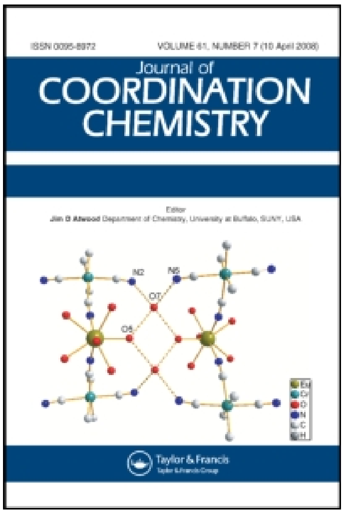

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Reactions of chromium, molybdenum and tungsten carbonyls with a tetradentate schiff base

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To cite this Article El-Medani, Samir M.(2004) 'Reactions of chromium, molybdenum and tungsten carbonyls with a tetradentate schiff base', Journal of Coordination Chemistry, 57: 6, 497 — 507

To link to this Article: DOI: 10.1080/0095897042000213055

URL: http://dx.doi.org/10.1080/0095897042000213055

J. Coord. Chem., Vol. 57, No. 6, 15 April 2004, pp. 497–507

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REACTIONS OF CHROMIUM, MOLYBDENUM AND TUNGSTEN CARBONYLS WITH A TETRADENTATE SCHIFF BASE

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(Received 17 August 2003; Revised 6 October 2003; In final form 11 March 2004)

Interaction of metal carbonyls $M(CO)_6$ (M = Cr, Mo and W) with the tetradentate Schiff base bis(salicylaldehyde)phenylenediimine (salphenH_2) was studied in THF. Under reduced pressure, reaction of salphenH_2 with $M(CO)_6$ (M = Cr, Mo) yielded $Cr(CO)_2$(salphen) **1** and MoO(CO)(salphen) **2**. The complexes MoO_2(salphenH)$_2$ **3** and W_2O_6(salphenH_2) **4** were isolated from reactions in air. All the complexes were characterized by elemental analysis, mass spectrometry and IR and ^{1}H NMR spectroscopy. Spectroscopic studies of the reported complexes revealed the proposed structures. The UV-vis spectra of the complexes in different solvents showed bands due to either metal-to-ligand or ligand-to-metal charge transfer. Thermal properties of the chromium and molybdenum complexes were investigated by thermogravimetric techniques.

Keywords: Schiff base; Chromium; Molybdenum; Tungsten; Metal carbonyl; IR spectra; Thermal decomposition

INTRODUCTION

Complexes of transition metal ions with polydentate Schiff bases containing nitrogen and oxygen donor atoms play an important role in biological systems and represent interesting models for metalloenzymes that catalyze the reduction of dinitrogen and dioxygen [1,2]. Tetradentate ligands having N_2O_4 or N_4 donor sets such as bis(salicylaldehyde)ethylenediimine (salenH_2) and bis(salicylaldehyde)phenylenediimine (salphenH_2) were found to have catalytic activity for epoxidation reactions [3–7]. Electrochemical and spectrochemical studies of Co(salen) and Co(salphen) showed that both compounds formed adducts with oxygen and exhibited catalytic activities for oxygen reduction [6]. Furthermore, complexes of chromium, manganese, nickel and ruthenium with Schiff bases having N_2O_2 and N_4 donor atoms were found to be catalytic for epoxidation reactions [8]. These complexes bound reversibly to molecular oxygen with a change in the oxidation state of the metal [3,4,9,10].

ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/0095897042000213055

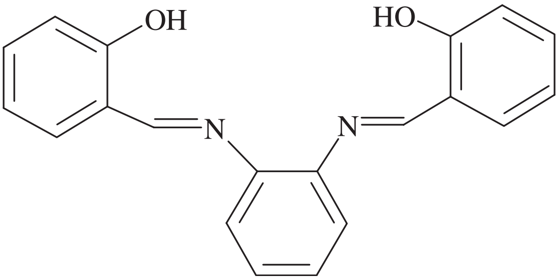


FIGURE 1 Bis(salicylaldehyde)phenylenediimine (salphenH_2).

Reactions of those Schiff bases with group 6 and 8 metal carbonyls have been studied recently [11–13]. Reactions of $M(CO)_6$ ($M = Cr$, Mo) with the Schiff base bis(2-hydroxyacetophenone)ethylenediimine (hapenH_2) in air gave the oxo derivatives M(O)(hapen) with the metal in the +4 formal oxidation state. The dihydride complex $MoH_2(CO)$(hapen) was also isolated under reduced pressure [11]. On the other hand, reaction of hapenH_2 with $Ru_3(CO)_{12}$ resulted in the formation of the dicarbonyl derivative $Ru(CO)_2$(hapenH_2) [12]. Reactions of bis(salicylaldehyde)ethylenediimine (salenH_2) with $M(CO)_6$ ($M = Cr$, Mo) in the presence of air gave the paramagnetic oxo metal complexes M(O)(salen) with a +4 metal oxidation state and a high-spin d^2 configuration [11], while reaction of $Cr(CO)_6$ with salenH_2 under reduced pressure yielded the dicarbonyl derivative $Cr(CO)_2$(salenH_2) with the chromium atom in the zero oxidation state. Recently, we reported the reactions of $M(CO)_6$, $M = Cr$ Mo and W) with *N*-salicylidene-2-hydroxyaniline (shaH_2) [14]. Under reduced pressure, the reactions yielded the two complexes $CrO_2(CO)_2$(shaH_2) and $W(CO)_2$(shaH)$_2$ while in air MoO(sha) and Mo_2O_4(sha)$_2$ were isolated. Structural studies of the complexes revealed that shaH_2 binds to the metal through the oxygen atoms of the hydroxyl groups and the nitrogen atom of the imine group. The type of ligand and the reaction conditions play a vital role in determining the type of products isolated. This has prompted us to investigate reactions of $M(CO)_6$ with bis(salicylaldehyde)phenylenediimine (salphenH_2), Fig. 1. The different structures of the two ligands salenH_2 and shaH_2 compared with the structure of salphenH_2, cause differences in the isolated products.

EXPERIMENTAL

Reagents

$M(CO)_6$ ($M = Cr$, Mo and W) were obtained from Aldrich. Bis(salicylaldehyde)-phenylenediimine (salphenH_2) was prepared as described in ref. [15]. All chemicals were of analytical reagent grade and used without further purification. All solvents were purified by distillation before use.

Synthesis of $Cr(CO)_2$(salphen) Complex

A mixture of $Cr(CO)_6$ (0.10 g, 0.45 mmol) and salphenH_2 (0.14 g, 0.45 mmol) was heated to 50°C for 25 h under reduced pressure in a sealed tube containing 25 cm^3 THF. The color of the reaction mixture changed from yellow to orange and then to brown. The reaction mixture was cooled and the solvent removed on a vacuum line. The residue was washed several times with boiling petroleum ether and then recrystallized from THF to yield brown crystals. The complex was left to dry *in vacuo* for several hours (yield 80%).

Synthesis of MoO(CO)(salphen) Complex

A similar procedure was employed as for $Cr(CO)_2$(salphen) but the reaction period was 10 h. Brown crystals (yield 85%) were obtained.

Synthesis of $MoO_2(salphenH)_2$ Complex

A mixture of $Mo(CO)_6$ (0.1 g, 0.38 mmol) and $salphenH_2$ (0.12 g, 0.38 mmol) in *ca.* 25 cm^3 THF was heated to reflux under atmospheric pressure for 4 h. The reaction mixture was left to cool and the solvent was removed on a vacuum line. The solid was washed with hot petroleum ether and then recrystallized from hot ethanol to give dark brown crystals (yield 85%).

Synthesis of $W_2O_6(salphenH_2)$ Complex

A similar procedure was used as for $MoO_2(salphenH)_2$ with a reaction period of seven days. Brown crystals (yield 80%) were obtained.

Instrumentation

Infrared measurements (KBr pellets) were carried out on a Unicam-Mattson 1000 FT-IR spectrophotometer. Electronic absorption spectra were measured on a Unicam UV2-300 UV-VIS spectrophotometer. Nuclear magnetic resonance measurements were performed on a Spectrospin-Bruker AC200 MHz spectrometer. Samples were dissolved in d_6-DMSO using TMS as an internal reference. Magnetic susceptibilities of the complexes in the solid state (Gouy method) were measured on a Sherwood Scientific magnetic susceptibility balance. Diamagnetic corrections were made using Pascal's constant and $Hg[Co(SCN)_4]$ was used as a calibrant. Elemental analyses were performed on a Perkin-Elmer 2400 CHN instrument. 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 with a heating rate of 10°C/min using a Shimadzu DT-50 instrument. Table I gives the elemental analysis and mass spectrometry data for the complexes.

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

Complex	*C (%)*		*H (%)*		*N (%)*		*Mass spectrometry*	
	Calcd.	*Found*	*Calcd.*	*Found*	*Calcd.*	*Found*	*Mol. Wt.*	*m/z*
1	62.6	62.8	3.3	3.5	6.6	6.8	422.4	$423(p)^+$
2	55.5	55.6	3.1	3.0	6.2	6.1	454.3	$426(p-CO)^+$
3	63.3	63.4	4.0	4.1	7.4	7.3	758.7	$759(p)^+$
4	30.8	30.5	2.1	2.0	3.6	3.8	780.0	$781(p)^+$

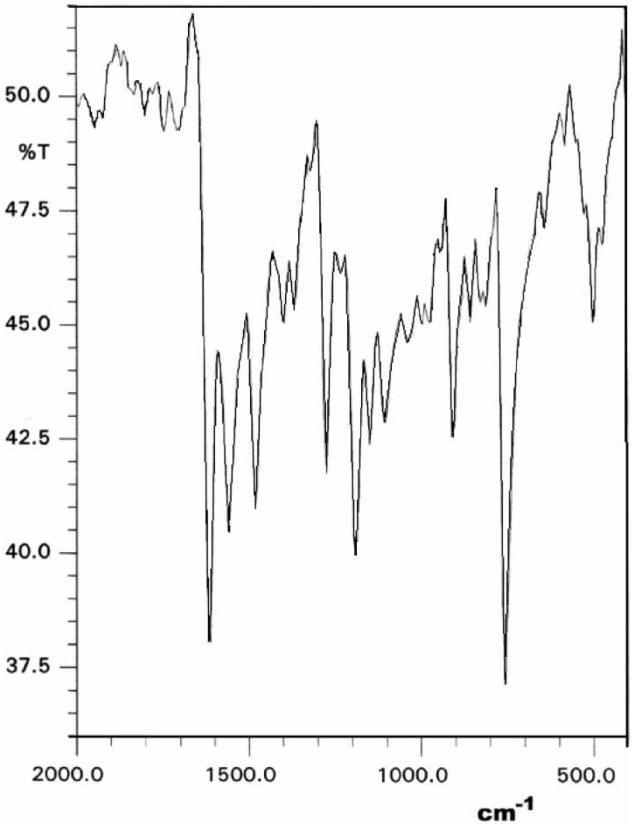


FIGURE 2 The IR spectrum of salphenH$_2$.

RESULTS AND DISCUSSION

Reaction of $Cr(CO)_6$ with bis(salicylaldehyde)phenylenediimine (salphenH$_2$) in THF under reduced pressure yielded the dicarbonyl derivative $Cr(CO)_2$(salphen). The IR spectrum of salphenH$_2$ displayed the characteristic bands due to the OH, C–O and C=N groups (Fig. 2 and Table II). The IR spectrum of the chromium complex showed the ligand bands with appropriate shifts as a result of complex formation (Fig. 3a and Table II). The IR spectrum of the complex also showed the disappearance of the OH bands of the salphenH$_2$ ligand, indicating that the ligand coordinated to the metal oxidatively with displacement of the OH protons [16,17]. In addition, the IR spectrum of the complex displayed two strong bands in the terminal metal carbonyl region at 1944 and 1859 cm^{-1} due to two *cis* CO groups [18]. Investigation of the complex by ^{1}H NMR spectroscopy gave no signals for the ligand moiety, owing to its paramagnetism. It is expected that chromium would have a Cr(II) d^4 configuration. Magnetic susceptibility measurement of the solid complex at 298 K gave a value of 1.2×10^{-5} e.m.u g^{-1} with an effective magnetic moment of 3.5 BM, less than the spin-only value for four unpaired electrons (4.8 BM). However, many paramagnetic chromium complexes exhibit effective magnetic moment values less than the spin-only one. Octahedral Cr(II) complexes may be either high spin or low spin. A number of

TABLE II Important IR and NMR data for salphenH$_2$ and its complexes

Compound	*IR data* (cm^{-1})[a]							*^1H NMR*[b] *data(ppm)*
	ν_{OH}	δ_{OH}	$\nu_{C=O}$	$\nu_{C\text{–}OH}$	$\nu_{C=N}$	$\nu_{M=O}$	$\nu_{M\text{–}O\text{–}M}$	
SalphenH$_2$	3425(m)	1456(m)	–	1273(s)	1612(s)	–	–	6.94(m,Ph), 7.43(m,Ph), 7.65(m,Ph), 8.93(s,CH), 12.86(s,OH)
1	–	–	1944(s) 1859(s)	1265(s)	1605(s)	–	–	–
2	–	–	1975(s)	1250(s)	1597(s)	880(s)	–	6.71(m,Ph), 7.03(m,Ph), 7.44(m,Ph), 9.54(s,CH)
3	3073(m)	1473(s)	–	1273(s)	1605(s)	918(m) 880(m)	–	5.20(m,Ph), 6.86(m,Ph), 7.67(m,Ph), 9.10(s,CH), 10.64(s,OH)
4	3200(m)	1450(m)	–	1258(m)	1605(m)	980(s) 894(s) 818(vs)	633(m) 509(w)	6.72(m,Ph), 6.81(m,Ph), 7.68(m,Ph), 9.05(s,CH) 9.93(s,OH)

[a] vs, very strong, s, strong; m, medium; w, weak.
[b] s, singlet; m, multiplet.

low-spin Cr(II) complexes have magnetic moments in the range 2.7–3.4 BM and their electronic spectra show clear evidence of extensive π-bonding. High-spin Cr(II) complexes are characterized by magnetic moments close to 4.9 BM and the UV-vis spectra include a broad band in the region of 628 nm with another band around 1000 nm [19]. The value of the effective magnetic moment of Cr(CO)$_2$(salphen) (3.5 BM) suggests a low-spin electronic configuration. In addition, the UV-vis spectrum of the complex did not show the characteristic band of the high-spin configuration at 628 nm (*vide infra*). Therefore, it is suggested that the complex has the structure shown in Fig. 4.

Reaction of Cr(CO)$_6$ with bis(salicylaldehyde)ethylenediimine Schiff base (salenH$_2$) under reduced pressure yielded the dicarbonyl derivative Cr(CO)$_2$(salenH$_2$) [11] while the corresponding reaction with salphenH$_2$ Schiff base produced the complex Cr(CO)$_2$(salphen). In Cr(CO)$_2$(salenH$_2$), the ligand binds to chromium through its two nitrogen atoms and two OH hydroxyl groups without proton displacement leaving the metal atom in the zero oxidation state. However, in Cr(CO)$_2$(salphen), the ligand binds to the metal similarly but the hydroxyl groups are bound to chromium oxidatively with proton displacement giving the metal a +2 oxidation state as shown in Fig. 4. Presumably, the presence of an extra phenyl group in the structure of salphenH$_2$ provides a mesomeric effect of the highly conjugated structure producing a partial positive charge on the hydroxyl oxygen and hence facilitating proton displacement.

Reaction of Mo(CO)$_6$ with salphenH$_2$ gave two different products according to the reaction conditions. Under reduced pressure, the monocarbonyl derivative

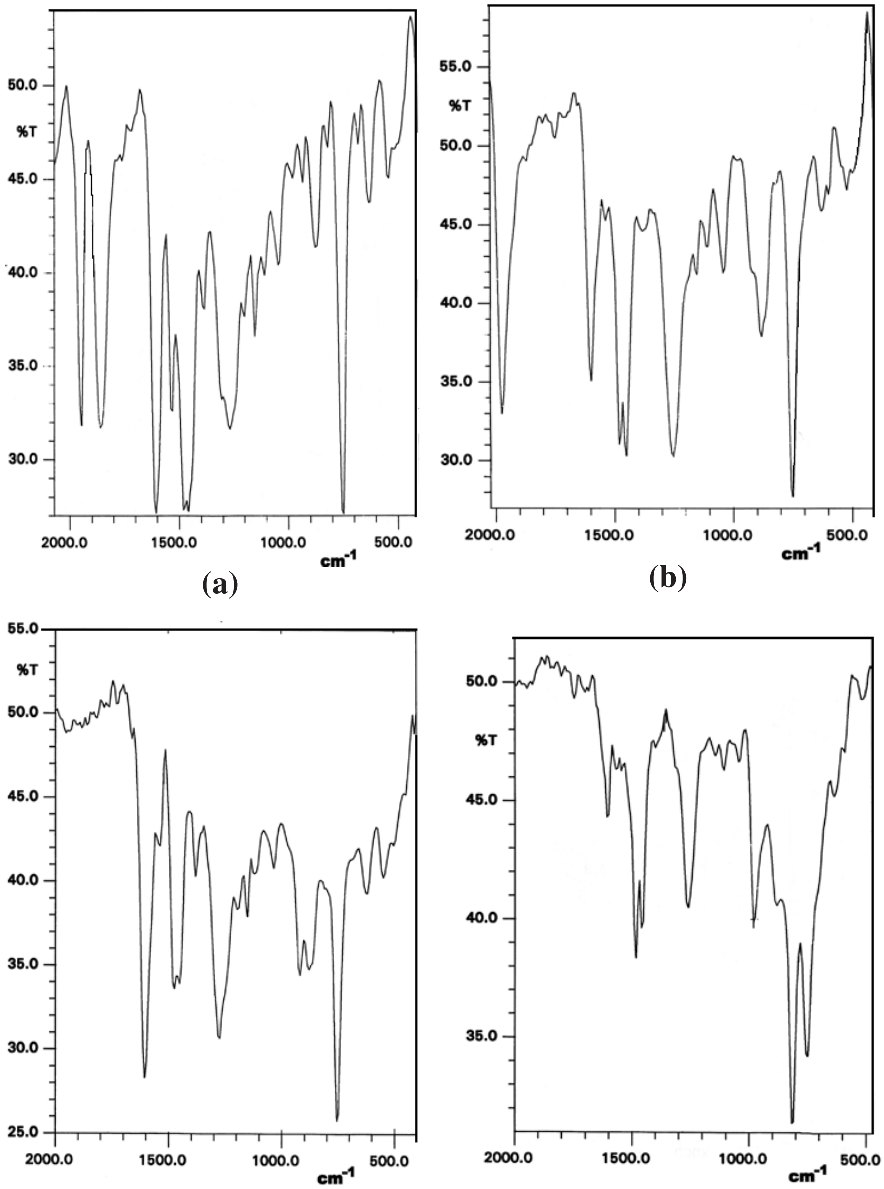
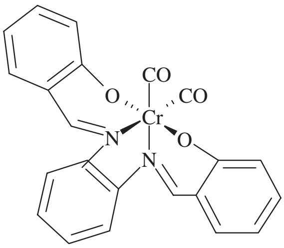


FIGURE 3 The IR spectra of (a) $Cr(CO)_2$(salphen), (b) MoO(CO)(salphen), (c) $W_2O_6(salphenH_2)$, (d) $MoO_2(salphenH)_2$.

MoO(CO)(salphen) was isolated. Although the reaction was carried out under reduced pressure, complete exclusion of oxygen was not possible. In air, the dioxo derivative $MoO_2(salphenH)_2$ was obtained. The IR spectrum of the two complexes displayed the bands of ligand moieties with the required shifts. The IR spectrum of MoO(CO)(salphen) displayed a $\nu(C{=}O)$ band in the terminal metal carbonyl region at 1975 cm^{-1} due to one CO group (Fig. 3b and Table II) [18]. Also, the IR spectrum



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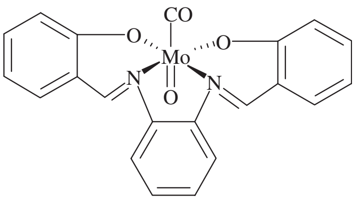

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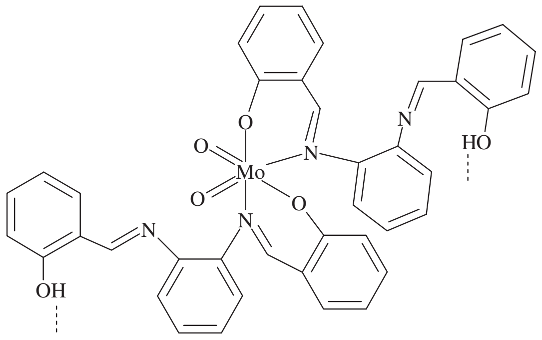

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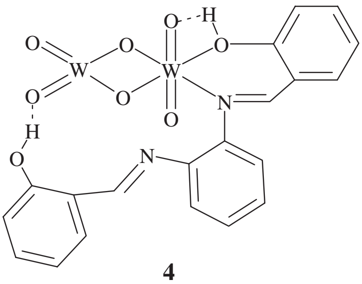

4

FIGURE 4

of the complex exhibited a strong band at 880 cm^{-1} due to stretching vibrations of the Mo=O bond [18]. The mono Mo=O bonds are usually displayed in the IR spectra in the range 900–950 cm^{-1} [18]. The appearance of the Mo=O of the present complex at a lower stretching frequency range could be due to the trans effect of the π-acceptor CO ligand. Furthermore, the IR spectrum of the complex showed disappearance of the OH bands of salphenH$_2$ ligand (Table II), which indicated that the ligand coordinated to the metal oxidatively. This was also confirmed by the disappearance of OH signals in the ^{1}H NMR spectrum of the complex (Table II). Therefore, the oxo complex contains Mo(IV) with a low-spin d^2 electronic configuration due to further splitting of the t$_{2g}$ orbitals in the low-symmetry complex, i.e., $d^2_{xy}\,d^0_{xz}\,d^0_{yz}\,d^0_{x^2-y^2}\,d^0_{z^2}$ Figure 4 gives the proposed structure of the complex.

Refluxing a mixture of salphenH$_2$ and Mo(CO)$_6$ in THF in the presence of air produced a dark-brown complex of molecular formula MoO$_2$(salphenH)$_2$. The IR spectrum of the complex displayed vibrational bands at 3073 and 1473 cm^{-1} due to ν(OH) and δ(OH), respectively. The presence of the OH groups was confirmed by

^{1}H NMR spectroscopy (Table II). The shift of the OH signal to higher field and the shift in its IR band indicated the presence of intermolecular hydrogen bonding [20]. Also, the IR spectrum of the complex displayed two bands at 918 and 880 cm^{-1} due to symmetric and asymmetric stretching frequencies of two Mo=O terminal bonds (Fig. 3c). Therefore, according to the spectroscopic data, the complex might have the structure shown in Fig. 4 with the metal in the +6, d^0 formal oxidation state.

Reaction of $Mo(CO)_6$ with salenH_2 Schiff base under reduced pressure gave the paramagnetic Mo(O)(salen) complex with a high-spin d^2 electronic configuration [11], while the corresponding reaction of $Mo(CO)_6$ with (salphenH_2) yielded a low-spin d^2 MoO(CO)(salphen) complex. The low-spin electronic configuration of the latter complex is due to the presence of the strong field CO ligand and the increased coordination number of the molybdenum–salphenH_2 complex. On the other hand, reactions of $Mo(CO)_6$ with the tridentate shaH_2 ligand in presence of air produced two complexes; MoO(sha) and Mo_2O_4(sha)$_2$. The tetradentate salphenH_2 ligand reacted with $Mo(CO)_6$ in air to give MoO_2(salphenH)$_2$. Both the tetraoxo Mo_2O_4(sha)$_2$ complex and the dioxo MoO_2(salphenH)$_2$ complex have d^0 electronic configuration but they differ in the type of ligation. In Mo_2O_4(sha)$_2$, the ligand coordinated oxidatively with the molybdenum as a tridentate ligand while salphenH_2, ligated through two donor atoms as a bidentate ligand leaving two OH groups to form hydrogen bonds with the oxygen of Mo=O moieties.

Interaction of $W(CO)_6$ with salphenH_2 in air resulted in formation of a dark-brown complex of molecular formula W_2O_6(salphenH_2). The IR spectrum of the complex showed a ν(OH) stretching frequency at 3200 cm^{-1} (Table II). This band was shifted 225 cm^{-1} into the hydrogen bonding region [13,20]. The ^{1}H NMR spectrum of the complex also showed a singlet at 9.93 ppm due to hydrogen-bonded hydroxyl groups. In addition, the δ(OH) frequency was shifted to 1450 cm^{-1}. The shift in the vibrational frequencies of ν(OH) and δ(OH) indicated participation of the two OH groups in bonding without proton displacement [13,21]. Furthermore, the IR spectrum of the complex showed two strong bands at 980 and 894 cm^{-1} as well as a very strong band at 818 cm^{-1} due to W=O stretching frequencies (Fig. 3d). The former two bands could be due to symmetric and asymmetric frequencies of two *cis* W=O bonds [22]. The structure of a binuclear oxo tungsten(VI) complex derived from reaction of 3-hydroxypicolinic acid (Hpic-OH) with WO_4^{2-} was studied [22]. The IR spectrum of the complex showed strong bands at 938 and 892 cm^{-1} due to symmetric and asymmetric metal *cis*-dioxo stretching frequencies. The band at 818 cm^{-1} in the IR spectrum of the present tungsten complex might be due to two *trans* W=O groups [18,23]. Also, the IR spectrum of the complex showed two bands at 633 and 509 cm^{-1}, probably due to symmetric and asymmetric stretching frequencies of W–O–W bonds. From the spectroscopic data, the complex can be formulated as $O_2W(\mu\text{-}O)_2WO_2$(salphenH_2). This formulation will give a +6 tungsten oxidation state. Figure 4 gives the proposed structure of the tungsten complex.

UV-VIS STUDIES

The electronic absorption spectra of the salphenH_2 ligand and its complexes were investigated in different solvents (Table III). Two regions of absorption were observed for salphenH_2 in THF, DMF, hexane, CH_2Cl_2 and ethanol. Absorption bands in the

TABLE III UV-vis data for salphenH$_2$ and its chromium, molybdenum and tungsten complexes

Compound	λ (nm)[a]				
	DMF	*EtOH*	*THF*	*CH_2Cl_2*	*Hexane*
SalphenH$_2$	269	270	270	271	269
			286		
	331	331	336	334	337
1	267	273	278	273	274
			285		
	320	311	310(sh)	320(sh)	302(sh)
			328(sh)		
	427	422		422(b)	423(b)
2	276	274	279	274	269
			284		
	325(sh)	314	323	311(sh)	337
	381(sh)	328		540(b)	442(b)
	530(b)	537(b)			
3	267(sh)	274	265	274	269
			288		
	328(sh)	315(sh)	332	316	337
	364	380(sh)	370(sh)	422	375(sh)
4	277	276	278	275	270
	329(sh)	330(sh)	330(sh)	322(sh)	327(sh)
	459(b)	468(b)	434(b)	454(b)	451(b)

[a] sh, shoulder; b, broad.

range 269–286 nm were due to π–π^* electronic transitions and the bands at 331–337 nm corresponded to n–π^* transitions. On going from ligand to complex, the π–π^* electronic transitions showed bathochromic shifts while the *n*–π^* electronic transitions exhibited hypsochromic shifts (Table III). In addition, the complexes showed absorption bands in the range 422–537 nm, which could be due to metal-to-ligand charge transfer as for the chromium complex (salphen $\pi^* \leftarrow$ Cr dπ) or due to ligand-to-metal charge transfer as for molybdenum and tungsten complexes (salphen $\pi^* \rightarrow$ M dπ) [24].

Thermal Studies

To provide more insight into the composition and structure of the complexes, their thermal stability was investigated by thermogravimetry (Table IV). The observed decomposition processes in the DTG plots are summarized in the following equations:

$$(\mathbf{1})\quad \mathrm{Cr(CO)_2(C_{20}H_{14}O_2N_2)} \xrightarrow{340\text{–}483\,\mathrm{K}} \mathrm{Cr(CO)(C_{20}H_{14}O_2N_2)}$$

$$\xrightarrow{490\text{–}733\,\mathrm{K}} \mathrm{Cr(C_{18}H_{12}O_2)} \xrightarrow{740\text{–}933\,\mathrm{K}} \mathrm{Cr(C_{15}H_6O_2)} \xrightarrow{940\text{–}1273\,\mathrm{K}} \mathrm{CrO_2}$$

$$(\mathbf{2})\quad \mathrm{MoO(CO)(C_{20}H_{14}O_2N_2)} \xrightarrow{353\text{–}488\,\mathrm{K}} \mathrm{MoO(C_{20}H_{14}O_2N_2)}$$

$$\xrightarrow{490\text{–}733\,\mathrm{K}} \mathrm{MoO(C_{14}H_{10}O_2N_2)} \xrightarrow{773\text{–}1083\,\mathrm{K}} \mathrm{MoO(C_3H_3ON_2)} \xrightarrow{1090\text{–}1273\,\mathrm{K}} \mathrm{Mo}$$

TABLE IV Thermal analysis data for the chromium and molybdenum complexes of salphenH_2

Complex	*Decomposition step (K)*	*Weight loss (%)*	*Mol. Wt*	*Species eliminated*	*Solid residue (%)*
$Cr(CO)_2(C_{20}H_{14}O_2N_2)$	340–483	6.63	28.01	CO	18.74
	490–733	19.41	82.00	$CO + C_2H_2N_2$	
	740–933	9.96	42.08	C_3H_6	
	940–1273	44.10	186.21	$C_{15}H_6$	
$MoO(CO)(C_{20}H_{14}O_2N_2)$	353–488	6.16	28.01	CO	21.13
	490–733	16.75	76.10	C_6H_4	
	773–1083	34.15	155.18	$C_{11}H_7O$	
	1090–1273	21.80	99.06	$C_3H_3 + N_2 + O_2$	
$MoO_2(C_{20}H_{15}O_2N_2)_2$	350–453	4.22	32.00	O_2	13.10
	460–653	17.06	129.45	$C_5H_{10} + N_2 + O_2$	
	660–1083	49.34	374.37	$2(C_{12}H_{13}) + N_2 + O_2$	
	1093–1268	16.28	123.50	$C_{11}H_4$	

$$(\mathbf{3})\quad MoO_2(C_{20}H_{15}O_2N_2)_2 \xrightarrow{350\text{–}453\,K} MoO_2(C_{20}H_{15}ON_2)_2$$

$$\xrightarrow{460\text{–}653\,K} MoO_2(C_{35}H_{20}N_2) \xrightarrow{660\text{–}1083\,K} Mo(C_{11}H_4) \xrightarrow{1090\text{–}1273\,K} Mo$$

Studies of the three complexes indicate comparable thermal stability.

CONCLUSION

Schiff-base complexes were found to have applications in homogeneous catalytic reactions such as hydrogenation, carbonylation and epoxidation reactions. The two carbonyl complexes $Cr(CO)_2$(salphen) and MoO(CO)(salphen) were isolated from reactions of $M(CO)_6$ with salphenH_2 under reduced pressures. The ligand added to the metal oxidatively. The oxo metal complexes MoO_2(salphenH)$_2$ and W_2O_6(salphenH_2)$_2$ were isolated from reactions in air. Spectroscopic studies of the two complexes revealed the presence of hydrogen bonding between the OH proton of ligand and the M=O bonds.

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