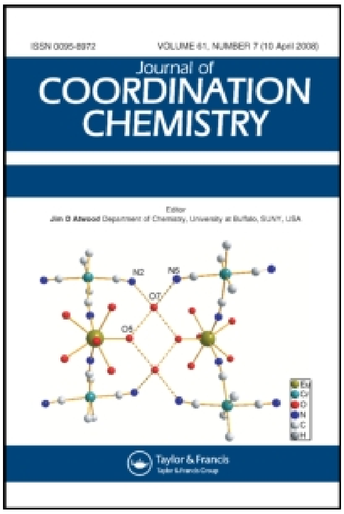

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Reactions of group 6 metal carbonyls with salicylaldehyde isonicotinic acid hydrazone

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Reactions of group 6 metal carbonyls with salicylaldehyde isonicotinic acid hydrazone

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Sunlight irradiation of the reactions of $[M(CO)_6]$, M = Cr, Mo and W with salicylaldehyde isonicotinic acid hydrazone (H_2salnah) in THF were investigated. Interaction of $[Cr(CO)_6]$ with H_2salnah resulted in formation $[Cr_2O_2(H_2salnah)_2]$. The corresponding reactions of molybdenum and tungsten carbonyls yielded dinuclear oxo complexes $[M_2O_6(H_2salnah)]$. All complexes were characterized by elemental analysis, IR, mass spectrometry and ^{1}H NMR spectroscopy. The IR spectra of complexes exhibited bands due to either terminal or bridged metal oxygen bonds. Magnetic measurement of $[Cr_2O_2(H_2salnah)_2]$ showed it has paramagnetic characteristics with high spin d^4 configuration and μ_{eff} of 1.27 BM. Electronic spectra of the complexes in DMF displayed visible bands due to ligand-to-metal charge transfer. Thermal properties of the complexes were investigated by thermogravimetry technique.

Keywords: Metal carbonyls; Hydrazones; Spectra; Thermal analysis

1. Introduction

Transition metal carbonyl derivatives are used as catalysts in reactions such as carbonylation, hydrogenation, and hydroformylation [1–3]. Also, molybdenum is involved in complexes that catalyze nitrogen fixation in plants by some microorganisms [4]. Hydrazones are versatile ligands able to coordinate to metal atoms in different manners [5–8]. Complexes of such ligands have been studied due to the established biological activity [9]. Zinc, mercury, cadmium, thorium and dioxouranium(VI) complexes of hydrazone derivatives have been characterized [10–15].

Recently, we reported the reactions of $[M(CO)_6]$, M = Cr and Mo, with the biological active isoisonicotinic acid hydrazide (inh). The photochemical process resulted in dimerization of inh with elimination of a hydrazine molecule to give *N′*-isonicotinoyliso-nicotino hydrazide (ininh). Complexes with the molecular formula $[MO_2(ininh)]$, ininh = *N′*-isonicotinoylisonicotino hydrazide were formed [16]. In this article, reactions of group 6 metal carbonyls with salicylaldehyde isonicotinic acid hydrazone (H_2salnah) (scheme 1) are reported.

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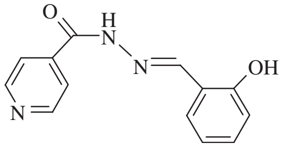


Scheme 1. Salicylaldehyde isonicotinic acid hydrazone (H_2salnah).

Table 1. Melting point, colour and elemental analysis data for the complexes.

			Found			Calculated		
Complexes	M.p. (°C)	Colour	%C	%H	%N	%C	%H	%N
[$Cr_2O_2(H_2$salnah$)_2$]	>300	Brown	50.45	3.73	13.50	50.49	3.56	13.59
[$Mo_2O_6(H_2$salnah)]	>300	Brown	29.33	2.18	8.01	29.5	2.08	7.94
[$W_2O_6(H_2$salnah)]	>300	Light brown	22.17	1.65	5.75	22.13	1.56	5.96

2. Experimental

2.1. *Reagents*

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

2.2. *Instrumentation*

Infrared measurements (KBr pellets) were carried out on a Unicam-Mattson 1000 FT-IR spectrometer. Nuclear magnetic resonance measurements were performed on a Spectrospin-Bruker AC 200 MHz spectrometer. Samples were dissolved in deuterated DMSO, using TMS as internal reference. Magnetic susceptibility measurements of the complexes in the solid state (Gouy method) were recorded on a Sherwood magnetic susceptibility balance. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. Mass spectra of the solid complexes (70 eV, EI) were carried out on a Finnigan MAT SSQ 7000 spectrometer. Thermogravimetric analyses were carried out under nitrogen with a heating rate of $10^\circ C\,min^{-1}$ using a Schimadzu DT-50 thermal analyzer. Table 1 gives melting point, color and elemental analysis data for the complexes.

2.3. *Synthesis of salicylaldehyde isonicotinic acid hydrazone (H_2salnah)*

Salicylaldehyde isonicotinic acid hydrazone(H_2salnah) was prepared by refluxing equimolar amounts of isoisonicotinic acid hydrazide and salicylaldehyde in ethanol for 2 h. Partial removal of solvent on the water bath followed by cooling produced a crystalline product which was suction filtered, washed with cold alcohol and dried in *vacuo* as described [11]. The mass spectrum of the (H_2salnah) showed the molecular ion peak at $m/z = 241$.

Table 2. Important IR data for H_2salnah and chromium, molybdenum and tungsten complexes.

Compound	IR data (cm^{-1})[a]				
	ν(C=O)	ν(C=N)	ν(OH)	ν(M=O)	ν(M–O–M)
H_2salnah	1682(s)	1617(s)	3426(b)	–	–
[Cr_2O_2(H_2salnah)$_2$]	1632(s)	1575(m)	3405(b)	–	697(m) 638(m)
[Mo_2O_6(H_2salnah)]	1607(s)	1556(m)	3425(b)	986(s) 910(s)	699(sh) 630(s)
[W_2O_6(H_2salnah)]	1679(s)	1610(s)	3420(b)	960(s) 881(m)	761(s) 685(m)

[a] s, strong; m, medium; b, broad; sh, shoulder.

2.4. *Synthesis of [Cr_2O_2(H_2salnah)$_2$]*

A mixture of [$Cr(CO)_6$] (0.10 g, 0.45 mmol) and salicylaldehyde isonicotinic acid hydrazone (0.11 g, 0.45 mmol) in THF was exposed to sunlight for 12 h, during which a brown precipitate formed. The residue was filtered off and washed several times with hot petroleum ether. The complex was recrystallized from DMSO to give brown crystals which were dried *in vacuo* for several hours (yield 70%)

2.5. *Synthesis of [Mo_2O_6(H_2salnah)] and [W_2O_6(H_2salnah)]*

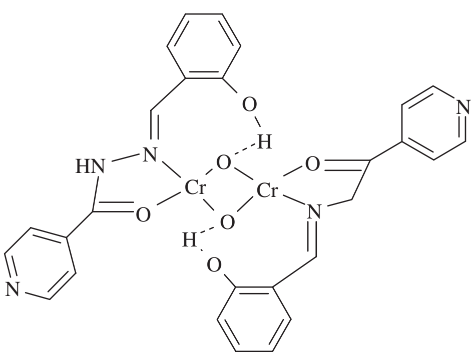
Similar procedure was employed as for [Cr_2O_2(H_2salnah)$_2$] with sunlight irradiation periods of 6 and 8 h, respectively. Brown precipitate of [Mo_2O_6(H_2salnah)] (yield 71%) and light brown precipitate of [W_2O_6(H_2salnah)] (yield 73%) were obtained.

3. Results and discussion

Interaction of [$M(CO)_6$], M = Cr, Mo and W, with salicylaldehyde isonicotinic acid hydrazone under sunlight irradiation resulted in formation of oxo complexes with molecular formulas [Cr_2O_2(H_2salnah)$_2$], [Mo_2O_6(H_2salnah)] and [W_2O_6(H_2salnah)]. The source of oxygen in the oxo complexes could be due to dissolved oxygen in the used solvent.

The IR spectra of [Cr_2O_2(H_2salnah)$_2$], [Mo_2O_6(H_2salnah)] and [W_2O_6(H_2salnah)] displayed ligand bands with appropriate shifts due to complex formation (table 2). The chromium complex exhibited larger shift than the corresponding Mo and W complexes in the OH band. The position of this band may indicate the presence of either inter or intramolecular hydrogen bonding (scheme 2). Two bands at 697 and 637 cm^{-1} were assigned to Cr–O–Cr stretching vibrations [17]. In addition, the IR spectrum of the complex also displayed bands due to ring deformation of pyridine moieties in the range 697–513 cm^{-1} [16]. From elemental analysis and spectroscopic data, the complex may have the structure in scheme 2.

Sunlight irradiation of the reactions of [$M(CO)_6$], M = Cr, Mo and W with either *N*-salicylidene-2-hydroxyaniline (shaH_2) or *bis*-(salicylaldehyde) phenylenediimine



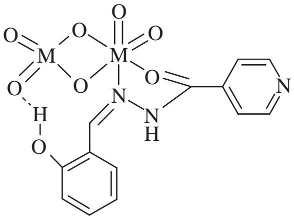
Scheme 2. The proposed structure for $[Cr_2(\mu\text{-}O)_2(H_2salnah)_2]$.

($salphenH_2$) in THF gave the complexes $[Cr(shaH_2)_3]$, $[MoO_2(shaH_2)_2]$, $[W_2O_5(shaH)_2]$, $[CrO(salphenH_2)]$, $[Mo_2O_6(salphenH_2)_2]$ and $[W_2O_6(salphenH_2)]$ [18]. Interaction of $[M(CO)_6]$, M = Cr or Mo, and isoisonicotinic acid hydrazide (inh) in dioxane under sunlight resulted in formation of complexes $[MO_2(ininh)]$ [16]. Numerous oxo molybdenum and tungsten complexes have been reported. For example, interaction of *bis*-(salicylaldehyde)ethylenediimine ($salenH_2$) and *bis*-(2-hydroxyacetophenone) ethylenediimine ($hapenH_2$) with $[Mo(CO)_6]$ in THF gave [Mo(O)(salen)] and [Mo(O)(hapen)] with the metal atom in +4 oxidation state [19, 20]. Also, reactions of the Schiff base salicylideneimine-2-anisole (salanH) with $[M(CO)_6]$, M = Mo or W, gave the dinuclear oxo complex $[M_2O_4(salan)_2]$ [21].

Investigation of $[Cr_2O_2(H_2salnah)_2]$ by ^1H NMR spectroscopy gave no signal because it is paramagnetic. Magnetic measurements of the complex at 298 K gave a magnetic susceptibility value of 1.09×10^{-6} emug^{-1} with an effective magnetic moment (μ_{eff}) 1.27 BM. Therefore, the paramagnetic oxo complex may contain Cr(II), d^4, in a high-spin configuration. The value is slightly less than the spin-only value of two unpaired electrons. However lowering in μ_{eff} could be due to strong antiferromagnetic coupling between the two Cr(II) centers through the two (μ–O) groups. Many paramagnetic chromium complexes show less magnetic moment than the corresponding spin-only value. For example, $[Cr(phenSQ)_3]$, phen SQ = phenanthrenesemiquinone, $[Cr(Cl_4SQ)_3]$, Cl_4SQ = tetrachlorosemiquinone [22], [Cr(O)(hapen)], $hapenH_2$ = *bis*-(2-hydroxyacetophenone)ethylenediimine [20] and $[(MH)Cr(\mu\text{-}O)_2(MH)]$, MH_2 = maleic hydrazide [23].

The sunlight irradiation of a mixture of $[M(CO)_6]$, M = Mo or W with ($H_2salnah$) ligand in THF produced the dinuclear oxo complexes $[M_2O_6(H_2salnah)]$. The infrared spectra of the two complexes displayed ligand bands with the corresponding shifts due to complex formation (table 2). The IR spectra of the two complexes also displayed bands due to ring deformation of pyridine in the range 557–524 and 565–445 cm^{-1} for the molybdenum and tungsten complexes, respectively [16]. Furthermore, the IR spectra of $[Mo_2O_6(H_2salnah)]$ and $[W_2O_6(H_2salnah)]$ displayed bands due to asymmetric and symmetric stretching frequencies of O=M=O indicating that the two oxo groups were *cis*. IR spectra of the complexes exhibited two bands in the range 761–630 cm^{-1} due to two ν(M–O–M) stretching vibrations. (table 2) [24, 25].

The infrared spectra of the molybdenum and tungsten complexes exhibited bands due to OH groups (table 2), due to either inter- or intramolecular hydrogen



Scheme 3. The proposed structure for $[M_2(\mu\text{–}O)_2O_4(H_2salnah)]$ (M = Mo and W).

Table 3. The UV-vis data for H_2salnah and its complexes.

Compound	λ(nm)
H_2salnah	289(1229.9), 334(1421.3), 394(1676.6)
$[Cr_2O_2(H_2salnah)_2]$	268(7108.8), 310(8222.8), 340(9018.7), 439(11,644.6)
$[Mo_2O_6(H_2salnah)]$	271(16,937), 301(18,812), 352(22,000), 430(26,875)
$[W_2O_6(H_2salnah)]$	271(7527.8), 328(9111.1), 400(11,111.1)

Molar extinction coefficients, ε, are given in parentheses.

bonding (scheme 3). The presence of the OH group was also confirmed by ^1H NMR spectroscopy. ^1H NMR spectrum of the H_2salnah ligand exhibited signal at 12.2 ppm due to OH. Investigation of $[Mo_2O_6(H_2salnah)]$ and $[W_2O_6(H_2salnah)]$ complexes by ^1H NMR spectroscopy gave signals at 9.02 ppm. The OH signal displayed shifts to the higher field. The shift in the ^1H NMR signals and the IR bands indicated that the OH groups form hydrogen bond. Also, the ^1H NMR spectra showed two multiplets at 8.1 and 7.2 ppm due to pyridine.

3.1. *Electronic aborption studies*

The electronic absorption spectra of salicylaldehyde isonicotinic acid hydrazone (H_2salnah) and its complexes were measured in DMF table 3. The UV-Vis spectrum of H_2salnah displayed three bands at 289, 334 and 394 nm. The former two bands could be due to π–π* and n–π* transitions. The band at 394nm could be due to charge transfer transition between the ligand and the solvent. The UV-Vis spectra of the complexes in DMF displayed four bands at 268, 310, 340 and 439 nm for chromium complex; 271, 301,352 and 430 nm for molybdenum complex and three bands at 271, 328 and 400 nm for tungsten complex. The absorption bands in the visible range could be due to ligand to metal charge transfer (LMCT). Such LMCT bands are common for these and similar complexes such as $[CrO_2(CO)_2(shaH_2)]$, $[MoO(sha)]$, $[Mo_2O_4(sha)]$ and $[W(CO)_2(shaH)]$, $(shaH_2)$ = *N*-salicylidene-2-hydroxy-aniline [26].

3.2. *Thermogravimetric analysis*

The reported chromium, molybdenum and tungsten complexes were air stable and have high thermal stability. Such characteristics prompted us to investigate their thermal decomposition. This study was carried out using the thermogravimetry (TG) and differential thermogravimetry (DTG) techniques. The decomposition ranges along with

Table 4. Thermal analysis data for the chromium, molybdenum and tungsten complexes.

Molecular formula	Molecular weight	Decomposition step (K)	Weight loss (%)	Mass loss found (calculated)	Eliminated species	Solid residue (%)
$C_{26}H_{22}N_6O_6Cr_2$	618	328–793	39	241.2(241)	$C_{13}H_{11}N_3O_2$	16.5
		793–1237	44.5	275(273)	$C_{13}H_{11}N_3O_2 + O_2$	(2Cr)
$C_{13}H_{11}N_3O_8Mo_2$	529	333–823	57.5	304.2(305)	$C_{13}H_{11}N_3O_2 + 2O_2$	–
		823–1198	42.4	224.3(224)	2MoO	
$C_{13}H_{11}N_3O_8W_2$	705	333–823	34	239.7(241)	$C_{13}H_{11}N_3O_2$	52.7
		823–1273	13.3	93.8(96)	$3O_2$	(2W)

the corresponding mass losses are given in table 4. The TG plot of $[Cr_2O_2(H_2salnah)_2]$ displayed two decomposition steps in the temperature range 328–1273 K (table 4). The first decomposition step consisted of three overlapped decomposition steps, occurred in the temperature range 328–793 K with a net weight loss of 39% corresponding to elimination of a $C_{13}H_{11}N_3O_2$ species. The second decomposition step occurred in the temperature range 793–1273 K with a net weight loss of 44.5% could be due to elimination of a $(C_{13}H_{11}N_3O_2 + O_2)$ species to leave metallic chromium as a residue (weight 16.5%).

The TG plot of $[Mo_2O_6(H_2salnah)]$ displayed two decomposition steps. The first decomposition step, composed of three overlapped decomposition steps, occurred in the temperature range 333–823 K with a net weight loss of 57.5% due to elimination of a $(C_{13}H_{11}N_3O_2 + 2O_2)$ species. The second decomposition step occurred in the temperature range 823–1198 K with a net weight loss of 42.4% corresponding to evaporation of the residue.

The $[W_2O_6(H_2salnah)]$ complex thermally decomposed in two well-defined steps. The first decomposition step occurred in the temperature range 333–823 K with a weight loss of 34% corresponding to loss of $(C_{13}H_{11}N_3O_2)$. The second decomposition step (823–1237 K, 13.3%) was due to the elimination of $(3O_2)$ to yield finally metallic residue (table 4).

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