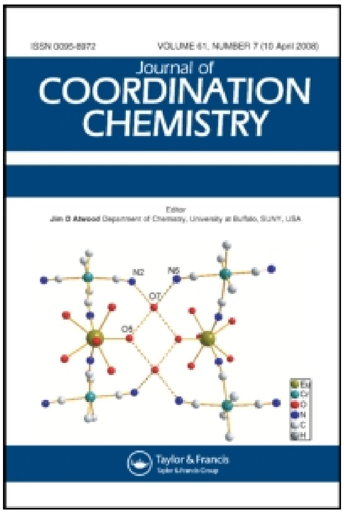

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Reactions of chromium and molybdenum carbonyls with *bis*-(salicylaldehyde)-1,3-propylenediimine Schiff base

Teraze A. Youssef[a]
[a] Faculty of Science, Department of Chemistry, Ain Shams University, Cairo, Egypt

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Reactions of chromium and molybdenum carbonyls with *bis*-(salicylaldehyde)-1,3-propylenediimine Schiff base

TERAZE A. YOUSSEF*

Faculty of Science, Department of Chemistry, Ain Shams University, Cairo, Egypt

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Interaction of a Schiff base, *bis*-(salicylaldehyde)-1,3-propylenediimine, salpenH_2, with $M(CO)_6$ ($M = Cr$ or Mo) in the presence of oxygen gave the oxo-complexes[M(O)(salpen)]. Magnetic studies for the two oxo-complexes showed chromium and molybdenum in the +4 formal oxidation state. In presence of pyridine, reaction of $Cr(CO)_6$ with salpenH_2 gave the identical product; [Cr(O)(salpen)]. Reaction of $Mo(CO)_6$ with salpenH_2 in presence of pyridine (py) resulted in formation of the square-pyramidal complex [Mo(py)(salpenH_2)]. Reactions of $M(CO)_6$ with salpenH_2 in presence of a ligand L ($L =$ bipyridine (bpy) or 3,3-dimethylbipyridine (dmbpy)) gave the octahedral complexes [M(L)(salpenH_2)]. All the complexes were characterized by elemental analyses, IR, mass and ^1H NMR spectroscopy. The spectroscopic studies revealed the proposed structures. UV-Vis spectra of the ligand and its complexes in DMSO exhibited visible bands due to metal-to-ligand or ligand-to-metal charge transfer.

Keywords: *Bis*-(salicylaldehyde)-1,3-propylenediimine; Complexes; Metal carbonyls; Spectra; Pyridine derivatives; Charge transfer

1. Introduction

Metal carbonyl derivatives play an important role in homogenous catalytic reactions such as hydrogenation, hydroformylation, carbonylation and oxygen transfer reactions [1]. Chromium, manganese, cobalt, nickel and ruthenium complexes with a wide variety of ligands having donor sets such as N_2O_2, NO_2 and N_4 around the metal ion have been used as catalysts for epoxidation reactions [2]. These complexes bind reversibly to molecular oxygen with a change in oxidation state of the metal [3–5]. Previous studies on reactions of Group 6 metal carbonyls with Schiff bases containing N_2O_2 and NO_2 donor sets showed complexes with interesting structural features [6–10]. Interaction of either *bis*-(salicylaldehyde) ethylene diimine(salenH_2) or *bis*-(2-hydroxyacetophenone) ethylene diimine(hapenH_2) with $M(CO)_6$, $M = Cr$ or Mo in air gave the oxo complexes, [M(O)(salen)] and [M(O)(hapen)], respectively [9, 6]. Magnetic studies showed the metal in the +4 oxidation state. Also, the IR spectra of the complexes revealed the presence of M=O bonds.

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*Email: trease_albert@yahoo.com

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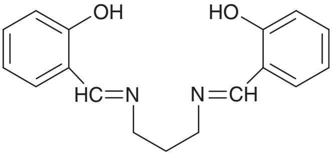


Scheme 1. SalpenH_2 ligand.

In this article we report reactions of $M(CO)_6$, M = Cr, Mo with *bis*-(salicylaldehyde)-1,3-propylenediimine(salpenH_2), (scheme 1), alone or in the presence of either pyridine, bipyridine or 3,3′-dimethylbipyridine.

2. Experimental

2.1. *Materials*

$M(CO)_6$, M = Cr and Mo were supplied by Aldrich. All solvents were of analytical grade and were purified by distillation before use.

2.2.1. Synthesis of *bis*-(salicylaldehyde)-1,3-propylenediimine(salpenH_2). The ligand was synthesized by refluxing an ethanolic solution of salicylaldehyde and 1,3-propylene diamine (2 : 1 molar ratio) for one hour. The reaction mixture was cooled and a bright yellow crystalline solid separated. The solid was filtered off and recrystallized from ethanol to give bright yellow crystals (yield 90%) [11].

2.2.2. Synthesis of Cr(O)(salpen). $Cr(CO)_6$ (0.1 g, 0.45 mmol), salpenH_2 (0.126 g, 0.45 mmol) and 30 mL THF in the presence and absence of pyridine were refluxed for 30 h. The color of the reaction mixture changed from yellow 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 ethanol to give brown crystals. The complex was left to dry under vacuum for several hours (yield 68%).

2.2.3. Synthesis of Cr(bpy)(salpenH_2). $Cr(CO)_6$ (0.10 g, 0.45 mmol), salpenH_2 (0.13 g, 0.45 mmol) and bipyridine (0.07 g, 0.45 mmol) were mixed together in 30 mL THF and heated to reflux under atmospheric pressure for 48 h. The color of the reaction mixture was changed from yellow to brown. The reaction mixture was cooled and the solvent was removed as mentioned before to give brown crystals (yield 83%).

2.2.4. Synthesis of Cr(dmbpy)(salpenH_2). Similar procedure was employed as for synthesis of [Cr(bpy)(salpenH_2)]. Dark brown crystals were obtained (yield 85%).

2.2.5. Synthesis of Mo(O)(salpen). Similar procedure was employed as for [Cr(O)(salpen)] but the reaction period was 20 h. Dark brown crystals with a yield of 65% were obtained.

Table 1. Elemental analysis and mass spectrometry data for the complexes.

	Found (Calcd) (%)			Mass spectrometry	
	C	H	N	Mol. wt	m/z (p^+)
salpenH_2	72.4(72.3)	6.4(6.3)	9.6(9.9)	282.3	283
Cr(O)(salpen)	58.9(58.6)	4.8(4.6)	8.2(8.0)	348.3	349
Cr(bpy)(salpenH_2)	66.5(66.1)	5.1(4.9)	11.7(11.4)	490.5	491
Cr(dmbpy)(salpenH_2)	67.8(67.2)	5.5(5.8)	10.4(10.8)	518.6	519
Mo(O)(salpen)	51.9(52.0)	4.3(4.1)	7.2(7.1)	392.3	393
Mo(py)(salpenH_2)	58.0(57.8)	4.9(5.0)	9.4(9.2)	457.4	458
Mo(bpy)(salpenH_2)	60.6(60.7)	4.7(4.9)	10.8(10.5)	534.5	535
Mo(dmbpy)(salpenH_2)	62.1(61.9)	5.4(5.3)	10.2(10.0)	562.6	563

2.2.6. Synthesis of Mo(py)(salpenH_2). $Mo(CO)_6$ (0.10 g, 0.38 mmol), salpenH_2 (0.11 g, 0.38 mmol) and 30 mL toluene/1 mL pyridine were refluxed for 10 h. The color of the reaction mixture changed from yellow 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 ethanol to give brown crystals. The complex was left to dry under vacuum for several hours (yield 50%).

2.2.7. Syntheses of Mo(bpy)(salpenH_2) and Mo(dmbpy)(salpenH_2) complexes. Similar procedure was employed as for [Cr(bpy)(salpenH_2)] complex. The reaction periods were 15 and 12 h, respectively, and the complexes were brown (yield 75 and 80%, respectively).

3. Instrumentation

Infra red (IR) measurements (KBr pellets) were carried out on a Unicam-Mattson 1000 FTIR. ^1H NMR measurements were carried out on a Spectrospin-Bruker AC 200 MHz NMR spectrometer. The samples were dissolved in deuterated DMSO using TMS as an internal reference. UV-Vis spectra were measured on a Unicam UV 2–300 UV-Vis spectrophotometer. Magnetic susceptibility measurements in the solid state (Gouy method) at 298 K were performed on a Sherwood magnetic susceptibility balance. Diamagnetic corrections were made by Pascal's constants and $Hg[Co(SCN)_4]$ was used as a calibrant. Elemental analyses were carried out on a Perkin-Elmer 2400 CHN elemental analyzer. Mass spectra of the complexes (70 eV, EI) were performed on a Finnigan MATSSQ 700 spectrometer. Table 1 gives the elemental analysis and mass spectrometry data for the complexes.

4. Results and discussion

Reactions of $M(CO)_6$ (M = Cr or Mo) with *bis*-(2-salicylaldehyde)-1,3-propylenediimine(salpenH_2) in THF in presence of air gave the oxo-complexes [M(O)(salpen)]. Also, in presence of pyridine, identical product for chromium was

Table 2. Important IR data for salpenH_2 and their complexes.

	IR data (cm^{-1})			
	$\nu_{(OH)}$	$\nu_{(C–O)}$	$\nu_{(C=N)}$	δpy
salpenH_2	3433(m)	1280(s)	1635(s)	–
Cr(O)(salpen)[a]	–	1288(s)	1620(m)	–
Mo(O)(salpen)[b]	–	1290(s)	1618(m)	–
Cr(bpy)(salpenH_2)	3389(m)	1316(m)	1617(s)	667(m), 614(m), 575(m)
Cr(dmbpy)(salpenH_2)	3419(m)	1319(m)	1618(s)	669(m), 614(m), 570(m)
Mo(py)(salpenH_2)	3440(m)	1285(s)	1620(vs)	756(m), 694(m), 632(m)
Mo(bpy)(salpenH_2)	3419(m)	1282(m)	1607(vs)	766(m), 712(m), 669(m), 628(m)
Mo(dmbpy)(salpenH_2)	3423(s)	1282(m)	1616(vs)	765(m), 715(m), 671(m), 627(m)

[a] ν(Cr=O): 902 (m) cm^{-1}.
[b] ν (Mo=O): 918 (m) cm^{-1}.

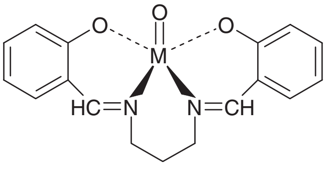
Table 3. Important ^1H NMR data for salpenH_2 and its complexes.

Complex	^1H NMR data (ppm)
salpenH_2	2.50(t, CH_2), 6.88(m, Ph), 7.31(m, Ph), 7.41(m, Ph), 8.58(s,CH), 13.4(s, OH)
Mo(O)(salpen)	2.52(t, CH_2), 6.77(m, Ph), 6.87(m, Ph), 7.41(m, Ph), 8.68(s, CH)
Mo(py)(salpenH_2)	2.84(m, CH_2), 6.85–7.45(m, Ph), 8.76(s, CH), 13.29(s, OH)
Mo(bpy)(salpenH_2)	2.83(m, CH_2), 6.51–7.98(m, Ph), 8.71(s, CH), 10.3(s, OH)
Mo(dmbpy)(salpenH_2)	2.86(m, CH_2), 6.87–7.84(m, Ph), 8.76(s, CH), 10.3(s, OH)

s, singlet; t, triplet; m, multiplet.

obtained. The IR spectra of the two complexes displayed the ligand characteristic bands with the appropriate shifts due to complex formation (table 2). Interestingly, the IR spectra of the two complexes displayed no bands due to OH groups. The ^1H NMR spectra of [Mo(O)(salpen)] complex also showed the disappearance of the OH signal confirming the IR data. The shifts in ν(C–O) and ν(C=N) stretching frequencies and the absence of OH groups indicated that the ligand is coordinated oxidatively to the metal via the hydroxyl oxygen atoms and the azomethine nitrogen atoms [12–15]. Stretching frequencies due to Cr=O and Mo=O were observed at 902 and 918 cm^{-1}, respectively, indicating oxoderivatives. Another two non-ligand bands were observed at 610 and 471 cm^{-1} due to ν(Mo–O) and ν(Mo–N) frequencies, while the ν(Cr–O) and ν(Cr–N) frequencies were observed at 580 and 445 cm^{-1} [14]. Magnetic measurements of [Cr(O)(salpen)] gave an effective magnetic moment (μ_{eff}) value of 2.38 BM, less than the spin only value of two unpaired electrons (2.83 BM). The μ_{eff} value indicates Cr in the +4 (d^2) oxidation state. Several previous Cr(IV) complexes showed lower μ_{eff} values. For example, [Cr(O)(salen)] showed a value of $\mu_{eff} = 2.34$ [11]. [Mo(O)(salpen)] was diamagnetic and the ^1H NMR spectrum of the complex showed signals due to the ligand (table 3). The diamagnetism of the complex would be due to Mo (IV) species with a low-spin d^2 configuration arising from splitting of the t_{2g} orbital in the low symmetry complex [6, 16]. (scheme 2) gives the proposed structures for [M(O)(salpen)] complexes.

Interaction of $Mo(CO)_6$ with the salpenH_2 in presence of pyridine gave a complex with molecular formula [Mo(py)(salpenH_2)]. The IR spectrum showed characteristic bands due to both salpenH_2 and py with the corresponding shifts (table 2).

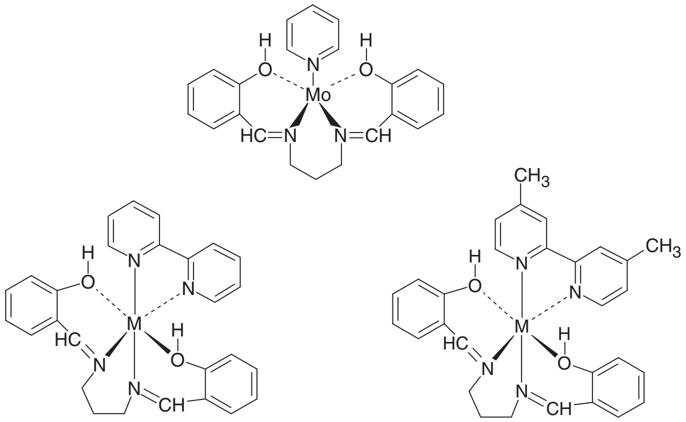


Scheme 2. The proposed structure for M(O)(salpen), [M = Cr and Mo].

Therefore, it could be concluded that molybdenum in [Mo(py)(salpenH$_2$)] exists in a square pyramidal environment with the pyridine monodentate in the apical position. A similar complex was previously obtained from reaction of Mo(CO)$_6$ with *bis*-(salicylaldehyde)ethylenediimine, salenH$_2$, in the presence of pyridine [11]. Interaction of M(CO)$_6$, M = Cr or Mo with salpenH$_2$ in the presence of L, L = bpy or dmbpy gave complexes with molecular formula [M(L)(salpenH$_2$)]. The IR spectra of the complexes showed the characteristic bands due to both salpenH$_2$ and L with the appropriate shifts (table 2). The [M(L)(salpenH$_2$)] complexes also showed in-plane ring deformation bands of pyridines at 624–585 cm^{-1} which were shifted to higher frequencies due to bonding through the pyridyl nitrogen (table 2) [17]. In addition, the IR spectra showed shifts for ν(C = N), ν(C–O) and ν(OH) stretching frequencies indicating bonding to metal through azomethine and hetero nitrogen atoms as well as to the hydroxyl oxygen atoms. The magnetic susceptibilities of the solid complexes were measured at 298 K. The effective magnetic moment (μ_{eff}) for [Cr(bpy)(salpenH$_2$)] and [Cr(dmbpy)(salpenH$_2$)] were found to be 2.47 and 2.84 BM, respectively. These values indicate the presence of two unpaired electrons in the complexes from a Cr(0) species with electronic configuration $d_{xz}^2 d_{yz}^2 d_{xy}^1 d_{z^2}^1 d_{x^2-y^2}^0$. The ^{1}H NMR spectra of the molybdenum complexes, [Mo(L)(salpenH$_2$)], displayed signals due to OH groups (table 3). Also, the ^{1}H NMR spectra showed a set of multiplets due to bipyridine or 3,3′-dimethylbipyridine ligands with the corresponding shifts with respect to free ligands [18]. The presence of OH stretching frequencies in the IR spectra and the OH signals in the ^{1}H NMR spectra indicated bonding of the hydroxyl oxygen to the metal without proton displacement. Scheme 3 gives the proposed structures for the chromium and molybdenum complexes. The proposed structures of [M(bpy)(salpenH$_2$)] and [M(dmbpy)(salpenH$_2$)] have an octahedral structure with bidentate bpy and dmbpy (scheme 3).

4.1. *UV-Vis studies*

The absorption spectra of salpenH$_2$ and its complexes were measured in DMSO. The salpenH$_2$ displayed bands at 265 and 319 nm due to π–π* and n–π* transitions, respectively (table 4). The electronic spectra of the oxo chromium and molybdenum complexes showed a pattern similar to that of ligand. The UV-Vis spectra of the complexes exhibited a new weak band in the visible range (385–499 nm). These bands could be attributed to metal-to-ligand charge transfer transitions (salpenH$_2$ $\pi^* \leftarrow$ Mdπ) for [M(L)(salpenH$_2$)] or ligand-to-metal charge transfer transitions (salpenH$_2$ $\pi^* \rightarrow$ Mdπ) for [M(O) (salpen)] complexes. The charge transfer bands for the molybdenum complexes were observed at longer wavelengths than for chromium



Scheme 3. The proposed structure for Mo(py)(salpenH_2); M(bpy)(salpenH_2) and M(dmbpy)(salpenH_2) complexes, [M = Cr or Mo].

Table 4. Electronic spectra of salpenH_2 and its complexes in DMSO.

Complex	λ (nm)
salpenH_2	247, 265, 319
Cr(O)(salpen)	269, 298, 385
Cr(bpy)(salpenH_2)	265, 315, 385
Cr(dmbpy)(salpenH_2)	265, 314, 388
Mo(O)(salpen)	263, 315, 452
Mo(py)(salpenH_2)	263, 323, 499
Mo(bpy)(salpenH_2)	265, 315, 493
Mo(dmbpy)(salpenH_2)	265, 313, 490

derivatives. Other mono- and bimetallic centers bound to different imine derivatives were found to be highly absorbing in the visible region of the spectrum, attributed to the lower energy of MLCT *versus* LF bands [19–23].

5. Conclusion

The oxo metal complexes [M(O)(salpen)], (M = Cr, Mo) were isolated from reactions of salpenH_2 with $M(CO)_6$ in air. In the presence of pyridine, the square pyramidal complex [Mo(py)(salpenH_2)] was obtained. In the presence of bpy and dmbpy, octahedral complexes with the formula [M(L)(salpenH_2)] were isolated.

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