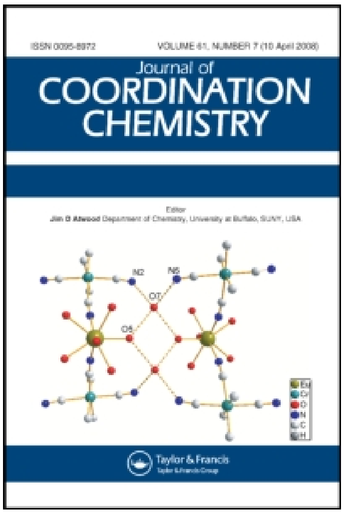

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Novel chromium and molybdenum complexes of a dimerized isonicotinic acid hydrazide

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Sunlight irradiation of $[M(CO)_6]$, M = Cr and Mo with isonicotinic acid hydrazide (inh) was investigated. The photochemical process resulted in dimerization of inh with elimination of a hydrazine molecule to give *N′*-isonicotinoylisonicotino hydrazide (ininh). Two complexes with molecular formulas $[MO_2(ininh)]$ were isolated and characterized by elemental analysis, infrared, mass and ^1H NMR spectroscopy. The UV-vis spectra of the complexes in DMSO showed visible bands due to ligand-to-metal charge transfer. Thermal properties of the complexes were investigated by TG thermogravimetry.

Keywords: Metal carbonyls; Isonicotinic acid hydrazide; Spectra; Thermal analysis

1. Introduction

Isonicotinic acid hydrazide (inh) and its derivatives are antibacterial agents that have been used to treat tuberculosis, interacting with microbial cell walls [1, 2]. Pyridoxal isonicotinoyl hydrazone (pih), an orally available iron chelator for excretion of the excess iron acquired by chronic blood transfusion, is found to be effective at mobilizing iron *in vivo* and *in vitro* at doses that are not toxic [3]. Furthermore, transition metal complexes of inh and its derivatives showed promising application as biologically active materials. For example, complexes of the type $[Cr(inh)_2Cl_2]Cl \cdot 2H_2O$, $VO(inh)_2Cl_2$ and $TiO(inh)_2Cl$ were prepared, characterized by spectroscopic tools and showed significant tuberculostatic activity [4]. Also, studies on *N*-methylaceto-acetanilide isonicotinylhydrazone and its metal chelates revealed that they are active

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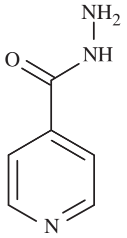


Scheme 1. Isonicotinic acid hydrazide (inh).

against pathogenic fungal strains [1]. Inh and its derivatives were also shown to be excellent chelating agents for lanthanides and actinides [5, 6].

Recently, we have reported the reactions of $M(CO)_6$, M = Cr and Mo, with maleic hydrazide (a biologically active substance) producing complexes with interesting structural features [7]. As a continuation of the investigation of reactions of Group 6 metal carbonyls with biologically active hydrazide derivatives, we report here the reactions of $M(CO)_6$, M = Cr and Mo, with isonicotinic acid hydrazide (inh), scheme 1.

2. Experimental

2.1. *Reagents*

$Cr(CO)_6$, $Mo(CO)_6$ and isonicotinic acid hydrazide (inh) were purchased from Aldrich. All solvents were of analytical grade and purified by distillation before use.

2.2. *Instrumentation*

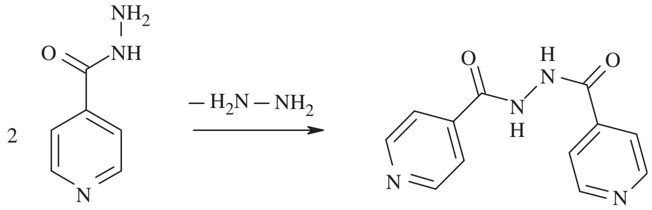
Infrared measurements were carried out on a Unicam-Mattson 1000 FT-IR spectrometer using KBr pellets. Nuclear magnetic resonance measurements were performed on a Spectrospin-Bruker AC 200 MHz spectrometer. Samples were dissolved in DMSO-d_6 using TMS as internal reference. UV-vis measurements were carried out on a Unicam UV2-300 spectrophotometer with 10 mm quartz cell. Magnetic susceptibilities of the paramagnetic chromium complex in the solid state (Gouy method) were recorded on a Sherwood magnetic susceptibility balance. Diamagnetic corrections were made by Pascal's constant and $Hg[Co(SCN)_4]$ was used as a calibrant. 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 Shimadzu DT-50 thermal analyzer. Table 1 gives the elemental analysis and mass spectrometry data for the complexes.

2.3. *Synthesis of complexes*

2.3.1. Synthesis of [CrO_2(ininh)] (1). A mixture of $Cr(CO)_6$ (0.1 g, 0.45 mmol), isonicotinic acid hydrazide (inh) (0.062 g, 0.4 mmol) in dioxane was exposed to sun irradiation for 14 h. The color of the solution was changed from yellow to brown with isolation of a pale brown precipitate. The residue was filtered off and

Table 1. Elemental analysis and mass spectrometric data for the chromium and molybdenum complexes.

	%C		%H		%N		Mass spectrometry	
Complex	Calcd	Found	Calcd	Found	Calcd	Found	Mol. Wt.	*m*/*z*
1	44.2	43.9	4.0	3.9	17.1	17.2	325.95	326 (p^+)
2	38.9	39.2	2.7	2.8	15.1	14.7	369.99	370 (p^+)



Scheme 2. Dimerization of isonicotinic acid hydrazide to *N*′-isonicotinoyl-isonicotino hydrazide (ininh).

washed several times by boiling dioxane followed by hot petroleum ether. The complex was recrystallized from DMSO to give brown crystals (yield 75%).

2.3.2. Synthesis of [MoO$_2$(ininh)] (2). Similar procedure was employed as for CrO$_2$(ininh) with sun irradiation for 10 h. Dark brown crystals were obtained (yield 88%). An identical product was obtained when the reaction was carried out in THF.

3. Results and discussion

UV photolysis by sunlight irradiation was found to be excellent for preparing many interesting complexes, which cannot be prepared by thermal reactions. 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 gave [Cr(shaH$_2$)$_3$], [MoO$_2$(shaH$_2$)$_2$], [W$_2$O$_5$(shaH)$_2$], [CrO(salphenH$_2$)], [Mo$_2$O$_6$(salphenH$_2$)$_2$] and [W$_2$O$_6$(salphenH$_2$)] [8]. Sun irradiation of a mixture of M(CO)$_6$, M = Cr or Mo, and isonicotinic acid hydrazide (inh) in dioxane gave unexpected complexes with the molecular formula [MO$_2$(ininh)], ininh=*N*′-isonicotinoylisonicotino hydrazide. These products were formed *via* dimerization of isonicotinic acid hydrazide probably with the elimination of a hydrazine molecule, scheme 2. It is well established that the hydrazone derivatives have the capability to give dimers with the elimination of either hydrazine or NH$_3$ molecules. The catalytic role of metal carbonyls in organic and organometallic synthesis is also known [9, 10]. Reactions of W(CO)$_6$ with salicylaldehyde hydrazone (shH) in air or under reduced pressure led to formation of the salicylaldehyde azine dimer *via* elimination of a hydrazine molecule. The structure of the dimer was confirmed by crystal structure determination and by FTIR and FT-Raman spectroscopy [11]. This dimer was presumably formed through attack of an shH molecule on the tungsten complex with the formation of a tetracyclic intermediate (*vide infra*).

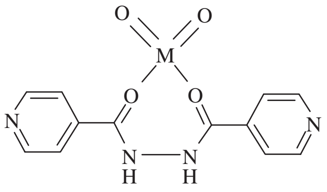
The IR spectrum of isonicotinic acid hydrazide ligand showed characteristic bands due to ν(NH), ν(C=N) and ν(C=O) bands (table 2). The IR spectra of complexes **1** and **2** also showed bands due to the stretching frequencies of NH, C=O and C=N, corresponding to the ininh moiety (table 2). Unfortunately, we were not able to isolate the ininh dimer in its free form and comparison between the IR spectra of complexes and ininh was not possible. However, comparison with the IR spectrum of the parent molecule (inh) gives useful information about the bonding. The IR spectra of the two complexes also displayed bands due to ring deformation of pyridine moieties in the range of 691–531 and 697–569 $\mathrm{cm^{-1}}$ for the chromium and molybdenum complexes, respectively [12]. Furthermore, the IR spectra of **1** and **2** displayed two bands due to symmetric and asymmetric stretching frequencies of M=O bonds, table 2 [13]. Therefore, from the elemental analysis, mass spectrometry and IR spectra, it can be concluded that the metal species in the complexes existed in a tetrahedral environment, coordinated to an ininh moiety from its carbonyl groups and two terminal oxos (scheme 3).

The magnetic measurements of the chromium complex (Cr(IV), d^2) in the solid state (Gouy method) at 298 K gave a magnetic susceptibility value of $1.67 \times 10^{-6}\,\mathrm{emu\,g^{-1}}$ with an effective magnetic moment (μ_{eff}) of 1.14 BM. This value is less than the spin-only value of one unpaired electron. However, many paramagnetic chromium(III) and (IV) complexes have a smaller moment than the corresponding spin-only value. For example, [Cr(phenSQ)$_3$], phenSQ = phenanthrenesemiquinone, [Cr(Cl$_4$SQ)$_3$], Cl$_4$SQ = tetrachlorosemiquinone [14], [Cr(O)(hapen)], hapenH$_2$ = 2-hydroxyacetophenoneethylenediimine [15] and [(MH)Cr(μ–O)$_2$(MH)], MH$_2$ = maleic hydrazide [7]

Table 2. Important IR data for isonicotinic acid hydrazide (inh) and the chromium and molybdenum complexes.

	IR data ($\mathrm{cm^{-1}}$)[a]			
Compound	ν(C=O)	ν(C=N)	ν(NH)	ν(M=O)
Inh	1667(s) 1634(s)	1603(s) 1556(s)	3304(m) 3113(s) 3050(s) 3014(s)	–
1	1615(sh) 1612(s)	1549(s)	3225(s,b)	847(m) 769(m)
2	1679(s) 1611(s)	1551(s)	3202(m,b)	883(m) 850(m)

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



M = Cr or Mo

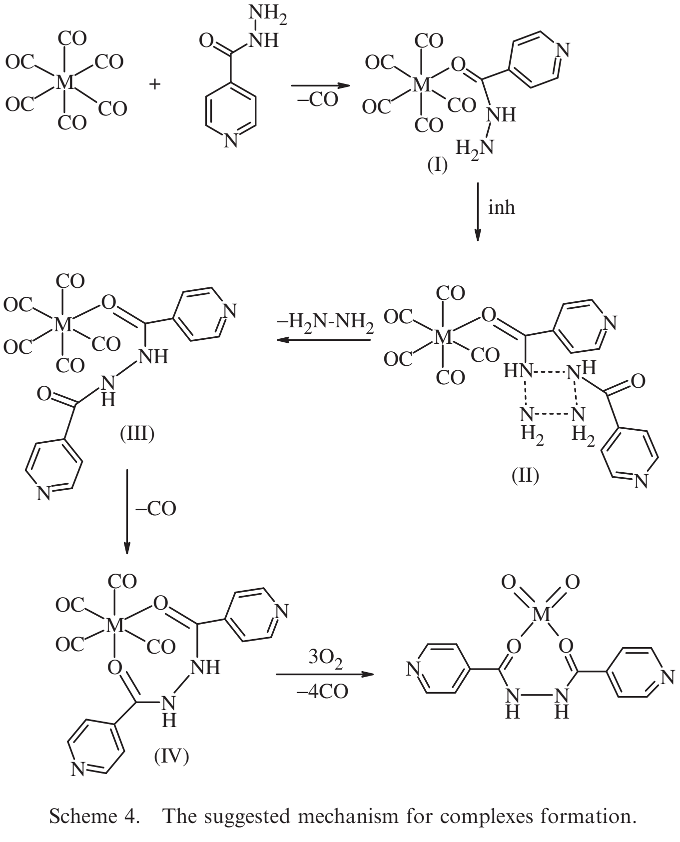
Scheme 3. The proposed structure for complexes.

exhibited μ_{eff} values of 1.15, 1.08, 2.25 and 1.39 BM, respectively. Investigation of the molybdenum complex by ^{1}H NMR spectroscopy showed two multiplets at 8.7 and 7.9 ppm due to the pyridine moieties. Also, the NMR spectrum displayed a broad singlet at 10.98 ppm corresponding to NH.

We have previously found that the reaction of $W(CO)_6$ with salicylaldehyde hydrazone (shH) led to the formation of the salicylaldehyde azine dimer. It was suggested that the dimerization proceeded *via* a tetracyclic intermediate [11]. It is interesting to speculate that the chromium and molybdenum complexes reported here were formed through the mechanism illustrated in scheme 4. Reaction of isonicotinic acid hydrazide with $M(CO)_6$ would form the pentacarbonyl derivative (intermediate I). The amino group of the isonicotinic acid moiety was thus activated through complex formation. Attack of another molecule of inh on the metal complex (intermediate I) would result in formation of the tetracyclic intermediate II. Elimination of a hydrazine molecule would subsequently form intermediate III. Successive elimination of CO groups and reaction with oxygen results in formation of complexes **1** and **2**.

3.1. *Electronic aborption studies*

The electronic absorption spectrum of isonicotinic acid hydrazide in DMSO showed no bands in the visible region, but the spectra of the complexes displayed two bands



Scheme 4. The suggested mechanism for complexes formation.

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

Molecular formula	Molecular weight	Decomposition step (K)	Weight loss (%)	Mass loss found (calculated)	Eliminated species	Solid residue (%)
$C_{12}H_{10}N_4O_4Cr$	325.95	315–527	19.55	63.73(64)	$2O_2$	16.1
		533–830	64.35	209.78(210)	$C_{12}H_{10}N_4$	(Cr)
$C_{12}H_{10}N_4O_4Mo$	369.99	342–470	17.4	64.38(64)	$2O_2$	25.9
		473–730	56.7	209.9(210)	$C_{12}H_{10}N_4$	(Mo)

at 327, 420; and 317, 497 nm for the chromium and molybdenum derivatives, respectively. The higher energy band was assigned to a n–π^* transition. The absorption band appearing at higher wavelength was due to ligand-to-metal charge transfer (LMCT) [16]. The CT band of the molybdenum complex occurred at higher wavelength and was more intense.

3.2. *Thermogravimetric analysis*

To examine the structure and thermal stability of the chromium and molybdenum complexes, the thermal studies were carried out using thermogravimetry (TG) and differential thermogravimetry (DTG) techniques.

The TG plot of $[CrO_2(ininh)]$ (**1**) displayed two resolved and well-defined decomposition steps (table 3). The first decomposition step occurred in the temperature range 315–527 K with a net weight loss of 19.55%, which could be due to elimination of two moles of oxygen ($2O_2$). The second decomposition step occurred in the temperature range 533–830 K with a net weight loss of 64.35% corresponding to material decomposition with elimination of $C_{12}H_{10}N_4$ fragments to give the metallic residue (Cr) with a net weight of 16.1%.

Thermal decomposition of $[MoO_2(ininh)]$ (**2**) displayed an identical pattern to that of the chromium complex with two decomposition steps in the temperature range 342–730 K, indicating higher thermal stability with respect to the first decomposition step, table 3. The first decomposition step occurred in the temperature range 342–470 K with a net weight loss of 17.4% corresponding to elimination of $2O_2$ molecules. The second decomposition step occurred in the temperature range 473–730 K with a weight loss of 56.7% due to material decomposition of $C_{12}H_{10}N_4$ species to give finally the metallic residue of Mo with a net weight of 25.9%.

4. Conclusion

Photochemical reactions of $M(CO)_6$, M = Cr and Mo, with isonicotinic acid hydrazide through sunlight irradiation resulted in dimerization of the hydrazide ligand to *N′*-isonicotinoylisonicotino hydrazide followed by coordination to the metal to give oxo complexes. Both metals were found to have +4 formal oxidation states. The chromium derivative was paramagnetic with a high spin electronic configuration, while the molybdenum was diamagnetic with a low spin configuration.

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