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Spectral and thermal studies of some chromium and molybdenum complexes with ONO donor Schiff bases

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Abstract

Reactions of $M(CO)_6$, where M = Cr and Mo with Schiff bases prepared by the condensation of ethanolamine with either acetylacetone or benzoylacetone were investigated. The reactions of $Cr(CO)_6$ in benzene resulted in the formation of the tricarbonyl drivatives $[Cr(CO)_3(HL)]$, HL = acaceaH or baceaH. The HL proved to act as a tridentate ligand. The corresponding reactions with $Mo(CO)_6$ in dioxane gave the oxo complexes $[Mo_2O_6(HL)_2]$ with HL was a bidentate. All prepared complexes were investigated using elemental analysis, IR, mass spectrometry, UV–vis absorption spectra and magnetic measurement. Thermal behaviors of the complexes were studied using by thermogravimetry (TG). Schemes for the thermal decomposition were proposed along with their mass fragmentation patterns.

Keywords: Chromium; Molybdenum; Metal carbonyls; Schiff bases; IR Spectra; Thermogravimetry

1. Introduction

Metal carbonyls have been proved as reactive species in homogeneous catalytic reactions such as hydrogenation, hydroformylation and carbonylation. Carbon monoxide serves simply as a ligand providing the complex with the necessary reactivity and/or stability to allow reaction to ensue [1]. On the other hand, a large number of Schiff bases and their complexes have been studied for their interesting and important properties, such as their ability to reversibly bind oxygen [2], catalytic activity in the hydrogenation of olefins [3], transfer of amino groups [4], photochromic properties [5] and complexing ability towards some toxic metals [6]. In addition, the metal complexes of Schiff bases simulate the interaction between metal ions and amino acids for metal–protein systems as well as they have been considered as interesting models in a variety of biological systems [7].

The reactions of chromium and molybdenum hexacarbonyls with the Schiff bases bis-(2-hydroxyacetophenone)ethylenediimine, hapenH_2 [8] and 2-hydroxylacetophenonepropylimine, happramH [9] have been reported. Several complexes with interesting structural features were isolated. The aim of this investigation is to study the reactions of chromium and molybdenum hexacarbonyls with two Schiff bases of ONO donor system derived from ethanolamine with either acetylacetone (HL_1) or benzoylacetone (HL_2), Scheme 1.

2. Experimental

$Cr(CO)_6$ and $Mo(CO)_6$ were supplied by Aldrich. Acetylacetoneethanolimine (HL_1) and benzoylacetoneethanolimine (HL_2) were prepared as described in literature [10]. All solvents were of analytical grade.

IR measurements (KBr pellets) were carried out on a Unicam-Mattson 1000 FT-IR. Electronic absorption spectra were measured on a Unicam UV2-300 UV–vis spectrophotometer with 10.0 mm quartz cells. Thermogravimetric analysis (TG) was carried out using a Shimadzu DT-50 thermal analyzer under nitrogen atmosphere with a heating rate of 10 °C/min. Elemental analyses were carried out on a Perkin-Elmer 2400 CHN elemental analyzer. Mass spectra of the solid complexes were performed on a Finnegan MAT SSQ 7000 spectrometer. Table 1 gives the elemental analysis, UV–vis, mass spectrometry and magnetic moments data for the complexes.

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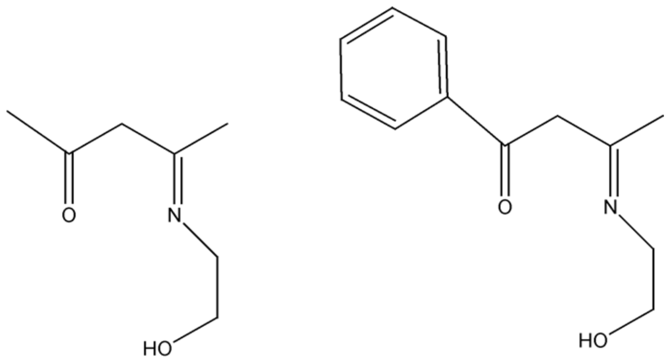

HL_1 HL_2

Scheme 1.

2.1. Synthesis of $[Cr(CO)_3(HL_1)]$ complex

$Cr(CO)_6$ (0.10 g, 0.45 mmol) and acetylacetoneethanolimine (HL_1) (0.07 g, 0.45 mmol) were mixed together in a sealed tube containing 20 ml benzene. The mixture was degassed and heated for 10 h at 60 °C. The color of the solution was changed to brown. The reaction mixture was cooled and the solvent was evaporated on a vacuum line. The brown residue was washed several times with hot petroleum ether and recrystallized from hot ethanol. The brown crystals were dried under vacuum for few hours to give a yield of 45%.

2.2. Synthesis of $[Cr(CO)_3(HL_2)]$ complex

Similar procedure was used as employed for $[Cr(CO)_3(HL_2)]$ with a reaction period of 48 h. Brown crystals with a yield of 54% were obtained.

2.3. Synthesis of $[Mo_2O_6(HL_1)_2]$ complex

A mixture of $Mo(CO)_6$ (0.10 g, 0.38 mol) and HL_1 (0.05 g, 0.38 mmol) in 30 ml dioxane was refluxed in air for 7 h. The color of the reaction mixture was changed from yellow to brown. The reaction mixture was cooled and the brown solid was isolated by filtration. The isolated brown complex was washed several times with dioxane and then recrystallized from DMSO and redried *in vacuum* for several hours (yield 53%).

2.4. Synthesis of $[Mo_2O_6(HL_2)_2]$ complex

Similar procedure was used as for $[Mo_2O_6(HL_1)_2]$ with a reaction period of 7 h. Brown crystals with a yield of 58% were obtained.

3. Results and discussion

The results of elemental analyses of the isolated complexes are given in Table 1. A good agreement between the calculated and experimental values was observed. The parent molecular ion peaks are in good agreement with the molecular masses of the complexes.

3.1. Spectral study

The IR spectra of HL_1 and HL_2 showed a strong and broad νOH at 3350–3850 cm^{-1} and strong νCH=N stretching frequencies at 1620–1600 cm^{-1}, Table 2. Reactions of chromium hexacarbonyl with acaceaH (HL_1) and baceaH (HL_2) in benzene under reduced pressure resulted in the formation of $[Cr(CO)_3(HL_1)]$ and $[Cr(CO)_3(HL_2)]$, respectively. Upon complexation, the νOH bands of the ligands moities were shifted to lower wave numbers indicating that the OH group has participated in the coordination without proton displacement. Participation of the OH in coordination is also further confirmed by the shift of the νC–O to lower frequencies [11–13], Table 2. The νCH=N stretching band was also found to be shifted in the spectra of the complexes indicating the participation of the azomethine group in coordination. Therefore, the ligand coordinates as a tridentate with a facial structure. In addition, the IR spectrum of the $[Cr(CO)_3(HL_1)]$ complex showed two strong ν(CO) bands in the terminal metal carbonyl region at 1962 and 1878 cm^{-1} with a shoulder at 1841 cm^{-1}, while the IR spectrum of $[Cr(CO)_3(HL_2)]$ complex exhibited two strong ν(CO) bands at 1962 and 1882 cm^{-1} and a weak ν(CO) band at 2003 cm^{-1}. The number and pattern of the CO bands indicated the coordination of three carbonyl groups to chromium in both complexes [14,15].

From the spectroscopic and elemental analyses data, it can be concluded that zero valent chromium exists in an octahedral environment with the HL ligand coordinated as a tridentate (Scheme 2) [16].

Interaction of molybdenum hexacarbonyl with HL_1 and HL_2 in dioxane resulted in the formation of dinuclear complexes

Table 1
Elemental, UV–vis and mass spectral data of the chromium and molybdenum complexes

Complex	Mol. weight	Elemental analysis found (calc.)				UV–vis[a] λ_{max} (nm) (DMSO)	Mass spectral data *m/z* (p+)
		%C	%H	%N	%M		
$[Cr(CO)_3(HL_1)]$ $C_{10}H_{13}NO_5Cr$	279.21	44.23 (43.02)	5.5 (4.69)	2.86 (2.54)	18.45 (18.62)	317, 352	278.0
$[Cr(CO)_3(HL_2)]$ $C_{15}H_{15}NO_5Cr$	341.28	51.80 (52.79)	5.80 (4.43)	2.73 (2.80)	15.31 (15.24)	308, 372	341.0
$[Mo_2(O)_6(HL_1)_2]$ $C_{14}H_{26}N_2O_{10}Mo_2$	574.24	28.84 (29.28)	4.26 (4.56)	4.80 (4.88)	33.78 (33.41)	320	576.1
$[Mo_2(O)_6(HL_2)_2]$ $C_{24}H_{30}N_2O_{10}Mo_2$	698.38	41.90 (41.27)	4.19 (4.33)	4.00 (4.01)	27.04 (27.47)	320	698.5

[a] (HL_1): 255 and 350 nm; (HL_2): 250 and 350 nm.