Thermal Degradation of Some New Metallic Complexes and Environmental Impact Assessment

ANCA MIHAELA MOCANU*, CONSTANTIN LUCA
"Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Organic, Biochemical and Food Engineering, 71 A D.Mangeron Blvd, 700050, Iasi, Romania

The environmental impact is studied regarding the gaseous emissions resulted from the thermal degradation of the studied compounds, due to the practical importance of these compounds, part of the class of biological active substances with various pharmaceutical uses. Quantification of environmental impact applied in the case of assessment of gaseous emissions generated from thermal degradation of new metallic synthesized complexes by using the TG-FTIR method, at a constant temperature between 30 – 500°C is done by applying the alternative methodology of global pollution index (I^*_{PG}). This study proposes major contributions in the air quality impact assessment expressed in air quality index (EQair), an air quality assessment index (ESair) in thermal degradation. The EQair value represents the reference index regarding the air quality – air quality degraded by the investigated activity. The results of the environmental impact assessment are corresponding to real air quality index values set in the admissible limits in thermal degradation.

Keywords: metallic complexes, TG-FTIR, thermal degradation, global pollution index, environmental impact, air pollution.

The coordinative chemistry, the chemistry of complex combinations with organic ligands, began being intensively studied due to their major role in revealing the transamination and racemization mechanisms at biological systems level. Both their flexibility and their structural variety have lead to the use of hydrazides as ligands to obtain complex metallic combinations with diverse biological activity [1-4].

Researches connected to synthesis and characterization of biological compounds of metallic ions are very important since they can be used in pharmaceutics, medicine, agronomy, ecology and nutrition [5-10].

The biological activity of complex combinations is strictly connected to the type of both ligand and metals, as most studies point out there is a superior antimicrobial activity in the case of complexes than in the case of free ligands [8, 11-13].

The use of metallic complexes as anti-infective agents is determined by their interaction ability with microorganisms (bacteria, fungi, viruses) causing infectious diseases [11-15].

As a continuation of these studies undertaken by us on the thermal behavior of new metal complexes to elucidate the correlation structure-thermal stability, degradation mechanism, this paper aims to provide important contributions related to environmental impact assessment due to gaseous emissions generated by thermal degradation new metal complexes, where the initial temperature is exceeded during their processing.

It was used a technique coupled: thermogravimetry (TG) –IR analysis (FTIR), efficient to analyze it thermally in order to obtain useful information on revealing the environmental assessment impact (the air quality) due to gaseous emission resulted from the thermal degradation.

In previous studies [16-22] the thermogravimetric curves recorded with the thermal degradation of the samples in nitrogen were found to superimpose on those in air only within the endothermic domain of the thermal degradation, between 30-400°C. Over this temperature range of the degradation in air the gas species evolved occur by splitting of the bonds in the compounds submitted to degradation with no reaction with the oxygen in air.

All gaseous emissions resulting from the thermal degradation released in the air must be in accordance with the environmental legislative regulations and requirements. An excellent quality indicator of gaseous emissions is characterized by 'zero pollutant emissions' which promotes the sustainability concept, namely a healthy ecosystem.

In order to fulfill these requirements, studies on the quantity and quality of gaseous emissions in air during the thermal degradation of the tested compounds was conducted. The experimental values were compared to current maximum allowable concentrations (C.M.A.) and also evaluated individually for each of the tested compounds.

The quantification of environmental impact assessment generated by the gaseous emissions of the tested compounds was performed by application of the alternative methodology of global pollution index (I^*_{PG}) taking into consideration a single environment component: *air*, as the only potentially polluted component [23-26].

Experimental part

Materials

The obtaining stages of the metallic complexes under study are presented in figure 1, and their chemical structures and formulae, IUPAC denominations, molecular weights and melting points in figure 2.

* email: ancamocanu2004@yahoo.com

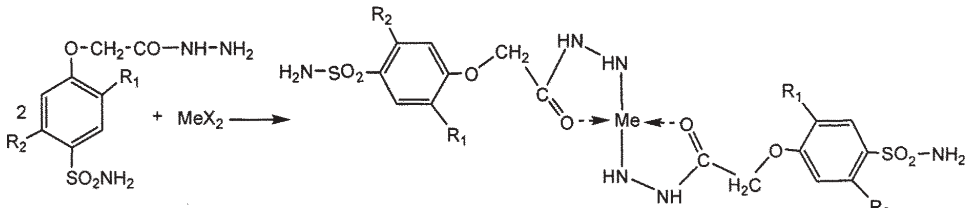
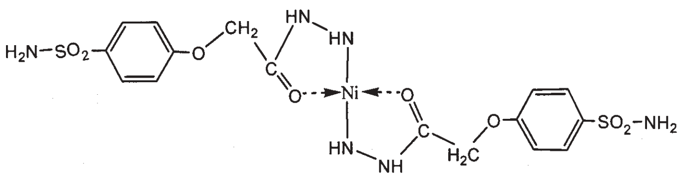
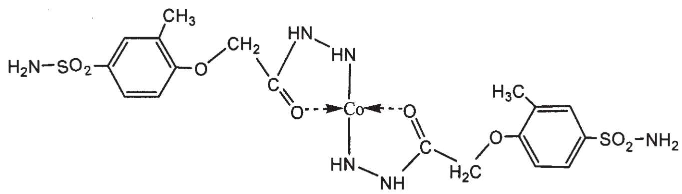


Fig. 1. General obtaining scheme of the new metallic complexes under study

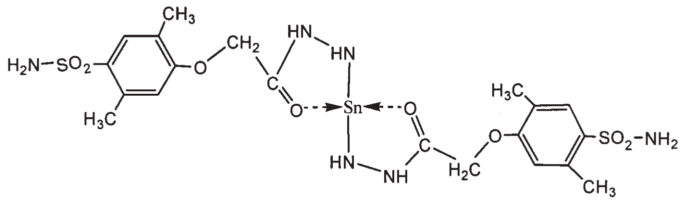
MeX_2= Ni $(CH_3COO)_2 \cdot 4H_2O$, $SnCl_2 \cdot 4H_2O$, Co $(CH_3COO)_2 \cdot 4H_2O$
R_1, R_2 = -H, $-CH_3$



Complexe with Ni of di {2-[4-(sulfonamido)phenoxy]acetohydrazide} **(a)**
Chemical Formula: $C_{16}H_{20}N_6O_8S_2Ni$
Molecular Weight: 547
Melting Point: 220-222°C



Complexe with Co of di {2-[4 (sulfonamido)-2methylphenoxy]acetohydrazide} **(b)**
Chemical Formula: $C_{18}H_{24}N_6O_8S_2Co$
Molecular Weight: 575
Melting Point: 215-217°C



Complexe with Sn of di {2-[4-(sulfonamido)-2,5dimethylphenoxy]acetohydrazide} **(c)**
Chemical Formula: $C_{20}H_{28}N_6O_8S_2Sn$
Molecular Weight: 663
Melting Point : 231-233°C

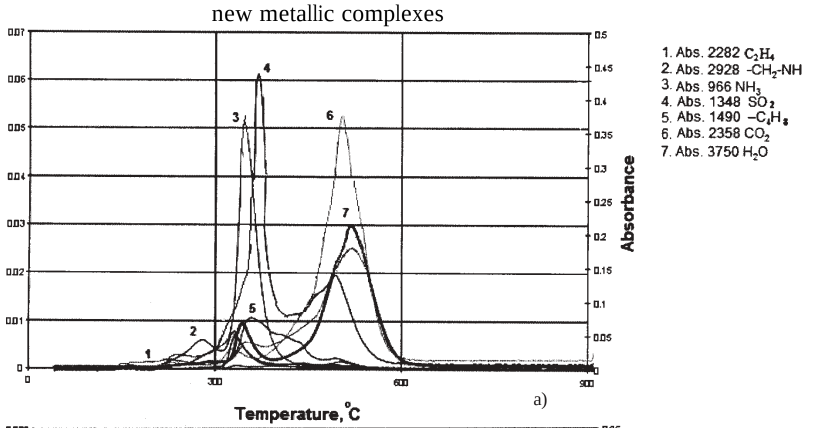
Fig. 2. Chemical structures and some main charcteristics of the new metallic complexes

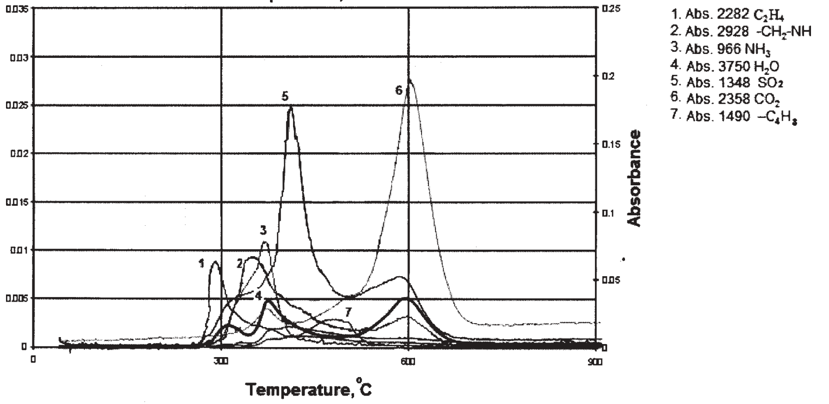
Analysis method: TG-FTIR

The TG-FTIR analyzer consists of a TG/DTA Diamond (Perkin Elmer) thermo-balance and a FTIR spectrometer, Spectrum 100 (Perkin Elmer), provided with a TG-FTIR (Perkin Elmer) gas transfer accessory and a gas cell of 100 mm length and KBr windows, heated at 150°C. The FTIR spectra were recorded within the 700 - 4000 cm range at a resolution of 4 cm and scanning rate of 200 cm/s, a single spectrum being recorded every 15 s by means of the Spectrum Time Bose Perkin Elmer program. A G7 gas analyzer (Dominic Hunter) supplies the dry air (pearl point: -50°C) entering the TG/DTA analyzer at a flow rate of 100 mL/min as well as the nitrogen for purging the analysis room of the FTIR spectrophotometer. The analysis was run with 10 mg sample placed into a platinum crucible, at a heating rate of 10K/m in within the 30 - 900°C temperature range. The gaseous species resulting by the thermal degradation of the samples were identified by means of the standard IR spectra.

Results and discussions

From the thermal degradation in the air of new metallic complexes two domains of temperature were observed: the endodermic one, identical to that of thermal degradation of N_2 (30 - 500°C) in the air and an exothermal one (500 – 900°C), domains which were grouped and gaseous species which result from the thermal degradation, marked in curves representing the absorbance-temperature dependence for **b** and **c** samples (fig. 3).





b)

Fig.3. IR absorbance vs. temperature for the thermal degradation of: a) compound **b**; b) compound **c**

Temperature domain, °C	Thermal degradation compounds	Average measured value, (mg.m^{-3}) x 10^{-3} (for the compounds)			M.A.C.[a] (mg.m^{-3})x10^{-3}
		a	b	c	
30-500	NH_3	1.579	1.503	1.304	30
	SO_2	5.961	5.671	4.917	500
	CO_2	4.096	3.898	3.378	100.000.000 kg/an [b]
	CH_2NH	2.700	2.568	2.226	1
	C_4H_8	5.212	4.957	4.300	150
	C_2H_4	2.603	2.476	2.150	150

Table 1
GASEOUS SPECIES ELIMINATED BY THE THERMAL DEGRADATION OF THE NEW COMPOUNDS AND AVERAGE MEASURED VALUE OF THE RELEASED GASES

The gaseous species emitted in the endothermic domain (30 - 500°C) are formed by breaking of covalent bonds of new tested compounds and the gaseous species emitted in the exothermal domains are formed by burning of intermediates from the endothermic domain.

The following gaseous species resulted from the thermal degradation of analyzed compounds which are assessed from the global impact of emissions in the air are: NH_3, SO_2, CO_2, CH_2NH, C_4H_8, C_2H_4, H_2O, in the endothermic domain and CO_2, H_2O in the exothermal domains.

The gaseous species eliminated by the thermal degradation of the metallic complexes under study that are evaluated in view of estimating the overall impact of their releasing in air are given in table 1.

It also can be noticed that all gaseous species eliminated by the thermal degradation are included in the category of air quality pollutants, some of them have a toxic effect on human health or lethal effect in case of long-term exposure. The most important pollutants which are continuously controlled are: CH_2NH (carcinogenic effects), $C_6H_3SO_2$ (carcinogenic effects), but also NH_3, C_4H_8 and C_2H_4.

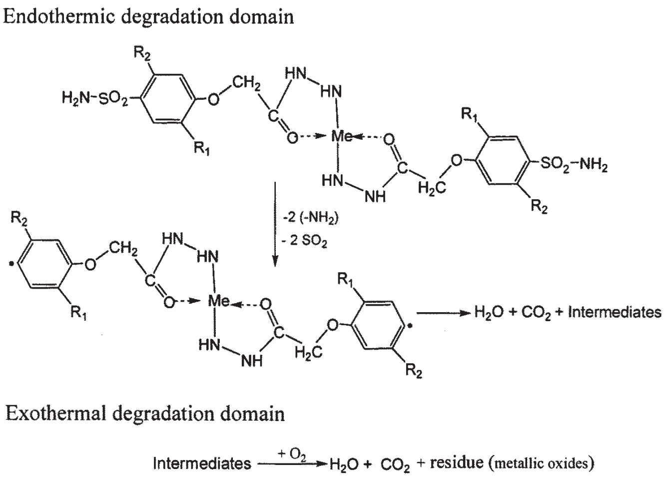


Fig. 4. The general thermal degradation mechanism of the new metallic complexes

The general mechanism of the thermal degradation of metallic complexes proceeds into two stages: endothermic domain and exothermal domain (fig. 4).

The average value of the released gases expressed as (mg x m^{-3} x 10^3) was calculated by means of their quantitative analysis and then compared to the maximum accepted concentration of the gas component in air according to the environmental legislative rule [24], while the quality index (EQ_i) was estimated for the compounds under study by the relationship.

$$EQ_i = C_{i,measured} / CMA_i$$

where:

i- identification number of every gas component resulting by thermal degradation;

$C_{i\ measured}$- experimenta concentration of the resulting gas component;

CMA – the maximum admitted concentration of the gas component according to the environmental legislative rule [27].

The value of the quality index (EQ_i) and the evaluation score (ES_i) of the analyzed gaseous components are given in table 2.

The synergetic action of every gas component released by thermal degradation is expressed by means of the arithmetic average value of all of the EQ_i indices, denoted by EQ_{air}, (table 2) and the evaluation score of the air quality, ES_i, is estimated based on the data in table 3 [24, 28] correlating the evaluation score ES_i to the values of the quality index, EQ_i.

The EQ_i values and also the global index of air quality indicated a great attention on the control and monitoring of air quality. The application of preventive measures to capture and destroy the pollutants before their release in the air using treatment techniques specially designed to convert these pollutants to harmless compounds is therefore considered.

Every variation range EQ_i is characterized by an evaluation score in air ES_i (table 4) [28].

The minimum and maximum values of the evaluation score, ES_i, are of 1 and 10, respectively, representing an irreversible major degradation state of the atmosphere andthe natural unaffected state, respectively [23, 24, 26,28].

Thermal degradation compounds	Air quality index (EQ_i) (for the compounds)			Evaluation Score (ES_i) (for the compounds)		
	a	b	c	a	b	c
NH_3	0.0526	0.0501	0.0434	9	9	9
SO_2	0.0119	0.0113	0.0098	9	9	9
CO_2	-	-	-	-	-	-
CH_2NH-	2.700	2.5680	2.2260	5	5	5
C_4H_8	0.0347	0.0330	0.0286	9	9	9
C_2H_4	0.0173	0.0165	0.0143	9	9	9
	$EQ_{1.\ air}$ = 0.4694	$EQ_{2.\ air}$ = 0.4464	$EQ_{3.\ air}$ = 0.3870	$ES_{1.\ air}$ = 8.2	$ES_{2.\ air}$ = 8.2	$ES_{3.\ air}$ = 8.2

Table 2
AIR QUALITY INDEX AND EVALUATION SCORE VARIATION

Evaluation score (ES_i)	Values of (EQ_i) quality index	Effects on the environmental component (air) and human health
10	0	The environmental component is not affected by the economic activity. Environment state: natural
9	(0.0-0.2]	The environmental component is affected by the economic activity. The effect can not be quantified
8	(0.2-0.7]	The environmental component is affected, but under the maximum admissible limits – level 1. Alert level: potential effects
7	(0.7-1.0]	The environmental component is affected, but into maximum admissible limits – level 2. Intervention level: potential effects
6	(1.0-2.0]	The environmental component is affected, over the maximum admissible limits – level 1. The effects are pronounced
5	(2.0-4.0]	The environmental component is affected, over the maximum admissible limits – level 2. The effects are harmful
4	(4.0-8.0]	The environmental component is affected, over the maximum admissible limits – level 3. The harmful effects are pronounced
3	(8.0-12.0]	Degraded environmental component – level 1 The effects are lethal to the average exposure
2	(12.0-20.0]	Degraded environmental component – level 2 The effects are lethal at short times of exposure
1	> 20.0	The environmental component is improper for life

Table 3
CORRELATION SCALE FOR POLLUTION LEVEL OF THE AIR COMPONENT (QUALITY INDEX SCALE)

No.	New tested compounds	EQ_i	ES_i		
			Calculated value	Minimum	Maximum
1	Compound **a**	0.4694	8.2		
2	Compound **b**	0.4464	8.2	*1*	*10*
3	Compound **c**	0.3870	8.2		

Table 4
SPECIFIC AIR QUALITY DATA OF THERMAL DECOMPOSITION OF THE NEW AZOMETINES TESTED

No.	New tested products / abbreviation	$\overline{ES^2_{air}}$	I^*_{PG} value	Real situation of the air pollution
1	Compound **a**	67.2400	1.4872	Air environment modified by thermal degradation activities within admissible limits
2	Compound **b**	67.2400	1.4872	
3	Compound **c**	67.2400	1.4872	

Table 5
AIR EVALUATION SCORES, THE VALUES OF GLOBAL POLLUTION INDEX AND ESTIMATION OF THE REAL SITUATION OF THE AIR POLLUTION

Values of I^*_{GP}	Real situation of air environment pollution
$I^*_{PG}=1$	Natural environment, not affected by economic activities
$1 < I^*_{PG} < 2$	Environment modified by economic activities within admissible limits
$2 < I^*_{PG} < 3$	Environment modified by economic activities generating discomfort effects
$3 < I^*_{PG} < 4$	Environment modified by economic activities generating distress to life forms
$4 < I^*_{PG} < 6$	Environment modified by economic activities, dangerous for life forms
$I^*_{PG} \geq 6$	Degraded environment, not proper for life forms

Table 6
CORRELATIONS INTO THE ALTERNATIVE METHODOLOGY OF GLOBAL POLLUTION INDEX (I^*_{GP})

The global pollution index (I^*_{PG}) is estimated by the equation [29] :

$$I^*_{PG} = \frac{100}{\overline{ES^2_{air}}}$$

where:

$\overline{ES^2_{air}}$ – the arithmetic average of the square values of the evaluation score for every quality index under consideration.

The values of the $\overline{ES^2_{air}}$, global pollution index and the estimation of the real pollution state are given in table 5 based on the correlation between the value of the global pollution index I^*_{PG} and the real pollution state of the atmospheric air (table 6).

Appling the alternative methodology of global pollution index, the value of global pollution index is 1.48 for all studied compounds in the process of thermal degradation and corresponds to an 'atmospheric environment modified by thermal degradation activities within admissible limits'.

The environmental impact was estimated by means of the quantitative analysis of the gaseous species eliminated by the thermal degradation of the samples in air.

The air quality index (EQi), the evaluation score (ESi) as well as the global pollution index were evaluated.The evaluation scores were calculated for every component as potential polluting agent resulting by thermal degradation of the samples.

The obtained values indicate that the quality of air is modified within the accepted limits, estimated based on the influence of the gaseous species emitted by the thermal degradation of the new metallic complexes under study.

These I^*_{GP} values represent some reference/baseline pollution indexes that clearly impose the obligation of periodical air emission control and monitoring but also concern on depollution of air discharges emitted from the thermal degradation of the new studied synthetic compounds for no air dangerous polluting effect.

Conclusions

The gaseous components resulting by thermal degradation of new metallic complexes were identified by applying the TG-FTIR coupled technique.

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