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NEW COMPLEX COMPOUNDS WITH β -AMINOISOBUTYRIC ACID BIDENTATE LIGAND FOR POTENTIAL APPLICATION IN SUSTAINABLE AGRICULTURE

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Abstract

The synthesis and the study of the complexes obtained in this paper represent the beginning of our research for applied coordinative compounds of this type in agriculture. The analysis and the study of Mn(II) complexes with DL- β -Aminoisobutyric acid as ligand were accomplished in aqueous and alcoholic solution and also in solid state. The composition ratios and the stability of the synthesised compounds were analysed with specific methods: conductance, pH measurements, spectrophotometry and thermogravimetry. There were obtained two complexes, at the metal:ligand molar ratio 1:1 and 1:2. In order to determine the structures of the new compounds, the following methods were applied: chemical analysis, IR, UV-VIS and XRD spectroscopy. The $[\text{MnLCl}]_2 \cdot 2/5\text{H}_2\text{O}$ and $[\text{MnL}_2] \cdot 1/2\text{H}_2\text{O}$ presented a triclinic and respectively, monoclinic crystalline structure. From the thermal decomposition data, the kinetic parameters of the studied compounds were calculated observing that both new complex compounds have a higher thermal stability than the ligand. The experimental data confirmed that ligand DL- β -Aminoisobutyric acid presented a bi-dentate behavior towards Mn(II) ions in solution.

Key words: DL- β -aminoisobutyric acid, complex compounds, manganese (II)

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1. Introduction

The interest for amino acids is very well known from different fields of research presenting a lot of application areas as: food industries for their bacteriostatic and antioxidant properties, enhancement of aliment flavours (alanine, arginine, aspartate); as supplement feed in livestock breeding in order to increase nutritional value; in agriculture for growth and plants protection (Wang et al., 2016). In the last decade, this class of compounds is extensively used in pharmaceutical industries for many organ dysfunction treatment (Hwang et al., 1997; Marcucci et al., 2010) and more recent in textile industry as new

compounds for ecological leather tanning (Crudu, 2008; Crudu et al., 2009).

The aminobutyric acids are safe enough to use in food industry inducing resistance against a broad organisms as: bacteria (Cohen, 1994; Cohen et al., 1994; Cohen, 2000), viruses (Cohen, 2002; Cohen et al., 2011), fungi (Tamm et al., 2011), nematode and aphids and reduce plant diseases from tomatoes (Cohen et al., 1994), potatoes, cucumbers (Sahebani et al., 2011), grapevines (Barillia et al., 2012; Cohen et al., 1999). The aminobutyric acids are known to induce resistance to microbial pathogens, nematodes and insects in several host plant/pest systems (Tiwari et al., 2013), improving early growth (Li et al., 2016)

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and protection from salts stress injury by improving photosynthesis processes (Wang et al., 2017). Also, it play an important role in degradation and interorganellar transport of lipids in plant (Mitrofanova et al., 2018) or animal cells (Kammoun et al., 2014, Molfino et al., 2017) acting as O_2^- , H_2O_2 and HO-scavenger (Signorelli et al., 2015).

Regarding the main interest for amino acids used in various fields of research, mentioned above, we selected DL- β -aminoisobutyric acid (BAIBA). Our intention was to test the behavior of this acid along with its new coordination compounds with Mn(II) chloride compared to DL- β -Amino-n-butyric acid (BABA) found in literature as an important biological reagent against soybean aphid, for example *Aphis glycines* increasing the activity of some defense enzymes (Yunpeng et al., 2014). Supplemental Mn(II) reduce uptake of some heavy metal cations (Cd, Cu, Pb) from soil (Iordache et al., 2016) and their toxic effects (Cd, Pb) on plant physiology (Rahman et al., 2016; Secu, 2016). We have chosen Mn(II) for coordination with the BAIBA as ligand, due to its $3d^5$ electronic configuration (Chandra et al., 2005; Tutulea et al., 2011) with high tendency of accomplishing coordinative bonds, especially with oxygen and nitrogen donor-ligands (Crudu et al., 2009; Gerey et al., 2016; Mei et al., 2017) and greater their antibacterial activity (Kim and Park, 2017; Maurya et al., 2016).

This research represents a preliminary stage for studying the effects of different concentrations of BAIBA treatment on the growth of soybean seedlings compared to the biological activity of the new synthesized compounds.

2. Experimental

All the reagents used were of analytical grade, Fluka, 99% - 99.9% purity. The concentrations of the solutions in double distilled water were 10^{-2} M for $MnCl_2 \cdot 6H_2O$ and DL- β -aminoisobutyric acid (BAIBA), respectively. The Mn(II): BAIBA molar ratios were determined in aqueous solution by pH-metric and conductometric methods at room temperature and the values of stability constants were calculated using the Harvey-Manning method (Foca et al., 2006; Sibiescu, 2012).

The compounds were synthesized in aqueous medium by mixing the isomolar 10^{-2} M solutions in molar ratio of 1:1 and 1:2. Then the solutions were submitted to a refluxing process for three hours at $30^\circ C$ temperature. The solid compounds were obtained by the solvent evaporation at room temperature. The recrystallization process of complexes was applied both in aqueous and 80% ethylic alcohol solutions at low ($8^\circ C$) temperature (Spătărescu et al., 2010). The final products are presented as slightly pink microcrystalline powders, very soluble in water and alcohol. Chemical elemental analysis was performed on Thermo Fisher Scientific Flash EA-10 1112 CHNS/O equipment provided with Eager 300 software. Chemical elemental analysis was

accomplished for the synthesized complex compounds, in order to determine the content of carbon, hydrogen, nitrogen and manganese and to compare the results with the theoretical one.

The IR absorption spectra of crystalline complexes were recorded in $4000-200\text{ cm}^{-1}$ domain, using a Jasco FTIR 660 Plus Spectrometer, in order to determine changes of specific chemical bonds frequencies of ligand induced by the presence of manganese (II) cations. The UV-VIS absorption spectra of aqueous solution samples and study of substitution of manganese ions in solution were performed spectrophotometrically with CAMSPEC 501M single beam spectrophotometer (equipped with kinetic motorization software) using $5 \cdot 10^{-2}$ M and 10^{-3} M solution of BAIBA (HL), $[MnLCl]_2$, $[MnL_2]$, $FeSO_4 \cdot 7H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and $Cd(NO_3)_2$, at ionic strength, $I=5 \cdot 10^{-2}$ M (NaCl), pH = 6.7 (HCl - NaOH balance), at $25 \pm 0.2^\circ C$ solution temperature (HAAKE thermo-stating system), in 0.2 and 0.5 cm quartz cell, in the 190 - 800 nm range at specific wavelength of every system (Fe(II)-301 nm, Co(II)-293 nm and Cd(II)-217 nm). Each set of kinetic determination run was repeated at least twice.

XRD patterns were recorded in the $10 - 90$ degree 2θ range on a PanalyticalX'Pert Pro diffractometer, provided with a Cu $K\alpha$ radiation ($k = 1.5418740 \text{ \AA}$), Step size: 0.0131303, 45 kV - 40 mA. Unit cell parameters of the investigated complexes were further refined with PanalyticalX'Pert High Score Plus and Celref software.

The thermogravimetric study was conducted using a Mettler Toledo SDTA 851°derivatograph. Thermogravimetric curves (TG) and derivative thermogravimetric curves (DTG) were recorded in the nitrogen atmosphere, in the temperature range $25-700^\circ C$, at $10^\circ C/min$ heating rate. The sample subjected to analysis weighted between 3 and 5 mg. The data used to obtain the main thermogravimetric and kinetic characteristics were processed with STAR software, using the "Kinetics n^{th} order" module from Mettler Toledo.

3. Results and discussion

3.1. Combination molar ratio and stability constants

From the conductivity and pH versus molar ratio L/M graphs, (Figs.1a and 1b) it is observed, for each experiment, a curve that changes the slope in the points corresponding to the 1:1 and 2:1 for DL- β -aminoisobutyric acid / Mn^{2+} ratio values, indicating that two complex compounds are formed in solution. The stability constants values of the two compounds are $\beta_1=2.617 \cdot 10^6 \text{ L} \cdot \text{M}^{-1}$ and $\beta_2=1.728 \cdot 10^{12} \text{ L}^2 \cdot \text{M}^{-2}$. The highest stability is presented by the complex with maximum combination ratio, L/Mn=1/2 at pH= 3.7.

3.2. Chemical-elemental analysis

The experimental and theoretical results are presented in Table 1.

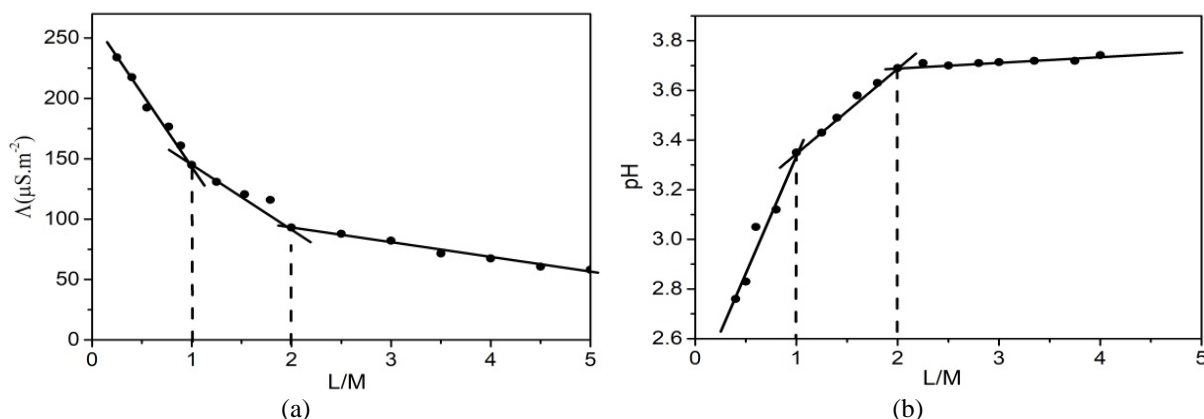


Fig. 1. The conductivity (a) and pH (b) values of $Mn(II)_{aq}$ - $BAIBA_{aq}$ solutions at different L/M molar ratio

Table 1. Content of carbon, hydrogen, nitrogen, oxygen, chlorine and manganese for the obtained complex compounds

Comp.	C%		H%		N%		O%		Cl%		Mn%	
	Exp.	Calc.	Exp.	Calc.	Exp.	Cal.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
L:M 1:1	24.111	24.462	4.812	4.280	7.010	7.134	117.471	17.939	18.131	18.091	28.421	28.029
L:M 2:1	35.411	35.788	6.109	6.337	10.191	10.438	26.141	26.841	-	-	20.101	20.504

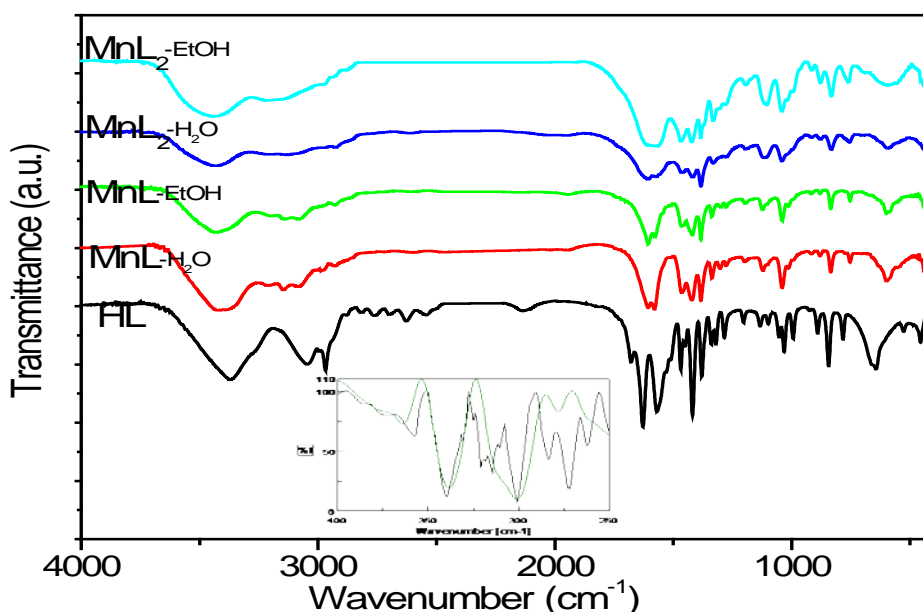
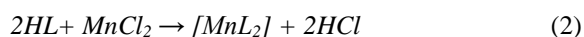
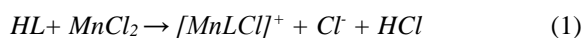


Fig. 2. IR spectra of HL, $[MnLCl]_2 \cdot 2/5H_2O$ (MnL) and $[MnL_2] \cdot 1/2H_2O$ (MnL₂) crystallized from water and ethylic alcohol and inset IR spectra of $[MnL]$ and $[MnL_2]$ in 400-250 cm^{-1} range

The experimental data were in accordance with calculated values with errors included 0.3-0.69 %. From the L:Mn(II) molar ratio and elemental chemical analysis of the obtained compounds, resulted the (1) and (2) chemical preparing reactions, in solution:



The process was followed by the separation of $[MnLCl]_2 \cdot 2/5H_2O$ (ML) and $[MnL_2] \cdot 1/2H_2O$ (ML₂) crystallized complexes.

3.3. FTIR spectra

The FTIR spectra of solid HL and Mn(II)-L coordinative compounds are shown in Fig. 2. The significant IR frequency bands values of the complexes $[ML]$ and $[ML_2]$ do not depend on the obtaining method. Among the various vibrational modes of the BAIBA, the study of the NH_2 and $COOH$ group vibrations are useful for establishment of the mode of coordination of amino acid ligand toward to manganese cation. The IR spectra of BAIBA shown a broad band centred at 3370 cm^{-1} assignable to $\nu(OH)$

vibration of carboxylic group and two other bands at 3046 cm^{-1} and 2969 cm^{-1} due to the symmetric (ν_s) and asymmetric (ν_{as}) vibration modes of NH_2 group. Lower value of $\nu(\text{OH})$ can be explained by the involving of O-H group in a hydrogen bond. The $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{O})$ vibration modes of carboxylic group are observed at 1628 cm^{-1} and, respectively, 1418 cm^{-1} . In [ML] and [ML₂] complexes the $\nu(\text{OH})$ and vibration band is shifted to higher frequency (3433 cm^{-1} and 3439 cm^{-1}) and overlap with (NH) modes. These can be related with the coordinated or lattice water molecules. Also, the bands observed at 3146 , 3083 (for [ML]), 3213 and 3131 cm^{-1} (for [ML₂]), assigned to $\nu(\text{NH})$ vibration modes, have higher values compared to uncoordinated ligand.

The disappearance of $\nu(\text{OH})$ carboxylate and shift of $\nu(\text{NH})$ modes clearly suggest the deprotonization of $-\text{COOH}$ and involving of $-\text{COO}^-$ and $-\text{NH}_2$ groups in the coordination process. These are confirmed by the shifting of $\nu(\text{C}=\text{O})$ vibration mode to lower wave numbers from 1628 cm^{-1} (for HL) to 1607 cm^{-1} ([ML]) and 1605 cm^{-1} ([ML₂]), until $\nu(\text{C}-\text{O})$ vibration mode values are very close (1421 cm^{-1} and 1417 cm^{-1}) to the free HL. The $\Delta\nu(\text{COO}^-)$ values for ligand and complexes are 210, 190 and 185 cm^{-1} , fact that suggest a mono-dentate interaction of $-\text{C}-\text{O}$ carboxylate group with Mn(II) ion and involvement of sp^2 oxygen atom ($-\text{C}=\text{O}$) of the same group in a bridged bond with manganese cation of neighbouring complex molecule (Nakamoto, 1997). The phenomenon is more evident for ML₂. In the $700-400\text{ cm}^{-1}$ domain, the IR spectra show new bands assigned to $\nu(\text{Mn}-\text{N})$ and $\nu(\text{Mn}-\text{O})$, respectively: 599 , 442 cm^{-1} ([ML]) and 596 , 430 cm^{-1} ([ML₂]). The electronic and thermal analyses suggest a possible Mn-Cl bond in [ML]. Literature data located $\nu(\text{Mn}-\text{Cl})$ vibration mode from [MnL₄Cl₂] coordinative compounds below 300 cm^{-1} (Nakamoto, 1997; Boucher et al., 2013). The IR spectra of [ML] show a new bands at 283 and 263 cm^{-1} which may be ascribed to $\nu(\text{Mn}-\text{Cl})$ stretching vibrations.

3.4. Electronic spectra

The electronic spectrum of HL (Fig. 3) exhibits an asymmetric absorption band which is centered below 190 nm . The Gaussian deconvolution of BAIBA spectrum, revealed three absorption bands at 199 , 209 and 212 nm assigned to $\pi-\pi^*$ (50251 cm^{-1}), $n_{\text{O}}-\pi^*$ (47846 cm^{-1}), and $n_{\text{N}}-\pi^*$ (47170 cm^{-1}), respectively.

The spectra of aqueous solution of [ML] and [ML₂] complexes are similar, with an intense and asymmetric absorption band in $190-250\text{ nm}$ range and a number of weak bands in visible domain, more evident for [ML₂] compound, assigned to d-d transition of Mn(II)- d^5 . After the deconvolution of spectra, the bands of coordinated ligand shifted to the lower energy values in case of [ML₂] due to electronic effect determined by the second L- ion from coordination sphere of manganese cation: 191 nm

(52356 cm^{-1}), 197 nm (50761 cm^{-1}), 204 nm (49019 cm^{-1}) for [ML] and 197 nm (50761 cm^{-1}), 212 nm (47170 cm^{-1}), 217 nm (46083 cm^{-1}) for [ML₂].

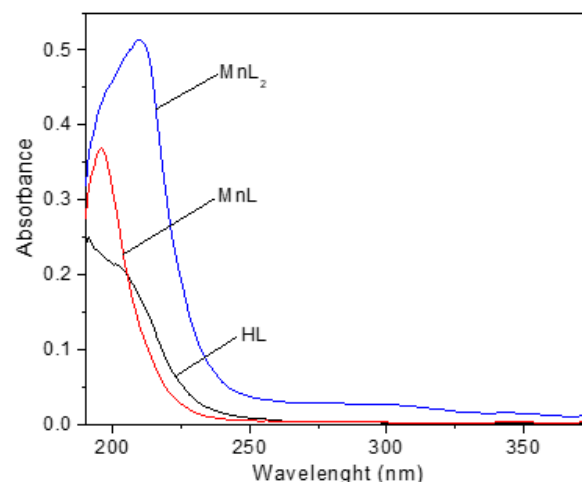
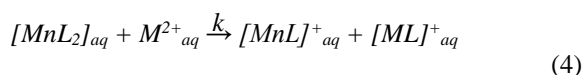
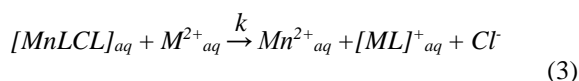


Fig. 3. Electronic spectra of HL, [MnL] and [MnL₂] in aqueous solution: $C_{\text{HL}} = C_{\text{compl}} = 10^{-3}\text{ M}$, $l = 0.2\text{ cm}$

Additional bands assigned to ligand – metal charge transfer, LMCT, overlapped with ligand absorption bands, centred at 220 nm (45454 cm^{-1} , [ML]) and 283 nm (35336 cm^{-1} , [ML₂]), respectively, were identified. The [ML₂] complex displays the d-d absorption bands at 462 nm (21645 cm^{-1}) and 343 nm (29154 cm^{-1}) attributed to ${}^6\text{A}_{1g} - {}^4\text{T}_{1g}(\text{G})$ and ${}^6\text{A}_{1g} - {}^4\text{T}_{2g}(\text{G})$ forbidden electronic transitions which are characteristic for octahedral Mn(II)-high spin coordinative compound (Boucher, 2013; Mei et al., 2017).

3.5. Substitution reactions of Mn(II) in aqueous solution

Mixing $1\text{ mL } 5 \cdot 10^{-2}\text{ M } [\text{MnLCl}]_2 \cdot 2/5\text{H}_2\text{O}$ complex solution and $[\text{MnL}_2] \cdot 1/2\text{H}_2\text{O}$, respectively, with 1 mL solution $10^{-3}\text{ M } \text{Fe}^{2+}_{\text{aq}}$, $\text{Co}^{2+}_{\text{aq}}$ and $\text{Cd}^{2+}_{\text{aq}}$ respectively, the substitution of Mn^{2+} ions from complexes takes place. The monitored absorbance, at specific wavelengths, change in time for each reaction systems (Astilean, 2002). In Fig. 4 is presented the concentration traces of $[\text{FeL}]^+_{\text{aq}}$, $[\text{CoL}]^+_{\text{aq}}$ and $[\text{CdL}]^+_{\text{aq}}$ in time for all studied systems. The formation of [ML] species and the movement of equilibrium to the direct reactions 1 is presented below (Eqs. 3, 4):



It is evidenced by the evolution of [ML] concentration complexes determined at the wavelengths corresponding to the coordination compounds of L (BAIBA) with M^{2+} from mixed solutions. The most pronounced increase of concentration is recorded for [MnL] – Fe^{2+} and [MnL₂] – Fe^{2+} systems.

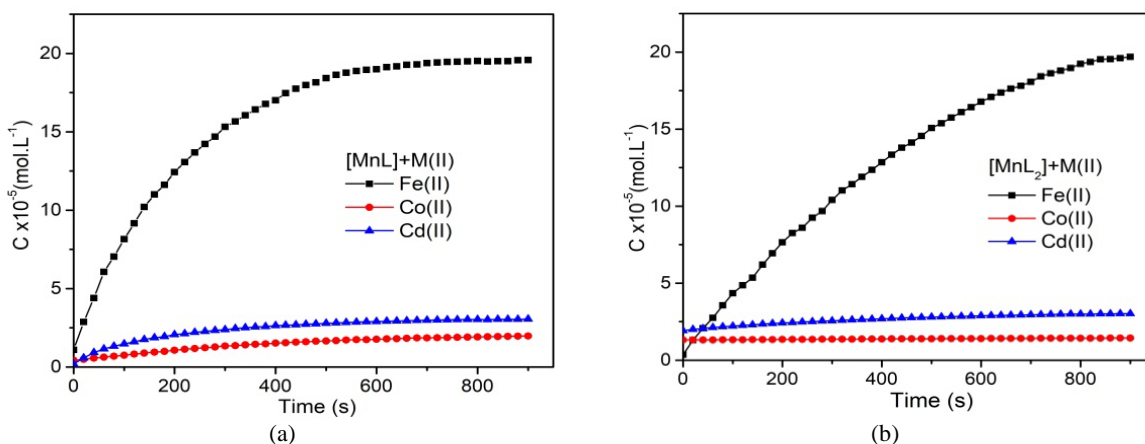


Fig. 4. Concentration evolution of new [ML] (M= Fe, Co and Cd) complexes during the Mn(II) substitution from $[MnL]aq$ (a) and $[MnL_2]aq$ (b) in aqueous solution at pH=6.7, T= 298 K and scan time of every 20 s

Table 2. Values of observable rate constant, k_{obs} , for $n=1$ and $n=2$ kinetic models, for the reversible first step of reactions (1) and (2)

Reaction system		$n=1$		$n=2$	
Complex	Metal cation	k_{obs}, s^{-1}	r	$k_{obs} mol \cdot L^{-1}$	r
[MnL]	Fe ²⁺	1.250·10 ⁻²	0.9927	8.630·10 ⁻²	0.8433
	Co ²⁺	3.777·10 ⁻³	0.9928	1.116·10 ⁻²	0.8802
	Cd ²⁺	8.597·10 ⁻⁴	0.9989	8.093·10 ⁻³	0.9339
[MnL ₂]	Fe ²⁺	6.556·10 ⁻³	0.9836	7.039·10 ⁻³	0.861
	Co ²⁺	4.993·10 ⁻⁴	0.9855	5.539·10 ⁻²	0.9066
	Cd ²⁺	6.469·10 ⁻⁴	0.9927	1.063·10 ⁻²	0.9090

r - correlation coefficient

Based on the obtained data, the rate constants were calculated (Table 2) for the determining step of reaction rate (the slowest step). The observable rate constants, k_{obs} , were determined graphically by applying the pseudo-first and second order kinetic models (Eqs. 5, 6) (Bugarcic et al, 2015; Topolski et al., 2017).

$$n=1 \\ \ln(C_t - C_o) = \ln(C_o) - k_{obs}t \quad (5)$$

$$n=2 \\ 1/(C_t - C_o) = 1/C_o + k_{obs}t \quad (6)$$

The correlation coefficients presented in Table 2 show the higher values for first order rate constant ($n=1$) which correspond to a linear dependence of ligands interchange (BAIBA – H₂O). The comparison of the first order rate constants k_1 of all reaction systems shows that the compatibility between Lewis hardness of M²⁺ and O-, N-donor ligand plays an important role, more evident in case of [MnL] – Co²⁺ system ($k_1 = 3.777 \cdot 10^{-3} s^{-1}$). Also, the presence of supplementary Cl⁻ ions (Eq. 3) has a direct consequence on the increasing of products solvation process and of k_{obs} values, respectively.

Extension of Mn²⁺ coordination sphere in [MnL₂] increases the influence of elemental solvation process of the reactants and reaction intermediates. In

this case, the proton donor species can interfere in elementary first step of mechanism, favouring a certain type of movement – associative (nucleophile substitution SN_2 by A-associative or I_a - associative interchange mechanism) or dissociative (nucleophile substitution SN_1 by D – dissociative or I_d - dissociative interchange mechanism). In hydrogen bond formation the water molecules, supplementary polarized by coordination at M²⁺cations, participate with higher probability. The rate of proton transfer depends on electronegativity and polarizability of metal cation. This stage could be the determining rate step which corresponds of I_d mechanism. The cumulative influence of all mentioned factors can explain the k_{obs} lower values for [ML₂] – M²⁺ systems and the small difference between them.

3.5. X-ray diffraction analysis

The possible crystal structures of $[MnLCl]_2 \cdot 2/5H_2O$ and $[MnL_2] \cdot 1/2H_2O$ complexes have been determined on the X-ray powder diffraction analysis. The X-ray data were refined with Celref program at maximum deviation of $2\theta=0.07^\circ$ and h, k, l Miller indices were assigned (Fig. 5).

The final results show that $[MnLCl]_2 \cdot 2/5H_2O$ belongs to triclinic crystal system ($P(-1)$ space group) with unit cell parameters: $a=5.4286 \text{ \AA}$, $b=7.2745 \text{ \AA}$, $c=15.0061 \text{ \AA}$, $\alpha=50.43(4)^\circ$, $\beta=97.95(3)^\circ$, $\gamma=87.54(2)^\circ$

and $V=445,707 \text{ \AA}^3$ (Giacovazzo et al., 2008; Vainstein, 1989).

The $[\text{MnL}_2] \cdot 1/2\text{H}_2\text{O}$ solid compound crystallized in monoclinic system, $C2/c$ space group with $a=22.3911 \text{ \AA}$, $b=13.6913 \text{ \AA}$, $c=19.6709 \text{ \AA}$, $\beta=114.54(4)^\circ$ and $V=5489.446 \text{ \AA}^3$.

3.7. Thermal-gravimetric analysis and the kinetics of the decomposition reactions

Studying the TG curves for both ligand and complexes (Fig. 6) reveals that the thermal destruction takes place in four steps with the emission of gaseous compounds resulted from the organic part of the ligand. The final solid products of the thermal decomposition corresponds to MnO and some carbon

compounds residue (Freeman and Carroll, 1958; Segal and Fatu, 1983). Also, it is observed that the thermal stability of the compounds increases in order: $\text{HL} < \text{MnL}_2 < \text{MnL}$ as it is shown in the Fig. 6 and Table 3. The transport phenomena of the gaseous products through the solid compound, the interphase interactions and also the vaporization of the volatile products are related to the fraction reaction order values. The reaction order value increases with the dispersion degree of the resulted products (Table 4).

3.8. The proposed structure of the new synthesized complex compounds

Based on the above observation we proposed the possible structures of Mn(II) –BAIBA complexes, in aqueous solutions and solid state (Fig. 7).

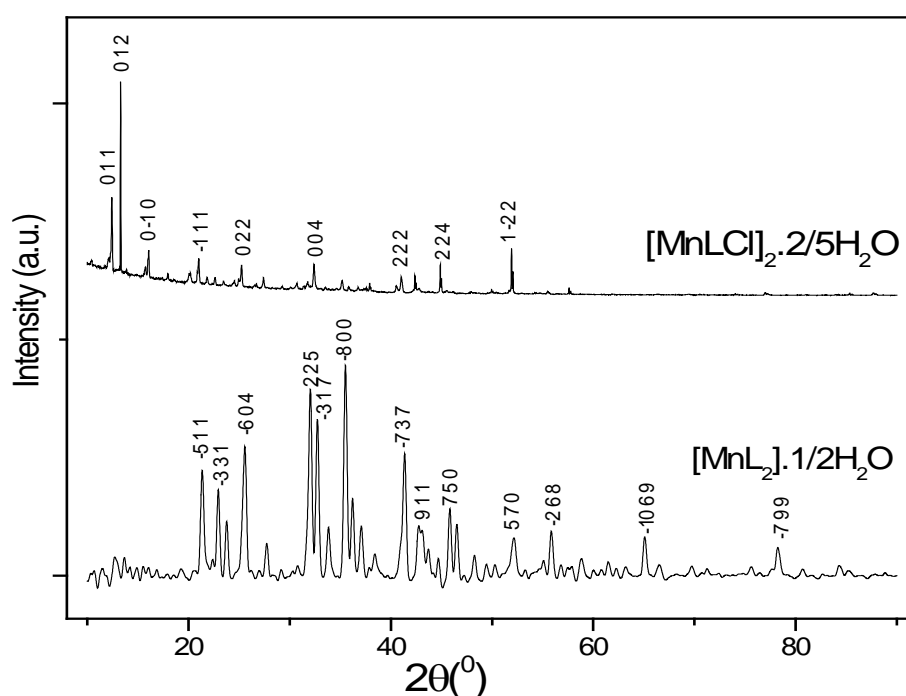


Fig. 5. Diffractograms of $[\text{MnLCl}_2]_2 \cdot 2/5\text{H}_2\text{O}$ and $[\text{MnL}_2] \cdot 1/2\text{H}_2\text{O}$

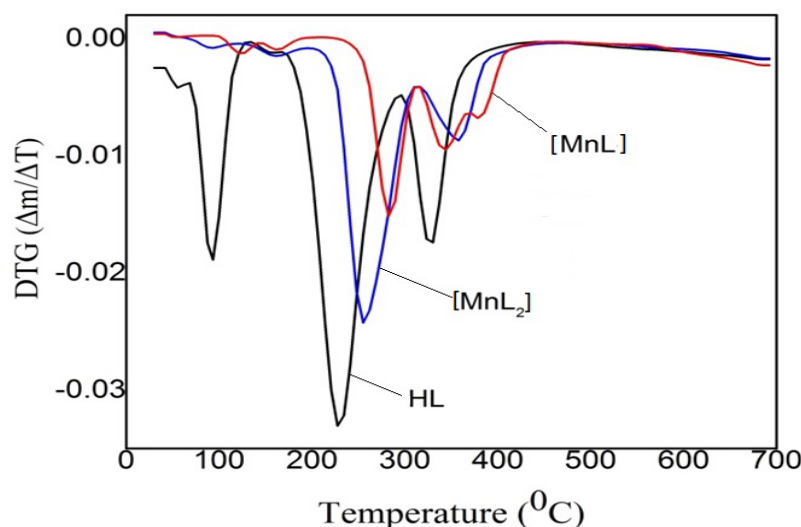


Fig. 6. The DTG curves of the ligand and the synthesized compounds

Table 3. Thermal characteristics of the degradation process of the ligand and synthesized manganese complexes

Sample	Step	$T_{onset},$ °C	$T_{peak},$ °C	$T_{endset},$ °C	Weight loss, %	Residue, %
HL	I	47.8	50	62.5	2.67	0
	II	84.4	92.1	102.1	15.67	
	III	198.7	229.2	259.2	53.28	
	IV	314.7	327.1	352.1	28.31	
[MnLCl] ₂ ·2/5H ₂ O	I	115.4	123.0	129.9	0.94	57.18
	II	154.1	162.3	175.8	0.80	
	III	270.8	283.0	300.2	15.78	
	IV	328.9	381.4	395.7	25.30	
[MnL ₂]·1/2H ₂ O	I	81.6	89.2	109.0	0.96	38.66
	II	143.7	160.2	189.2	2.42	
	III	240.0	253.7	292.0	37.81	
	IV	330.2	358.7	372.2	20.15	

Table 4. The kinetic parameters (activation energy, E_a ; reaction order, n ; pre-exponential factor, lnk_0) of the decomposition reactions of the ligand and the synthesized Mn(II) complexes

Sample	Step	$E_a,$ kJ/mol	n	lnk_0
HL	I	137.63±2.77	0.82	46.69±1.03
	II	111.14±0.53	0.50	32.39±0.18
	III	157.82±0.47	1.56	33.31±0.12
	IV	288.59±3.53	0.95	53.69±0.71
[MnLCl] ₂ ·2/5H ₂ O	I	129.10±8.48	0.47	35.18±2.61
	II	132.50±11.00	0.59	32.34±3.06
	III	270.70±13.97	1.04	54.68±3.06
	IV	111.05±2.48	0.90	13.17±2.68
[MnL ₂]·1/2H ₂ O	I	133.78±18.18	0.74	40.45±6.06
	II	148.54±7.63	0.62	37.60±2.18
	III	282.03±11.81	1.34	60.69±2.76
	IV	111.90±6.22	0.14	16.44±1.20

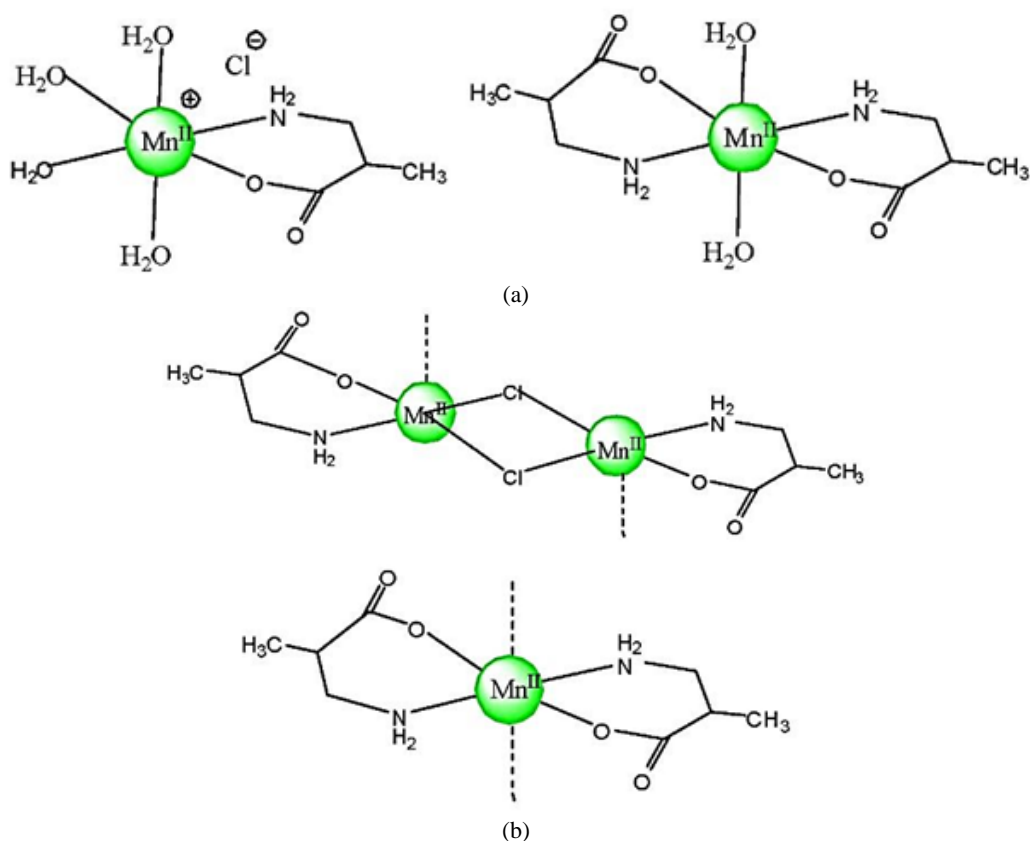


Fig. 7. Proposed structure of [ML] and [ML₂] coordination units in aqueous solution (a) and solid state (b)

4. Conclusions

We have synthesized two new complexes of Mn (II) with DL- β -Aminoisobutyric acid in 1:1 and 1:2 molar ratio in aqueous solution. They were characterized by physical-chemical methods in order to determine their structures and properties: pH-metry, conductometry, chemical analysis, IR-absorption spectra, XRD and the thermal analysis. Both 1:1 and 1:2 molar ratio compounds are slightly pink crystalline solids.

Thermal decomposition begins at 100°C for both complexes and at above 50°C for the ligand, showing the increased thermal stability of the coordinative compounds due to the coordination process.

The experimental data were in agreement with the literature indications and we proposed the structures of the new complex compounds with Mn(II), revealing the bi-dentate properties of the ligand.

In further studies, this research will be continued for testing the biological properties of the ligand BAIBA and its coordinative compounds in agriculture.

References

- Astilean S., (2002), *Methods and Modern Techniques of Optical Spectroscopy* (in Romanian), Book Publishing House of Science, Cluj-Napoca, Romania.
- Barillia E., Rubialesa D., Castillejo M.Á., (2012), Comparative proteomic analysis of BTH and BABA - induced resistance in pea (*Pisumsativum*) toward infection with pea rust (*Uromycespisi*), *Journal of Proteomics*, **75**, 5189-5205.
- Bugaric Z.D., Bogojeskia J., van Eldik R., (2015), Kinetics, mechanism and equilibrium studies on the substitution reactions of Pd(II) in reference to Pt(II) complexes with bio-molecules, *Coordination Chemistry Reviews*, **292**, 91-106.
- Boucher L.J., Kotowski M., Koeber K., Tille D., (2013), *Mn Manganese: Coordination Compounds 7, Handbook of Inorganic and Organometallic Chemistry - 8th Edition*, Springer Science & Business Media.
- Chandra S., Kumar U., (2005), Spectral and magnetic studies on manganese(II), cobalt(II) and nickel(II) complexes with Schiff bases, *Spectrochimica Acta Part A*, **61**, 219-224.
- Cohen Y., (1994), 3-Aminobutyric acid induces systemic resistance against *Peronospora tabacina*, *Physiological and Molecular Plant Pathology*, **44**, 273-288.
- Cohen Y., Niderman T., Möisinger E., Fluhr R., (1994), β -Aminobutyric acid induces the accumulation of pathogenesis - related proteins in tomato (*Lycopersicon esculentum* L.) plants and resistance to late blight infection caused by *Phytophthora infestans*, *Plant Physiology*, **104**, 59-66.
- Cohen Y., Reuveni M., Baider A., (1999), Local and systemic activity of BABA (DL-3-aminobutyric acid) against *Plasmopara viticola* grapevines, *European Journal of Plant Pathology*, **105**, 351-361.
- Cohen Y., (2000), Method for protecting plants from fungal infection, USA Patent, No. 6075051.
- Cohen Y., (2002), β -Aminobutyric acid - induced resistance against plant pathogens, *Plant Disease*, **86**, 448-457.
- Cohen Y., Rubin A.E., Vaknin M., (2011), Post infection application of DL- β -aminobutyric acid (BABA) induces multiple forms of resistance against *Bremialactuae*, *European Journal of Plant Pathology*, **130**, 13-27.
- Crudu M., (2008), *Study on the use of inorganic processing of natural leather concerning the prevention of environmental pollution* (in Romanian), PhD Thesis, "Gheorghe Asachi" Technical University of Iasi, Romania.
- Crudu M., Sibiescu D., Rosca I., Sutiman D., Vizitiu M., Apostolescu G., (2009), New coordination compounds of Cr(III) used in leather tanning, *Proceedings of SPIE*, The International Society for Optical Engineering, 7297, DOI: 10.1117/12.823638.
- Crudu M., Sibiescu D., Rosca I., Sutiman D., Vizitiu M., (2009), Studies of obtaining and stability in aqueous medium of new complex compounds of Ti(IV) and Zr(IV) used in ecological leather tanning, *Proceedings of SPIE*, The International Society for Optical Engineering, 7297.
- Foca N., Sibiescu D., Oancea S., (2006), *Physico-Chemical Methods Applied in the Complex Combination Studies*, Tehnopress, Iasi, Romania, 58-97.
- Freeman S.E., Caroll B., (1958), The application of thermoanalytical techniques to reaction kinetics. The thermogravimetric evaluation of the kinetics of the decomposition of calcium oxalate monohydrate, *The Journal of Physical Chemistry*, **62**, 394-397.
- Gerey B., Goure E., Fortage J., Pecaut J., Collomb M.N., (2016), Manganese-calcium/strontium heterometallic compounds and their relevance for the oxygen-evolving center of photosystem II, *Coordination Chemistry Reviews*, **319**, 1-24.
- Hwang B.K., Sunwoo J.Y., Kim Y.J., Kim B.S., (1997), Accumulation of β -1,3-glucanase and chitinase isoforms, and salicylic acid in the DL- β -amino-n-butyric acid induced resistance response of pepper stems to *Phytophthora capsici*, *Physiological and Molecular Plant Pathology*, **51**, 305-322.
- Kammoun H.L., Mark A., Febbraio M.A., (2014), Come on BAIBA Light My Fire, *Cell Metabolism*, **19**, 1-2, <http://dx.doi.org/10.1016/j.cmet.2013.12.007>.
- Kim J.W., Park J.K., (2017), Synergistic antimicrobial properties of active molecular chitosan with EDTA-divalent metal ion compounds, *Journal of Phytopathology*, **165**, 641-651, DOI: 10.1111/jph.12603.
- Iordache M., Branzoi I.V., Popescu L.R., Iordache I., (2016), Evaluation of heavy metal pollution into a complex industrial area from Romania, *Environmental Engineering and Management Journal*, **15**, 389-394.
- Li W., Liu J., Ashraf U., Li G., Li Y., Lu W., Gao L., Han F., Hu J., (2016), Exogenous α -aminobutyric acid (GABA) application improved early growth, net photosynthesis, and associated physio-biochemical events in maize, *Frontiers in Plant Science*, **7**, doi: 10.3389/fpls.2016.00919.
- Giacovazzo C., Monaco H.L., Artioli G., Viterbo D., Ferraris G., Gilli G., Zanotti G., Catii M., (2008), *Fundamentals of Crystallography*, 2nd Edition, reprinted, Oxford University Press, Oxford.
- Maurya R.C., Bohre P., Sahu S., Martin M.H., Sharma A.K., (2016), Manganese(II) chelates of bioinorganic and medicinal relevance: Synthesis, characterization, antibacterial activity and 3D-molecular modelling of

- some penta-coordinated manganese(II) chelates in O,N-donor coordination matrix of b-diketoenolates and picolinate, *Arabian Journal of Chemistry*, **9**, S54-S63.
- Marcucci E., Aleandri M.P., Chilosi G., Magro P., (2010), Induced resistance by β -aminobutyric acid in artichoke against white mould caused by *Sclerotinia clerotiorum*, *Journal of Phytopathology*, **158**, 659-667.
- Mei Y.X., Hui Yu H., Wei E.H., Mei G.Q., Cai H., (2017), Two coordinated geometries of Mn^{2+} ions in one single molecule: organic-inorganic hybrids constructed with tris(2-aminoethyl)amine and manganese halide and fluorescent properties, *Polyhedron*, **127**, 458-463.
- Molfino A., Amabile M.I., Ammann T., Alessio Farcomeni A., Lionetto L., Simmaco M., Lai S., Laviano A., Rossi Fanelli F., Chiappini M.G., Muscaritoli M., (2017), The metabolite beta-aminoisobutyric acid and physical inactivity among hemodialysis patients, *Nutrition*, **34**, 101-107.
- Nakamoto K., (1997), *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley and Sons, New-York.
- Rahman A., Nahar K., Hasanuzzaman M., Masayuki Fujita M., (2016), Manganese-induced cadmium stress tolerance in rice seedlings: Coordinated action of antioxidant defense, glyoxalase system and nutrient homeostasis, *Comptes Rendus Biologies*, **339**, 462-474.
- Sahebani N., Hadavi N.S, Zade F.O., (2011), The effects of β -aminobutyric acid on resistance of cucumber against rootknot nematode *Meloidogyne javanica*, *Acta Physiologiae Plantarum*, **33**, 443-450.
- Segal E., Fatu D., (1983), *Introduction to Kinetic Non-Isotherm Reactions*, Romanian Academy Publishing House, Bucharest, Romania.
- Sibiescu D., (2012), *Chemistry of Coordination Compounds*, (in Romanian), Pim Publishing House, Iasi, Romania.
- Signorelli S., Dans P.D., Coitino E.L., Borsani O., Monza J., (2015), Connecting proline and γ -aminobutyric acid in stressed plants through non-enzymatic reactions, *PLoS ONE*, **10**, e0115349, doi:10.1371/journal.pone.0115349.
- Tiwari S., Meyer W.L., Stelinski L., (2013), Induced resistance against the Asian *Citrus psyllid*, *Diaphorina citri*, by β -aminobutyric acid in citrus, *Bulletin of Entomological Research*, **103**, 592-600.
- Topolski A., Rozmarynowska P., Maj M., Czajkowski R., (2017), Kinetics and mechanism of chloride substitution by thiourea, L-methionine and glutathione in bimetallic $[Pt_2(6NNqui)Cl_4]$ complex in water-DMF medium. Unusually slow reaction with thiourea, *Inorganica Chimica Acta*, **462**, 10-15.
- Secu C.V., (2016), Potentially toxic elements in urban soils of Iasi (Romania), *Environmental Engineering and Management Journal*, **15**, 687-698.
- Spătărescu I., Sibiescu D., Roșca I., (2010), The characterization and the synthesis of a new coordination compound for removal of Cr(III) from wastewaters, *Environmental and Engineering and Management Journal*, **9**, 443-447.
- Tamm L., Thürig B., Fliessbach A., Goltlieb A.E., Karavani S., Cohen Y., (2011), Elicitors and soil management to induce resistance against fungal plant diseases, *Journal of Life Sciences*, **58**, 131-137.
- Tutulea M.D., Rosca I., Cretescu I., Cailean A., Bistricianu I.L., (2011), New coordinative compounds of Mn(II) and Cu(II) using as ligand N-hydroxy-succinimide, *Revista de Chimie*, **62**, 293-298.
- Vainstein K.B., (1989), *Modern Crystallography*, (in Romanian), vol. 1, Scientific and Encyclopaedic Publishing House, Bucharest, Romania.
- Yunpeng Z., Biao W., Junhui Y., Linjing C., Luming Y., Liang X., Tianlong W., (2014), DL- β -Aminobutyric Acid induced resistance in soybean against *Aphis glycines* Matsumura (Hemiptera: Aphididae), *PLoS ONE*, **9**, e85142, <https://doi.org/10.1371/journal.pone.0085142>.
- Wang Y., Gu W., Meng Y., Xie T., Li L., Li J., Wei S., (2017), γ -Aminobutyric acid imparts partial protection from salt stress injury to maize seedlings by improving photosynthesis and upregulating osmoprotectants and antioxidants, *Scientific Reports*, **7**, Article number:43609, DOI: 10.1038/srep43609.
- Wang L., Zhang H., Jin P., Guo X., Li Y., Fan C., Wang J., Zheng Y., (2016), Enhancement of storage quality and antioxidant capacity of harvested sweet cherry fruit by immersion with β -aminobutyric acid, *Postharvest Biology and Technology*, **118**, 71-78