

Photochemical reactions of $[M(CO)_6]$ ($M=Cr, Mo, W$) with Quadridentate Schiff-bases

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ABSTRACT

The new complexes $[(\mu-CO)_2Cr_2(\eta^4-H_2L)_2]$, 1; $[(\mu-CO)M_2(CO)_2(\eta^4-H_2L)_2]$, $[M= Mo; 2, W; 3]$; $[(\mu-CO)\mu_2Cr_2(\eta^4-H_2L)_2]$, 4 and $[(\mu-CO)M_2(CO)_2(\eta^4-H_2L)_2]$, $[M=Mo;5, W;6]$ have been synthesized by the photochemical reactions of photogenerated intermediate, $M(CO)_5THF$ ($M=Cr, Mo, W$) with two oxygen and nitrogen donor Schiff base ligands, N-N'-bis(2-hydroxy acetophenoneimine)-1,2-bis (p-aminophenoxy) ethane [H_2L] and N-N'-bis(2-hydroxy acetophenoneimine)-1,4-bis (p-aminophenoxy) butane [H_2L']. The complexes have been characterized by elemental analysis, magnetic studies, I.R. spectroscopy. The spectroscopic studies show that H_2L and H_2L' ligands are coordinated to the central metal as tetra-dentate ligands coordinating via their imine N and O donor atoms in (1-6).

Key words: Schiff Bases, Metal Carbonyl, N-N'-bis(2-hydroxy acetophenoneimine)-1,2-bis (p-aminophenoxy) ethane, N-N'-bis(2-hydroxy acetophenoneimine)-1,4-bis (p-aminophenoxy) butane

INTRODUCTION

The Schiff bases derived from the condensation of aldehyde or ketone with primary amines represent an important class of chelating ligands, the metal complexes of which have been studied widely¹. Many of the Schiff bases in general are found to possess physiological, biological and pharmaceutical activities like antibacterial, antidiabetic, antihelminthic and antidipressant²⁻⁷. Recently, interest in the chemistry of transition metal compounds that contain Schiff bases has increased greatly⁸. The interest in the synthesis and characterization of transition metal complexes containing a Schiff base lies in their biological and catalytic activity in many reactions. The transition metal complexes having oxygen and nitrogen donor Schiff bases possess unusual configuration, structural libility and are sensitive to molecular

environment. The environment around the metal centre "as coordination geometry, number of coordinated ligand and their donor group" is the key factor for metalloprotein to carryout specific physiological function^{1,9,10}. Numerous Schiff base compounds are often used as ligand in coordination chemistry for their metal binding ability. Important and interesting characteristic properties of Schiff bases-metal complexes are their ability to reversibly binding oxygen in expoxidation reactions, complexing ability towards some toxic metals, catalytic activity in hydrogenation of olefins and photochromic properties¹¹⁻¹⁴. The Schiff base complexes have continued to attract attention in past because of the different possible coordination geometries that the ligand may adopt^{11,7,15}. Their low energy metal to ligand charge transfer (MLCT) transitions make these molecules attractive for luminescence and electron transfer reactions¹⁶.

In the light of the above, we have now investigated the six new complexes¹⁻⁶ that have been prepared for the first time by the photochemical reactions of photogenerated intermediate $M(\text{CO})_5\text{THF}$ ($M=\text{Cr, Mo, W}$) with two Schiff base ligands, N-N'-bis(2-hydroxy acetophenoneimine)-1,2-bis (p-aminophenoxy) ethane [H_2L] and N-N'-bis(2-hydroxy acetophenoneimine)-1,4-bis (p-aminophenoxy) butane [$\text{H}_2\text{L}'$] (Figure 1). Then the spectral and magnetic properties of all complexes were studied in detail.

EXPERIMENTAL

Reactions were carried out under dry argon or in vacuo. All solvents were dried and degassed prior to use. Infrared spectra were recorded on a Perkin-Elmer spectrophotometer (Model-577) in KBr discs. All the melting points were determined in an open capillary and are uncorrected. All glassware was oven dried at 120°C, molecular weight of the complexes were determined cryoscopically in benzene. Organic solvent and silica gel were purchased from E. Merck, and $M(\text{CO})_6$ ($M = \text{Cr, Mo, W}$), were purchased from Aldrich.

The Schiff bases H_2L and $\text{H}_2\text{L}'$ were prepared by the literature method¹⁷. Magnetic susceptibility measurements of the complexes were carried out by Gouy method. UV irradiation were performed with a medium pressure 125W mercury lamp through a quartz bulb.

General procedure for the synthesis of complexes (1-6)

Complexes $[(\mu\text{-CO})_2\text{Cr}_2(\eta^4\text{-H}_2\text{L})_2]$, 1; $[(\mu\text{-CO})\text{M}_2(\text{CO})_2(\eta^4\text{-H}_2\text{L})_2]$, [$M = \text{Mo; 2, W; 3}$]; $[(\mu\text{-CO})_2\text{Cr}_2(\eta^4\text{-H}_2\text{L}')_2]$, 4 and $[(\mu\text{-CO})\text{M}_2(\text{CO})_2(\eta^4\text{-H}_2\text{L}')_2]$, [$M=\text{Mo;5, W;6}$] were prepared by the photochemical reactions of $M(\text{CO})_5\text{THF}$ ($M=\text{Cr, Mo, W}$) with N-N'-bis(2-hydroxy acetophenoneimine)-1,2-bis (p-aminophenoxy) ethane [H_2L] and N-N'-bis(2-hydroxy acetophenoneimine)-1,4-bis (p-aminophenoxy) butane [$\text{H}_2\text{L}'$] and obtained in 65-73% yield by similar methods of which the following is typical; A solution of $\text{Cr}(\text{CO})_6$ (0.22g; 1mmole) in 70ml of THF was irradiated to obtain $\text{Cr}(\text{CO})_5\text{THF}$ with UV light in a quartz vessel under a stream of argon for 1½Hr. at room temperature. A solution of H_2L (0.16g; 0.33mmole) in 25ml of THF was added to the

resulting solution of $\text{Cr}(\text{CO})_5\text{THF}$ intermediate. The reaction mixture was irradiated again at room temperature for 2½Hr. at same conditions. During this irradiation the solution changed from yellow to brown. The solvent was removed under vacuum afford a brown airstable solid. Which was shown to be $[(\mu\text{-CO})_2\text{Cr}_2(\eta^4\text{-H}_2\text{L})_2]$, 1 (65% yield). Unreacted $\text{Cr}(\text{CO})_6$ removed by washing the residue several times with light petroleum (40-60°C). The product was recrystallised in benzene

RESULTS AND DISCUSSION

Since the quadridentate H_2L and $\text{H}_2\text{L}'$ ligands are strong electron donors, the imine and phenol groups will assure strong binding to the metal as found the quadridentate salen type complexes¹⁸⁻²¹.

Recently, photogeneration of $M(\text{CO})_5$ from $M(\text{CO})_6$ ($M = \text{Cr, Mo, W}$) has been extensively studied²²⁻²⁸. These 16-electron containing $M(\text{CO})_5$ fragment react quickly with any available donor. The photochemical reactions of $M(\text{CO})_5\text{THF}$ ($M = \text{Cr, Mo, W}$) with quadridentate Schiff bases H_2L and $\text{H}_2\text{L}'$ proceed in this expected manner to yield hitherto unknown series of complexes 1-6. The synthetic route shown in Fig. 2 can be suggested for the formation of complexes 1-6. Irradiation of $M(\text{CO})_5\text{THF}$ ($M = \text{Cr, Mo, W}$) in the presence of N-N'-bis(2-hydroxy acetophenoneimine)-1,2-bis (p-aminophenoxy) ethane [H_2L] and N-N'-bis(2-hydroxy acetophenoneimine)-1,4-bis (p-aminophenoxy) butane [$\text{H}_2\text{L}'$] results in conversion into new $[(\mu\text{-CO})_2\text{Cr}_2(\eta^4\text{-H}_2\text{L})_2]$, 1; $[(\mu\text{-CO})\text{M}_2(\text{CO})_2(\eta^4\text{-H}_2\text{L})_2]$, [$M = \text{Mo; 2, W; 3}$]; $[(\mu\text{-CO})_2\text{Cr}_2(\eta^4\text{-H}_2\text{L}')_2]$, 4 and $[(\mu\text{-CO})\text{M}_2(\text{CO})_2(\eta^4\text{-H}_2\text{L}')_2]$, [$M=\text{Mo;5, W;6}$] which are isolated and characterized by elemental analyses, IR spectra.

The analytical results and some physical properties of the complexes 1-6 are given in Table-1. The stoichiometries of the ligands and their complexes were confirmed by their elemental analysis. The complexes are air stable and soluble in all chlorinated solvents. The absorption frequencies of all $[(\mu\text{-CO})_2\text{Cr}_2(\eta^4\text{-H}_2\text{L})_2]$, 1; $[(\mu\text{-CO})\text{M}_2(\text{CO})_2(\eta^4\text{-H}_2\text{L})_2]$, [$M = \text{Mo; 2, W; 3}$]; $[(\mu\text{-CO})_2\text{Cr}_2(\eta^4\text{-H}_2\text{L}')_2]$, 4 and $[(\mu\text{-CO})\text{M}_2(\text{CO})_2(\eta^4\text{-H}_2\text{L}')_2]$, [$M=\text{Mo;5, W;6}$] complexes are listed in Table 2.

The IR spectra of 1 and 4 exhibit one prominent band at 1717 and 1714 cm^{-1} , respectively in the CO stretching vibrational region. One band $\nu(\text{CO})$ pattern at this region clearly indicates the presence of two bridging CO groups, which are at similar positions. The IR spectrum of 2 contains two bands at 1971 cm^{-1} and 1715 cm^{-1} in the CO stretching vibrational region. The band at 1715 cm^{-1} indicates the presence of a bridging CO group between the metal atoms, the band at 1971 cm^{-1} belongs to two terminal CO groups. Terminal CO groups and Schiff base ligand in 2 are at trans position with each other. As indicated in [29], trans- $[(i\text{-CO})_2\text{Fe}_2(\text{CO})_2 \text{cp}_2]$, which has similar structure with 2, has possessed two CO bands at 1962 cm^{-1} and 1794 cm^{-1} like 2. In addition some literature

explaining that $[(i\text{-CO})\text{Fe}_2(\text{CO})_2 \text{cp}_2]$ which has one bridging CO group and two terminal CO group at cis- positions, indicate three bands in the CO stretching vibrational region. The situation supports that the coordination of CO and Schiff base ligands to the metal centers is at trans position rather than cis- positions. The IR spectra of 3,5,6 contain essentially the same $\nu(\text{CO})$ absorption pattern as observed for 2. These vibrational modes shift to lower wave numbers when compared with these of $\text{M}(\text{CO})_6$ and $\text{M}(\text{CO})_5\text{THF}$ (M= Cr, Mo, W).

The IR spectra of the complexes 1-6 showed the characteristic bands of H_2L and $\text{H}_2\text{L}'$ with the appropriate shifts due to complex formation. The bands in the IR spectra of the Schiff bases

Table 1: Physical and analytical data of Complexes 1-6

Complexes	Empirical Formula	Yield %	Found (Calculated), %			
			C	H	N	Mol. Wt
1	$\text{Cr}_2\text{C}_{62}\text{H}_{56}\text{N}_4\text{O}_{10}$	65	65.43 (66.43)	4.90 (5.00)	4.90 (5.00)	1114 (1121)
2	$\text{Mo}_2\text{C}_{63}\text{H}_{56}\text{N}_4\text{O}_{11}$	69	59.95 (61.17)	4.49 (4.53)	4.47 (4.53)	1232 (1237)
3	$\text{W}_2\text{C}_{63}\text{H}_{56}\text{N}_4\text{O}_{11}$	64	56.33 (57.19)	4.20 (4.24)	4.19 (4.24)	1408 (1413)
4	$\text{Cr}_2\text{C}_{66}\text{H}_{64}\text{N}_4\text{O}_{10}$	68	65.67 (67.35)	5.33 (5.44)	4.36 (4.76)	1163 (1170)
5	$\text{Mo}_2\text{C}_{67}\text{H}_{64}\text{N}_4\text{O}_{11}$	72	60.99 (62.23)	4.89 (4.95)	4.27 (4.33)	1289 (1293)
6	$\text{W}_2\text{C}_{67}\text{H}_{64}\text{N}_4\text{O}_{11}$	73	57.42 (58.35)	4.59 (4.64)	4.02 (4.06)	1465 (1469)

Table 2: Selected I.R. spectral bands (cm^{-1}) of H_2L and $\text{H}_2\text{L}'$ and 1-6

Complexes	$\nu(\text{CO})$	$\nu(\text{C}=\text{N})$	Intramolecular $\nu(\text{O}-\text{H})$ hydrogen bonding	$\nu(\text{OH})$	$\nu(\text{phen C}-\text{O})$
H_2L	-	1612s	2885w	3420m	1285m
$\text{H}_2\text{L}'$	-	1613s	2874w	3445m	1294w
1	1717s	1615s	2890w	3413s	1291w
2	1971s, 1715m	1615s	2890w	3388w	1301w
3	1965s, 1716m	1618s	2881w	3427s	1308w
4	1714s	1614s	2881w	3423s	1298w
5	1965s, 1721m	1614s	2877w	3435m	1289w
6	1974s, 1720m	1615s	2881w	3415s	1294w

H_2L and H_2L' at 2885 cm^{-1} and 2875 cm^{-1} respectively are assigned to the stretch of the intra molecular hydrogen bonded $-OH$ [1,17]. The bands have appeared and displayed shifts considerably in the IR spectra of the complexes 1-6. However, appearance of the intramolecular hydrogen bonded $-OH$ bands, the broad and medium $\mu(OH)$ bands occurring 3420 cm^{-1} and 3445 cm^{-1} in the IR spectra of H_2L and H_2L' , respectively, show shift considerably in the IR spectra of complexes. The strong bands at nearly 1612 cm^{-1} in the IR spectra of complexes. The strong bands at nearly 1612 cm^{-1} in the IR spectra of free H_2L and H_2L' belong to the $C=N$ stretching vibration^{1,17}. This band contain shifts in compounds 1-6, showing that H_2L and H_2L' ligands coordinate to the metal via the imine ($HC=N$)

nitrogen donor atom and the donation of the a lone pair of nitrogen atom with almost no involvement of $C=N$ π -bonds [7]. The bands observed at 1285 cm^{-1} and 1294 cm^{-1} relating, phenolic $C-O$ stretching vibrations in the IR spectra of H_2L and H_2L' are found in the regions $1291-1308\text{ cm}^{-1}$ and $1289-1298\text{ cm}^{-1}$ in the IR spectra of complexes. These changes suggests that the ortho- hydroxyl ($o-OH$) groups of H_2L and H_2L' moieties have taken part in complex formation without elimination of hydrogen atoms from the OH groups, which were also confirmed by the appearance of the new band in the spectra of the metal complexes at $520-583\text{ cm}^{-1}$ and $406-445\text{ cm}^{-1}$ ascribed to the $M-O$ and $M-N$ vibrations^{1,17}, which were not seen in the spectra of the ligands. In addition, magnetic susceptibility measurement

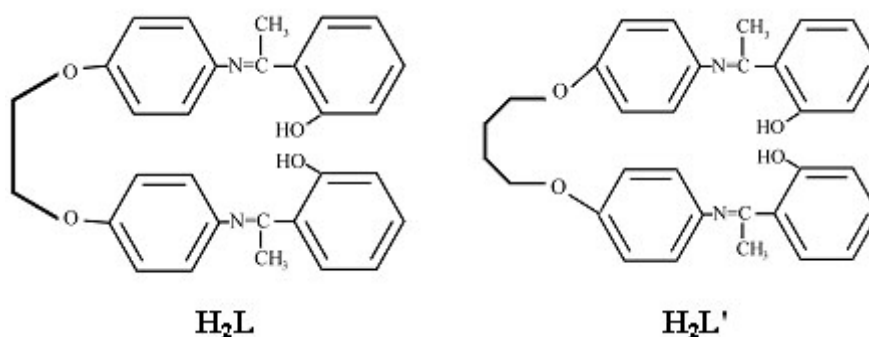


Fig. 1: H_2L and H_2L' , N,N' -bis(2-hydroxy acetophenoneimine)-1,2-bis (p-aminophenoxy) ethane, N,N' -bis(2-hydroxy acetophenoneimine)-1,4-bis (p-aminophenoxy) butane

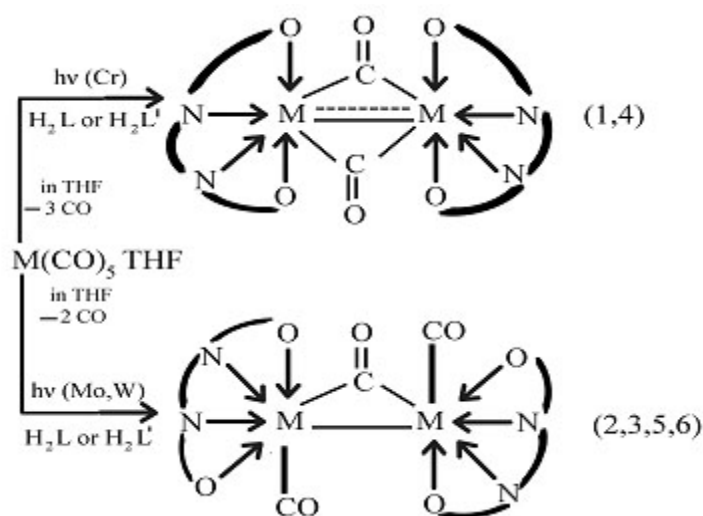


Fig. 2: Representation of photogeneration of $[(\mu-CO)_2Cr_2(\eta^4-H_2L)_2]$, 1; $[(\mu-CO)M_2(CO)_2(\eta^4-H_2L)_2]$, [M= Mo; 2, W; 3]; $[(\mu-CO)_2Cr_2(\eta^4-H_2L')_2]$, 4 and $[(\mu-CO)M_2(CO)_2(\eta^4-H_2L')_2]$, [M=Mo;5, W;6]

shows that 1-6 complexes were diamagnetic. Since these complexes have M(o) [M=Cr, Mo, W] with a low spin d^6 configuration. Such diamagnetism might arise from further splitting of the d-orbital in the low symmetry complexes. i.e. d_{xy}^2 , d_{xz}^2 , d_{yz}^2 , $d(x^2-y^2)^0$, dz^2^0 .

In homoleptic binuclear metal carbonyls, the pair of metal atoms provides two fewer electrons for bonding, so that additional ligands are required for each metal atom to attain the favored 18-electron noble gas configuration [30]. According to the 18-electron rule, two metal atoms must interact with each other to stabilize the complexes (1-6). Cr=Cr double bond is required to give each chromium atom the favored 18-electron rare gas configuration if the single terminal CO group is a normal two electron donor and bridging CO group is a one –electron donor in 1 and 4. In 2,3,5,6 complexes, a single bond between M atoms (M=Mo, W) is enough to reach 18-electrons rare gas configuration.

CONCLUSION

IR spectra of the complexes show that the

H_2L and H_2L' ligands coordinate to the metal atoms via both azomethines' nitrogen and oxygen donor atoms, behaving like quadridentate natural ligand. The C=N stretching vibrations and the stretch of the intramolecular hydrogen bonded –OH in the IR spectra of the complexes exhibit shifts compared with that of ligands. One and two prominent carbonyl bands in the CO stretching vibrational region belonging to two bridging and one bridging–two terminal carbonyl complexes are displayed in 1, 4 and 2, 3, 5, 6 are in good agreement with the expected structure of 1–6.

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