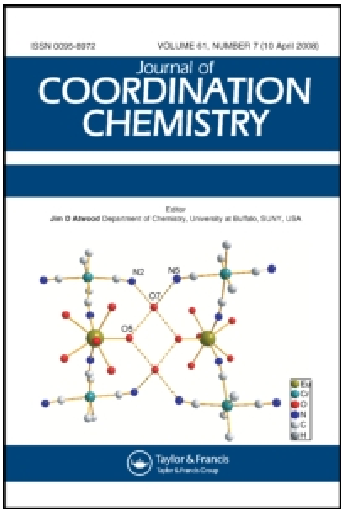

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Structural Studies of some Chromium, Molybdenum and Tungsten Complexes of *N*-Salicylidene-2-Hydroxyaniline

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STRUCTURAL STUDIES OF SOME CHROMIUM, MOLYBDENUM AND TUNGSTEN COMPLEXES OF *N*-SALICYLIDENE-2-HYDROXYANILINE

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Interaction of the Schiff base *N*-salicylidene-2-hydroxyaniline (shaH_2) with $M(CO)_6$ (M=Cr and W) in THF under reduced pressure resulted in the formation of $CrO_2(CO)_2(shaH_2)$ (**1**) and $W(CO)_2(shaH)_2$ (**4**). The two complexes MoO(sha) (**2**) and $Mo_2O_4(sha)_2$ (**3**) were isolated from the reaction of $Mo(CO)_6$ with shaH_2 in air, depending on the reaction period. All complexes were characterised by elemental analysis, IR, mass and ^{1}H NMR spectroscopy. The structural studies of the complexes revealed that the ligand shaH_2 bonds to the metal through the oxygen atoms of the hydroxyl groups and the nitrogen atom of the imine group. Magnetic studies of **1** showed it to be paramagnetic with $\mu_{eff} = 2.8$ BM, suggesting that Cr is in a high-spin (d^2) electronic configuration. The other complexes **2**–**4** showed diamagnetic behaviour. Electronic spectra of the complexes in different donor solvents displayed weak visible bands due to ligand-to-metal charge transfer. The thermal properties of the complexes were investigated by thermogravimetry techniques.

Keywords: Chromium; Molybdenum; Tungsten; Schiff-base; Spectra; Thermal analysis

INTRODUCTION

Schiff base ligands are widely used in coordination chemistry because of their structures and applications in catalytic reactions [1]. For example, salicylaldeneimine derivatives such as *N*-(2-carboxyphenyl)salicylideneimine were found to be useful precursors for the synthesis of transition metal complexes [2–8]. Numerous studies have been reported concerning the reversible solid-state photochromic or thermochromic reactions of this type of *N*-salicylideneimine compounds [6,9–13]. The hexacarbonyls of group 6 transition metals, however, are useful intermediates in the synthesis of either organometallic or coordination compounds. Studies of the reactions of hexacarbonyls of group 6 metals with some selected Schiff bases containing oxygen and nitrogen donors have been reported. Interaction of the Schiff base 2-hydroxyacetophenonepropylimine (happramH) with $M(CO)_6$ (M=Cr or Mo) gave the dicarbonyl complex $M(CO)_2$ $(happramH)_2$. The oxo molybdenum complex $MoO(happram)_2$ was formed in the presence of air. Reactions of $M(CO)_6$ with bis(2-hydroxyacetophenone)ethylenediimine

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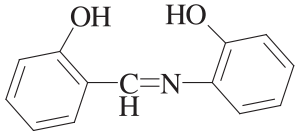


SCHEME 1 The $shaH_2$ Schiff base.

TABLE I Elemental analysis and mass spectrometric data for the chromium, molybdenum and tungsten complexes

Complex	*%C*		*%H*		*%N*		*Mass spectrometry molecular weight*	*m/z* (p^+)
	Calculated	*Found*	*Calculated*	*Found*	*Calculated*	*Found*		
1	51.0	51.1	3.1	3.2	4.0	4.1	353.25	354
2	48.3	48.2	2.8	2.9	4.3	4.2	323.08	324
3	46.0	46.1	2.7	2.6	4.1	4.0	678.32	679
4	50.6	50.5	3.0	3.1	4.2	4.3	664.33	665

($hapenH_2$) under atmospheric pressure gave the oxo derivatives M(O)(hapen) with the metal atom in the +4 formal oxidation state [14,15].

In this article, reactions of group 6 metal carbonyls with *N*-salicylidene-2-hydroxyaniline ($shaH_2$) are reported (Scheme 1).

EXPERIMENTAL

Reagents

$M(CO)_6$ (M=Cr, Mo and W) were supplied by Aldrich. All chemicals were of analytical reagent grade and used without further purification.

Instrumentation

Infrared measurements were carried out on a Unicam-Mattson 1000 FT-IR spectrometer using KBr discs. Electronic absorption spectra were measured on a Unicam UV2-300 UV–VIS spectrometer. Nuclear magnetic resonance measurements were performed on a Spectrospin-Bruker AC 200-MHz spectrometer. Samples were dissolved in DMSO-d_6 using tetramethylsilane as internal reference. Magnetic susceptibilities of the complexes in the solid state (Gouy method) were recorded on a Sherwood Scientific magnetic susceptibility balance. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyser. Mass spectra of the solid complexes (70 eV, EI) were carried out on a Finnigan MAT SSQ 7000 spectrometer. Measurements for the thermogravimetric analysis (TGA) and differential thermogravimetry (DTG) were carried out under a nitrogen atmosphere at a heating rate of 10°C/min using a Schimadzu DT-50 thermal analyser. Table I gives the elemental analysis and mass spectrometry data for the complexes.

Synthesis of *N*-Salicylidene-2-hydroxyaniline ($shaH_2$)

The ligand $shaH_2$ was synthesized as reported in the literature [16], by refluxing a mixture of 0.1 mol of salicylaldehyde and 0.1 mol of *o*-aminophenol in 50 cm^3 of ethanol for 1 h. The reaction mixture was cooled. The solid product formed was separated by filteration and then recrystallised from hot ethanol to yield red crystals.

Synthesis of $CrO_2(CO)_2(shaH_2)$ Complex

$Cr(CO)_6$ (0.10 g, 0.45 mmol) and $shaH_2$ (0.11 g, 0.45 mmol) were mixed in a sealed tube containing *ca.* 25 cm^3 THF. The mixture was degassed with one freeze–thaw cycle and then heated to 50°C for 10 h. The colour changed from yellow to reddish-brown with formation of a brown precipitate. The reaction mixture was then left to cool and the solid residue was isolated by filteration and washed several times with boiling petroleum ether. The complex was recrystallised from hot THF to yield brown crystals and then left to dry *in vacuo* for several hours (yield 70%).

Synthesis of MoO(sha) Complex

A mixture of $Mo(CO)_6$ (0.10 g, 0.38 mmol) and $shaH_2$ (0.08 g, 0.38 mmol) in *ca.* 25 cm^3 THF was heated to reflux in air for 6 h. The colour of the solution changed from yellow to brown. The reaction mixture was cooled and the solvent was removed on a vacuum line. The solid residue was washed several times with boiling petroleum ether and then recrystallised from hot THF to yield brown crystals which were dried *in vacuo* for several hours (yield 90%).

Synthesis of $Mo_2(O)_4(sha)_2$ Complex

A similar procedure for MoO(sha) was used but the reaction period was 20 h. A dark brown residue was separated and recrystallized from hot THF (yield of 75%).

Synthesis of $W(CO)_2(shaH)_2$ Complex

A similar procedure was performed as in the synthesis of $CrO_2(CO)_2(shaH_2)$ with the exception that the reaction period was 4 days. The residue was washed several times with hot petroleum ether and then recrystallised from hot THF to give reddish-brown crystals (yield of 85%).

RESULTS AND DISCUSSION

Reaction of $Cr(CO)_6$ with *N*-salicylidene-2-hydroxyaniline ($shaH_2$) in THF under reduced pressure resulted in the formation of the dicarbonyl complex $Cr(O)_2(CO)_2$ ($shaH_2$) (**1**), while reaction between $W(CO)_6$ and $shaH_2$ under reduced pressure resulted in the formation of the dicarbonyl bis derivative $W(CO)_2(shaH)_2$ (complex **4**). $Mo(CO)_6$ reacted with $shaH_2$ in air to give two different complexes, MoO(sha) (**2**) and $Mo_2O_4(sha)_2$ (**3**), depending on the reaction period.

The IR spectrum of $shaH_2$ showed characteristic bands due to the functional groups OH, C=N and C–O (Table II) [17]. The IR spectrum of the chromium, molybdenum and tungsten complexes displayed the ligand characteristic bands with appropriate shifts due to complex formation (Table II). In addition, the IR spectrum of $Cr(O)_2(CO)_2(shaH_2)$ complex exhibited two bands in the terminal metal carbonyl

TABLE II Important IR data (cm^{-1})[a] for $shaH_2$ and its chromium, molybdenum and tungsten complexes

Compound	*ν(C=N)*	*ν(C–O)*	*δ(OH)*	*ν(OH)*
$ShaH_2$	1632(s)	1273(m) 1242(m)	1369(m)	3422(m)
1[b]	1613(m)	1280(m) 1156(m)	1400(m)	3450(s)
2[c]	1620(s)	1315(m) 1150(m)	–	–
3[d]	1601(s)	1292(m) 1150(m)	–	–
4[e]	1597(m)	1282(m) 1258(m)	1457(m)	3484(s)

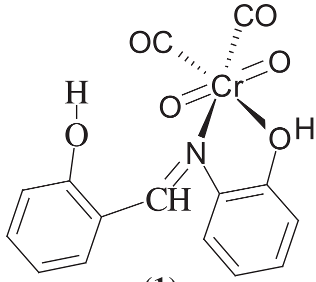
[a] s, strong; m, medium.

[b] ν(C=O): 1948 and 1863 cm^{-1}; ν(Cr–O): 522 cm^{-1}; ν(Cr–N): 419 cm^{-1}; ν(Cr=O): 875 and 925 cm^{-1}.

[c] ν(Mo–O): 459 cm^{-1}; ν(Mo–N): 424 cm^{-1}; ν(Mo=O): 976 cm^{-1}.

[d] ν(Mo–O): 532 cm^{-1}; ν(Mo–N): 467 cm^{-1}; ν(Mo=O): 914 and 934 cm^{-1}; ν(Mo–O–Mo): 847 and 876 cm^{-1}.

[e] ν(C=O): 1921 cm^{-1}; ν(W–O): 502 cm^{-1}; ν(W–N): 476 cm^{-1}.



(1)

SCHEME 2 The $CrO_2(CO)_2(shaH_2)$ Complex.

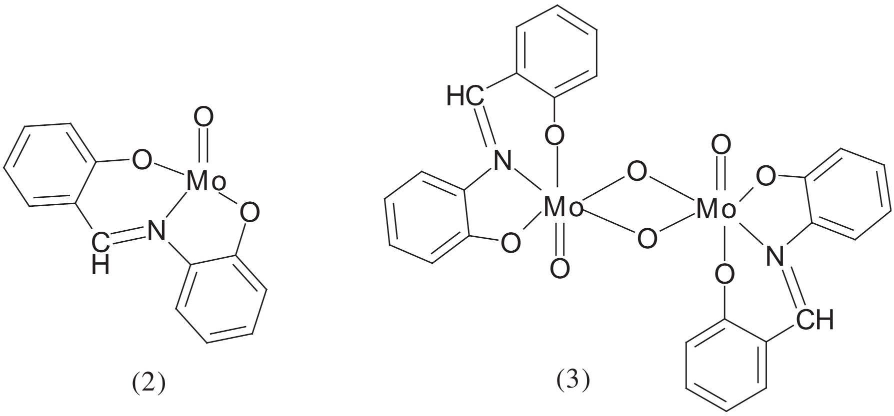
range at 1863 and 1948 cm^{-1} [18]. The presence of two CO bands in the IR spectrum suggested that they were bound to the metal in *cis* positions of a distorted octahedral arrangement [14]. The distortion may be attributed to the non-coplanar characteristic of the ligand [19]. The IR spectrum of **1** also showed two strong bands at 975 and 925 cm^{-1} due to the presence of two M=O bonds [18]. In the far IR spectrum of the chromium complex, the non-ligand bands observed at 522 and 419 cm^{-1} due to Cr–O and Cr–N bonds, respectively, provided conclusive evidence regarding the bonding of phenolic oxygen and azomethine nitrogen of the $shaH_2$ Schiff base to the metal ion [19,20]. The chromium complex was paramagnetic and gave no ^1H NMR spectrum. Magnetic susceptibility measurements of the complex at 298 K gave a value of 9.24×10^{-6} e.m.u.g.$^{-1}$ with an effective magnetic moment (μ_{eff}) of 2.80 BM. The μ_{eff} value indicated a high-spin d^2 electronic configuration. This electronic configuration indicates a +4 formal oxidation state of the chromium in the complex. Accordingly, the complex may have the following structure (Scheme 2).

A similar Schiff base to $shaH_2$, salicylideneimine-2-anisole (salanH), reacted with $Cr(CO)_6$ to give the dicarbonyl derivative $Cr_2O_2(CO)_2(salan)_2$. The IR spectrum of the complex displayed bands due to the CO and Cr–O–Cr bonds [21].

The IR spectrum of the two oxo complexes MoO(sha) and $Mo_2O_4(sha)_2$ showed that the ν(OH) and δ(OH) frequencies of the ligand disappeared. The absence of the OH

TABLE III Important ^1H NMR data for $shaH_2$ and its chromium, molybdenum and tungsten complexes

Compound	*^1H NMR data* (ppm)
$ShaH_2$	13.75(s) [OH, 1H], 9.70(s) [OH, 1H], 9.03(s) [N=CH, 1H], 7.55(m) [Ph, 4H], 7.06(m) [Ph, 4H]
2	9.33(s) [N=CH, 1H], 7.52(m) [Ph, 4H], 6.82(m) [Ph, 4H]
3	9.14(s) [N=CH, 1H], 7.82(m) [Ph, 4H], 7.54(m) [Ph, 4H]
4	9.89(s) [OH, 1H], 9.38(s) [N=CH, 1H], 7.47(m) [Ph, 4H], 6.74(m) [Ph, 4H]



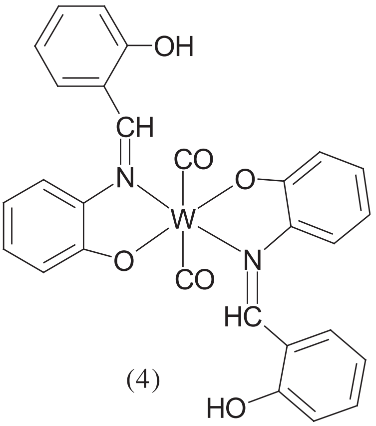
(2)

(3)

SCHEME 3 (2). The MoO(sha) Complex. (3). The $Mo_2(O)_4(sha)_2$ Complex.

group was also confirmed by ^1H NMR spectroscopy. Elimination of the hydrogen from the OH groups indicates that the metal coordinates to the ligand oxidatively [22,23]. However, the IR spectra of the two complexes showed a strong band at 976 cm^{-1} for **2** and two strong bands at 914 and 934 cm^{-1} for **3** indicating the presence of terminal Mo=O bonds in the two complexes [18]. Furthermore, the IR spectra of the molybdenum complexes showed bands corresponding to Mo–O and Mo–N bonds (Table II) and the dinuclear complex **3** showed two strong bands at 849 and 876 cm^{-1} due to Mo–O–Mo bridged bonds. Magnetic studies showed that the two oxo complexes are diamagnetic. In addition, the ^1H NMR spectra of the two complexes exibited signals due to the ligand moieties (Table III). Scheme 3 represents the proposed structures of MoO(sha) (**2**) and $Mo_2O_4(sha)_2$ (**3**) complexes. Interaction of the Schiff base 2-hydroxyacetophenoneethylenediimine ($hapenH_2$) with $Mo(CO)_6$ under atmospheric pressure resulted in the formation of the oxo derivative M(O)(hapen) with the metal atom in the +4 formal oxidation state. Furthermore, the IR spectrum of the complex revealed the presence of an Mo=O band [15]. However, reaction of salan with $Mo(CO)_6$ gave the dinuclear molybdenum complex $Mo_2O_4(salan)_2$. The IR spectrum of the complex showed the disappearance of the OH band of the ligand moieties. In addition, the spectrum displayed asymmetric and symmetric stretching frequencies due to Mo=O and Mo–O–Mo bonds [21]. According to the proposed structures, the molybdenum atom in MoO(sha) has a +4 formal oxidation state with a low-spin d^2 electronic configuration. The $Mo_2O_4(sha)_2$ complex, however, has a +6 (d^0) formal oxidation state. The dinuclear molybdenum complex **3** might be formed through the reaction of **2** with oxygen followed by dimerisation (Eq. (1)) [14,24].

$$2MoO(sha) + O_2 \rightarrow Mo_2O_4(sha)_2 \qquad (1)$$



(4)

SCHEME 4 The $W(CO)_2(shaH)_2$ Complex.

Reaction of $W(CO)_6$ with $shaH_2$ under reduced pressure gave the dicarbonyl bis derivative $W(CO)_2(shaH)_2$. The IR spectrum of the complex showed a ν(OH) stretching frequency at $3484\,cm^{-1}$ (Table II). This band was shifted $62\,cm^{-1}$ to higher frequency and occurred in the free OH region [17]. In addition, the δ(OH) frequency was shifted to $1457\,cm^{-1}$. The shifts in ν(OH) and δ(OH) to higher frequencies indicated the presence of one free OH group [17]. The presence of one OH group was also confirmed by the ^{1}H NMR spectrum. In addition, the IR spectrum of the complex exhibited a strong band in the terminal metal carbonyl region at $1921\,cm^{-1}$ probably due to two CO groups in *trans* positions of an octahedral derivative [18]. Scheme 4 gives the proposed structure for the tungsten complex.

UV–VIS Studies

The electronic absorption spectra of the $shaH_2$ Schiff base and its complexes were investigated in different solvents (Table IV). Two absorption bands were observed for $shaH_2$ in EtOH, THF, CH_2Cl_2 and benzene in the ranges 260–270 and 349–356 nm due to π–π^* and n–π^* transitions, respectively. In the UV–VIS spectra, on going from ligand to complex, the π–π^* electronic transition band showed a bathochromic shift, while the n–π^* band exhibited a hypsochromic shift with a considerable change in absorbance. These observations are consistent with complex formation (Table IV). In addition, the four complexes exhibited absorption bands at 430–440 nm that could be due to ligand-to-metal charge transfer transitions [25–27].

Thermogravimetric Analysis

The thermal studies of the chromium, molybdenum and tungsten complexes were carried out using thermogravimetry (TG) and DTG techniques.

The TG plot of $Cr(O)_2(CO)_2(shaH_2)$ displayed four resolved and well-defined decomposition steps. The first and second decomposition steps occurred in the temperature ranges 330–410 K and 420–460 K, with a net weight loss of 7.95% for each step, probably due to successive elimination of two CO groups (Table V). The third decomposition step occurred in the temperature range 544–702 K with a net weight loss

TABLE IV UV–VIS data for shaH$_2$ and its chromium, molebdenum and tungsten complexes

Compound	λ (nm)			
	EtOH	*CH$_2$Cl$_2$*	*THF*	*Benzene*
ShaH$_2$	260	270	268	268
	349	356	352	356
1	270	282	280	262
	443	444(b)	454(b)	274
				326(b)
				448(b)
2	277	275	278	276
	422(sh)	314(sh)	426(sh)	318(sh)
		428		442(sh)
3	269	269	270(b)	268
	347(sh)	323	332(b)	280
	428	422	428(b)	340
				434(b)
4	276	270	274	280
	347	330(b)	328(sh)	330(b)
	438(sh)	430(b)	434(b)	440

sh, shoulder; b, broad.

TABLE V Thermal analysis data for the chromium, molybdenum and tungsten complexes

Complex	*Decomposition step*, K	*% Weight loss*	*Molecular weight*	*Species eliminated*	*% Solid residue*
1	330–410	7.95	28.01	CO	23.74
	420–460	7.95	28.01	CO	
	544–702	30.33	107.13	C_7H_7O	
	705–806	30.04	106.11	C_6H_4NO	
2	490–700	28.50	92.10	C_6H_4O	39.59
	720–820	31.91	103.12	C_7H_5N	
3	493–619	31.87	216.20	$2(C_6H_4+O_2)$	28.30
	625–760	30.99	210.23	$2(C_7H_5O)$	
	773–890	8.85	60.01	N_2O_2	
4	337–400	4.21	28.01	CO	30.08
	450–820	36.17	28.01 + 212.25	$CO + 2(C_7H_6O)$	
	830–950	29.54	180.21 + 16.00	$2(C_6H_4N) + \frac{1}{2}O_2$	

of 30.33%, due to the loss of a C_7H_7O moiety. The fourth decomposition step (705–806 K, 30.04%) was due to elimination of C_6H_4NO species to leave the residue CrO_2 (Table V).

The TG plot of the MoO(sha) complex (**2**) displayed two decomposition steps in the temperature range 490–820 K (Table V). The first decomposition step occurred in the temperature range 490–700 K with a net weight loss of 28.50% corresponding to elimination of a C_6H_4O moiety. The second decomposition peak occurred in the temperature range 720–820 K with a weight loss of 31.91% and corresponded to the material decomposition of C_7H_5N to give finally the residue MoO_2.

The Mo_2O_4(sha)$_2$ complex (**3**) was found to thermally decomposed in three well-defined steps in the temperature range 493–890 K (Table V). The first decomposition step, at 493–619 K with a net weight loss of 31.87%, corresponds to elimination of two C_6H_4 species and two oxygen molecules. The second decomposition step

(625–760 K, 30.99%) was due to elimination of two C_7H_5O species. The third decomposition step occurred in the temperature range 773–890 K (weight loss 8.85%) probably due to elimination of an N_2O_2 moiety to leave molybdenum metal as a residue.

The $W(CO)_2(shaH)_2$ complex (**4**) decomposed in three well-defined steps with a total mass loss of 69.92%. The first decomposition step occurred in the temperature range 337–400 K and corresponded to the loss of a CO group. The second decomposition step (450–820 K, 36.17%) was due to the elimination of a CO group and two C_7H_6O species. The third decomposition step occurred in the temperature range 830–950 K with a weight loss of 29.54% corresponding to the decomposition of two C_6H_4N and an oxygen atom to leave the metallic oxide WO.

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