Studies on Some Transition Metal Chelate Monomers

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Some metal chelates of monomers have been synthesized by the interaction of Ni(II), Cu(II), Cr(III) and Fe(III) acrylate with 2,2'-bipyridylamine in alcohol. All these metal chelate monomers are coloured, crystalline powders insoluble in many of the organic solvents. They are characterized by UV-visible spectra, infrared spectra, elemental analysis, thermogravimetric analysis and megnetic susceptibility measurements. All metal chelate monomers show a six coordinated structure and suggest octahedral geometry. Conductometric studies indicate that these metal chelate monomers are non-electrolytes.

INTRODUCTION

The progress in many fields of science and engineering is connected to macromolecular metal chelates, which are high molecular weight compounds that incorporate metal chelate cycles[1]. The major achievements in synthesis and investigation of macromolecular metal chelates have been summarized recently[2]. To date, the number of metal chelate monomer studied is extremely limited, mainly due to the difficulty of their synthesis[1]. The present communication deals with the synthesis and characterization of metal chelate monomers of Ni(II), Cu(II), Cr(III) and Fe(III). We have studied their elemental analysis, magnetic susceptibilities, infrared spectra, UV-visible spectra and thermogravimetric properties.

EXPERIMENTAL

All chemicals used were of analytical grade purity. Ni(II), Cu(II), Cr(III) and Fe(III) acrylates were prepared according to a procedure suggested as earlier[3].

Synthesis of metal chelate monomers: The complexes of metal acrylate with 2,2'-bipyridylamine were synthesized by dropwise addition of an alcoholic solution of 2,2'-bipyridylamine (0.012 M) to an alcoholic solution of metal acrylate (0.01 M) followed by stirring of reaction mixture for 2 h at 40°C. After solvent evaporation in vacuum the solid product was extracted in soxhlet by using ether to ensure complete removal of excess of 2,2'-bipyridylamine. The prepared complexes were recrystallized from ethanol and dried in vacuum at room temperature.

The complexes of Ni(II), Cu(II), Cr(III), Fe(III) are synthesized by the same method. All the complexes were dried and kept in vacuum desiccator.

All the physico-chemical measurements were made at 30°C. The carbon, hydrogen and nitrogen analyses of the complexes were carried out using a Coleman C H N analyzer. The metal content was determined by using titration method with a standard solution of disodium salt of EDTA solution after decomposing the complexes with a mixture of concentrated nitric acid, perchloric acid and sulphuric acid in 5 : 2 : 3 ratio respectively[4]. IR spectrum was recorded on a Perkin-Elmer 983 spectrophotometer as KBr pellets. The UV-visible reflectance spectra were measured on a Backman DK-2A spectrophotometer using MgO as a reference material. Conductance was measured on a Systronics μ-conductometer. Magnetic measurements are made at room temperature on a Sartorius semimicro Gouy balance using $Hg[Co(CNS)_4]$ as a calibrant.

RESULTS AND DISCUSSION

All the metal chelate monomers are bright coloured crystalline substances partly soluble in DMSO, water and alcohol; and insoluble in ether, benzene, chloroform and dioxane. The % yield, colour, melting point, elemental analysis and magnetic moment data are presented in Table-1. However, the low values of specific conductance indicated that all of the complexes were non-electrolytes. The elemental analysis of all these complexes indicates 1 : 1 : 2 stoichiometry for divalent metal ions.

Infrared Spectra: IR spectra show bands corresponding to 2,2′-bipyridyl-amine and metal chetale monomers and various bands are presented in Table-2. Bands were observed in far IR region. It is well known that various vibration modes of the resulting chelate rings undergo coupling. So normal interpretation of these bands is not possible without normal coordinate analysis. The broad band observed in the range of 4000 to 3300 cm^{-1} is attributed to —OH stretching (antisymmetric and symmetric) and bands at *ca.* 1630–1600 cm^{-1} also can be assigned for H—O—H stretching frequencies. Also there are variable bands *ca.* 920, 680, 630 cm^{-1} corresponding to $M—OH_2$ band[5]. This indicates the presence of water which is either lattice or coordinated water. There is a band corresponding to carboxylate ion at *ca.* 1510 cm^{-1}; however, this band remains independent of nature of metal ion, as it was in initial metal acrylate and absorption frequency of C=C band is lowered slightly[6]. The M—N stretching frequency in 2,2′-bipyridylamine complex is obtained at higher wave number due to the double bond character of M—N bond originated because of M—N π-interaction[7]. It is well established that M—N stretching frequency undergoes coupling with other stretching vibrations resulting in a number of bands[8].

Thermogravimetric Analysis: The thermograms of metal chelate monomers are compared with that of 2,2′-bipyridylamine. Decomposition of Ni(II) and Cu(II) chelate monomers starts above 175°C and for Cr(III) and Fe(III) chelate momomers starts above 125°C. Thermogravimetric analysis data is presented in Table-3. The water molecules are lost on heating the compounds up to 110°C indicating the presence of water of crystallization. It is certain that water

TABLE-1
ANALYTICAL DATA AND SOME PHYSICAL PROPERTIES OF METAL CHELATE MONOMERS

Compound (empirical formula)	m.w. (Colour)	m.p. (°C)	Yield (%)	Analysis (%), found (calculated)				μ_{eff} (B.M.)
				M	C	H	N	
$Ni(CH_2=CHCOO)_2 \cdot A \cdot 2H_2O$ ($NiC_{16}H_{19}N_3O_6$)	407.71 (Lilac)	195	65	14.10 (14.40)	46.93 (47.09)	4.59 (4.66)	10.38 (10.30)	3.11
$Cu(CH_2=CHCOO)_2 \cdot A \cdot 2H_2O$ ($CuC_{16}H_{19}N_3O_6$)	412.54 (Dark green)	175	70	14.97 (15.40)	46.12 (46.54)	4.12 (4.10)	10.72 (10.08)	1.87
$Cr(CH_2=CHCOO)_3 \cdot A \cdot H_2O$ ($CrC_{19}H_{20}N_3O_7$)	454.0 (Green)	140	72	11.15 (11.45)	50.18 (50.22)	4.97 (4.41)	9.08 (9.25)	4.45
$Fe(CH_2=CHCOO)_3 \cdot A \cdot H_2O$ ($FeC_{19}H_{20}N_3O_7$)	457.85 (Brown)	160	68	12.00 (12.20)	49.11 (49.79)	4.30 (4.37)	9.12 (9.17)	5.60

Where A = 2,2'-bipyridylamine

TABLE-2
INFRARED SPECTRA OF METAL CHELATE MONOMERS (V IN CM^{-1})

Compound	$\bar{\nu}$(O—H)	$\bar{\nu}$(N—H)	$\bar{\nu}$(C=C)	$\bar{\nu}$(C=N)	$\bar{\nu}$(C=N-C)	$\bar{\nu}$(C—C)	$\bar{\nu}$(COO$^-$)	$\bar{\nu}$(M—N)	$\bar{\nu}$(M—O)
A	—	3240 m	1620 s	1660 s	2020 w	1160 m 1020 w			
$Ni(CH_2=CHCOO)_2 \cdot A \cdot 2H_2O$	3400 b	3240 m	1620 s	1660 s	2020 w	1160 m 1020 w	1510 m 1480 m	780 m 630 s	480 m 410 s
$Cu(CH_2=CHCOO)_2 \cdot A \cdot 2H_2O$	3400 b	3240 m	1620 s	1670 s	2015 w	1160 m 1010 w	1500 m 1440 m	780 m 630 s	480 m 420 s
$Cr(CH_2=CHCOO)_3 \cdot A \cdot H_2O$	3400 b	3240 m	1620 s	1665 s	2020 w	1150 m 1100 w	1500 m 1440 m	780 m 630 s	490 m 415 s
$Fe(CH_2=CHCOO)_3 \cdot A \cdot H_2O$	3400 b	3240 m	1620 s	1660 s	2020 w	1160 m 1000 w	1510 m 1430 m	780 m 620 s	495 m 410 s

A = 2,2'-bipyridylamine

eliminated below 150°C can be considered as water of crystallization and water eliminated above 150°C may be due to its coordination of the metal[9]

TABLE-3

THERMAL DATA OF PRIMARY LIGAND AND ITS METAL CHELATE MONOMERS

Compound	% weight loss at temperature (°C)										
	100	150	200	250	300	350	400	450	500	550	600
A	3.0	15.0	88.0	92.0	92.0	93.0	95.0	95.0	95.0	95.0	95.0
$Ni(CH_2=CHCOO)_2 \cdot A \cdot 2H_2O$	4.0	7.0	12.0	33.0	40.0	51.0	76.0	88.0	88.0	88.0	88.0
$Cu(CH_2=CHCOO)_2 \cdot A \cdot 2H_2O$	4.0	8.0	25.0	50.0	59.0	63.0	65.0	66.0	70.0	83.0	83.0
$Cr(CH_3=CHCOO)_3 \cdot A \cdot H_2O$	5.0	13.0	55.0	63.0	66.0	72.0	77.0	80.0	81.0	82.0	82.0
$Fe(CH_3=CHCOO)_3 \cdot A \cdot H_2O$	4.0	7.0	27.0	36.0	45.0	52.0	68.0	79.0	82.0	82.0	82.0

where A = 2,2′-bipyridylamine

Magnetic moment and electronic spectra study: The electronic spectral parameters are presented in Table-4 and Racah parameters are calculated by equations[10]. The electronic spectrum of Ni(II) chelate monomer shows three bands which are assigned as $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}$, $^3A_{2g} \rightarrow {}^3T_{1g}(p)$ transitions. The observed values of magnetic moment (3.11 B.M.) and v_2/v_1 ratio suggest for the high spin octahedral geometry for the Ni(II) chelate monomer[11]. The magnetic moment value (1.87 B.M.) and a shoulder band at 26171 cm^{-1} is attributed to $^2E_g \rightarrow {}^2T_{2g}$, transition, *i.e.*, 10 Dq as predicted by Orgel diagram for $3d^9$ system of Cu(II), exhibits distorted octahedral geometry as suggested earlier[12]. In Cr(III) chelate monomer, only two bands are observed at 14594 cm^{-1} and 24739 cm^{-1} asigned as v_1 and v_2. The transitions from $^4T_{1g}$ are weaker than the other d-d transitions; so third band has very poor resolution. The magnetic moment value (4.45 B.M.) and v_1/v_2 ratio gives indication of octahedral geometry[13]. The three bands at 14438 cm^{-1} (v_1), 16492 cm^{-1} (v_2) and 25678 cm^{-1} (v_3) are corresponding to $^6A_{1g} \rightarrow {}^4T_{1g}$, $^6A_{1g} \rightarrow {}^4T_{2g}$ and $^6A_{1g} \rightarrow {}^4A_{1g}(P)$ transitions in Fe(III) chelate monomer[14]. The higher values of nephelauxetic parameter indicate the covalent character for various metal chelate monomers.

TABLE-4

PARAMETERS OF THE ELECTRONIC SPECTRA OF
THE METAL CHELATE MONOMERS

Compound	d-d transitions (cm^{-1})		Dq (cm^{-1})	B′ (cm^{-1})	β (β′/B)	β$_0$ (%)
	v_2	v_3				
$Ni(CH_2=CHCOO)_2 \cdot A \cdot 2H_2O$	7640	25044	1015.5	875.2	0.82	18
$Cu(CH_2=CHCOO)_2 \cdot A \cdot 2H_2O$	—	26177	—	—	—	—
$Cr(CH_2=CHCOO)_3 \cdot A \cdot H_2O$	24739	28994	1459.4	663.4	0.72	28
$Fe(CH_2=CHCOO)_3 \cdot A \cdot H_2O$	16492	25678	1443.8	671.5	0.64	36

where A = bipyridylamine

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