, A. Castineiras, R. Domínguez, C. M.- Mossmer, J. Strahle and D.X. West, *Polyhedron*, 18, 3695 (1999).
- 34- D. K.-Demertzi, A. Domopoulou, M. A. Demertzis, A. Papageorgiou and D. X. West, *ibid.*, 16, 3625 (1997).
- 35- D. K.-Demertzi, C. Vidjeluc, M. A. Demertzis, E. Siapi and T. Mavromoustakos, *Thermochim. Acta.*, 424, 53 (2004).
- 36- D. X. West, I. S. Billeh, J. P. Jasinski, J. M. Jasinski and R. J. Butcher, *Transition Met. Chem.*, 23, 209 (1998).
- 37- D. X. West, J. S. Ives, J. Krejci, M. Salberg, T. L. Zumbahlen, G. Bain, A. Liberta, J.V. Martinez, S.H. Ortiz and R. Toscano, *Polyhedron*, 14, 2189 (1995).
- 38- D. Kovala-Demertzi, J. R. Miller, N. Kourkouvelis, S. K. Hadjikakou and M. A. Demertzis, *ibid.*, 18, 1005 (1999).
- 39- D. Kovala-Demertzi, A. Domopoulou, M. A. Demertzis, A. Papageorgiou and D. X. West, *ibid.*, 16, 3625 (1997).
- 40- D. K.-Demertzi, A. Domopoulou, M. A. Demertzis, J. V.-Martnez, S. H.-Ortega, G. E.-Perez, D. X. West, M. M. Salberg, G. A. Bain and P. D. Bloom, *ibid.*, 15, 2587 (1996).
- 41- M. Mikuriya, H. Okawa and S. Kida, *Inorg. Chim. Acta.*, 34, 13 (1979).
- 42- A. W. Coats and J. P. Redfern, *Nature*, 20, 68 (1964).
- 43- H. H. Horowitz and G. Metzger, *Anal. Chem.*, 35, 1464 (1963).
- 44- H. F. Cordes., *J. Phys. Chem.*, 72, 2135 (1968).
- 45- B. R. Shannon., *Trans. Faraday Soc.*, 60, 1902 (1964).
- 46- A. A. M. Aly, I. M. A. Awad, M. Abd El-Mottaleb and K. Abd El-aal, *Chem. Pap.*, 60, 143 (2006).