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Spectrochimica Acta Part A 65 (2006) 841–845
SPECTROCHIMICA ACTA PART A
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Spectral and thermal studies of some chromium and molybdenum complexes with ONO donor Schiff bases

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Received 5 October 2005; received in revised form 30 November 2005; accepted 16 January 2006

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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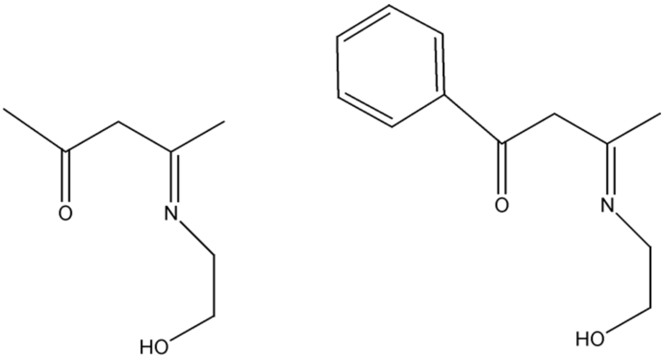
doi:10.1016/j.saa.2006.01.016



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$_2$O$_6$(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$_2$O$_6$(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.

Table 2
Important IR data of chromium and molybdenum complexes

Compound	IR data (cm^{-1})						
	νOH	νC=N	νC=O	νC—O	ν_{as} Mo—O—Mo	ν_s Mo=O	$\nu_{\alpha s}$ Mo=O
HL_1	3415(s,b)	1620(s)		1266(s)			
HL_2	3355(s,b)	1610(s)		1279(s)			
$[Cr(CO)_3(HL_1)]$	3388(s,b)	1589(s)	1962(s), 1882(s), 2003(w)	1249(m)			
$[Cr(CO)_3(HL_2)]$	3386(s,b)	1600(s)	1962(s), 1841(sh), 1878(s)	1256(m)			
$[MoO_2(O)_6(HL_1)]$	3411(s,b)	1612(s)		1266(m)	724(m)	900(s)	942(m)
$[MoO_2(O)_6(HL_2)]$	3412(s,b)	1600(s)		1278(m)	716(m)	904(s)	940(m)

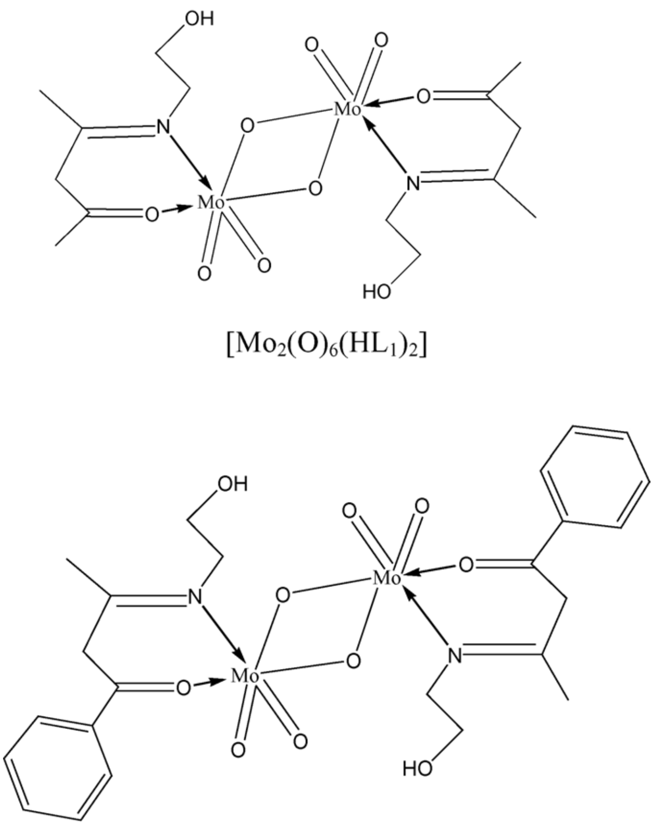
s, strong; m, medium; w, weak; sh, shoulder; b, broad.

$[Mo_2(O)_6(HL_1)_2]$ and $[Mo_2(O)_6(HL_2)_2]$, respectively. The IR spectra of complexes showed that the νOH bands were not shifted with respect to those of free ligands indicating that the ligands acted as bidentate with non-facial structure in which the OH is oriented away from the coordination center (Scheme 3). The IR spectra of complexes also displayed two strong to medium bands at 942 and 904–900 cm^{-1} assigned for the asymmetric and symmetric stretching frequencies of the Mo=O bonds, respectively. This has been found to be common for Mo=O bonds reported for a *cis* MoO_2 fragments of a dimeric structures having the Mo_2O_6 core [17–19]. In addition, the IR spectra of the molybdenum complexes showed two stretches $\nu_{as}(Mo_2O)$ and $\nu_s(Mo_2O)$ of the oxo-bridging groups at 724 and 716 cm^{-1}, respectively [15,17]. Several complexes having the Mo_2O_6 or Mo_2O_5 cores have been recently reported, where molybdenum atoms bonded to a *cis* dioxo group and the two Mo atoms were bridged by one or two oxygen atoms [14,17]. The dimeric structures of the two complexes were further confirmed from the mass spectral data in which the molecular ion peaks were found to be 576.1 (38.0%) and 698.50 (5.57%) for $[Mo_2(O)_6(HL_1)_2]$ and $[Mo_2(O)_6(HL_2)_2]$, respectively. These structures were also found to be consistent with the TG data and the proposed decomposition scheme (*vide infra*). Scheme 3 gives the proposed structures of the complexes.

The electronic absorption spectra of both HL_1 and HL_2 displayed two bands at 250, 350 and 255, 355 nm, which are assigned for the π–π^* and n–π^* transitions, respectively. Upon complexation with chromium and molybdenum the two bands were red shifted. In addition, the monomeric chromium complexes displayed additional bands in the range 252–372 nm, which may be attributed to metal-to-ligand charge transfer (MLCT) [14,20,21].

3.2. Thermal analysis and mass spectrometry

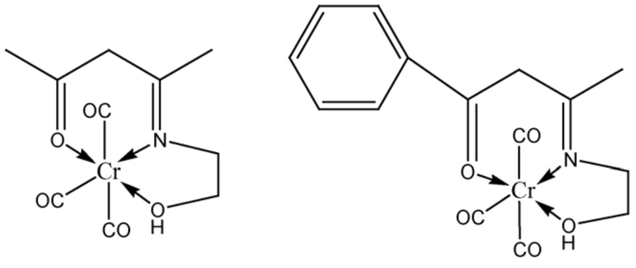
A deeper insight on the structures of the investigated complexes was undertaken using thermogravimetry (TG) and derivative thermogravimetry (DTG) techniques. Fig. 1 shows the TG and DTG curves of the complexes. The $[Cr(CO)_3(C_7H_{13}NO_2)]$ complex (*m*/*e*: 278; 24.5%) decomposed in three decomposition steps covering the temperature range 98–426 °C (Scheme 4). Two carbon monoxide molecules were eliminated in the first two steps while the third carbonyl was eliminated along with



$[Mo_2(O)_6(HL_1)_2]$

$[Mo_2(O)_6(HL_2)_2]$

Scheme 3.



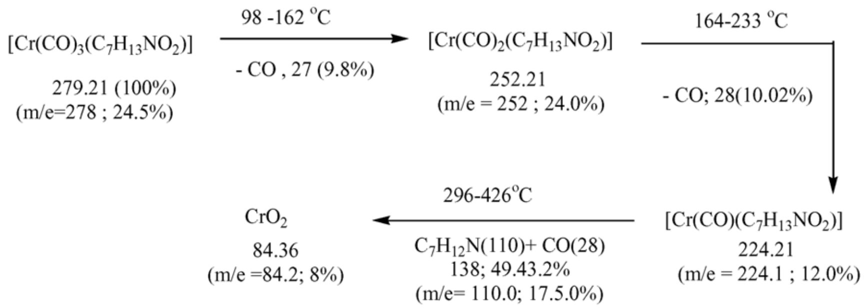
$[Cr(CO)_3(HL_1)]$

$[Cr(CO)_3(HL_2)]$

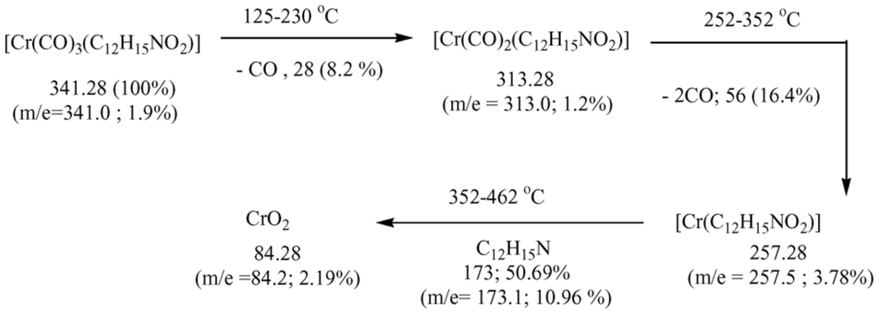
Scheme 2.

Table 3
Selected mass spectral data of the complexes

Complex	Molar mass	m/*z* values
$[Cr(CO)_3(HL_1)]$ $C_{10}H_{13}NO_5Cr$	279.21	278.0, 252.0, 244.9, 224.21, 213.9, 190.9, 157.9, 154.6, 129.9, 125.0, 110.0, 84.2, 78.0, 52.0
$[Cr(CO)_3(HL_2)]$ $C_{15}H_{15}NO_5Cr$	341.28	341.0, 313.0, 299.4, 269.4, 257.5, 210.1, 196.0, 187.1, 173.1, 169.1, 158.1, 143.3, 115.1, 91.2, 84.2, 77.1
$[Mo_2(O)_6(HL_1)_2]$ $C_{14}H_{26}N_2O_{10}Mo_2$	574.24	576.1, 500.1, 485.8, 424.1, 420.0, 393.8, 362.9, 344.0, 321.9, 278.8, 220.3, 176.4, 149.2, 128.0, 112.2, 91.0, 65.1
$[Mo_2(O)_6(HL_2)_2]$ $C_{24}H_{30}N_2O_{10}Mo_2$	698.38	698.5, 664.1, 632.9, 548.7, 526.9, 474.6, 424.3, 409.2, 374.1, 356.9, 348.2, 310.7, 289.1, 257.4, 218.1, 194.1, 183.2, 146.7, 128.2, 112.6, 105.2, 77.3



Scheme 4.

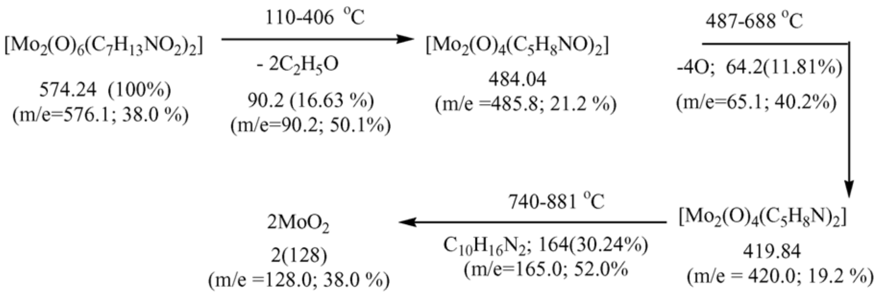


Scheme 5.

the decomposition of the organic part in the third step leaving CrO_2 (*m*/*e*: 84.2; 8.0%) as a metallic residue. The decomposition patterns were further confirmed from the mass spectral peaks, Table 3.

The $[Cr(CO)_3(C_{12}H_{15}NO_2)]$ complex (*m*/*e*: 341.0; 1.9%) was also shown to decompose in three steps within the temperature range 125–462 °C. Three carbonyl groups were eliminated in the first two steps. The organic part was decomposed in the last step with the formation of CrO_2 as a metallic residue, Scheme 5.

The dimeric structures of the two molybdenum complexes were further confirmed from their thermal decomposition schemes and mass spectra. Weight losses of the different species either eliminated or remained in each decomposition steps with the mass fragments in their mass spectra. The



Scheme 6.

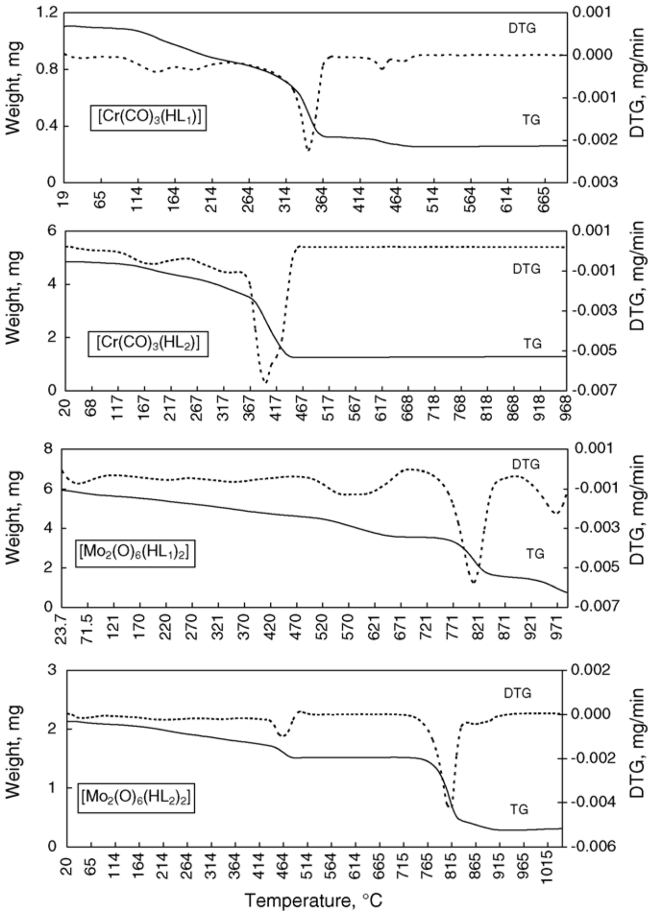
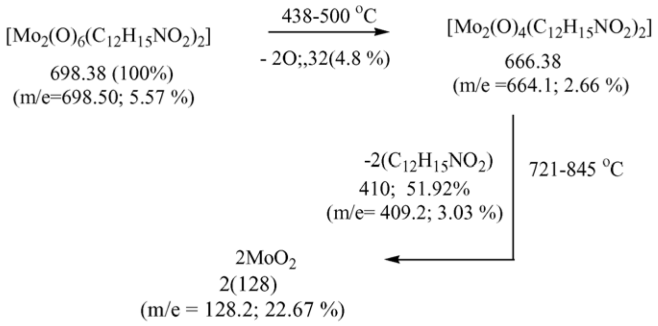


Fig. 1. TG and DTG curves of the chromium and molybdenum complexes.



Scheme 7.

$[Mo_2(O)_6(C_7H_{13}NO_2)_2]$ complex showed thermal decomposition patterns in four steps in the temperature range 110–996 °C with molybdenum oxide MoO_2 as the metallic residue (*m*/*e*: 128.0; 38.0%) (Scheme 6).

The $[Mo_2(O)_6(C_{12}H_{15}NO_2)_2]$ complex showed a relatively better thermal stability, Fig. 1, from the room temperature up to 438 °C before it decomposed in three steps within the temperature range 438–928 °C starting with the dimeric structure (*m*/*e*: 698.50; 5.57%) and ended with molybdenum oxide MoO_2 (*m*/*e*: 128.2; 22.67) (Scheme 7).

4. Conclusion

From the spectroscopic, elemental and thermal analyses data, it can be concluded that zero valent chromium exists in an octahedral environment with the HL ligand coordinated as a tridentate with a facial (O,N,O)donor. On the other hand molybdenum atoms bonded to a *cis* dioxo group and the two Mo atoms were bridged by one or two oxygen atoms in dimeric structures which were further confirmed from the mass spectral data in which the molecular ion peaks were found to be 576.1 (38.0%) and 698.50 (5.57%) for $[Mo_2(O)_6(HL_1)_2]$ and $[Mo_2(O)_6(HL_2)_2]$, respectively. These molybdenum dimeric structures were also found to be consistent with the TG data and the proposed decomposition scheme.

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