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Photochemical reactions of group 6 metal carbonyls with *N*-salicylidene-2-hydroxyaniline and bis-(salicylaldehyde)phenylenediimine

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Abstract

Sunlight irradiation of the reactions of $[M(CO)_6]$, M = Cr, Mo and W with either *N*-salicylidene-2-hydroxyaniline ($shaH_2$) or bis-(salicylaldehyde) phenylenediimine ($salphenH_2$) in THF were investigated. Three complexes with molecular formulas $[Cr(shaH_2)_3]$, **1**, $[MoO_2(shaH_2)_2]$, **2**, and $[W_2O_5(shaH)_2]$, **3** were isolated from the reactions with $shaH_2$. The corresponding reactions with $salphenH_2$ produced the oxo complexes $[CrO(salphenH_2)]$, **4**, $[Mo_2O_6(salphenH_2)_2]$, **5**, and $[W_2O_6(salphenH_2)]$, **6**. All complexes were characterised by elemental analysis, infrared, mass and ^1H NMR spectroscopy. The UV–vis spectra of the complexes in different solvents showed visible bands due to either ligand-to-metal or metal-to-ligand charge transfer. Thermal properties of the complexes were investigated by TG thermogravimetry technique.

Keywords: Chromium; Molybdenum; Tungsten; Metal carbonyl; Schiff base; Photochemistry; Thermal analysis

1. Introduction

A large number of Schiff base compounds are often used as ligands in coordination chemistry for their metal binding ability. Schiff base-metal complexes are characterised by interesting and important properties, such as their ability to reversibly binding oxygen in epoxidation reactions [1], biological activity [2–5], complexing ability towards some toxic metals [6], catalytic activity in hydrogenation of olefines [7] and photochromic properties [8,9]. Polydentate Schiff bases containing nitrogen and oxygen donor atoms such as bis-(salicylaldehyde)ethylenediimine ($salenH_2$), bis-(salicylaldehyde)phenylenediimine ($salphenH_2$), salicylideneimine-2-anisole (salanH), and *N*-salicylidene-2-hydroxyaniline ($shaH_2$) are useful for the synthesis of transition metal complexes which play important role in biological systems [10,11]. Such classes of ligands were also found to provide catalytic characteristics especially for epoxidation reactions [12–17].

Reactions of group 6 and 8 metal carbonyls with some selected Schiff bases having oxygen and nitrogen donors were investigated [18–20]. Reactions of the two Schiff bases, $shaH_2$ and $salphenH_2$, with $[M(CO)_6]$, M = Cr, Mo and W gave complexes with different structural features; $[CrO_2(CO)_2(shaH_2)]$, $[W(CO)_2(shaH)_2]$, $[Cr(CO)_2(salphen)]$, $[MoO(CO)(salphen)]$, $[MoO(sha)]$, $[Mo_2O_4(sha)_2]$, $[MoO_2(salphenH)_2]$ and $[W_2O_6(salphenH_2)]$ [21,22]. The versitile chemistry of these reactions has prompted us to investigate the reactions of Group 6 metal carbonyls with $shaH_2$ and $salphenH_2$, Scheme 1, under sunlight photolysis.

2. Experimental

2.1. Reagents

$[M(CO)_6]$, M = Cr, Mo and W were supplied by Aldrich. The $shaH_2$ and $salphenH_2$ ligands were prepared

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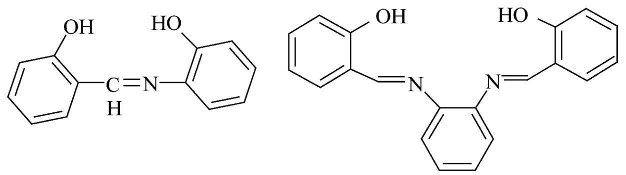

$shaH_2$ $salphenH_2$

Scheme 1.

as described in literatures [21,23]. All solvents were purified by distillation before use.

2.2. Instruments

Infrared measurements (KBr pellets) were carried out on a Unicam–Mattson 1000 FT-IR spectrometer. UV–vis spectra were measured on a Unicam UV2-300 spectrophotometer. NMR measurements were performed on a Spectrospin–Bruker AC 200 MHz spectrometer. Samples were dissolved in deuterated DMSO using TMS as internal reference. Elemental analyses were performed on a Perkin–Elmer 2400 CHN elemental analyzer. Mass spectrometry measurements of the solid complexes (70 eV, EI) were carried out on a Finnigan MAT SSQ 7000 spectrometer. Thermogravimetric analysis was performed under nitrogen atmosphere with a heating rate of 10 °C/min using a Schimadzu DT-50 thermal analyzer. Table 1 gives the elemental analysis and mass spectrometry data for the complexes.

2.3. Syntheses of complexes

A general procedure was employed for the synthesis of the reported complexes. A mixture of equimolar amounts of $[M(CO)_6]$, M = Cr, Mo and W, and either $shaH_2$ or $salphenH_2$ in a sealed tube containing 25 cm^3 of THF. Photolysis of the mixture with sunlight for a certain period of time (25 °C) was employed (Table 1). (The photoexcitation procedure is expected to be the UV range of light). The solvent was removed on a vacuum line. The residue was washed several times by boiling petroleum ether and then recrystallized from THF. The complex was left to dry in vacuo for several hours. Table 1 gives the reaction period, color of complex and % yield.

3. Results and discussion

3.1. Infrared and NMR studies

3.1.1. The $shaH_2$ complexes

Interaction of $[M(CO)_6]$, M = Cr, Mo and W, with *N*-salicylidene-2-hydroxyaniline ($shaH_2$) under sunlight irradiation resulted in the formation of different complexes depending on the metal type. While the reaction with $[Cr(CO)_6]$ gave the tris derivative $[Cr(shaH_2)_3]$, **1**, with the chromium atom in the zero formal oxidation state, the molybdenum and tungsten hexacarbonyls gave the oxo derivatives $[MoO_2(shaH_2)_2]$, **2**, and $[W_2O_5(shaH)_2]$, **3**, with +4 and +6 formal oxidation states, respectively. It is expected that the formation of complexes were proceeded via the $M(CO)_5$ intermediate through M–CO bond dissociation. This is a general route for the UV photolysis of the hexacarbonyls of Group 6 [24]. Such intermediate reacts with either the ligand alone to give the chromium derivative or with the ligand and oxygen to give the molybdenum and tungsten products. The source of oxygen in the oxo complexes could be originated from the dissolved oxygen in the used solvent. It is well established that both molybdenum and tungsten have higher affinity to react with oxygen [24,25]. Numerous oxo molybdenum and tungsten complexes were previously reported. For example, interaction of bis-(salicylaldehyde)etylenediimine ($salenH_2$) and 2-hydroxyacetophenoneethylenediimine ($hapenH_2$) with $Mo(CO)_6$ in THF under atmospheric pressure gave Mo(O)(salen) and Mo(O)(hapen) with the metal atom in +4 oxidation state [18,19]. Also, reactions of the Schiff base salicylideneimine-2-anisole (salanH) with $M(CO)_6$, M = Mo or W, gave the dinuclear oxo complex $M_2O_4(salan)_2$ [26]. The infrared spectrum of the chromium complex, **1**, displayed the characteristic bands of $shaH_2$ with the appropriate shifts due to complex formation (Table 2). The complex showed vibrational bands at 3354, 1379 and 1340 cm^{-1} due to ν(OH) and δ(OH) frequencies, respectively (Table 2). In addition, the infrared spectrum of **1** showed an appreciable shifts in the ν(C=N) and ν(C–O)

Table 1
Elemental analysis and mass spectrometry data for the chromium, molybdenum and tungsten complexes

Complex	Color	Reaction time (h)	% Yield	Elemental analysis						Mass spectrometry	
				%C		%H		%N		Mol. Wt.	*m/z* (p^+)
				Calc.	Found	Calc.	Found	Calc.	Found		
1	Brown	3	73	67.7	67.4	4.8	5.0	6.1	5.9	691.7	692
2	Dark-brown	4	68	56.3	56.1	4.0	4.2	5.7	5.5	554.4	555
3	Light-brown	10	75	35.8	35.6	2.3	2.4	3.2	3.0	872.2	873
4	Brown	6	84	62.5	62.3	4.2	4.5	7.3	7.1	384.4	385
5	Dark-brown	5	61	52.2	52.4	3.5	3.1	6.1	6.2	920.6	921
6	Light-brown	12	53	30.8	30.4	2.1	1.9	3.6	3.4	780.1	781