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A Review on Photosubstituted Metal Complexes of Transition Elements

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ABSTRACT

Literature survey reveals that innumerable photosubstituted metal complexes of iron, cobalt, chromium, molybdenum and tungsten were synthesized by irradiating an aqueous solution of metal complex using UV-visible photolamps followed by ligand substitution in secondary process of photochemical reaction. Ligands like ethylenediamine, diethylenetriamine, hexamine, pyrazine, pyridine, ethanolmine and imidazole were seen in the reported photosubstituted metal complexes. The insertion of such ligands in the metal complexes was confirmed from elemental analysis, UV-visible spectra, FTIR and thermogravimetric analysis. Thermogravimetric analysis revealed a good thermal stability of metal complexes. Now-a-days these photosubstituted metal complexes have been proved as potential fillers in the composite and nano-composite formation of conducting polymers of polyaniline, polypyrrole and polythiophene. These synthesized metal complex based composites were found to have wonderful thermal, electrical, magnetic and sensor applications.

Keywords: Iron, Metal complex, Photoirradiation, Thermogravimetric analysis

I INTRODUCTION

In the last few decades, photosubstituted metal complexes remain the main foci of chemists and researchers owing to their wonderful chemistry and applications. The aim of their synthesis was to augment the properties of metal complexes. In the reported photosubstituted metal complexes, most of the ligands incorporated were organic. The intention of photosubstituted metal complex synthesis was to produce a hybrid of organic-inorganic system. Due to synergic interaction of organic, inorganic components, the product formed was found to have better properties and applications in the thermal, electrical and magnetic fields.

There are innumerable photosubstituted metal complexes that contain both inorganic and organic parts synthesized via photochemical routes. Selection of organic ligands is based on the structure and properties. Incorporation of selected ligands like ethylenediamine, diethylenetriamine, hexamine, pyrazine, pyridine and imidazole have produced a desired results in the metal complexes of iron, cobalt, chromium, molybdenum and tungsten [1-3].

In the recent past, photosubstituted metal complexes were proved as potential fillers in the composite formation of conducting polymers of polyaniline, polypyrrole and polythiophene. They have augmented various properties of basic matrix of polymers like thermal stability, electrical conductivity, adsorption capacity, sensor ability etc [4-10]. The aim of this review is to highlight the importance of photosubstituted metal complexes and to explore them more and more in the advancement of science and technology.

II RESULTS AND DISCUSSION

2.1 UV-visible spectral characterization

The photoaquation of $K_4[Fe(CN)_6]$, $[Co(NH_3)_6]Cl_3$, $[Cr(NH_3)_6]Cl_3$, $K_4[Mo(CN)_8]$ and $K_4[W(CN)_8]$ are confirmed by recording UV spectra before and after irradiation. Irradiation of aqueous solution of metal cyanides and amines leads to the formation of the primary photoadduct where a CN^- ion or ammonia moiety is replaced by OH^-, which undergoes subsequent thermal substitution by entering ligand (monoethanolamine or pyridine or EDTA etc). The scheme of photosubstitution of CN ligand from $K_4[Fe(CN)_6]$ with monoethanolamine (MEOA) ligand
is shown below:

$$[Fe(CN)_6]^{4-}\ (aqu.) \xrightarrow{h\upsilon} [Fe(CN)_4(OH)_2]^{4-}$$

$$[Fe(CN)_4(OH)_2]^{4-} + MEOA \rightarrow [Fe(CN)_3(MEOA)(OH)]^{2-} + OH^-$$

The electronic absorption spectra of $K_4[Fe(CN)_6]$ shown in Fig.1. shows a characteristic peak at 325 nm, assigned as metal to ligand charge transfer transition. On exposure the solution turns red and then green and on prolonged exposure it turns blue with absorption maximum at 590 nm, which is assigned as d-d transition. The unexposed solution of $K_4[Fe(CN)_6]$ shows a d-d transition at 605 nm. On irradiation the d-d band shows a shift of about 15 nm towards higher frequency which justifies the photoaquation reaction and availability of aqua ligands for further substitution.

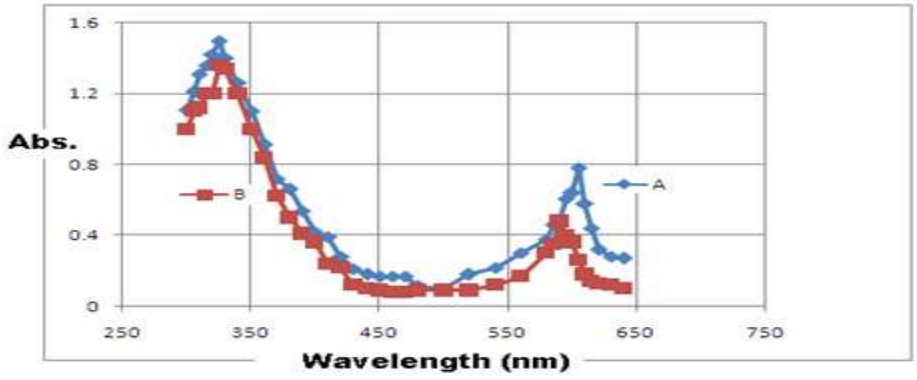

Figure 1: The UV-VIS spectrum of $K_4[Fe(CN)_6]$ (A) before and (B) after irradiation.

2.2. FTIR Characterization

Fourier transform infrared spectroscopy (FTIR) is a technique used to determine different moieties present in the complex. The insertion of organic ligands in the metal complex is confirmed from the FTIR spectra. Figure 2 shows the FTIR of (a) $K_4[Fe(CN)_6]$ and (b) $K_2[Fe(CN)_3(MEOA)(OH)]$. FTIR of photosubstituted metal complex $K_2[Fe(CN)_3(MEOA)(OH)]$ confirms the presence of monoethanolamine ligand, thus supporting the successful photosubstitution of ligands.

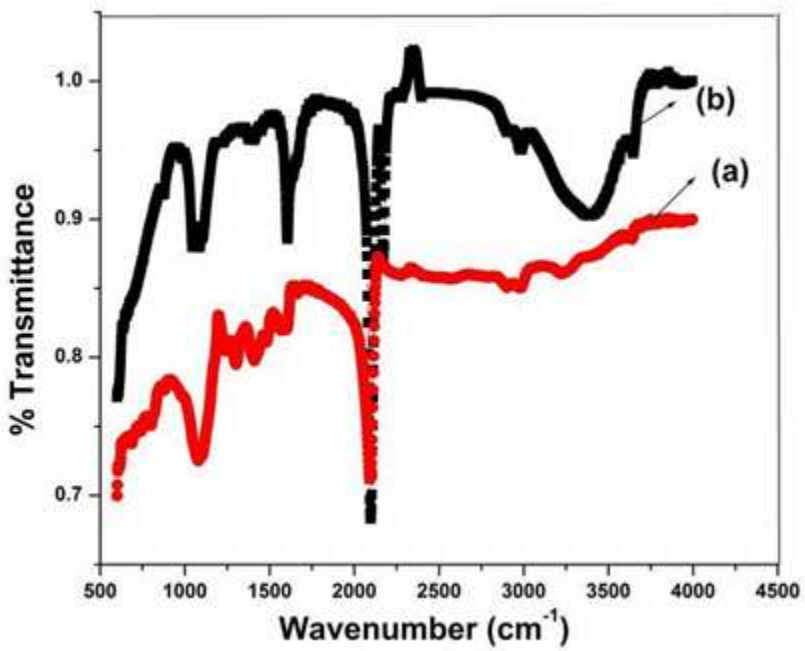

Figure 2: FTIR of (a) (a) $K_4[Fe(CN)_6]$ and (b) $K_2[Fe(CN)_3(MEOA)(OH)]$.

2.3. Thermogravimetric Analysis

Thermogravimetric analysis is a technique used to determine the thermal stability of the materials. Figure 3 (a) shows the thermal degradation of photosubstituted metal complex of cobalt with organic ligand hexamine. It is clear from the graph that even 900°C, cobalt complexehad not decomposed completely indicating its good thermal stability. Pure polyaniline shows thermal decomposition at 600°C. Polyaniline-metal complex composite shows thermal stability beyond 900°C as shown in Fig. 3(b). This proved that the complex after doped into polyaniline matrix has improved its stability to a large extent.

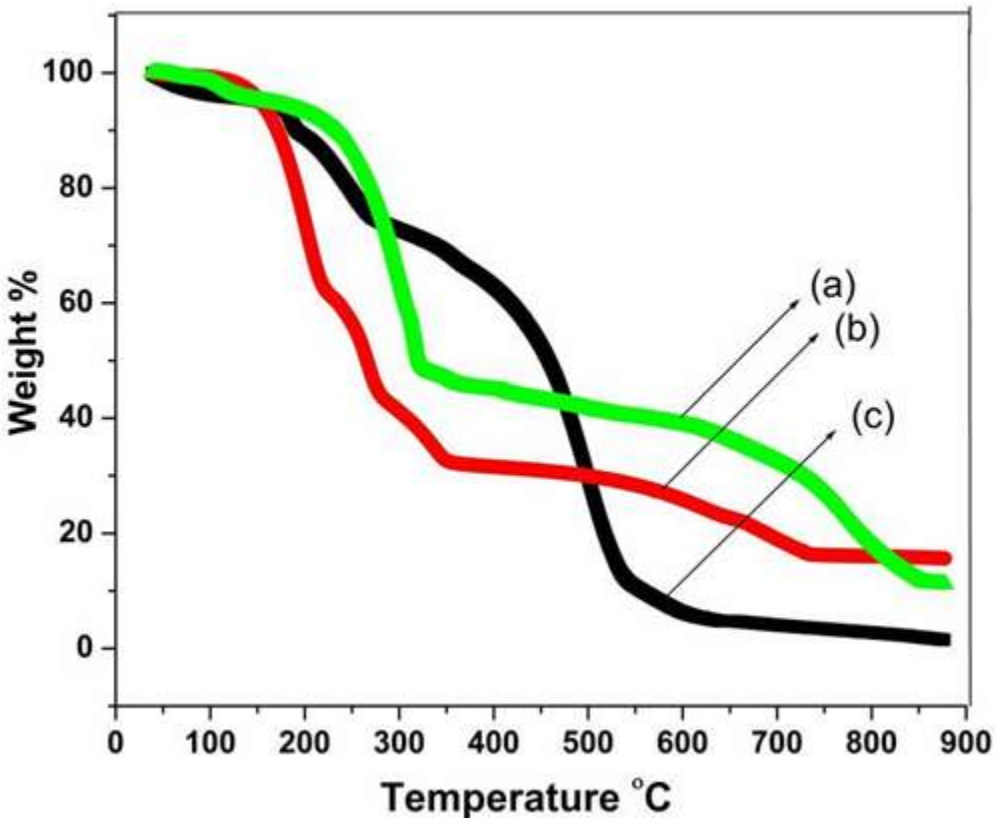

Figure 3: Thermogams of (a) $[Co(NH_3)_6]Cl_3$ with ligand hexamine, (b) Polyaniline-metal complex composite and (c) pure Polyaniline

III CONCLUSION

All metal complexes are not photochemically active. Among the metal complexes, Fe(II), W(IV), Cr(III), Co(III) and Mo(IV) have shown photochemical reactivity. Ligands with planar structure and π- conjugation network have been incorporated in the metal complexes during photochemical irradiation. Most reported photosubstituted metal complexes are water soluble that hinders them for further extensive investigation. Their latest application was seen them as potential fillers in the conducting polymers of polyaniline, polypyrrole and polythiophene for composite formation in the material sciences.

REFERENCES

1) K. Majid, S. I. Ali, Photoreactivity of ethanolamine with octacyanomolybdate(IV) and octacyanotungstate(IV), Transition Metal Chemistry 22(1), 1997, 53-57.

2) K. Majid, S. I. Ali, Photoreactivity of diethanolamine with octacyanomolybdate(IV) and -tungstate(IV), International Journal of Chemical Kinetics 29(11), 1997, 819-824.

3) K. Majid, F. A. Rafiqi, M. S. Rather, Photosubstituted synthesis, Characterization and thermal kinetics of potassium hexacyanoferrate with monoethanolamine, Chemical Physics, 36, 2011, 3245-3247.

4) W. Naqash, K. Majid, Synthesis and characterization of a high dielectric constant and ac-conducting PANI/$[Co(NH_3)_3(C_4H_4N_2)_3]Cl_3$ nanocomposite, Journal of Materials Science Materials in Electronics, September 2017, DOI: 10.1007/s10854-017-7778-5.

5) S. K. Moosvi, K. Majid, Spectroscopic, morphological, thermal and dielectrical analysis of composite of polythiophene with photoactive transition metal complex of W(IV), Bulletin of Materials Science 40(6), 2017, 1-8

6) S. K. Moosvi, K. Majid, T. Ara, Study of Thermal, Electrical, and Photocatalytic Activity of Iron Complex Doped Polypyrrole and Polythiophene Nanocomposites, Industrial & Engineering Chemistry Research 56(15), 2017. DOI: 10.1021/acs.iecr.7b00167

7) W. Naqash, K. Majid, Structural, optical, electrical, and thermal properties of PANI/$[Co(NH_3)_2(C_2H_8N_2)_2]Cl_3$ nanocomposite, Chemical Papers- Slovak Academy of Sciences · December 2016 . DOI: 10.1007/s11696-016-0093-4.

8) S. K. Moosvi, K. Majid, T. Ara, Synthesis and characterization of PTP/[Fe(CN)3(dien)].H2O nanocomposite; study of electrical, thermal and photocatalytic properties, April 2016 DOI: 10.1016/j.chemphys.2016.04.012.

9) M. H. Najar, K. Majid, M. A. Dar, Electric modulus based relaxation dynamics, ac-conductivity and I–V characteristics in PTh/[Co(EDTA)NH3Cl] H2O nanocomposite prepared by chemical oxidation method, Journal of Materials Science Materials in Electronics, 2017, DOI 10.1007/s10854-017-6913-7.

10) M. H. Najar, K. Majid, Synthesis and characterization of nanocomposite of polythiophene with $Na_2[Fe(CN)_3(OH)(NO)C_6H_{12}N_4]$ H_2O: a potent material for EMI shielding applications, 26, 2015, 6458–6470.