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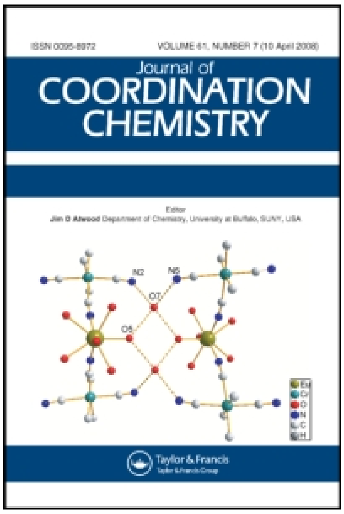

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REACTIONS OF CHROMIUM AND MOLYBDENUM CARBONYLS WITH BIS-(SALICYLALDEHYDE)ETHYLENEDIIMINE SCHIFF-BASE LIGAND

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Interaction of bis-(salicylaldehyde)ethylenediimine, salenH_2, with $M(CO)_6$ (M = Cr, Mo) in air gave M(O)(salen) complexes. Magnetic studies show that the metal exists in the +4 oxidation state. $Cr(CO)_6$ reacted with salenH_2 under reduced pressure to yield the dicarbonyl derivative $Cr(CO)_2$(salenH_2). Reactions of $M(CO)_6$ with salenH_2 in the presence of a secondary ligand L (L = H_2O, pyridine) resulted in the formation of the square pyramidal complex M(L)(salenH_2). UV-Vis spectra of the complexes exhibited visible bands due to metal-to-ligand charge transfer. Structures for the complexes are proposed on the basis of spectroscopic studies.

Keywords: Schiff base; Chromium; Molybdenum; Spectra; Charge transfer

INTRODUCTION

Transition metal carbonyl derivatives are intermediates in homogeneous catalytic reactions such as carbonylation, hydrogenation, hydroformylation and oxygen transfer [1]. Similarly, chromium, manganese, cobalt, nickel and ruthenium complexes with Schiff-base ligands, especially those containing donor atom sets such as N_2O_2, NO_2 and N_4, have found numerous applications in homogeneous catalytic epoxidation reactions [2–5]. These complexes were found to reversibly bind molecular oxygen with a change in oxidation state of the metal. Our interest in the reactions of Group 6 metal carbonyls with some selected Schiff bases containing N_2O_2 and NO_2 donor sets [6–8] has prompted us to study the reactions of $M(CO)_6$ (M = Cr, Mo) with bis-(salicylaldehyde)ethylenediimine, salenH_2, alone or in the presence of either pyridine or water.

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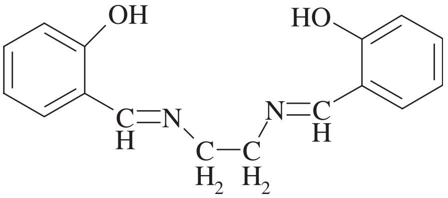


salenH_2

EXPERIMENTAL

Reagents

Metal carbonyls, $M(CO)_6$ (M = Cr, Mo), were purchased from Aldrich. Bis-(2-salicylaldehyde)ethylenediimine (salenH_2) was prepared as described in the literature [9]. All solvents were of analytical grade and purified by distillation before use.

Physical Measurements

IR measurements (KBr discs) were carried out on a Unicam-Mattson 1000 spectrometer. ^{1}H NMR measurements were carried out on a Spectrospin-Bruker AC 200 spectrometer. The samples were dissolved in deuterated DMSO using TMS as an internal reference. UV-Vis spectra were measured on a Unicam UV2-300 spectrophotometer. Magnetic susceptibilities of the paramagnetic complexes in the solid state (Gouy method) were recorded on a Sherwood magnetic susceptibility balance. Diamagnetic corrections were made using Pascal's constant and $Hg[Co(SCN)_4]$ was used as a calibrant. Thermogravimetric analysis (TG) was carried out under nitrogen with a heating rate of 10°C/min using a Shimadzu DT-50 thermal analyzer. Elemental analyses were carried out on a Perkin-Elmer 2400 CHN elemental analyzer. Mass spectra of the complexes (70 eV, EI) were obtained on a Finnigan MAT SSQ 7000 spectrometer. Table I gives the elemental analyses and mass spectrometry data for the complexes. All the chromium and molybdenum complexes reported here were found to be air stable.

Synthesis of $Cr(CO)_2(salenH_2)$

A mixture of $Cr(CO)_6$ (0.10 g, 0.45 mmol) and bis-(2-salicylaldehyde)ethylenediimine (0.12 g, 0.45 mmol) in a sealed tube charged with THF (*ca.* 30 cm^3) was degassed and

TABLE I Elemental analysis and mass spectrometry data for the complexes

Complex	*Found (Calcd.) (%)*			*Mass spectrometry*	
	C	*H*	*N*	*M*	*m/z*
$Cr(CO)_2(salenH_2)$	57.2 (57.5)	4.5 (4.3)	7.2 (7.4)	376.33	349$[P-CO]^+$
CrO(salen)	57.6 (57.5)	4.3 (4.2)	8.6 (8.4)	334.30	335 $[P]^+$
$Cr(H_2O)(salenH_2)$	56.5 (56.8)	5.7 (5.4)	8.2 (8.3)	338.33	338 $[P-H]^+$
$Cr(py)(salenH_2)$	63.0 (63.2)	5.1 (5.3)	10.7 (10.5)	399.41	321 $[P-py]^+$
MoO(salen)	50.6 (50.8)	3.4 (3.7)	7.1 (7.4)	378.24	379 $[P]^+$
$Mo(H_2O)(salenH_2)$	50.1 (50.3)	4.5 (4.7)	7.1 (7.3)	382.27	383 $[P]^+$
$Mo(py)(salenH_2)$	56.6 (56.9)	4.6 (4.8)	9.7 (9.5)	443.36	365 $[P-py]^+$

heated at 70°C in an oil bath for 20 h. The color of the reaction mixture changed from yellow to brown. The reaction mixture was cooled and the solvent was removed using a vacuum line. The residue was washed several times with boiling petroleum ether and then recrystallized from hot THF to give brown crystals. The complex was left to dry *in vacuo* for a few hours (yield 45%).

Synthesis of Cr(O)(salen)

$Cr(CO)_6$ (0.10 g, 0.45 mmol) and salenH_2 (0.12 g, 0.45 mmol) were mixed together in THF (30 cm^3) and heated to reflux in an oil bath under atmospheric pressure for 48 h. The color of the reaction mixture changed from yellow to brown with precipitation of a brown solid. The reaction mixture was cooled and the residue isolated by filtration. The complex was washed several times with hot THF then boiled in petroleum ether to remove impurities. The complex was recrystallized from hot ethanol to give fine dark-brown crystals. The complex was left to dry *in vacuo* for several hours (yield 62%).

Synthesis of Cr(H_2O)(salenH_2)

A mixture of $Cr(CO)_6$ (0.10 g, 0.45 mmol) and salenH_2 (0.12 g, 0.45 mmol) in a sealed tube charged with toluene (*ca.* 25 cm^3) and water (1 cm^3) was degassed and heated at 70°C in an oil bath for 20 h. The color of the reaction mixture changed from yellow to brown. The reaction mixture was cooled and the solvent was removed using a vacuum line. The residue was washed several times with boiling petroleum ether and then recrystallized from hot ethanol to give brown crystals. The complex was left to dry *in vacuo* for few hours (yield 45%).

Synthesis of Cr(py)(salenH_2)

$Cr(CO)_6$ (0.10 g, 0.45 mmol), salenH_2 (0.12 g, 0.45 mmol), toluene (30 cm^3) and pyridine (1 cm^3) were introduced into a sealed tube, degassed and then heated at 70°C in an oil bath for 30 h. The reaction mixture was cooled and the solvent was then removed using a vacuum line. The residue was washed several times with boiling petroleum ether and then recrystallized from hot ethanol to give brown crystals. The complex was left to dry *in vacuo* for several hours (yield 62%).

Synthesis of Mo(O)(salen)

A similar procedure was employed as for CrO(salen) but the reaction period was 20 h. Dark-brown crystals were obtained (yield 75%).

Synthesis of Mo(H_2O)(salenH_2)

A similar procedure was employed as for Cr(H_2O)(salen). The reaction period was 10 h and the complex was pale brown (yield 55%).

Synthesis of Mo(py)(salenH_2)

A similar procedure was employed as for Cr(py)(salen). The reaction period was 15 h and the complex was brown (yield 62%).

RESULTS AND DISCUSSION

Reactions of $Cr(CO)_6$ with salenH_2 in THF were found to be dependent on the reaction conditions. When the reaction was carried out in the absence of oxygen under reduced pressure, the dicarbonyl complex $Cr(CO)_2$(salenH_2) was isolated. On the other hand, an oxochromium complex, Cr(O)(salen), was isolated from reactions in the presence of air. The corresponding reactions of $Mo(CO)_6$ with salenH_2 resulted only in the formation of the oxomolybdenum derivative Mo(O)(salen). The IR spectrum of salenH_2 showed characteristic bands due to the OH, C=N and C–O functional groups (Table II). The IR spectrum of the chromium and molybdenum complexes displayed the characteristic ligand bands with appropriate shifts due to complex formation (Table II). In addition, the IR spectrum of the $Cr(CO)_2$(salenH_2) complex exhibited two bands in the terminal metal carbonyl range due to symmetric and asymmetric stretching frequencies of two CO groups [10]. The presence of two CO bands in the IR spectra suggested that they were bound to the metal in cis positions [10]. The IR spectrum of the oxo complex, M(O)(salen), showed that ν(OH) of the ligand disappeared (Table II). Elimination of hydrogen from the OH groups, which was also confirmed by the disappearance of the OH signal in the ^{1}H NMR spectrum (Table III), indicated that ligand coordinated oxidatively to the metal [1,6,11]. The IR spectra of the two complexes also showed a strong band due to the Cr=O or Mo=O bond (Table II) [10].

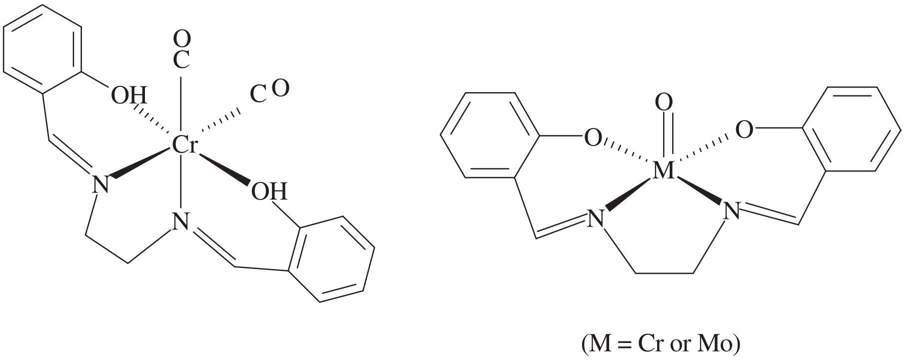
Investigations of the oxochromium and oxomolybdenum complexes by ^{1}H NMR spectroscopy showed no signals for the salen moieties. This behavior is characteristic for paramagnetic materials. The magnetic susceptibilities of the solid complexes were measured at 298 K. The effective magnetic moments (μ_{eff}) for the Cr(O)(salen) and Mo(O)(salen) complexes were found to be 2.34 and 2.21 BM, respectively. Therefore, the paramagnetic oxo complexes would contain M(IV) species with a high-spin d^2 configuration. Reactions of chromium and molybdenum hexcarbonyls with the Schiff base bis-(2-hydroxyacetophenone)ethylenediimine, hapenH_2, a ligand similar to salenH_2 with two methyl groups attached in the vicinity of the donor nitrogen atoms, gave the oxo derivatives M(O)(hapen) (M = Cr, Mo). Magnetic moment

TABLE II Important IR data for salenH_2 and its complexes

Compound	$\nu(OH)$	$\nu(C{=}O)$	$\nu(C–O)$	$\nu(C{=}N)$
SalenH_2	3425(m)	–	1281(s)	1636(s) 1574(m)
$Cr(CO)_2$(salenH_2)	3390(m)	1945(m) 1857(m)	1305(m)	1633(s) 1615(s) 1598(s)
CrO(salen)[a]	–	–	1275(m)	1630(s) 1598(m)
$Cr(H_2O)$(salenH_2)	3418(vs,b)	–	1304(m)	1636(vs) 1599(m)
Cr(py)(salenH_2)	–	–	1312(m)	1620(vs) 1535(m)
MoO(salen)[b]	–	–	1275(m)	1630(s) 1598(m)
$Mo(H_2O)$(salenH_2)	3425(vs,b)	–	1273(m)	1628(s,b)
Mo(py)(salenH_2)	–	–	1288(m)	1612(vs) 1543(m)

[a] $\nu(Cr{=}O) = 879(m)\,cm^{-1}$; [b] $\nu(Mo{=}O) = 889(s)\,cm^{-1}$.

measurements of these complexes showed that the metals were in the +4 oxidation state [6]. However, the μ_{eff} values for the chromium and molybdenum derivatives (2.25 and 1.42 BM) were also found to be less than the spin-only moment for two unpaired electrons. Scheme 1 gives the proposed structure of the chromium and molybdenum complexes.



Scheme 1.

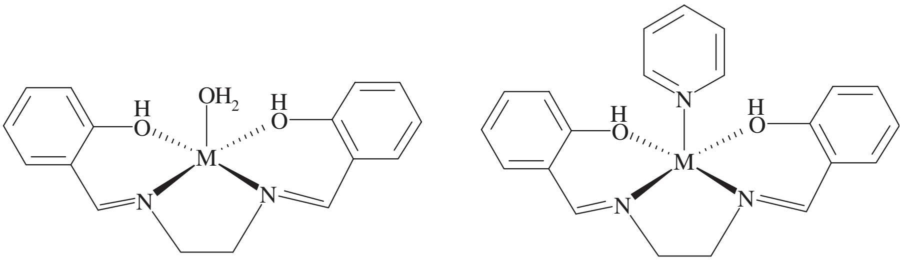
Interaction of either $Cr(CO)_6$ or $Mo(CO)_6$ with salenH_2 under reduced pressure and in the presence of a secondary ligand L (L = H_2O, py) gave complexes with the molecular formula M(L)(salenH_2). The IR spectra of the complexes showed the characteristic bands due to both salenH_2 and the secondary ligand with the corresponding shifts (Table II). In addition, the aquo complexes M(H_2O)(salenH_2) displayed a very strong band at the OH stretching frequency. On the other hand, the M(py)(salenH_2) complex showed that the in-plane ring deformation bands of pyridine, δ(py), at 585–624 cm^{-1} were shifted to higher frequency owing bonding through the pyridyl nitrogen [12]. The ^1H NMR spectra of the complexes displayed signals due to the salenH_2 moieties. Furthermore, the ^1H NMR spectra of the pyridine derivatives showed a set of three multiplets due to the pyridyl moiety (Table III); they exhibited shifts to lower field with respect to the corresponding signals of the free pyridine. Pyridine itself gives three multiplets at 7.0, 7.4 and 8.5 ppm [13]. Also, the ^1H NMR spectra of the aquo complexes exhibited signals due to the protons of water (Table III).

Thus, it can be concluded that the metal atom in the complexes exists in a square pyramidal environment with the ligand L in the apical position (Scheme 2).

TABLE III Important ^1H NMR data for salenH_2 and its complexes

Compound	*Shift* δ (ppm)
SalenH_2	2.50 (t, CH_2), 7.29 (m, Ph), 8.59 (s, CH), 13.32 (s, OH)
$Cr(CO)_2$(salenH_2)	2.56 (t, CH_2), 7.31 (m, Ph), 8.62 (s, CH), 13.41 (s, OH)
Cr(H_2O)(salenH_2)	2.53 (t, CH_2), 7.38 (m, Ph), 8.69 (s, CH), 13.39 (s, OH)
Cr(py)(salenH_2)	2.51 (t, CH_2), 7.18 (m, py), 7.37 (m, Ph), 7.77 (m, py), 8.57 (m, py), 8.65 (s, CH), 13.35 (s, OH)
Mo(H_2O)(salenH_2)	2.50 (t, CH_2), 3.25 (s, H_2O), 7.33 (m, Ph), 8.74 (s, CH), 13.32 (s, OH)
Mo(py)(salenH_2)	2.50 (t, CH_2), 7.15 (m, py), 7.36 (m, Ph), 7.81 (m, py), 8.53 (m, py), 8.71 (s, CH), 13.39 (s, OH)

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



4,6 (M = Cr or Mo)

5,7 (M = Cr or Mo)

Scheme 2.

TABLE IV Electronic spectral data for salenH$_2$ and its complexes

Complex	λ (nm)
SalenH$_2$	256 (22940), 316 (8600)
Cr(CO)$_2$(salenH$_2$)	248 (12310), 312 (6815)[a], 377 (4556)
CrO(salen)	251 (12400), 310 (3215)
Cr(H$_2$O)(salenH$_2$)	250 (13580), 267 (9648)[a], 383 (4650)
Cr(py)(salenH$_2$)	250 (12830), 269 (8680)[a], 386 (4935)
MoO(salen)	255 (12280), 316 (4493)
Mo(H$_2$O)(salenH$_2$)	254 (14675), 312 (7832), 394 (5430)
Mo(py)(salenH$_2$)	255 (12665), 312 (6795), 400 (4520)

Values of molar extinction coefficients, ε, are given in parentheses.
[a] Shoulder.

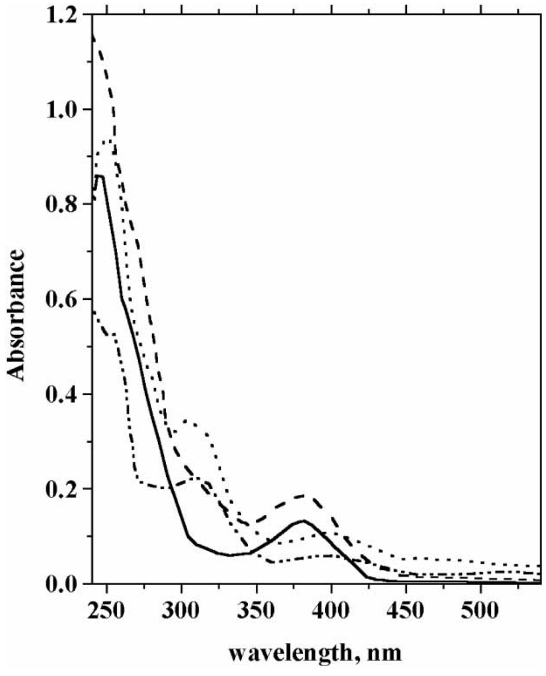


FIGURE 1 The UV-Vis spectra of: (——) Cr(H$_2$O)(salenH$_2$); (- - -) Cr(py)(salenH$_2$); (–· ·–· ·–) Mo(H$_2$O)(salenH$_2$); (······) Mo(py)(salenH$_2$).

UV-Vis Studies

The absorption spectra of salenH_2 and its complexes were measured in ethanol. SalenH_2 displayed two bands at 256 and 316 nm due to π–π^* and n–π^* transitions (Table IV). The electronic spectra of the oxo chromium and molybdenum complexes showed a pattern similar to that of the ligand. The UV-Vis spectra of the other complexes (Fig. 1) exhibited, in addition, a new weak visible band at 377–400 nm. This band could be attributed to metal-to-ligand charge transfer transitions (salen$H_2\pi^* \leftarrow$ Mdπ). Other mono- and bimetallic centers bound to different imine derivatives have been found to be highly absorbing in the visible region of the spectrum; this has been attributed to the lower energy of MLCT versus LF bands [14]. The charge transfer bands for the pyridyl complexes were observed at longer wavelengths than for the aquo derivatives probably, because of the basic nature of the pyridine ligand.

CONCLUSION

The Schiff-base complexes were found to have promising applications in homogeneous catalytic reactions such as hydrogenation, carbonylation and epoxidation. The oxo metal complexes M(O)(salen) (M = Cr, Mo) were isolated from reactions of salenH_2 with $M(CO)_6$ in air. In the presence of a secondary ligand L (L = H_2O, pyridine) the square-pyramidal complexes M(L)(salenH_2) were obtained. The ligand L can serve as a leaving ligand to facilitate catalytic processes.

References

[1] J.P. Collman and L.S. Hegedus, Principles and Applications of Organotransition Metal Chemistry (University Science Books, Mill Valley, California, 1980).
[2] T. Katsuki, *Coord. Chem. Rev.* **140**, 189 (1995).
[3] E.G. Samsel, K. Srinivasan and J.K. Kochi, *J. Am. Chem. Soc.* **107**, 7606 (1985).
[4] K. Srinivasan, P. Michaud and J.K. Kochi, *J. Am. Chem. Soc.* **108**, 2309 (1986).
[5] C.P. Horwitz, S.E. Creager and R.W. Murray, *Inorg. Chem.* **29**, 1006 (1990).
[6] R.M. Ramadan, M.S.A. Hamza and S.A. Ali, *J. Coord. Chem.* **43**, 31 (1998).
[7] S.A. Ali, A.A. Soliman, M.M. Aboaly and R.M. Ramadan, *J. Coord. Chem.* **55**, 1161 (2002).
[8] O.A.M. Ali, M.M.H. Khalil, G.M. Attia and R.M. Ramadan, *Spectroscopy Letters* **36**, 71 (2003).
[9] I.L. Finar, Organic Chemistry (Longman, London, 1967), 5th Edn.
[10] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds (Wiley, New York, 1986), 4th Edn.
[11] S.A. Ali, M.M.H. Khalil and R.M. Ramadan, *Transition Met. Chem.* **25**, 121 (2000).
[12] A.A. Abdel-Shafi, M.M.H. Khalil, H.H. Abdalla and R.M. Ramadan, *Transition Met. Chem.* **27**, 69 (2002).
[13] R.M. Silverstein, G.C. Bassler and T.C. Morrill, Spectrometric Identification of Organic Compounds (Wiley, New York, 1981), 4th Edn.
[14] C. Overton and J.A. Connor, *Polyhedron*, **1**, 53 (1982); K.J. Moore and J.D. Petersen, *Polyhedron* **2**, 279 (1983); R.R. Ruminski and J.O. Jonson, *Inorg. Chem.* **26**, 210 (1987); A.O. Youssef, M.M.H. Khalil, A.A. Soliman and R.M. Ramadan, *Transition Met. Chem.* **28**, 331 (2003); M.M.H. Khalil, H.A. Mohamed, S.M. El-Medani and R.M. Ramadan, *Spectrochim. Acta*, **59A**, 1341 (2003).