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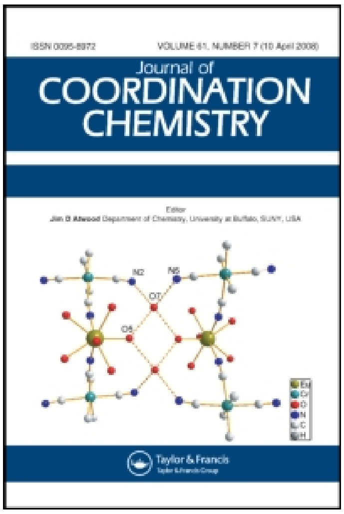

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Structural studies of new group 6 complexes of salicylidene-2-aminopyridine

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Structural studies of new group 6 complexes of salicylidene-2-aminopyridine

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Interaction of salicylidene-2-aminopyridine (Hsap) with $[M(CO)_6]$, M = Cr, Mo and W, in THF under sunlight resulted in formation of dinuclear complexes $[Cr_2O_4(sap)]$, **1**, $[Mo_2O_4(sap)]$, **2**, and $[W_2O_5(sap)_2]$, **3**. Elemental analysis, spectroscopic and magnetic studies of the reported complexes revealed the proposed structures. Magnetic studies of **1** and **2** suggested that the two metal centers have +3 and +6 formal oxidation states, while the tungsten complex **3** has +6 formal oxidation state with d^0 electron configuration. The thermal properties of the complexes were investigated by thermogravimetry.

Keywords: Chromium; Molybdenum; Tungsten; Schiff base; Spectra; Thermal analysis

1. Introduction

Schiff bases are widely used in coordination chemistry because of their promising applications in catalytic reactions [1]. The role of manganese(II) in its Schiff-base complexes derived from salicylaldehyde and aliphatic amines are of significance in green plant photosynthesis [2]. Bidentate Schiff bases and their complexes with ruthenium(III) were tested *in vitro* to evaluate their activity against fungi [2]. Furthermore, ruthenium(II) carbonyl complexes containing O, N donor ligands showed redox properties as well as biological activity [3]. Complexes of Cr(III), Mn(II), Fe(III), Ni(II) and Cu(II) containing a Schiff base resulting from condensation of salicylaldehyde and 2-aminopyridine have been synthesized [4].

Studies of the reactions of group 6 hexacarbonyls with Schiff bases containing oxygen and nitrogen donors have appeared [5–9]. The product and structural arrangements of these complexes were dependent on the reaction conditions such as energy source (thermal, UV), pressure, temperature and solvent. Many metal oxo derivatives in various oxidation states were isolated from these reactions [7–9]. 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 ($salphenH_2$) in THF

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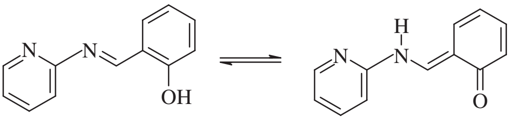


Scheme 1. The enol-keto forms of salicylidene-2-aminopyridine (Hsap).

showed several products [5]. For reactions with $shaH_2$, complexes with molecular formulas $[Cr(shaH_2)_3]$, $[MoO_2(shaH_2)_2]$, $[W_2O_5(shaH)_2]$, $[Cr(shaH_2)_3]$, Cr(III), $[MoO_2(shaH_2)_2]$, Mo(IV) and $[W_2O_5(shaH)_2]$, W(VI), were isolated. Oxo complexes $[CrO(salphenH_2)]$, $[Mo_2O_6(salphenH_2)_2]$ and $[W_2O_6(salphenH_2)]$ were isolated from reactions with $salphenH_2$ [5]; $[W_2O_6(salphenH_2)]$ was identical to that isolated from thermal reactions [6].

To continue our investigation of the reactions of group 6 metal carbonyls with different Schiff bases, here we report the reactions of $[M(CO)_6]$, M = Cr, Mo and W, with salicylidene-2-aminopyridine (scheme 1).

2. Experimental

2.1. *Reagents*

$[M(CO)_6]$, M = Cr, Mo and W were supplied by Aldrich. Salicylidene-2-aminopyridine (Hsap) was prepared as described in literature [10] by condensation of equimolar amounts of salicylaldehyde and 2-aminopyridine in ethanol for 2 h. The isolated yellow product was recrystallized from hot ethanol and dried under vacuum for several hours. All solvents were purified by distillation before use.

2.2. *Instruments*

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

2.3. *Syntheses of complexes*

A mixture of equimolar amounts (0.45 mmol) of $[M(CO)_6]$, M = Cr, Mo and W, and Hsap in ca. 25 mL of THF were exposed to sunlight irradiation for about 6 h in air. The solvent was then removed on a vacuum line. The residue was washed several times by boiling petroleum ether and then recrystallized from methanol/DMSO. The complex

Table 1. Color, yield, elemental analyses and mass spectrometry data for the complexes.

			Elemental analysis						Mass spectrometry	
			% C		% H		% N			
Complex	Color	% Yield	Found	Calcd	Found	Calcd	Found	Calcd	Mol. Wt	m/z $(p)^+$
1	Green	74	39.79	39.45	2.56	2.47	7.65	7.67	364.4	365
2	Light yellow	77	31.44	31.79	2.12	1.99	6.20	6.18	452.3	453
3	Yellow	76	34.34	34.20	2.22	2.14	6.55	6.65	841.6	842

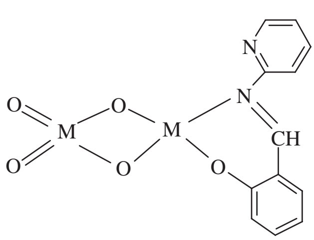
Table 2. Important IR and ^{1}H NMR data for Hsap and its chromium, molybdenum and tungsten complexes.

	IR data (cm^{-1})^a					
Compound	ν(C=N)	ν(C=C)	ν(NH···O)	ν(M=O)	ν(M-O-M)	^{1}H NMR^b data (ppm)
Hsap	1668(s)	1552(s)	3051(m)	–	–	6.96-8.48 (m, 8H, ph, py) 9.51 (s, CH) 13.03 (s, OH)
1	1614(s)	1530(s)	–	934(s) 903(s)	809(s) 761(s)	
2	1624(s)	1532(s)	–	940(s) 901(s)	866(sh) 767(s)	
3	1622(s)	1533(s)	–	974(s) 870(s)	813(s)	6.98–8.63 (m, 8H, ph, py) 9.76 (s, CH)

was left to dry *in vacuo* for several hours. Table 1 gives color, yield, elemental analyses and mass spectrometry data of the complexes.

3. Results and discussion

The reactions of chromium and molybdenum hexacarbonyls with salicylidene-2-aminopyridine (Hsap) under sunlight resulted in formation of two oxo complexes with general formula $[M_2O_4(sap)]$, **1** and **2**. Under similar conditions the reaction of $[W(CO)_6]$ with Hsap gave $[W_2O_5(sap)_2]$, **3**. The IR spectrum (KBr pellets) of Hsap showed characteristic bands due to the functional groups (table 2) [12]. The IR spectrum of the ligand did not show bands due to OH, previously observed in Schiff bases where a hydrogen transfers from a hydroxyl group to the adjacent nitrogen of the azo group forming a keto species [9, 12b]. Instead, it exhibited a medium sharp band at 3051 cm^{-1}, assigned to the intra-molecular hydrogen bond between the hydroxyl–imine or keto–amine of the ligand. The IR spectrum also showed some bands at 3001, 2980, 2924 and 2860 cm^{-1} due to different types of CH bonds. These observations indicate that Hsap exists in the solid state as a keto form (scheme 1). The spectrum of Hsap also displayed strong bands at 1668 and 1552 cm^{-1} due to νC=N and νC=C, respectively (table 2). ^{1}H NMR spectroscopy of Hsap in deuterated DMSO gave signals at 13.03

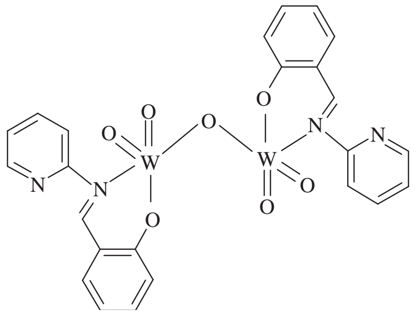


Scheme 2. The proposed structure of $[M_2O_4(sap)]$ complexes, M = Cr (**1**) or Mo (**2**).

and 9.51 ppm due to the presence of OH and azomethine groups, indicating the enol form in solution. Furthermore, the ^{1}H NMR spectrum showed a set of multiplets at 6.96–8.48 ppm due to phenyl and pyridyl protons. The IR spectra of the chromium and molybdenum complexes displayed the characteristic bands of the ligand with appropriate shifts due to complex formation (table 2). The shift in the stretching vibration of C=N bond indicates coordination of the azomethine nitrogen to the metal [6–8]. The IR spectra of the two complexes also displayed two strong symmetric and asymmetric stretching frequencies for Mo=O bonds, assigned for a *cis* MO_2 fragment of a dimeric structure (table 2) [5, 6, 12]. Furthermore, two stretches $\nu_{as}(Mo_2O)$ and $\nu_s(Mo_2O)$ of oxo-bridging groups were observed in the IR spectra of the chromium and molybdenum complexes (table 2). Several complexes having the Mo_2O_6, Mo_2O_5 or Mo_2O_4 cores have been prepared, where molybdenum has a *cis* dioxo and the two Mo atoms are bridged by one or two oxygens [9, 12b]. IR spectra of the complexes exhibit bands due to M–O and M–N bonds [7, 13] and bands due to ring deformation of the pyridine at 666–616 and 620–550 cm^{-1} [14]. IR spectra of the complexes did not show bands due to OH, indicating that the ligand coordinates oxidatively to the metal. It is expected that the metal bound to the sap would have +3 formal oxidation state, while the other metal could have +6 (scheme 2). Investigations of the oxochromium and oxomolybdenum complexes by ^{1}H NMR spectroscopy showed no signals for sap, characteristic for paramagnetic materials. Magnetic studies of the two complexes showed effective magnetic moments (μ_{eff}) of 3.99 and 4.39 BM for the $[Cr_2O_4(sap)]$ and $[Mo_2O_4(sap)]$, respectively. The μ_{eff} for the $[Cr_2O_4(sap)]$ is close to the spin-only moment of three unpaired electrons as expected; the molybdenum derivative showed a higher μ_{eff} than the spin-only moment for three unpaired electrons. The increase in the μ_{eff} value could be due to spin-orbit coupling. Many molybdenum complexes with +3 and +4 formal oxidation states exhibit higher μ_{eff} values than the spin-only moments [15]. Therefore, the chromium and molybdenum oxo complexes contain M(III) species with a high-spin d^3 configuration. Scheme 2 gives the proposed structure of the two complexes.

A similar reaction of $[M(CO)_6]$, M = Cr and Mo, with salicylaldehyde isonicotinic acid hydrazone (H_2salnah) in THF under sunlight resulted in formation of $[Cr_2O_2(H_2salnah)_2]$ and $[Mo_2O_6(H_2salnah)]$ [11].

$[W(CO)_6]$ reacts with Hsap under sunlight to give a yellow complex $[W_2O_5(sap)_2]$, **3**. The infrared spectrum shows ligand bands with appropriate shifts as a result of complex formation (table 2). The shift in stretching vibration of C=N indicates coordination of the azomethine nitrogen to the metal [16]. The infrared spectrum of **3** also has bands at 974 and 870 cm^{-1} due to symmetric and asymmetric frequencies of two terminal *cis* W=O bonds. The IR spectrum exhibited a strong band at 813 cm^{-1}, corresponding to



Scheme 3. The proposed structure for $[W_2O_5(sap)_2]$.

Table 3. Thermal analysis data for the chromium, molybdenum and tungsten complexes.

Complex	Decomposition step (K)	Weight loss (%)	Eliminated species	Solid residue (%)
$[Cr_2O_4(sap)]$	383–973	71.9	$C_{12}H_9N_2O + 4O$	28.1
$[Mo_2O_4(sap)]$	383–1073	58.0	$C_{12}H_9N_2O + 4O$	42.0
$[W_2O_5(sap)_2]$	373–723	27.3	$C_{12}H_9N_2O + 2O$	43.5
	723–1223	29.2	$C_{12}H_9N_2O + 3O$	

a stretching frequency of W–O–W bond. IR of the complex exhibited bands due to W–O and W–N bonds [5] and ring deformation of pyridine in the range 622–588 cm^{-1}. The IR spectrum of the dinuclear oxo complex $[W_2O_5(sap)_2]$ showed the disappearance of the OH band of the ligand (table 2). Elimination of hydrogen from OH, also confirmed by the disappearance of OH signal in the ^{1}H NMR spectrum, indicated that ligand coordinated oxidatively to the metal [7]. The ^{1}H NMR spectrum showed a set of multiplets at 6.98–8.63 ppm due to the phenyl and pyridyl protons. From the elemental analysis and spectroscopic data, it can be concluded that the tungsten complex has the configuration shown in scheme 3. According to the proposed structure, tungsten is +6 with d^0 electron configuration.

Oxo tungsten complexes have been previously reported. For example, reaction of salicylideneimine-2-anisole (salanH) with $[W(CO)_6]$ gave $[W_2O_4(salan)_2]$ [17], and $[W_2O_6(H_2salnah)]$ was isolated from reaction of $[W(CO)_6]$ with salicylaldehyde isonicotinic acid hydrazone **(H_2salnah)** under sunlight irradiation [11].

3.1. *Thermogravimetric analysis*

Thermal studies of the chromium, molybdenum and tungsten complexes were carried out using thermogravimetry (TG) and differential thermogravimetry (DTG). The decomposition ranges along with the corresponding mass losses are given in table 3. $[Cr_2O_4(sap)]$ decomposed in one resolved step with a total mass loss of 71.9% at 383–973 K, corresponding to loss of $C_{12}H_9N_2O + 4O$ to leave chromium as a metallic residue (table 3). Similarly, $[Mo_2O_4(sap)]$ thermally decomposed in one step at 383–1073 K with a weight loss of 58.0%, corresponding to elimination of $C_{12}H_9N_2O$ species and two oxygen molecules (table 3) to leave molybdenum as a metallic residue.

$[W_2O_5(sap)_2]$ displayed two decomposition steps in the temperature range 373–1223 K (table 3). The first, composed of two overlapped decomposition steps, occurred in the temperature range 373–723 K with a net weight loss of 27.3%, due to elimination of $C_{12}H_9N_2O$+2O. The second occurred in the temperature range 723–1223 K with a weight loss of 29.2% corresponding to loss of $C_{12}H_9N_2O + 3O$, leaving tungsten as a metallic residue.

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