

Physico-Chemical and Catalytic Studies on Complexation Behaviour of Polystyrene-1,10-phenanthroline-5,6-bis-4',5-dihydroxyimino-7-methoxy Isoflavone with Some Transition Metals

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A novel polymeric ligand (PS-PDMI) has been synthesized from the reaction of 5,6-diamino-1,10-phenanthroline with 4',5-dihydroxy-7-methoxy isoflavone and then polymerized with chloromethylated polystyrene unit. Metal complexes of 3d (VO^{2+} , Cr^{3+}), 4d (Mo^{6+} , Ru^{3+} , Rh^{4+}) and 5d (Os^{3+} , Ir^{4+}) series were prepared and characterized by elemental, spectroscopic, conductance and magnetic techniques. Coordination was found to be through the nitrogen (C=N), oxygen (O-H) and oxygen (lactone) in an octahedral environment. Ru(III)-chelate was found to be an effective catalyst for the oxidation of benzyl alcohol and cyclohexanol to benzaldehyde and cyclohexanone, respectively in the presence of co-oxidant N-methyl morpholine-N-oxide (NMO). Protonation constants of the ligand and the overall formation constants of the complexes have also been calculated from potentiometric data using the program TITFIT.

Key Words: Synthesis, Substituted isoflavone, Polystyrene anchored metal complexes, Catalytic activity.

INTRODUCTION

1,10-Phenanthroline (Phen) has been extensively used as a ligand in both analytical and preparative coordination chemistry. Systematic studies of substituted derivatives of phen and other α -diamines have been successfully undertaken¹. The photochemical and redox properties of complexes can be varied systematically through appropriate substitution on the phenanthroline rings²⁻⁴.

In literature, the synthesis of substituted amino, halogeno and oxo compounds and their derivatives including metal chelates have been a subject of study for a long period of time⁵⁻⁷ as analytical reagents and models for biological systems⁸⁻¹⁰.

The present paper describes the synthesis and characterization of coordination compounds of 3d (VO^{2+} , Cr^{3+}), 4d (Mo^{6+} , Ru^{3+} , Rh^{4+}) and 5d (Os^{3+} , Ir^{4+}) series metal ion with the polystyrene-anchored 1,10-phenanthroline-5,6-bis-4',5-dihydroxyimino-7-methoxy isoflavone (PS-PDMI).

EXPERIMENTAL

Double distilled water was used throughout the potentiometric experiments which were carried out under an atmosphere of nitrogen. All the chemicals employed were of the highest grade available. The ionic medium was 0.1 M NaClO₄ at the beginning of each potentiometric titration. A combined glass electrode was used for the potentiometric titrations using a thermostated titration vessel (100 mL) and the system was calibrated using buffer solutions of pH 4.0 and 7.0. Metal ion solutions (chlorides) were prepared and standardized by conventional methods¹¹.

The IR spectra (KBr discs) were recorded (4000-400 cm⁻¹ range) on a Beckman IR-12 spectrophotometer and ¹H NMR (DMSO) were obtained from a Bruker spectrospro 250 MHz. Melting points were determined using a Stuart scientific melting point apparatus. Magnetic susceptibility measurements were carried on Sherwood scientific magnetic balance. Conductance data were recorded on a digital NDC-732, systronics in dimethyl sulphoxide solution.

Synthesis of 1,10-phenanthrolino-5,6-bis-4,5-dihydroxyimino-7-methoxy isoflavone (PDMI): To solution of 5,6-diamino-1,10-phenanthroline (0.315 g, 1.5 mmol) in 100 mL of absolute alcohol was added solid NaHCO₃ (0.336 g, 4.0 mmol) and stirred for 10 min. Thereafter, 4',5'-dihydroxy-7-methoxy isoflavone (0.409 g, 3.0 mmol) in 10 mL of absolute alcohol was added dropwise to the above mixture during 1 h and then was stirred for 1.5 h at 65 °C. The hot solution which contained NaCl was filtered, washed with absolute alcohol (20 mL) until the filtrate became colourless. The combined ethanol filtrates were evaporated to one-third of their volume and petroleum ether (10 mL) was added at room temperature and a yellow precipitate was obtained. It was filtered and washed with diethyl ether. Yield (0.319 g) (52 %) m.p. > 380 °C. The product is slightly soluble in ethanol, methanol, chloroform and DMSO.

Synthesis of polystyrene-anchored PDMI (PS-PDMI): Chromomethylated polystyrene (1.0 g) is swelled in DMF (20 mL) in 45 mL and a DMF solution of PDMI (0.96 g, 20 mL) is added. Ethyl acetate (100 mL) and triethyl amine (1.5 g) are also added to the above mixture and is refluxed for 6-8 h. The solution is then allowed to cool. Pale yellow coloured resin is separated and washed with DMF and ethyl acetate and finally dried (yield-50 %).

Synthesis of metal-chelates: The synthesized PS-PDMI (1 g) is suspended in DMF (20 mL) for 45 min. To this suspension, a DMF solution (30 mL) of appropriate metal chlorides is added and refluxed for 8 h. The reaction product is cooled and washed with DMF, acetone and finally dried (yield-55 %).

Catalytic studies: To the solution of the benzyl alcohol (0.1 mL) in dichloromethane (10 mL), cooxidant N-methyl morpholine-N-oxide (NMO) (3 mmol) and the Ru-complex (2×10^{-2} mmol) was added. The mixture was refluxed for 3 h under vigorous stirring conditions in the presence of 4A molecular sieves. The solvent was evaporated and ether (5×5 mL) was used to extract the benzaldehyde.

To a solution of cyclohexanol (0.2 mL) in dichloromethane (15 mL), NMO (6 mmol) and the complex (4×10^{-2} mmol) was added. The mixture was refluxed for 3 h under vigorous stirring conditions. It was then concentrated and the cyclohexanone was separated by column chromatography (packed with silica gel) using hexane and ethyl acetate (3:2) as the eluent. The weight of the resulting ketone was then recorded.

RESULTS AND DISCUSSION

The synthesis of a new ligand and its reactions with metal ions of 3d (VO^{2+} , Cr^{3+}), 4d (Mo^{6+} , Ru^{3+} , Rh^{4+}) and 5d (Os^{3+} , Ir^{4+}) series of transition elements, leads to the formation of polymer anchored complexes with certain catalytic characteristics are reported.

Dissociation and formation constants: The calculated dissociation and formation constants using the TITFIT program¹² are depicted as: $\log k_1 = 9.50$, $\log \beta$; $\text{Cr(III)} = 4.60$, $\text{VO(II)} = 11.32$, $\text{Mo(VI)} = 13.81$, $\text{Ru(III)} = 15.6$, $\text{Rh(IV)} = 6.14$, $\text{Ir(IV)} = 7.08$, $\text{Os(III)} = 8.40$.

In the normal titration range, the proton from the OH group is released. Some general observation about the various metal systems-the complexation begins at pH = 3.5, at pH values 7-11 formation of MLH appears and the complete ML complex is formed around pH:8.

Spectral observations: IR spectrum indicate the presence of O-H stretching bands at 3412, 1280 and 1620 cm^{-1} for the lactone ring and C=N vibrations, respectively. In the spectra of the complexes, these bands were found to undergo shift (*ca.* 20 cm^{-1}), owing to their respective coordination to the metal ions¹³.

The polymer anchored ligand and its chelates show IR bands similar to the low molecular weight species, except for the very small shifts in spectral bands due to the presence of polymeric support. Bands due to $\nu(\text{CH}_2\text{-Cl})$ stretch at 1250 cm^{-1} (wagging) and 1440 cm^{-1} (scissoring) were observed, which was also seen in the metal complexes suggesting its non-participation. Another band at 1220 cm^{-1} $\nu(\text{C-O})$ was observed, but later in complexes disappeared, lends support for the covalent bond formation between oxygen and the polystyrene unit¹⁴.

¹H NMR spectrum of the ligand in DMSO confirmed the proposed structure of two exchangeable protons of 11.90 and 12.20 ppm for OH group. Aromatic protons at 6.0-8.5 ppm as multiplet and aliphatic C-H protons at 2.20 ppm as singlets were also observed.

The solubility of the metal complexes in organic solvents was insufficient to obtain ^1H NMR spectra, thus further investigations were not possible.

In the ESR spectrum for VO(II) and Cr(III), the g -factors are close to 2.0 and nearly isotropic. From the Table-1, $g_{\parallel} < g_{\perp}$ and $A_{\parallel} \gg A_{\perp}$, which is a characteristic for an axially compressed d_{xy} configuration^{15,16}. Mo(VI), Ru(III) and Rh(IV), being elements of second transition series with d^5 electrons reveal the corresponding octahedral behaviour¹⁷.

TABLE-1
ESR PARAMETERS

Ions	g_{\parallel}	g_{\perp}	$A_{\parallel} \times 10^{-4} \text{ cm}^{-1}$	$A_{\perp} \times 10^{-4} \text{ cm}^{-1}$
Cr(III)	1.90	1.91	63.00	–
VO(II)	1.93	1.95	187.51	76.79
MO(VI)	1.99	1.98	72.00	42.00
Ru(III)	2.18	2.16	137.00	–

In the case of Ir(IV) and Os(III), one most striking demonstration of electron delocalization into ligands is noticed. The molecular orbital interpretation visualizes pairing of the 5d-electrons into six electrons from the ligands, leaving an unpaired 'positive hole' which can interact with the Cl atoms ($\text{Na}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$) by overlap with a suitable combination of Cl 3p orbitals. Thus the hyperfine is well resolved¹⁷.

Conductivity data: The values of electrical conductivity (Ω) lies in the range of typical semiconductors¹⁸. A linear relationship is observed between logarithm of conductivity and reciprocal of absolute temperature, which shows the temperature dependence. The low and high temperature range exhibits the extrinsic and intrinsic behaviour of the semiconductors (Table-2).

TABLE-2
ELECTRICAL CONDUCTIVITY DATA

Ions	$\Omega \text{ cm}^{-1}$		Activation energy (ev)
	At 303 K	At 308 K	
Cr(III)	9.14×10^{-12}	6.57×10^{-10}	0.700
VO(II)	6.05×10^{-11}	4.47×10^{-10}	0.641
Mo(VI)	3.12×10^{-9}	2.01×10^{-10}	0.619
Ru(III)	1.15×10^{-9}	9.00×10^{-9}	0.315
Rh(IV)	1.58×10^{-9}	4.13×10^{-8}	0.713

Thermal analyses: TGA have also been carried out to evaluate the thermal stability. The curve for the complexes reveal first mass loss step from around 120-150 °C. The subsequent step shows mass loss upto 290 °C.

Almost 80 % mass loss occurs in both the steps. Corresponding oxides is presumed to be the end product. The compounds are stable as the first decomposition starts at 120 °C.

Magnetic measurements: The magnetic moments values (Table-3) are sufficiently low for Mo(VI), Ru(III), Rh(IV), Os(III) and Ir(IV) as compared to Cr(III) and VO(II). The reason is due to the complexes (4d, 5d) are invariably of the spin-paired type, because of larger 4d and 5d orbitals than 3d so that interelectronic repulsions, which tend to oppose spin pairing, are less.

TABLE-3
MAGNETIC MOMENT DATA AND SPIN-ORBIT COUPLING
CONSTANTS (cm⁻¹) FOR SPIN-PAIRED OCTAHEDRAL COMPLEXES

Ions	ζ	λ	μ_{eff}
Cr(III)	615	+87	3.80
VO(II)	410	+520	1.79
Mo(VI)	850	+450	1.83
Ru(III)	1250	-1250	2.00
Rh(IV)	1700	-1700	1.98
Os(III)	4000	-2000	2.10
Ir(IV)	5000	-5000	1.65

Another important reason for the low moments is that the spin orbit coupling constants are much higher for heavier atoms, which is again due to higher nuclear charge¹⁹.

Catalytic studies: Results for the catalytic oxidation by the ruthenium complex is given in Table-4 and was found to catalyze the oxidation of benzyl alcohol to benzaldehyde and cyclohexanol to cyclohexanone, but the yields and turn over vary with substrates. For the oxidation of alcohols to aldehyde or ketone, 65-95 % conversion was obtained. For these reactions refluxing was necessary to achieve high percentage yield (Table-4).

TABLE-4
CATALYTIC ACTIVITY OF Ru-CHELATE

Ion	No. of moles of complex	Substrate	Product	Yield*	Turn over**
Ru(III)	2.01×10^{-2}	Benzyl alcohol	Aldehyde	69.75	46.30
	4.00×10^{-2}	Cyclohexanol	Ketone	93.82	44.50

*Yield based on Substrate

**No. of moles of product/no. of moles of complex used.

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