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Analytical Studies of Ni(II), Co(II) and Mn(II) Complexes with 2′-Hydroxy-4′-Ethoxy-4-Methoxychalcone Oxime

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In the present work, the authors describe 2′-hydroxy-4′-ethoxy-4-methoxychalcone oxime (HEMCOX) as a gravimetric and spectrophotometric reagent for Ni(II), Co(II) and Mn(II).

INTRODUCTION

In the current scenario of analytical chemistry many reagents are available. Very few workers[1–3] have used chalcone oximes as analytical reagents. It was therefore intended to synthesize and to check the applicability of this reagent for various metal ions like Ni(II), Co(II) and Mn(II).

EXPERIMENTAL

Spectrophotometric measurements were done on Spectronic-20 and Hitachi U-2000 spectrophotometer. All pH measurements were done on Elico pH-meter. 2′-Hydroxy-4′-ethoxy-4-methoxychalcone oxime (HEMCOX) was prepared by the method reported earlier[4].

Stock solution of the reagent (0.05 M) was prepared by dissolving the oxime in 60% aqueous ethanol. Stock solutions of metal ions were prepared by dissolving pure $NiSO_4 \cdot 6H_2O$, $CoSO_4 \cdot 7H_2O$ and $MnSO_4 \cdot H_2O$ in doubly distilled water and were used after standardisation[5] with EDTA.

Gravimetric procedure

An aliquot containing a known amount of metal ions was diluted to 100 mL with distilled water and warmed. The pH of solution was adjusted in the range 75.–8.0 for Ni(II), 9.0–9.5 for Co(II) and 10.0–10.5 for Mn(II) using HCl-NH_4OH, HCl-borax and NaOH-borax buffers respectively. Then 0.05 M solution of HEMCOX in ethanol was added till precipitation was complete. The precipitate was digested on water bath at 60–70°C for 1h and filtered through a previously weighed sintered glass crucible (G_4). The precipitate was dried and weighed as M $(C_{18}H_{18}O_4N)_2$. Duplicate experiment was performed in each case and the mean values have been reported. The conversion factors (metal/metal complex) for Ni(II), Co(II) and Mn(II) were found to be 0.0857, 0.0863 and 0.0802 respectively.

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Spectrophotometric procedure

The precipitates of M(II)-HEMCOX were insoluble in absolute ethanol or methanol. Therefore, the complexes were directly extracted in chloroform layer. For this purpose, a suitable aliquot of metal(II) sulphate solution was taken and the required pH was adjusted with a suitable buffer and slight excess of HEMCOX solution was added. The complex thus precipitated was extracted with two or three portions of chloroform and the volume of chloroform extract was made to 20 mL. The absorbance of the organic layer was recorded against the reagent blank prepared under similar conditions.

RESULTS AND DISCUSSION

Gravimetric determination of Ni(II), Co(II) and Mn(II)

To determine the feasibility of the reagent for gravimetric estimations of Ni(II), Co(II) and Mn(II), the metal ions were precipitated from solutions having pH values in the range 3.0–9.0. Complete precipitation occurred at 7.5–8.0 for Ni(II), 9.0–9.5 for Co(II) and 10.0–10.5 for Mn(II). Estimations using different aliquots of metal ions were done at required pH. In all cases, the error in the metal contents did not exceed ± 0.5%.

Spectrophotometric determination of metal ions

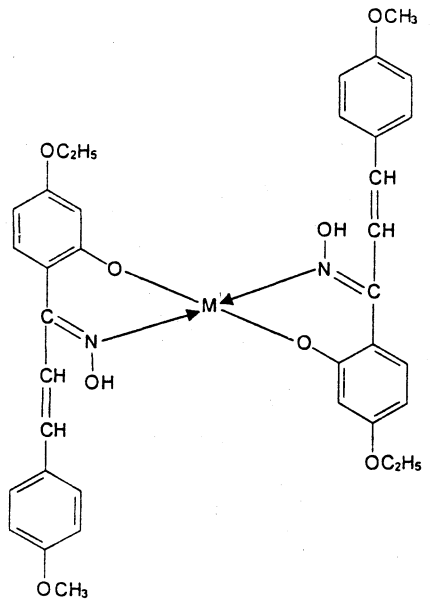
Selection of wavelength: For recording the absorption spectra, 1.5×10^{-4} M solution of the chelate in chloroform was used and the absorbances were measured in the range 330–1000 nm. It was observed that the absorbance of the coloured solution increases continuously towards the shorter wavelength. The absorption spectra show a shoulder at 420 nm for nickel, 410 nm for cobalt and 400 nm for mangenese chelates. Hence all the measurements were carried out at respective wavelengths.

Validity of Beer's law and optimum concentration range: The M(II)-HEMCOX chelates in chloroform obey Beer's law up to 14 ppm of Ni(II), 11 ppm of Co(II) and 13 ppm of Mn(II) in organic layer. Beyond these concentrations, the absorbance plots show a negative deviation from linearity. The molar absorptivities of the chelates obtained from the absorbance data were found to be 1.2500×10^4, 1.2019×10^4 and 1.2254×10^4 L mol^{-1} cm^{-1} at 420, 410 and 400 nm respectively.

Stoichiometry and structure of chelates: The stoichiometry of the M(II)-HEMCOX chelates was studied by (1) Yoe and Jones mole ratio method[6] and Job's method of continuous variation[7]. Both the methods gave the metal : ligand ratio of 1 : 2. The gravimetric determination as well as the elemental analysis of the chelates also confirmed this ratio. Comparison of IR spectra of ligand with those of chelates helped in establishing the nature of linkage and the site of coordination. IR spectrum of the ligand shows two bands in O—H stretching region; one band at 3438 cm^{-1} which disappears in the spectra of chelates is due to phenolic —OH group. Deprotonation of —OH group takes place and metal coordinates with the oxygen by covalent bond. The coordination

of metal through N of oximino group may be shown by the lowering of C=N frequency from 1622 cm^{-1} in ligand to 1605 cm^{-1} in chelates. The position of oximino —OH group (2980 cm^{-1}) remains unaffected in the ligand and chelates.

Based on above data the metal chelates may be assigned the following structure:



where, M = Ni(II), Co(II) and Mn(II)

Stability constant of the chelates: For evaluating stability constant of the chelates, the degree of dissociation (α) was calculated from the data of mole ratio method. The results obtained are as follows.

Chelate	E_m	E_s	A	$K_s = \frac{1-\alpha}{\alpha^2 c}$
Ni(II)-HEMCOX	0.1249	0.1125	0.0992	9.00×10^6
Co(II)-HEMCOX	0.1911	0.1701	0.1098	4.45×10^6
Mn(II)-HEMCOX	0.1775	0.1591	0.1036	8.96×10^6

The standard free energy change ($\Delta G°$) for the chelate formation reaction at room temperature was calculated using the relationship $\Delta G° = -RT \ln K$ and the values for $\Delta G°$ obtained were –9.54, –9.49 and –9.54 kcal/mole for Ni(II), Co(II) and Mn(II) respectively.

The Co(II) and Mn(II) chelates with HEMCOX were found to be paramagnetic with magnetic moments 4.49 B.M. and 5.08 B.M., respectively, corresponding to three and five unpaired electrons. The nickel chelate was found to be diamagnetic and hence these chelates have most probably square-planar configuration.

Interference from other ions

A definite quantity of interfering ions was added to the solutions of Ni(II), Co(II) and Mn(II) ions and the gravimetric determinations were carried out as described earlier. It was observed that anions like chloride, bromide, iodide, nitrate, sulphate and cations like Ba(II), Sr(II), Ca(II), Mg(II) and Zn(II) did not interfere. The error in any case did not exceed ± 0.6%.

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