

Research Article

Synthesis and Characterization of Metallic Gel Complexes Derived from Carboxymethyl Cellulose

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The oxaloyl carboxymethyl cellulose (OCMC) complexes of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) metal ions have been synthesized and the coordination of OCMC in these complexes has been investigated through IR spectra, reflectance spectra, and thermal analysis. On the basis of spectral and thermal data an octahedral geometry was assigned to $[\text{Mn(II)OCMC}(\text{H}_2\text{O})_2]_n$ and $[\text{Co(II)OCMC}(\text{H}_2\text{O})_2]_n$, square planar geometry was assigned to $[\text{Cu(II)OCMC}]_n$, and tetrahedral geometry was assigned to $[\text{Ni(II)OCMC}]_n$ and $[\text{Zn(II)OCMC}]_n$ Metallic Gel complexes.

1. Introduction

Cellulose is a naturally occurring polysaccharide and is the most abundant renewable resource available. It is a glucose polymer photosynthesized by solar energy in various plants and acts as the structural basis of the plant cell wall [1]. Cellulose is a linear polymer of anhydroglucose units linked at C-1 and C-4 by β -glycosidic bonds. This is confirmed by the presence of three hydroxyl groups with different acidity/reactivity, secondary OH at the C-2, secondary OH at the C-3, and primary OH at the C-6 position and, accordingly, by the formation of strong various intermolecular and intramolecular hydrogen bonds. Despite its simple molecular structure, cellulose shows a large complexity and variability in its supermolecular arrangement in cellulose fibrils [2]. Production of cellulose derivatives was done by reacting the free hydroxyl groups in the anhydroglucose units (AGU) with various chemical substitution groups. The introduction of the substituent disturbs the inter- and intramolecular hydrogen bonds in cellulose, which leads to liberation of the hydrophilic character of the numerous hydroxyl groups and restriction of the chains to closely associate [3]. Cellulose ether is the most widely used cellulose derivative in food and pharmaceutical industries. It is obtained by replacing the hydroxyl groups with either alkyl or hydroxy-alkyl groups.

Accordingly, a wide range of cellulose ethers was manufactured to meet specific needs of industrial applications [4]. This is the case with sodium carboxymethylcellulose (Na-CMC), an anionic linear cellulose ether. CMC presents the structure of a polyanion consisting of repeating units of anhydroglucose residues, substituted by sodium carboxymethyl groups. Cellulose derivatives such as carboxymethylcellulose (CMC) and hydroxypropylcellulose are biocompatible [5] and have been applied in drug delivery formulations [6–9] and as components of therapies for preventing postsurgical adhesions (e.g., Genzyme's Septrafilm) [10–14]. A number of papers have been published on the uses of chelating exchanges for trace element preconcentration from various matrices using cellulose as solids sorbents for the separation of the transition metals in analyses such as GFAAS spectrometry, ICP-MS for reduction and aggregation of silver, copper, and cadmium ions in aqueous solutions of gelatin and CMC, and with dichromate for separation of copper-lead in secondary copper minerals [15–18].

The Navy also makes use of polymers in load-bearing polymeric matrix composites, special coatings for signature control, coatings for corrosion reduction in waste-holding tanks, fuel storage tanks and metal pipe linings, and so on, where polymers have been often applied as part of a technology package to meet the needed performance criteria [19].

The present work is a part of systematic investigation undertaken in the laboratory which includes the synthesis of thermally stable Metallic Gel complexes, mechanism of their formation, structural aspects, and applications as coating materials. The metal ions selected for the present work belong to 3d block transition elements namely Mn(II), Co(II), Ni(II), Cu(II), and Zn(II). These metal ions have an ability to form complexes with ligands having one or more lone pair of electrons, which they can easily donate to the transition metal ion and thus complete the vacant orbital of cation through the formation of $L \rightarrow M$ bond. Since the electropositive nature decreases on moving down in each group of transition metals, the members of first transition series form more stable complexes with ligands containing nitrogen and oxygen. The resulting complexes formed due to interaction between metal ions and ligands were highly thermally stable and have numerous applications in various fields. Although a good amount of work has been reported in literature on solid complexes of first transition series metal ions with organic ligands containing Nitrogen, Oxygen, and Sulphur atoms as donors no much work has been done on solid complexes of these metals with ligands containing carboxymethyl cellulose.

2. Experimental Procedures

2.1. Materials Used. All the chemicals used as starting materials in the synthesis of ligand and its Metallic Gel complexes were of extra pure quality: Sodium carboxymethyl cellulose (E. Merck, Germany); Oxalic acid (E. Merck, Germany); Manganous acetate, Cobaltous acetate, Nickel acetate (E. Merck, Germany); Cuprous acetate and Zinc acetate (S. D. Fine Chem., India).

2.2. Instruments. Microanalysis of C, H, and N was carried out on Eassuperuser Elemental Analyser System GmbH, Access: VarioEL Superuser, NEERI. Infrared spectra in the region $4000\text{--}400\text{ cm}^{-1}$ were recorded in the solid state (KBr Pellets) in Pharmacy Department, RTMNU, Nagpur, using FTIR-101A SHIMADZU. The kinetics of thermal decomposition were investigated by using nonisothermal manual thermal analyzer at Department of Chemistry, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur. The heating rate employed was $10^\circ\text{C}/\text{min}$ and the mass loss was recorded continuously. Magnetic susceptibility of Metallic Gel complexes was determined by Gouy's method at room temperature using mercury tetrathiocyanatocobaltate(II) as standard.

2.3. Synthesis of Oxaloyl Carboxymethyl Cellulose (OCMC) Ligand. The ligand was synthesized by triturating the mixture of 10 g of finely powdered Na salt of CMC (low viscosity) and 30 mL of glycerol with mortar and pestle. The triturated mixture is added in small amounts into the vertex of 0.2 M aqueous Oxalic acid solution and stirred electrically until a clear gel was obtained. The synthesized ligand was stored in an airtight wide mouth bottle. The chemical reaction

for synthesis of Oxaloyl Carboxymethyl Cellulose ligand is shown in Figure 1.

2.4. Synthesis of Metallic Gel Complexes. The Metallic Gel complexes in the present work have been synthesized by refluxing 10 g of OCMC ligand and 100 mL of 0.2 M aqueous metal acetate at 100°C in an oil bath for 2 hrs. The Metallic Gel complexes obtained were then cooled, filtered and washed with hot water to remove any unreacted metal acetate and ligand.

3. Results and Discussions

3.1. Composition of the Metallic Gel Complexes. The composition of the Metallic Gel Complexes was assigned on the basis of elemental analysis. The presence of water of crystallization as well as water of coordination was ascertained on the basis of thermal studies. The composition of Metallic Gel complexes was found to be $[M(\text{II})L]_n$ and $[M'(\text{II})L \cdot 2\text{H}_2\text{O}]_n$, where $M = \text{Ni}(\text{II}), \text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$ and $M' = \text{Mn}(\text{II})$, and $\text{Co}(\text{II})$ and $L = \text{OCMC}$ ligand. The elemental analysis of OCMC has been reported in Table 1.

3.2. Infrared Spectral Studies. The IR spectral data for OCMC and its Metallic Gel complexes with Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) has been tabulated in Table 2. Characteristic peak of functional groups was observed in the IR spectra of OCMC: $-\text{OH}$ group at 3450 cm^{-1} , $-\text{CH}$ group at 2920 cm^{-1} , $\text{C}=\text{O}$ group of nonconjugated ketones, carbonyls and in ester groups at 1718 cm^{-1} [20, 21], and $-\text{COOH}$ group at 1650 cm^{-1} .

The IR spectra of complexes show few new weak absorption bands in the range of 600 to 660 cm^{-1} which may be assigned to the $M\text{--O}$ (Metal-Oxygen) bonds [22]. The weak band observed around 780 cm^{-1} may be assigned to coordinated water molecule. The infrared spectral assignments of ligand and Metallic Gel complexes have been tabulated in Table 2.

3.3. Magnetic Moment and Electronic Spectral Studies of OCMC Metallic Gel Complexes. The magnetic moment values of OCMC Metallic Gel complexes have been given in Table 3. These magnetic moment values supported the octahedral geometry for Mn(II) and Co(II) Metallic Gel complexes, the tetrahedral geometry for Ni(II), and square planar geometry for Cu(II) gel complexes.

Divalent manganese forms octahedral, tetrahedral, square planar or low symmetry compounds, but generally manganese gel complexes are either octahedral or tetrahedral. Bivalent manganese is known to form both high spin ($S = 5/2$) and low spin ($S = 1/2$) complexes. Octahedral as well as tetrahedral Mn(II) complexes show magnetic moment close to the spin only value, that is, 5.92 B.M., which is independent of temperature. However Venkateshwar Rao and Venkata Narasaiah, prepared Mn(II) complexes having magnetic moment 5.52 B.M., which is low as compared to spin only value for high spin Mn(II)

TABLE 1: Elemental analysis of oxaloyl carboxymethyl cellulose (OCMC) and its Metallic Gel complexes.

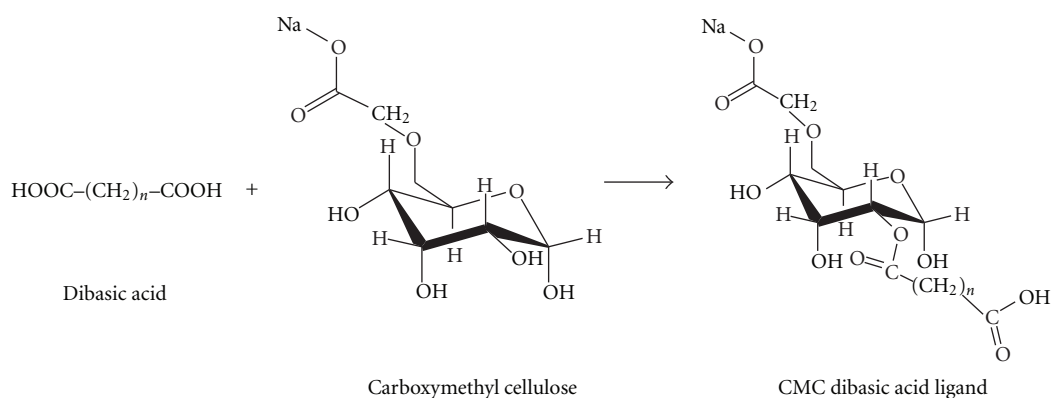
Proposed composition	Elemental analysis					
	Theoretical (%)			Experimental (%)		
	%C	%H	%M	%C	%H	%M
$[\text{Mn(II)(OCMC)(H}_2\text{O)}_2]_n$	31.41	3.92	14.38	31.50	3.90	14.29
$[\text{Co(II)(OCMC)(H}_2\text{O)}_2]_n$	31.09	3.88	15.26	31.63	3.80	15.11
$[\text{Ni(II)(OCMC)}]_n$	34.31	3.14	16.78	34.64	3.71	16.54
$[\text{Cu(II)(OCMC)}]_n$	33.84	3.10	17.92	34.12	3.00	17.26
$[\text{Zn(II)(OCMC)}]_n$	33.67	3.08	18.34	33.39	3.80	18.09

TABLE 2: IR spectral assignments of OCMC ligand and its Metallic Gel complexes.

Assignment	OCMC	Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)
O-H	3450	3450	3450	3450	3450	3450
C-H	2920	2920	2920	2876	2920	2924
C=O	1718	1718	1720	1720	1718	1718
COOH	1650	1650	1650	1650	1650	1650
COO ⁻	1460	1450	1450	1460	1458	1458
C-O-	1041	1024	1030	1040	1057	1030
H-O-H	—	780	781	—	—	—
Coordinated	—	660	650	660	600	620
M-O	—	660	650	660	600	620

TABLE 3: Magnetic moment data of OCMC Metallic Gel complexes.

Gel complexes	Gram susceptibility $\chi_g \times 10^{-6}$ (CGS Unit)	Atomic susceptibility $\chi_A \times 10^{-3}$ (CGS Unit)	Corrected atomic susceptibility $\chi_A \times 10^{-3}$ (CGS Unit)	Effective magnetic moment B.M.	Stereo chemistry
Mn-OCMC	39.36	15.03	15.12	5.95	Octahedral
Co-OCMC	28.93	11.16	11.25	5.13	Octahedral
Ni-OCMC	21.85	7.64	7.72	4.25	Tetrahedral
Cu-OCMC	4.42	1.57	1.65	1.97	Square planar

FIGURE 1: Synthesis of oxaloyl CMC Ligand. $n = 0$ for Oxalic acid.

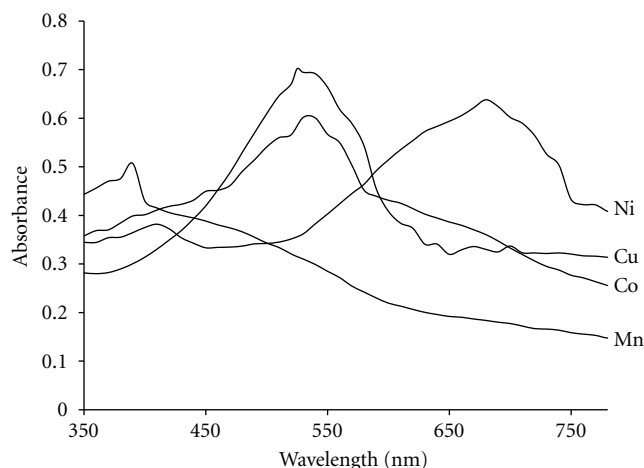


FIGURE 2: Electronic spectra of OCMC Metallic Gel complexes.

complexes. This can be attributed to the spin exchange in the solid state [23].

The theory of paramagnetic susceptibility of Co(II) was originally given by Schlapp and Penny [24]. The magnetic properties of high spin octahedral Co(II) complexes are governed by the orbitally degenerate ground term $^4T_{1g}$. This provides an orbital contribution to the magnetic moment so that at room temperature magnetic moment values are found to be in the range of 4.7–5.9 B.M.

In a tetrahedral ligand field, Ni(II), has an orbitally degenerate 3T_1 term which will give rise to a relatively large orbital contribution to the magnetic moment, which is temperature dependent. In a regular tetrahedral stereochemistry magnetic moment is around 3.5–4.5 B.M.

Since $[\text{Zn(II)(OCMC)}]_n$ is a d^{10} system and hence was diamagnetic in nature, though, on the basis of elemental analysis, infrared spectra, and thermal decomposition data, its most probable geometry was suggested to be tetrahedral.

Electronic spectral properties include the electronic transitions which take place between the ground levels of coordination clusters and the excited levels. The spectra of the coordination compounds may be classified into ligand field bands and charge transfer bands. The ligand field bands are essentially concerned with the transition between different d-orbitals which results from the application of the ligand field. On the basis of spectral assignments made by the workers as described in the literature and especially calculations made by Tanabe and Sugano [25] the electronic spectra of the Metallic Gel complexes can be suitably discussed [26]. Electronic spectral assignments of OCMC Metallic Gel complexes have been reported in Table 4. The electronic spectra of OCMC metallic gel complexes are shown in Figure 2.

3.4. Thermogravimetric Analysis of OCMC Metallic Gel Complexes. In the present study, thermogravimetric analysis of the Metallic Gel complexes of OCMC has been reported. No sharp weight loss was observed in any thermogram of these Metallic Gel complexes, which indicates their polymeric

complex nature. The thermogram for OCMC gel complexes has been shown in Figure 3.

TG curve of Mn(II)(OCMC) gel complex shows no mass loss up to 140°C due to the absence of water of crystallization. It shows mass loss of 9.5% between 140°C and 200°C due to the loss of two coordinated water molecules. After 240°C it shows a gradual decrease in mass up to 700°C, which may be due to the decomposition of the ligand attached to the metal ion; hereafter no further mass loss was observed, indicating the formation of stable metal oxide. The decomposition temperature was found to be 400°C.

The Co(II)(OCMC) gel complex also shows absence of water of crystallization since no mass loss was observed up to 140°C. It shows mass loss of 9.3% between 160°C and 230°C due to the removal of two coordinated water molecules and then after 260°C gradual loss in mass was observed up to 600°C which may be due to the decomposition of the organic species attached to the metal ion; hereafter no further mass loss was observed due to the formation of stable metal oxide. The decomposition temperature was found to be 380°C.

In TG curve of Ni(II)(OCMC) gel complex, no mass loss was observed up to 200°C. It then shows a gradual loss of mass up to 660°C, which may be due to decomposition of the ligand attached to the metal ion; hereafter no further mass loss was observed, due to the formation of stable metal oxide.

The Cu(II)(OCMC) gel complex was stable up to 230°C, since no weight loss was observed in thermogram up to 230°C. After 230°C, loss in weight was observed up to 640°C, which may be due to loss of organic species attached to the metal ion. After 640°C no mass loss was observed, which may be due to the formation of stable metal oxide. The decomposition temperature was found to be 410°C.

The Zn(II)(OCMC) gel complex was stable up to 220°C, due to absence of lattice and/or coordinated water. After 220°C gradual loss in mass was observed up to 640°C which may be due to the decomposition of the ligand attached to the metal ion. After 640°C, no further mass loss was observed, indicating the formation of stable species. The decomposition temperature was found to be 380°C.

The thermoanalytical data of these Metallic Gel complexes have been reported in Table 5.

4. Conclusions

On the basis of elemental analysis, infrared spectra, reflectance spectra, magnetic moment data, and thermal studies, the $[\text{Ni(II)(OCMC)}]_n$ and $[\text{Zn(II)(OCMC)}]_n$ metallic gel complexes have tetrahedral geometry, whereas $[\text{Mn(II)(OCMC)(H}_2\text{O)}_2]_n$ and $[\text{Co(II)(OCMC)(H}_2\text{O)}_2]_n$ metallic gel complexes were octahedral in nature; however, $[\text{Cu(II)(OCMC)}]_n$ metallic gel complex has square planar geometry. On the basis of thermal degradation studies, $[\text{Cu(II)(OCMC)}]_n$ has been found to be highly thermally stable than the rest of the complexes reported in this paper.

All these metallic gel complexes have high thermal stability more than 360°C and get decompose without melt. Hence, they may be used as temperature-resistant coating

TABLE 4: Electronic spectral assignments of OCMC Metallic Gel complexes.

Gel complexes	kK	Assignments	Stereochemistry
Mn-OCMC	25.64	${}^6A_{1g} \longrightarrow {}^4E_{(g)} (D)$	Octahedral
Co-OCMC	18.86	${}^4A_{1g} \longrightarrow {}^4T_{1(g)} (P)$	Octahedral
Ni-OCMC	14.70	${}^3T_1 \longrightarrow {}^3T_1 (P)$	Tetrahedral
Cu-OCMC	19.04	C.T.	Square planar

TABLE 5: Thermoanalytical data of OCMC Metallic Gel complexes.

Gel complex	% Loss due to coordinated water	% Loss due to decomposition	Decomposition temperature range ($^{\circ}\text{C}$)	Decomposition temperature ($^{\circ}\text{C}$)	Rate of heating ($^{\circ}\text{C}/\text{min}$)
$[\text{Mn(II)(OCMC)(H}_2\text{O)}_2]_n$	9.51	79	240–700	400	10
$[\text{Co(II)(OCMC)(H}_2\text{O)}_2]_n$	9.38	80	260–600	380	10
$[\text{Ni(II)(OCMC)}]_n$	—	78	200–660	360	10
$[\text{Cu(II)(OCMC)}]_n$	—	77	230–640	410	10
$[\text{Zn(II)(OCMC)}]_n$	—	77	220–640	380	10

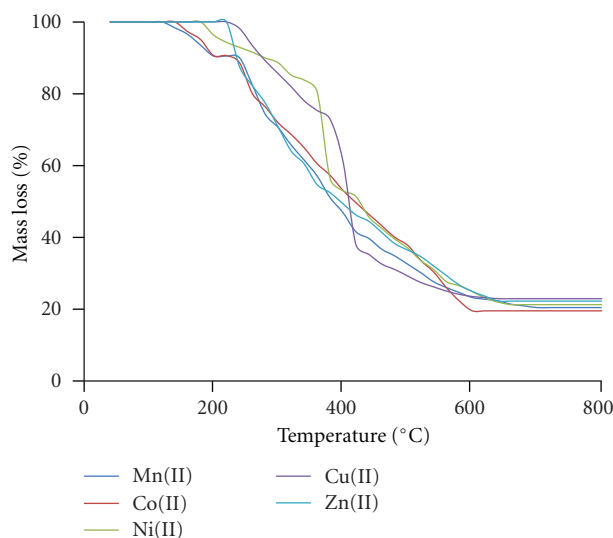


FIGURE 3: Thermogram of OCMC-M Metallic Gel complexes.

materials especially for plastic materials, electric wires, and so forth.

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