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Synthesis, Characterization and Thermal Behaviour of Manganese(II), Cobalt(II), Nickel(II), Copper(II) and Zinc(II) Complexes of Vanillin

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Five solid complexes of transition metal acetate with vanillin of the general formula $[ML_2(H_2O)_2]$, where M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II), HL = vanillin *i.e.*, 4-hydroxy-3-methoxy benzaldehyde ($C_8H_8O_3$) have been synthesized in boiling water system and characterized by elemental analysis, IR spectra and conductivity measurements. The M(II) ion in the complexes coordinates with two vanillin ligand *via* four oxygen atoms of the phenol hydroxy groups and methoxy groups and two water molecule *via* their two oxygen atoms. Their coordination number are six. The thermal behaviour of these complexes has been studied by TG and DTA. These complexes show two, three or four steps weight loss upon heating up to 450 ºC and show almost similar mode of decomposition. The residues after heating correspond to metal oxide. Nickel forms the most thermally stable complex.

Key Words: Thermoanaytical behaviour, Transition metal complex, Vanillin.

INTRODUCTION

The role of transition metals in human life is very important. Manganese is the component of nucleic acid, it can accelerate synthesizing cholesterine. Cobalt has a certain function to cure pernicious anemia and also has some function to coordination cure about antibiotics, especially penicillin[1]. Zinc is a important life element and some activity centers of enzyme[2-4]. Vanillin is a natural aldehyde existed in Andropogen nardus.

In this paper, the complexes with the general composition $[ML_2(H_2O)_2]$, where M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and HL = vanillin have been synthesized and characterized. The molecule of vanillin behaves as a bidentate ligand. In spite of the considerable importance of this biologically active molecule, little work has been done on the synthesis of transition metal complexes of this ligand in solid form.

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The aim of the present work is to pursue a more detail study of these complexes, which they undergo upon heating and to understand the mechanism of their decomposition to examine the conditions and products of their thermal decomposition.

EXPERIMENTAL

All the chemicals used were of analytical grade. The metal contents were determined by EDTA complexometric titration after decomposition a known amount of the complexes with concentrated nitric acid by published method[5]. Elemental analysis was performed on CHN analyzer, CARLO ERBA 1100 made in Italy. The molar conductance of the prepared complexes in DMSO was measured using the conductivity bridge made by Shanghai China. IR spectra of prepared complexes on a Nicolet NEXUS 670 FTIR using KBr dises in the range 4000-400 cm^{-1}. A Mettler Toledo thermal analyzer-TGA/SDTA 851^e was used to carry out the thermoanalytical analysis. The thermal experiments were performed in nitrogen from ambient 25 ºC temperature to 900 ºC with a heating rate of 10 ºC min^{-1}. Al_2O_3 crucibles were used to hold about 5 mg samples for analysis.

Preparation of the complexes: $M(vanillin)_2(H_2O)_2$ were prepared by mixing ligand vanillin (2 mmol) with corresponding transition metals acetate (1 mmol), then adding proper water. When the mixture was boiling, NaOH (2 mmol) liquid was added drop-wise. The solid formed is collected, filtered it, washed it several times with boiling water. Yield 80-90 %.

RESULTS AND DISCUSSION

The compositions of ligand and prepared complexes are summerized in Table-1. The C, H percentage both theoretically calculated values and actual values are in accordance. So the complexes are consist of one central metal, two ligands (vanillin), two water molecule. Their molar conductance in DMSO (1.0×10^{-3} mol dm^{-3}) solvent lie in the range of 3.0-7.0 S cm^2 mol^{-1}. The conductance value are in accordance with the non-electrolytic nature of the complexes[6], which clearly indicates that anions are coordinated with metal atom.

IR spectra of complexes (Table-2) suggests that the C-O stretching frequencies are shifted to lower and some to higher frequencies with changes in sharpness and intensities. This is caused by the withdrawal of electron density from C-O band where oxygen atom is believed to have coordinated to the metal ion.

The absorption band at around 3184 cm^{-1} was attributed to OH stretching. This band is a little stronger in the complexes than that of ligand. The reason may be the decrease of the electron density of OH after being coordinated. The absorbption band around 1667 cm^{-1} was due to C=O stretching,

TABLE-1
ELEMENTAL ANALYSIS, MOLAR CONDUCTANCE
DATA OF METAL COMPLEXES

Complex	Colour	Elemental analysis (%)			Λ_M (S cm^2 mol^{-1})
		C	H	M	
$MnL_2 \cdot 2H_2O$	Yellow	48.65 (48.87)	4.87 (4.61)	13.45 (13.97)	7.0
$CoL_2 \cdot 2H_2O$	Dark red	48.30 (48.37)	4.80 (4.57)	14.84 (14.84)	4.2
$NiL_2 \cdot 2H_2O$	Bright green	48.63 (48.40)	4.85 (4.57)	14.68 (14.78)	6.0
$CuL_2 \cdot 2H_2O$	Brown	47.93 (47.82)	4.70 (4.52)	15.74 (15.81)	3.2
$ZnL_2 \cdot 2H_2O$	Light yellow	47.55 (47.60)	4.42 (4.49)	15.97 (16.20)	2.7

*Percentages in parentheses are theoretically calculated values.

TABLE-2
KEY IR BANDS (cm^{-1}) FOR LIGAND AND ITS METAL COMPLEXES

Compd.	ν(O-H)	ν(C=O)	ν(HOH)	ν(Ar-OCH_3)	ν(C-O)	ν(M-O)
Vanillin	3184 m	1667 s	–	1299 m	1266 m	–
$MnL_2 \cdot 2H_2O$	3217 m	1647 s	927 m	1274 m	1234 m	433 w
$CoL_2 \cdot 2H_2O$	3217 m	1647 s	929 m	1272 m	1234 m	428 w
$NiL_2 \cdot 2H_2O$	3166 m	1645 s	929 m	1274 m	1232 m	428 w
$CuL_2 \cdot 2H_2O$	3256 m	1650 s	928 m	1272 m	1232 m	428 w
$ZnL_2 \cdot 2H_2O$	3196 m	1647 s	930 m	1274 m	1236 m	425 w

when in the complexes they are shifted lower frequencies about 20 cm^{-1}. The absorption band at around *ca.* 930 cm^{-1} was attributed to HOH stretching. Thus, H_2O coordinated with metal in these complexes. A weak intensity band at *ca.* 430 cm^{-1} was due to (M-O) stretching. Thus, the coordination bond were formed between metal ion and oxygen atoms of phenol-hydrogy and methoxy[7].

Thermal analysis was carried out systematically for all complexes in nitrogen atmosphere. The actual weight losses reported in Table-3, for the decomposition process of the complexes appeared to be comparable with the calculated values.

The TG and DTA curves reveal that in the first step all the complexes loses two coordinate water, by breakage of M-O bond around 75-218 ºC with an accompanying weak endothermic effect. Second and third step are similar that liberate two water molecule, two carbonyl group, with an accompanying weak exothermic around 218-355 ºC. The last step is than decomposed exothermally in the temperature range 280-450 ºC librating all ligands.

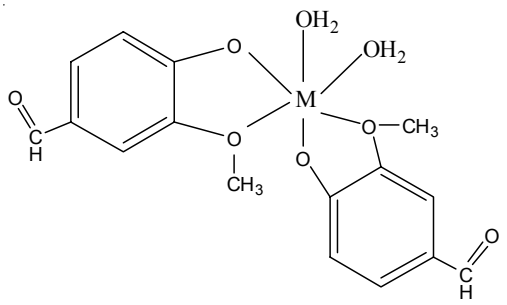
TABLE-3
THERMOANALYTICAL RESULTS OF COMPLEXES IN NITROGEN ATMOSPHERE

Complex	TG results temp. range (ºC)	Stage	DTA results temp. peak (ºC)	Weight loss	Loss (%) calcd.	Evolved moiety
$MnL_2 \cdot 2H_2O$	76-143	1	123.31	9.05	9.11	$2H_2O$
	216-315	2	298.45	72.39	72.08	Other ligands
	> 315	Residue	–	18.56	18.81	Mn_3O_4
$CoL_2 \cdot 2H_2O$	107-212	1	188.02	9.17	9.02	$2H_2O$
	212-286	2	234.32	14.13	14.04	2C=O
	286-326	3	320.84	15.18	15.54	$2\text{-}OCH_3$
	326-415	4	381.87	42.51	42.62	Other ligands
	> 415	Residue	–	19.01	18.78	CoO
$NiL_2 \cdot 2H_2O$	141-233	1	203.76	9.12	9.03	$2H_2O$
	223-283	2	243.52	7.13	7.02	C=O
	283-338	3	336.06	22.55	22.57	C=O $2\text{-}OCH_3$
	338-444	4	381.57	42.26	42.64	Other ligands
	> 444	Residue	–	18.94	18.74	NiO
$CuL_2 \cdot 2H_2O$	80-217	1	137.08	8.88	8.92	$2H_2O$
	217-289	2	208.93	29.95	29.24	2C=O $2\text{-}OCH_3$
	289-355	3	348.11	41.36	41.13	Other ligands
	> 355	Residue	–	19.81	19.71	CuO
$ZnL_2 \cdot 2H_2O$	84-155	1	131.13	8.81	8.88	$2H_2O$
	155-291	2	295.30	13.84	13.81	2C=O
	291-449	3	325.95	57.47	57.24	Other ligands
	> 449	Residue	–	19.88	20.07	ZnO

The DTA curves of the complexes show two, three or four peaks, endothermic and exothermic corresponding to the first and the last step of the TG curves. First step in the decomposition of complexes (75-218 ºC) is accompanied by exothermic effects in the DTA curves with the evolution of two moles of coordinate water. Second, third and four steps in the thermal decomposition involves the decomposition of intermediates and oxidation of metal by atmosphere nitrogen. The second moiety is two carbonyl group, two methoxyl group. The combined effect of loss of these moieties corresponds to large exothermic effect as indicated by DTA curves, accompanied by the oxidation of metal. The TG curves of process causing an increase in the mass of residue of the expected production of the decomposition in nitrogen of metal[8-12] after heating up to 900 ºC. The TG-DTA curves permit following conclusions: complex 1 is thermally stable up to 123 ºC, complex 2 to 188 ºC, complex 3 to 203 ºC, complex 4 to 137 ºC, complex 5 to 131 ºC (according the beginning of mass loss)[13].

Conclusion

The TG, DTA curves permit the following conclusion: (i)The thermal stabilize of these complexes is $NiL_2 \cdot 2H_2O$ > $CoL_2 \cdot 2H_2O$ > $CuL_2 \cdot 2H_2O$ > $ZnL_2 \cdot 2H_2O$ >$MnL_2 \cdot 2H_2O$. (ii) The strength of metal and coordinate oxygen atom in complexes is Ni-O > Co-O > Cu-O > Zn-O > Mn-O. (iii) All the coordinate water are easy to liberate at lower temperature. (iv) The structure of the complexes may be octahedral. The suggested structure is



REFERENCES

1. S.L. Xu, (Inorganic Chemistry Series) [M], Science Press, p. 9 (1996).
2. C.F. Naumann and B. Prijs, *Eur. J. Biochem.*, **41**, 209 (1974).
3. S.K. Burley, P.R. David, R.M. Sweet, A. Taylor and W.N. Lipscomb, *J. Mol. Biol.*, **224**, 113 (1992).
5. M. Eerck, Complexometric Assay Method with Titriplex, Darmstadt, edn. 3, p. 25, 55 (1964).
6. W.J. Geary, *Coord. Chem. Rev*, **7**, 81 (1971).
7. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, edn. 4 [M]. New York, Wiley & Sons, p. 273 (1986).
8. A. Bujewski, K. Grzedzicki and Z. Warnke, *J. Thermal Anal. Color.*, **33**, 961 (1988).
9. I. Tossidis and A. Syngollitou-Kourakou, *J. Thermal Anal. Color.*, **32**, 491 (1987).
10. J. Maslowska and A. Baranwska, *J. Thermal Anal. Color.*, **29**, 309 (1984).
11. J. Cernak and J. Chomic, *J. Thermal Anal. Color.*, **32**, 527 (1987).
12. B.N. Sivasankar and S. Govindarajan, *J. Thermal Anal. Color.*, **46**, 117 (1996).
13. E. Jona, M. Jamnicky and I. Kostelny, *J. Thermal Anal. Color.*, **32**, 513 (1987).

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