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Physico-chemical Studies and Thermodynamics of Some Transition Metal Complexes with 2-*cis*-3,7-Dimethyl 2,6-Octadiene-1-al

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Acyclic monoterpenoids form complexes with many transition metals. 2-*cis*-3,7-dimethyl 2,6-octadiene-1-al (citral) forms complexes with Fe(III), Co(II) and Ni(II). Stereochemistry of the complexes has been studied by physico-chemical methods.

INTRODUCTION

Citrals and their metal complexes have been the subject of intensive research due to their structural features, interesting spectral and magnetic properties and their industrial and biological importance. The complexes of Fe(III) with citral have been reported[1]. The optimum condition required for the complete formation of a complex may be predicted on the basis of its stability constants in solution and their thermodynamics has been carried out by conductometric, pH-metric, spectrophotometric studies, elemental analysis, infrared spectral measurements and magnetic susceptibility measurements[2].

EXPERIMENTAL

All other chemicals and solvents were of AR grade. All the conductometric titrations were performed by using Toshniwal conductivity bridge type CL.01/02A and a dip type cell having 0.804 cell constant.

A Philips pH-meter, model pH-9404, was employed for pH measurements. A special glass electrode (0–14 pH range) was used in conjunction with a saturated calomel electrode. The pH-meter was standardized against buffer solutions prepared from standard buffer tablets.

Spectroscopic studies for coloured complexes were carried out on Bausch and Lomb's spectronic-20 spectrophotometer with glass cuvette of 1 cm thickness. The infrared spectra were recorded on Perkin-Elmer infrared spectrophotometer by KBr technique and elemental analysis on Perkin-Elmer spectrophotometer. Magnetic measurements were however recorded on Gouy balance using $Co[Hg(SCN)_4]$ as calibrant.

Citral, the ligand for our purpose, procured from M/s H. Kelkar Co., Kerala, was purified by column chromatography and its purity was further checked on TLC plates.

Preparation of Stock Solutions and Complexes

(I) **Citral Solutions:** A 0.1 M stock solution of citral (pure b.p. 228°C) was prepared by dissolving the weighed amount of it in absolute ethyl alcohol (w/v).

(II) **Metal Ion Solutions:**

(1) *Ferric chloride solutions*—A weighed amount of ferric chloride (AR) was dissolved in ethanol to prepare 0.1 M stock solution.

(2) *Cobalt nitrate solution*—A 0.1 M stock solution of cobalt was prepared by dissolving weighed amount of cobalt nitrate (BDH) in doubly distilled ethyl alcohol.

(3) *Nickel chloride solution*—A weighed amount of nickel chloride (AR) was dissolved in doubly distilled ethanol to prepare 0.1 M stock solution.

Physico-chemical studies have been carried out in order to find out the composition and stability of the complexes.

Reverse conductometric titration, by Job's Molar Ratio method, was carried out by taking 40 mL of solution of citral (ten times diluted with respect to metal salt solution) in the cell and by addition of metal salt solution. By plotting a graph between conductance and volume of metal ion added, an inflection in the curve was obtained at the point of complexation. Molar conductance was calculated by measuring the conductance at the complexation point.

pH-metric titrations were carried out at two different temperatures with 10°C difference. The method of Calvin and Bjerrum modifed by Irving and Rossotti was used to obtain log k value. Kinetics of the complexes, *i.e.*, free energy changes of the reaction (ΔG_1°, ΔG_2°), enthalpy (ΔH°) and entropies (ΔS_1°, ΔS_2°) were calculated at 10°C temperature difference by Gibbs-Helmholtz equation.

Frequency of monochromatic radiation has been calculated. Energy per photon-ergs, electron-volt, joules/einstein and calorie/einstein are also given. Elemental and physical analyses have been done. Infra-red spectra of the ligand and isolated complexes have been recorded separately by KBr technique. Another interesting aspect was non-isolation of cobalt and nickel complexes due to their more stability in solution than in solid. Then non-isolation of these complexes was due to weak σ donor properties of the ligand.

TABLE-1
FORMATION CONSTANTS, FREE ENERGY, ENTHALPY AND ENTROPY CHANGES IN THE COMPLEXATION EQUILIBRIA OF TRANSITION METAL IONS WITH LIGAND R

Complex	log K_1	log K_2	log β	$-\Delta G_1$	$-\Delta G_2$	$-\Delta H$	ΔS_1	ΔS_2
Fe(III) R	14.400	11.800	26.200	20.296	17.170	116.520	312.34	312.35
Co(II) R	14.800	14.400	29.200	20.182	20.295	16.800	11.34	11.34
Ni(II) R	9.600	9.200	18.800	13.531	13.308	17.927	14.27	14.27

R = (Citral) $C_{10}H_{16}O$ or 2-*cis*,3,7-dimethyl, 2,6-octadiene-1-al.

TABLE-2
PARTIAL IR SPECTRA DATA (cm^{-1}) OF CITRAL AND ITS METAL COMPLEXES

	ν(CHO)	ν(C=C)	ΔCH_3	Additional frequencies
Citral	1760s	1655 wb	1460 s	–
$Fe{\cdot}C_{10}H_{16}O{\cdot}Cl{\cdot}2H_2O$	disappear	1670 ms	1470 ms	2296 b

TABLE-3
ELEMENTAL ANALYSIS AND MAGNETIC SUSCEPTIBILITY OF ISOLATED COMPLEX

Complexes	% Analysis					
	C		H		Fe	
	Found	Calculated	Found	Calculated	Found	Calculated
Citral iron complexes	55.57	55.40	8.09	8.33	12.93	12.75

TABLE-4
REVERSE CONDUCTOMETRIC AND pH-METRIC TITRATION OF METAL WITH CITRAL

Volume of reagent (in the cell) = 40 mL
Concentration of the reagent = 0.01 M
Concentration of cobalt nitrate = 0.1 M
Concentration of nickel chloride = 0.1 M

Complexes	Conductance at complexation point	Specific conductance	Molar conductance (mhos)
Ferric citral complexes	0.80×10^{-3}	0.6432×10^{-4}	6.432
Cobalt citral complexes	0.96×10^{-2}	0.7718×10^{-3}	7.718
Nickel citral complexes	0.82×10^{-2}	0.6592×10^{-3}	6.592

RESULTS AND DISCUSSION

The complexes are non-hygroscopic and stable at room temperature. They are soluble in DMF and DMSO, slightly soluble in acetonitrile and chloroform and insoluble in water and other common organic solvents. Composition of the complexes formed by the interaction of citral with metal ions was firstly determined by conductometric titrations. In iron complexes 1 : 1 ratio is observed indicating the formation of complex in the solution. The formation of 1 : 2 (metal : citral) complexes was indicated from the conductometric studies.

These titrations were performed by using buffer of pH 4 and pH 9.2 respectively. The lowering in the value of pH was due to complex formation reaction in solution.[4,5]

Electronic spectra: Electromagnetic radiations[6] of monochromatic light have been studied in the visible range between 4000–7500 Å. The electronic spectrum of citral showed $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. Citral gives suitable colour change with iron. Iron gives a 1 : 1 complex with citral as there is a

constant decrease in absorbance after 35% decrease in absorbance at complexation point in the vicinity of 480 nm wavelength by Job's continuous variation method. The molar extinction coefficient, *i.e.*, molar absorptivity (Σ) was calculated by Beer's law.[7]

TABLE-5

Volume of metal ion soltuion	Conductance of $FeCl_3$ (mhos in 10^{-3})	Conductance of $Co(NO_3)_2$ (mhos in 10^{-2})	Conductance of $NiCl_2$ (mhos in 10^{-2})
0.00	0.09	0.07	0.08
0.50	0.20	0.43	0.40
1.00	0.34	0.67	0.61
1.50	0.47	0.90	0.78
2.00	0.56	0.96	0.82
2.50	0.62	1.10	1.00
3.00	0.70	1.15	1.01
3.50	0.77	1.20	1.03
4.00	0.80	1.21	1.03
4.50	0.93	1.24	1.03
5.00	0.95	1.26	1.04
5.50	0.96	1.28	1.04

Thermal studies: Stability constants of the complexes were calculated by measuring pH at complexation point. The most convincing correlation regards the stability of citral complex upon pK_a value[8]. Aldehydes and ketones[9] add on to many metal ion forming covalent molecules. Citral complexes do not follow the Irving-william's order of stability (*i.e.*, $Co^{2+} > Fe^{3+} > Ni^{2+}$). Literature survey[10] reveals greater coordination tendency of nitrogen as compared to oxygen. In case of citral available coordination sites are oxygen and π-allylic bonds; therefore the stability constant values are somewhat low.

Thermodynamic parameters, *i.e.*, free energy changes (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated by usual relations[11] at 10°C temperature difference and showed that reactions are spontaneous. The negative values of free energy were found in the range of –1.486–22.909 kcal/mole (*i.e.*, $Fe^{3+} > Co^{3+} > Ni^{2+}$).

The enthalpy change of the reactions shows negative values in the range of 7.171 kcal/mole to 116.18 kcal/mole (*i.e.*, $Fe^{3+} > Ni^{2+} > Co^{2+}$).

All the values of entropy were found positive in the range 2.181–312.36 cal/mole (*i.e.*, $Fe^{3+} > Ni^{2+} > Co^{2+}$).

The excitation of molecular vibrations and rotations gives rise to absorption bands in the infrared regions[12] of the spectrum. In the spectrum of citral we assign sharp band at 1760 cm^{-1} due to aldehyde group[13], weak band at 1655 cm^{-1} due

to π-allylic bond and medium sharp peaks at 1460 cm^{-1} may be assigned to methyl group. The shift of 1760 cm^{-1} to either lower frequency region or higher frequency region and disappearnce or weakening of 1655 cm^{-1} is clearly indicative that citral acting as a bidentate ligand.

The elemental analysis of isolated complexes shows that the observed values of percentage of C, H and metal are in good agreement with the calculated values. All the complexes of citral were found to be diamagnetic except Cu and Ni complexes with $\sqrt{1}$ and $\sqrt{9}$ B.M.

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