

Complexes of some binuclear transition metals with isoniazid

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The synthesized binuclear complexes have the general formulae: $[M(\text{INH})(\text{SO}_4)(\text{H}_2\text{O})_2]_2$, M= Co(II), Ni(II), Mn(II).

The obtained complexes were thermally stable and they are insoluble in common organic solvents (methanol, ethanol, acetone, DMF and acetonitrile). Elemental analysis and some physical properties of the complexes are given in Table I.

Table I The elemental analysis and physical and chemical properties of binuclear complexes

	Compound	Colour	Melting point, (°C)	Elemental analysis			
				Found (calcd)			
				M%	C%	H%	N%
1	$[\text{Co}(\text{INH})(\text{SO}_4)(\text{H}_2\text{O})_2]_2$	pink	>325	16.84 (17.18)	21.85 (22.15)	3.12 (3.41)	12.74 (12.92)
2	$[\text{Ni}(\text{INH})(\text{SO}_4)(\text{H}_2\text{O})_2]_2$	Blue crystals	314*	18.38 (17.90)	22.28 (21.96)	2.87 (3.38)	13.06 (12.81)
3	$[\text{Mn}(\text{INH})(\text{SO}_4)(\text{H}_2\text{O})_2]_2$	yellow	>325	17.30 (16.95)	21.80 (22.22)	3.12 (3.42)	12.79 (12.96)

IR spectra

The position and intensity of the absorption bands from IR spectra of complexes compared with the ligand ones provide details about the type of chemical bond involved in the complex formation.

The IR spectra (4000 – 400 cm^{-1}) for the ligand and its complexes **1 - 3** are presented in Table II.

In the IR spectrum of isoniazid the medium intensity bands appear at 3304 cm^{-1} and 3110 cm^{-1} , which are assigned to the vibration frequency $\nu(\text{NH}_{\text{as}})$, $\nu(\text{NH}_{\text{sym}})$. The very intense bands from 1669 cm^{-1} and 1558 cm^{-1} , are due to amide-I and amide-II groups. The band of medium intensity from 887 cm^{-1} is due to the vibration frequency N-N.

The vibration frequencies ν N-H are strongly displaced towards lower values in all complexes, suggesting the involvement of the amino nitrogen in coordination with metallic ions. For the same thing pleads the movement to lower values of the vibration frequency ν N-N as compared with the ligand spectrum.

In the complexes, the corresponding band of amide-I group appears displaced towards lower values, which indicates the involvement of carbonyl group in coordination.

The bands in the domains 3381 - 3444 cm^{-1} and 894 - 905 cm^{-1} , respectively from the IR spectrum of $[\text{M}(\text{INH})(\text{SO}_4)(\text{H}_2\text{O})_2]_2$ complex, suggest the existence of coordination water.

The characteristic bands of pyridine nitrogen appeared in the spectra of the ligand and the complexes at the same position, confirming that the nitrogen of pyridine group does not participate in the coordination.

All of these IR data confirm a bidentate ligand (isoniazid) coordination, through the carbonyl oxygen and imine nitrogen to the metallic ions.

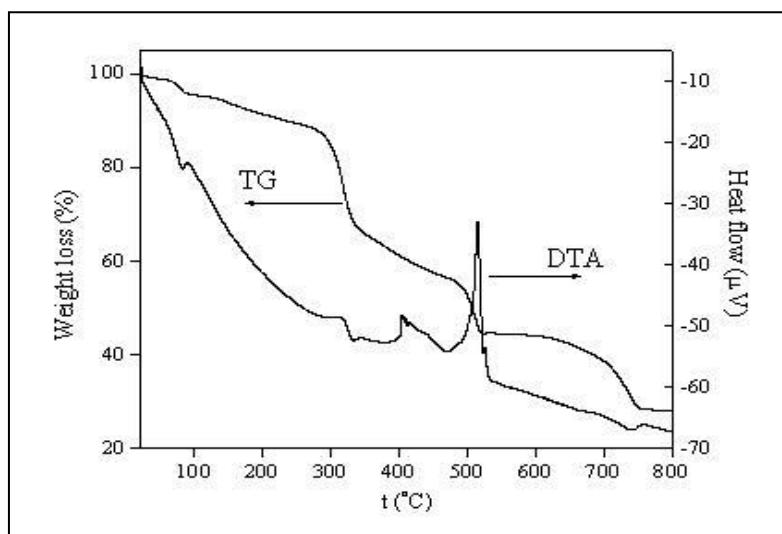
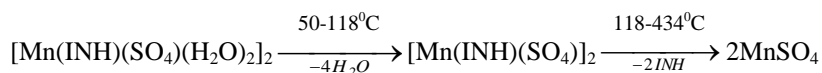
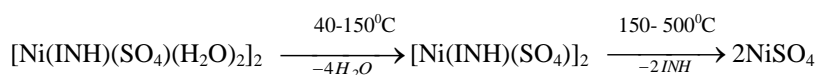
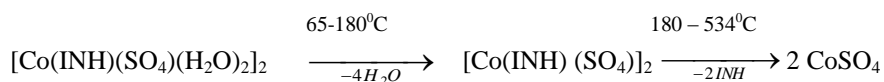
According to literature data, a low symmetry of SO_4^{2-} group from the complexes are

probably due to the reducing of T_d arrangement towards C_{2v} and the ν_3 and ν_4 frequencies are each split into three bands. The bands from the domains 967 - 984 cm^{-1} , 1060 - 1070 cm^{-1} and 1107 - 1118 cm^{-1} are attributed to the ν_3 vibration mode. The bands from the domains 480-529 cm^{-1} , 538 - 616 cm^{-1} and 601 - 705 cm^{-1} from the IR spectra of complexes **1-3** are attributed to the ν_4 vibration mode. It can be concluded that the anion is being coordinated in a bridge binding mode.

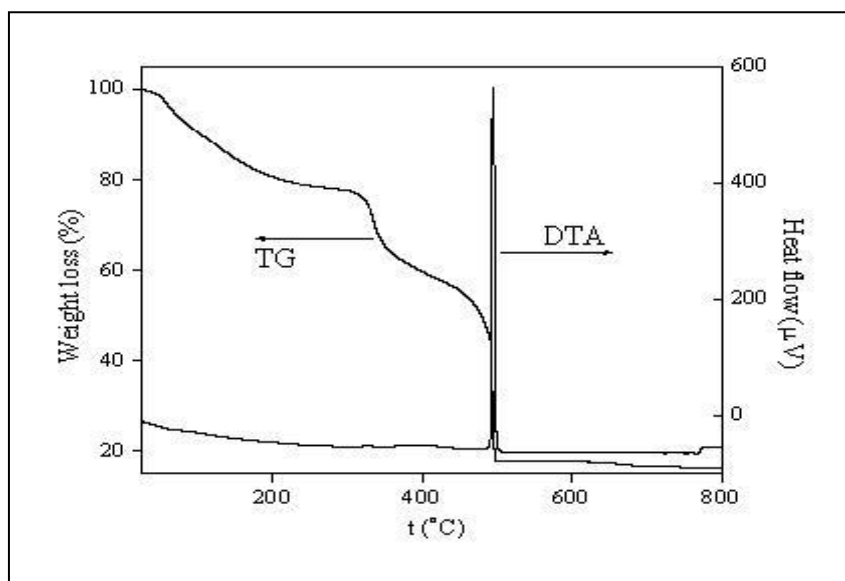
	Compound	$\nu(\text{OH})$	$\nu\text{N-H}$	$\nu\text{C=O}$ amide I	ν amide II	$\delta\text{H}_2\text{O}$ coord	$\nu\text{N-N}$	νSO_4^{2-} dicoor	
								ν_3	ν_4
	INH	-	3304 3110	1669	1558	-	888	-	
1	$[\text{Co}(\text{INH})(\text{SO}_4)(\text{H}_2\text{O})_2]_2$	3444	3270 3158	1656	1547	894	855	1116 1063 984	601 538 480
2	$[\text{Ni}(\text{INH})(\text{SO}_4)(\text{H}_2\text{O})_2]_2$	3381	3215	1658	1550	905	852	1107 1060 967	705 616 480
3	$[\text{Mn}(\text{INH})(\text{SO}_4)(\text{H}_2\text{O})_2]_2$	3443	3281 3187	1664	1547	894	858	1118 1079 978	667 609 529

Thermogravimetric analysis

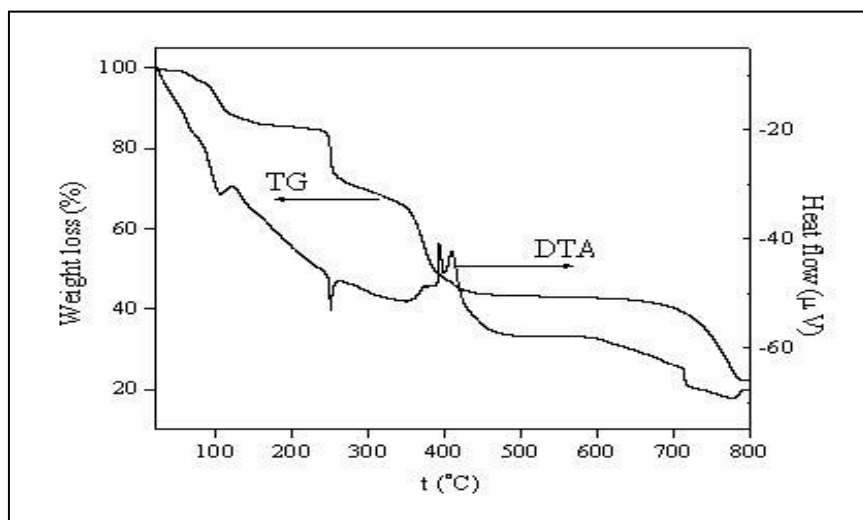
The TG and DTA curves and thermal data of investigated compounds are given in Table III and Figures 1 a-c; The final residue of Co(II), Ni(II) and Mn(II) complexes obtained from sulphate compounds are estimated as metal sulphate.



a



b



c

Fig. 1 a-c The TG/DTA curves for the complexes

- a. $[\text{Co}(\text{INH})(\text{SO}_4)(\text{H}_2\text{O})_2]_2$
- b. $[\text{Ni}(\text{INH})(\text{SO}_4)(\text{H}_2\text{O})_2]_2$
- c. $[\text{Mn}(\text{INH})(\text{SO}_4)(\text{H}_2\text{O})_2]_2$

Table III. The thermal results for complexes 1-3

	Compound	TG range/C	Loss	Mass loss	
				Exp	calc
1	[Co(INH)(SO ₄)(H ₂ O) ₂] ₂	65-180	-4H ₂ O	10,034	10,98
		180-534	-2INH	42,795	41,796
		534-800	residue 2CoSO ₄	46,171	47,27
2	[Ni(INH)(SO ₄)(H ₂ O) ₂] ₂	40-150	-4H ₂ O	12,086	11,12
		150-357	-INH	21,217	21,169
		357-500	-INH	21,422	21,169
		500-800	residue 2NiSO ₄	45,275	46,56
3	[Mn(INH)(SO ₄)(H ₂ O) ₂] ₂	50-118	-4H ₂ O	11,243	11,954
		118-344	-INH,	22,27	21,396
		344-434	-INH	21,661	21,396
		434-800	residue 2MnSO ₄	43,102	44,12

Magnetic moments

It is known that in the approximation “spin only” can be calculated magnetic moment of a compound based on the hypothesis non-matched numbers of electrons, so the value of the spin associated with the paramagnetic ions components. The validity of the hypothesis results from comparing the magnetic moment calculated with that determined from measurements.

Nothing is changed if it is considered only one or more molecules, as long as the assumption of no interaction between the paramagnetic centers within a molecule, intermolecular dipolar interaction or orbital contributions will be used.

Based on this hypothesis and the determined susceptibilities values at room temperature, the magnetic moments for dimmer complexes were calculated. Thus:

- for the Cu(II) complex, the experimentally determined magnetic moments is 2.1 BM, which corresponds to an octahedral geometry.

- for the complex Co (II), the experimentally determined magnetic moment is 5.7 BM, indicating a high spin and excluding the oxidation to Co(III). The value determined is perfectly in the 4.3 - 5.7 BM range, which corresponds to an octahedral geometry for the Co(II) ion.

- for the complex of Ni (II) the value determined for the magnetic moment is 3.2 BM.

This value is in the range of (2.8 - 3.5) BM for Ni (II) complexes with an octahedral geometry.

- the magnetic moment determined for Mn(II) complex is 5.65 BM. This value falls in the range (5.65 – 6.10) BM, which corresponds to the Mn(II) ion with an octahedral environment.

The spectral, thermal and magnetic susceptibility data show that in all complexes, the metallic ions are in an octahedral environment and the ligand acts as neutral bidentate being coordinated through the imine nitrogen and carboxylic oxygen. All four studied complexes are dimmer ones. The thermal analysis indicates the presence of molecules of crystallization water.

Structural formula proposed for complexes are given in Figure 2.

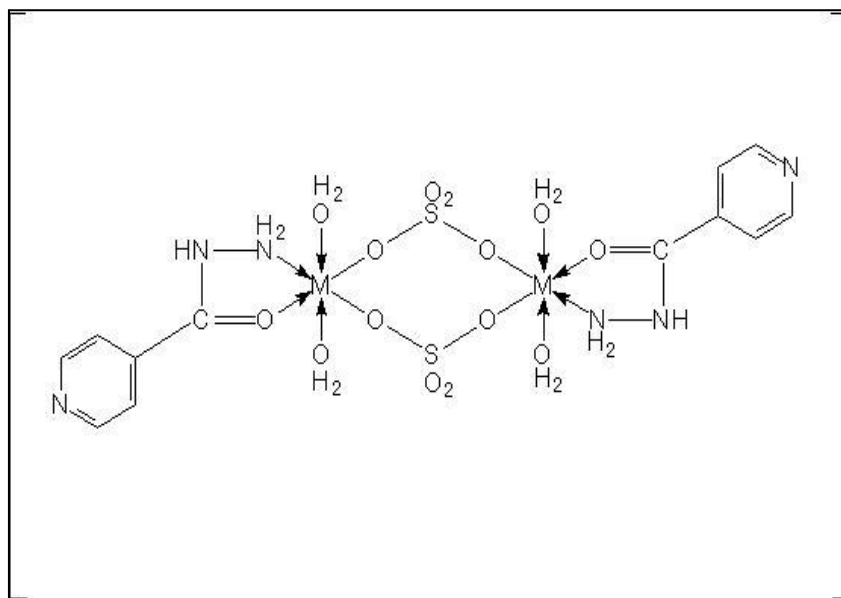


Fig. 2. Proposed structural formula of binuclear complexes of isoniazid $[ML(SO_4)(H_2O)_2]_2$, $M= CoII, NiII, MnII$.

REFERENCES

[Aba12] Ababei, L. V., “ Transition metal complexes with hydrazones derived from isonicotinic acid hydrazide” **Doctoral thesis, 2012**