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Synthesis and characterization of isatin complexes with $M(\text{CO})_6$, $M = \text{Cr}$ or Mo

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The reactions of $M(\text{CO})_6$, $M = \text{Cr}$ or Mo with isatin (isatH) were investigated. Three complexes with molecular formulae $[\text{Cr}(\text{CO})_5(\text{isatH})]$ (1), $[\text{Cr}_2\text{O}_2(\text{isatH})_2]$ (2) and $[\text{Mo}_2\text{O}_4(\text{isatH})_2]$ (3) were isolated from the reactions with isatH. In presence of bipyridine, bpy, two derivatives $[\text{Cr}(\text{CO})_4(\text{isatH})]\cdot\text{bpy}$ (4) and $[\text{Mo}(\text{CO})_4(\text{isatH})]\cdot\text{bpy}$ (5) were isolated. All complexes were characterized by elemental analysis, infrared, mass, ESR and ^1H NMR spectroscopy. The UV–Vis spectra of the complexes in different solvents showed bands due to either metal-to-ligand or ligand-to-ligand charge transfer transition. Thermal properties of the complexes were investigated by TG technique.

Keywords: Isatin; Chromium; Hexacarbonyl; Molybdenum

1. Introduction

Isatin (2,3-dihydroindole-2,3-dione, isatH) is an endogenous compound identified in humans that possesses a wide range of biological activities [1] and central nervous system activities [2, 3]. Isatin possess three centers for coordination, NH and the carbonyl functions. Very little research exists on the coordination of isatin through NH; a platinum complex $[\text{PtH}(\text{isat})(\text{PPh}_3)_2]$ has been formed by oxidative addition of the NH bond of isatin to zerovalent platinum complex [4]. Also, platinum(II) and palladium(II) complexes containing the monoanion of isatin have been synthesized by reaction of the metal halide complex with isatin [5]. Gold(I) complexes of isatin, its 5-bromo derivative and some related dye molecules have also been reported [6]. Complexation through NH leaves the carbonyl functions, which might themselves possess ligand properties towards other metals, leading to the formation of bi- and multi-metallic co-ordination assemblies. There are few examples for complexes of transition metals with isatin in the presence of a second ligand (mixed ligand complexes); extra stability might be

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given by the second ligand [4, 7, 8]. However, transition metal complexes of isatin derivatives such as isatin-3-imines [9–12], isatin-3-hydrazones [13–16], have been synthesized and characterized.

To the best of our knowledge, there is no previous work on the reaction of isatin or any of its derivatives with metal carbonyls. In this article, we report the synthesis and characterization of chromium and molybdenum complexes of isatin as the first example of reaction of isatin with metal carbonyls.

2. Experimental

2.1. Reagents

$\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$ and isatin were supplied from Aldrich. All solvents used were of analytical reagent grade and purified by distillation prior to use.

2.2. Instrumentation

Infrared measurements were carried out on a Beckman infrared spectrophotometer PU 9712 using KBr pellets. Nuclear magnetic resonance measurements were performed on a Varian Mercury 300 MHz NMR spectrometer. Samples were dissolved in DMSO (d_6) and tetramethylsilane (TMS) was used as an internal reference. Electronic absorption spectra were measured on a Unicam UV2-300 UV-Vis spectrophotometer with 10.0 mm quartz cells. Electron spin resonance spectra of powdered paramagnetic complexes were carried out on a Bruker electron spin resonance spectrometer model EMX. Magnetic susceptibility measurements for the solid paramagnetic complexes (Gouy method) were performed on a Sherwood Scientific Magnetic Susceptibility Balance. Elemental analyses of the complexes were carried out on a Perkin-Elmer 2400 CHN elemental analyzer. Mass spectra of the complexes (70 eV, EI) were performed on a Finnigan MAT SSQ 7000 spectrometer. Table 1 gives the elemental analyses and mass spectrometry data for the complexes.

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

Complex	Elemental analysis						Mass spectroscopy	
	Calculated			Found			Mwt	$m/z(\text{P}^+)$
	%C	%H	%N	%C	%H	%N		
$[\text{Cr}(\text{CO})_5(\text{isatH})]$	46.03	1.48	4.13	46.10	1.52	4.43	339.14	311(P^+-2CO)
$[\text{Cr}_2\text{O}_2(\text{isatH})_2]$	44.66	2.34	6.51	44.63	1.91	6.26	430.23	430(P^+)
$[\text{Mo}_2\text{O}_4(\text{isatH})_2]$	34.93	1.83	5.09	33.08	1.55	4.75	550.11	550(P^+)
$[\text{Cr}(\text{CO})_4(\text{isatH})]\cdot\text{bpy}$	56.54	2.80	8.99	57.02	3.05	8.76	467.34	311(P^+-bpy)
$[\text{Mo}(\text{CO})_4(\text{isatH})]\cdot\text{bpy}$	51.68	2.56	8.21	51.98	2.48	7.96	511.28	355(P^+-bpy)

2.3. Synthesis of $[\text{Cr}(\text{CO})_5(\text{isatH})]$

$\text{Cr}(\text{CO})_6$ (0.20 g, 0.9 mmol) and isatin (0.13 g, 0.9 mmol) were mixed together in a sealed tube containing ca 30 cm^3 of tetrahydrofuran (THF) as solvent. The mixture was refluxed 1 h. The solution changed from pale yellow to gray; finally a brown solid was separated by filtration and washed several times with boiling petroleum ether. It was recrystallized from benzene to give brown crystals which were dried on a vacuum line (yield 65%).

2.4. Synthesis of $[\text{Cr}_2\text{O}_2(\text{isatH})_2]$ complex

0.10 g $\text{Cr}(\text{CO})_6$ (0.45 mmol) and 0.067 g isatin (0.45 mmol) were mixed in ca 25 mL THF. The solution was then refluxed in air for 30 h. The color of the solution changed from pale yellow to yellowish green with a dark precipitate. The reaction mixture was cooled and the solvent was then evaporated. The obtained brown residue was washed several times by a mixture of ethyl alcohol/petroleum ether (1/5) and then recrystallized from benzene to give dark green crystals (yield 73%).

2.5. Synthesis of $[\text{Mo}_2\text{O}_4(\text{isatH})_2]$ complex

A solution of $\text{Mo}(\text{CO})_6$ (0.20 g, 0.76 mmol) and isatin (0.11 g, 0.76 mmol) in THF was refluxed in air for 20 h. The reaction mixture was cooled and the solvent was then evaporated. The obtained brown residue was washed several times with petroleum ether and then recrystallized from benzene to give brown crystals (yield 73%).

2.6. Synthesis of $[\text{Cr}(\text{CO})_4(\text{isatH})] \cdot \text{bpy}$ complex

$\text{Cr}(\text{CO})_6$ (0.15 g, 0.68 mmol), 0.1 g isatin (0.68 mmol) and 0.11 g bpy were mixed together in a sealed tube containing ca 30 cm^3 of THF as solvent. The solution was degassed and then heated to reflux. The color of the reaction mixture changed from orange to light brown after 1 h and the reaction continued for 2 h to give a red solution. The reaction mixture was cooled and the solvent was then evaporated. The obtained orange-red residue was washed several times by hot petroleum ether (60–80) and recrystallized from benzene to give orange-red crystals (yield 42%).

2.7. Synthesis of $[\text{Mo}(\text{CO})_4(\text{isatH})] \cdot \text{bpy}$ complex

A similar procedure was used as for $[\text{Cr}(\text{CO})_4(\text{isatH})] \cdot \text{bpy}$, giving orange crystals (yield 65%).

3. Results and discussion

3.1. IR and magnetic studies

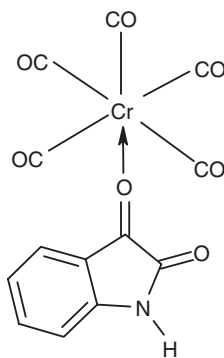
The IR spectrum of isatin showed characteristic bands for CO, C=C and NH groups. The carbonyl groups exhibited a shoulder at 1748 cm^{-1} and strong stretching band at 1727 cm^{-1} (table 2), while the strong bands at 1620 and 1461 cm^{-1} could be assigned to $\nu(\text{C}=\text{C})$ [17]. The ^1H NMR spectrum of isatH in deuterated DMSO showed resonance at 6.9(d), 7.06(t), 7.5(t), 7.61(d) ppm due to protons of the benzene ring and a signal at 10.98(s) ppm due to the NH group [18].

Table 2. Important IR data for isatin and its complexes.

Compound	IR data (cm ⁻¹) ^a				
	$\nu(\text{NH})$	$\nu(\text{C}=\text{C}) + \delta_{\text{CH}}$	$\nu(\text{CO})$	$\nu(\text{C}=\text{N})$	δ_{py}
Isatin	3191(s)	1615(vs), 1461(s)	1748(sh), 1727(vs)	–	–
Cr(CO) ₅ (isatH)	3190(m)	1469(s)	2059(m), 1979(m), 1922(vs), 1871(sh), 1719, 1653	–	–
[Cr ₂ O ₂ (isatH) ₂] ^b	3187(w)	1471(m) 1460(m)	1728(s), 1705(s), 1585(s)		
[Mo ₂ O ₄ (isatH) ₂] ^c	3186(w)	1585(s), 1620(s)	1653(s), 1554(s)		
[Cr(CO) ₄ (isatH)]·bpy	3021(m)	1463(s), 1620(vs)	2003(m), 1910(s), 1871(s), 1814(s), 1730(m), 1653(s)	1600(s), 1560(s)	626, 598
[Mo(CO) ₄ (isatH)]·bpy	3018(w)	1470(s), 1617 (s) 1443(m)	2010(m), 1901(sh), 1873(s), 1819(s), 1722 (w,sh), 1705 (s)	1623(s)	639(mw), 579(m)

^avs, very strong; s, strong; m, medium; w, weak; sh, shoulder. ^b $\nu_{\text{Cr-O-Cr}}$ at 549(m), 530(m). ^c $\nu_{\text{Mo=O}}$ at 959(s), $\nu_{\text{Mo-O-Mo}}$ at 722 cm⁻¹(m).

The products obtained from the reactions between Cr(CO)₆ with isatin were found to be dependent on the time of reaction and the solvent used. Heating an equimolar mixture of Cr(CO)₆ and isatH in THF under reduced pressure resulted in the formation of the pentacarbonyl monosubstituted derivative [Cr(CO)₅(isatH)] (**1**). The IR spectrum of the complex displayed the bands of the ligand with the corresponding shifts (table 2). On the other hand, the presence of $\nu(\text{NH})$ at 3191 cm⁻¹ in the IR spectrum and the two $\nu(\text{CO})$ bands at 1719 and 1653 cm⁻¹ suggesting that the ligand remains in the keto form and bonding takes place through the carbonyl groups, table 2. In addition, the IR spectrum exhibited a pattern ($2a_1 + b_1 + e$) due to stretching frequencies of five carbonyl groups attached to the chromium atom in a pyramidal structure [19], table 2, suggesting an octahedral structure with the isatH ligand occupying one axial position [20], (**1**). Such a structure arrangement gives three active IR bands, two weak bands a_1 and strong broad band of e symmetry. For example, Cr(CO)₅L, where L = 2,6-diaminopyridine [20] displayed three bands in the range 2068–1890 cm⁻¹. Unsymmetrical ligands will lead to distortion in the CO arrangement and splitting of e and the complex can display four bands. The ¹H NMR spectrum of the complex showed a signal at 10.98 ppm, suggesting that NH does not participate in coordination.



(1)

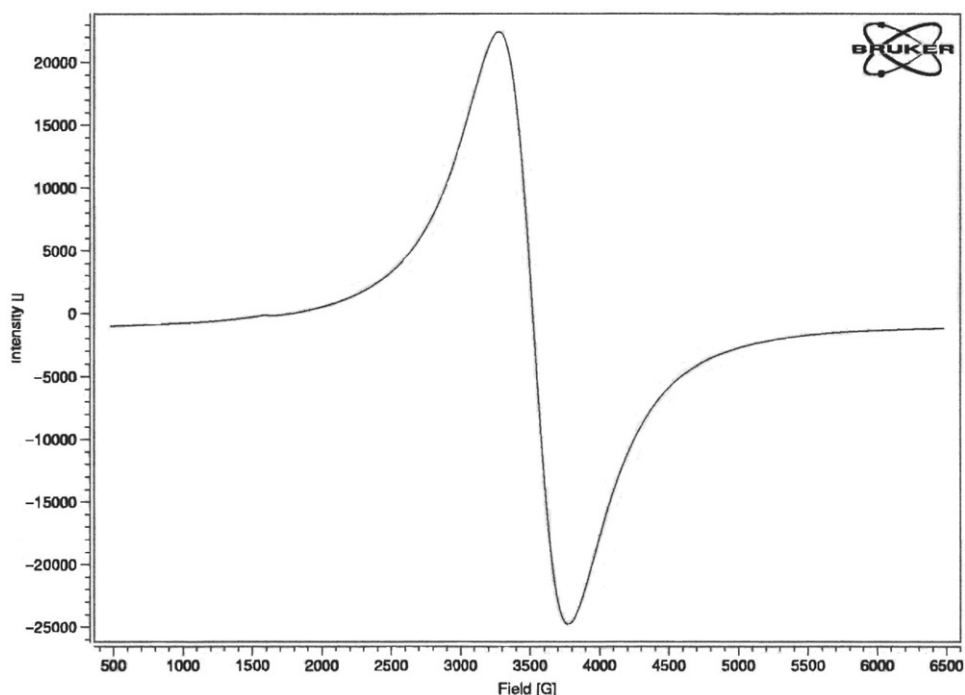
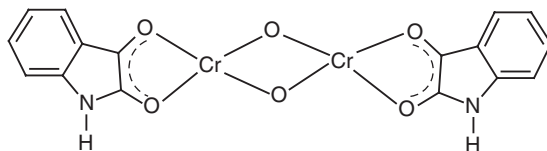


Figure 1. The X-band ESR spectrum of polycrystalline $[\text{Cr}_2\text{O}_2(\text{isatH})_2]$ at room temperature.

Reaction of isatin with $\text{Cr}(\text{CO})_6$ in benzene/ethyl alcohol at atmospheric pressure yielded a dinuclear complex with molecular formula $\text{Cr}_2\text{O}_2(\text{isatH})_2$. The IR spectrum of the complex, exhibited strong bands at 1728 and 1705 cm^{-1} that could be due to carbonyl groups and a strong band at 1558 cm^{-1} due to the stretching frequencies of CO bonds in the semiquinone mode. Investigation of $\text{Cr}_2\text{O}_2(\text{isat})_2$ (complex **2**) by ^1H NMR spectroscopy showed no signal, a characteristic of paramagnetic species. Measurements of the magnetic susceptibility of **2** at 298 K (Gouy method) gave a value of $2.02 \times 10^{-3}\text{ e.m.u. g}^{-1}$ with an effective magnetic moment of (2.21 B.M.). The observed μ_{eff} indicated that the corresponding value for each chromium species (1.105 B.M.) was less than the spin-only momentum of one unpaired electron which was not expected for a d^3 metal center with three unpaired electrons. This could indicate the existence of strong antiferromagnetic coupling between the two metal centers. However, small effective magnetic moment values for Cr(III) have been observed for many chromium complexes. For example, $\text{Cr}(\text{PhenSQ})_3$, PhenSQ = phenanthrene-semiquinone, $\text{Cr}(\text{Cl}_4\text{SQ})_3$, Cl_4SQ = tetrachlorosemiquinone [21], $\text{Cr}(\text{ChrySQ})_3$ ChrySQ = chrysene semiquinone [22] and $\text{Cr}(\text{H}_2\text{CA})_3$, H_2CA = chloranilic acid [23] exhibited μ_{eff} values of 1.15, 1.08, 2.55 and 1.82 B.M., respectively.

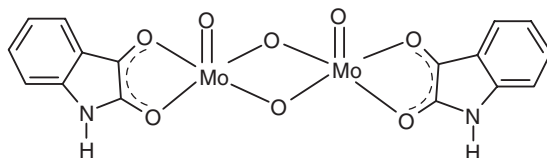
Furthermore, the EPR spectra of the complex recorded as polycrystalline sample, figure 1, gives one broad isotropic signal centered at the free electron (g) value of 1.9982. Broadening of the spectra is due to spin relaxation [24]. Therefore, from elemental analysis and spectroscopic studies of the complex, each chromium exists in a tetrahedral environment, bonded to two bridged oxygen atoms. Furthermore, each chromium was bound to isatin as a semiquinone. Such structural arrangements would result in a chromium atom with a +3 formal oxidation state. Tetrahedral chromium(III)

complexes are rare, found only with sterically-demanding ligands [25]. Since a single crystal of the complex was difficult to obtain, we cannot exclude the possibility that complex **2** exists as a tetramer with cubane Cr_4O_4 arrangement and the highest mass peak in the mass spectrum represents a fragment product.



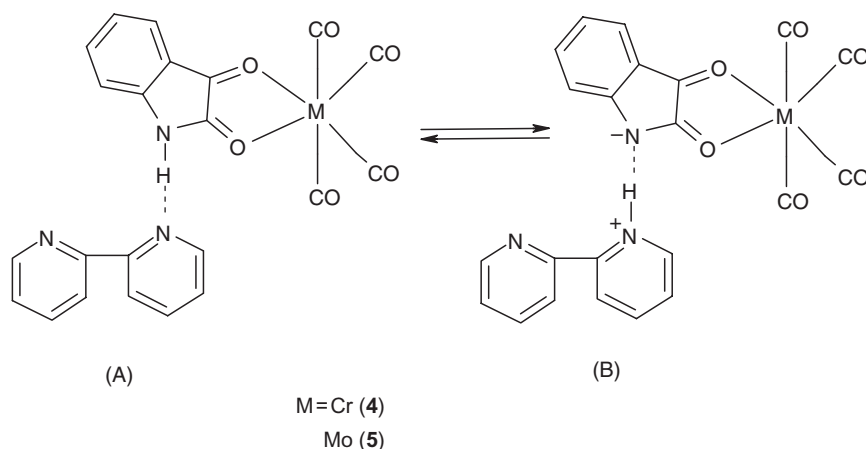
(2)

Thermal reaction of $\text{Mo}(\text{CO})_6$ with isatin in THF gave a dinuclear oxomolybdenum complex with molecular formula $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_8\text{Mo}_2$, table 1. The IR spectrum of the complex exhibited strong bands at 1664 and 1654 cm^{-1} that could be assigned to the coordinated $\text{C}=\text{O}$ groups of isatin at lower values compared to those of the free ligand. In addition, the spectrum displayed two bands at 959 and 722 cm^{-1} . The strong absorption maximum at 959 cm^{-1} belongs to $\text{Mo}=\text{O}$ (terminal), while the band at 722 cm^{-1} to the $\text{Mo}-\text{O}$ (bridging) stretching frequencies. For dinuclear oxomolybdenum complexes, the two $\text{Mo}=\text{O}$ groups are *cis* [25], leading to formation of a paramagnetic oxo complex $\text{Mo}(\text{V})$, d^1 . Magnetic susceptibility measurement of the complex at 298 K showed a value of 12.7×10^{-3} e.m.u. mol^{-1} with an effective magnetic moment μ_{eff} of 2.54 B.M., a μ_{eff} of 1.27 B.M. obtained for each Mo atom. This value is smaller than the spin-only moment of an unpaired electron (1.73 B.M.). On the other hand, the EPR spectra of the molybdenum complex recorded as polycrystalline sample at room temperature gave two sharp signals at (g) 2.004 , 1.9421 . The former and more intense signal assigned to the electron on isatin and the other signal at (g) 1.9421 retained the free electron on molybdenum. Thus, the molybdenum atom in **3** exists in a pyramidal environment with two terminal oxygen groups in axial positions and two ligands in equatorial positions, in addition to two bridging oxygens. Such bonding gives the opportunity for the sixth coordination place around molybdenum to be completed by a monodentate solvent molecule, easily removed by standing at room temperature. For example, freshly prepared molybdenum(V) complexes of general formula $[\text{Mo}_2\text{O}_4\text{L}_2\text{D}_2]$, where $\text{L} = \beta'$ -hydroxy- β -enaminones and $\text{D} = \text{ethanol}$ showed loss of two ethanol molecules upon standing in the desiccator at room temperature [26].



(3)

When the reaction of $\text{M}(\text{CO})_6$; $\text{M} = \text{Cr}$ or Mo with isatin was carried out under reduced pressure in the presence of 2,2'-bipyridine, the $[\text{M}(\text{CO})_4(\text{isatH})]\cdot\text{bpy}$ complexes were isolated. The IR spectra of the complexes exhibited characteristic bands of the isatin and bipyridine ligands with the corresponding shifts, table 2. In addition, the IR spectra of the complexes showed that the ν_{CO} of isatin ligand exerted $18\text{--}70\text{ cm}^{-1}$ shift



Scheme 1. Equilibrium between the two isomers of $M(\text{CO})_4(\text{isatH})$ with hydrogen bond formation between bpy and isatH.

suggesting that coordination of isatin occurred by ketone bonding. IR spectra of the complexes also exhibited IR patterns ($2a_1 + b_1 + b_2$) in the metal terminal carbonyl region with shifts toward the low frequency region, table 2, suggesting an octahedral structure with the isatH ligand occupying two equatorial positions [27]. The elemental analysis and mass spectra of the complexes, table 2, proposed that the complexes should contain bpy. Therefore, the bonding of bpy to the two complexes $[M(\text{CO})_4(\text{isatH})]$ was probably through hydrogen bonding between the nitrogen of the bipyridine and the N–H group of the isatin part, scheme 1. This conclusion is supported by the lower frequency shift of the NH group to give medium weak bands at $3015\text{--}3022\text{ cm}^{-1}$ which could be assigned to the stretching frequency of $\text{N-H}\cdots\text{N}$ bands [28]. Solvent effects, in charge-transfer (CT) transitions of some ruthenium-amine complexes was interpreted by a hydrogen bonding type interaction involving electron-pair donation from a solvent molecule to the N–H bond [28, 29].

The ^1H NMR spectra of **4** and **5** exhibited resonances due to both the isatH and bpy moieties. Furthermore, the chromium complex exhibited two new broad signals at 11.01 and 10.22 ppm; 10.61 and 10.26 ppm for the molybdenum complex. These results can be explained as an equilibrium between the two isomers (A) and (B), scheme 1 [28]. For the molybdenum complex, another complex was isolated from the reaction (yield 22%) and found to have the structure of complex **3** obtained from the reaction of $\text{Mo}(\text{CO})_6$ with isatin.

3.2. UV-Vis studies

Electronic spectra of isatin and its complexes have been measured in four different solvents; DMSO, EtOH, toluene and CH_2Cl_2 , table 3. In ethanol, isatin exhibited a band at 296 nm due to a $\pi\pi^*$ transition of the benzene ring, and a broad band at 420 nm due to an $n\pi^*$ transition. The solvent effect on the position of the longer wavelength absorption band of isatin shows that the bathochromic shift of the longest-wavelength absorption band of isatin on increasing polarity of the solvent indicates that the $n\pi^*$ transition has some CT character; the nitrogen atom is the electron donor and the

Table 3. UV-Vis data for isatH and its chromium, molybdenum complexes.

Compound	λ (nm) ^a			
	DMSO	Ethanol	Toluene	CH ₂ Cl ₂
IsatH	334	249	295	296
	418	296 420	405	416
[Cr(CO) ₅ (isatH)]	338	210	Insoluble	Insoluble
	375	302 375		
[Cr ₂ O ₂ (isatH) ₂]	281 ^a	282 ^a	Insoluble	Insoluble
	343	353		
[Mo ₂ O ₄ (isatH) ₂]	284	256	296	Insoluble
	384	284 372	368 ^a	
[Cr(CO) ₄ (isatH)]·bpy	284	287 ^a	283	288
	460	297	293	299
		373 ^a	302	334
		497	377	511
			536	
[Mo(CO) ₄ (isatH)]·bpy	296	243	301	229
	396	286	359	247
	448	294	379	297
		330 ^a	499	341
		465		480

^aShoulder.

β -carbonyl group the acceptor. Investigating the absorption spectra of the complexes obtained from the reaction of M(CO)₆; M = Cr or Mo with isatin only as a ligand showed a shift or disappearance of the CT band due to complexation through a carbonyl group in isatin. Interestingly, the chromium and molybdenum complexes that contain bpy [M(CO)₄(isatH)]·bpy exhibited bands at longer wavelength in the range 480–500 nm, especially in toluene. Since these complexes have isatin coordinated to the metal and bpy bound to isatH through hydrogen bonding, the new bands at 480–500 nm must be due to ligand–ligand charge transfer (LLCT) from bpy to isatin.

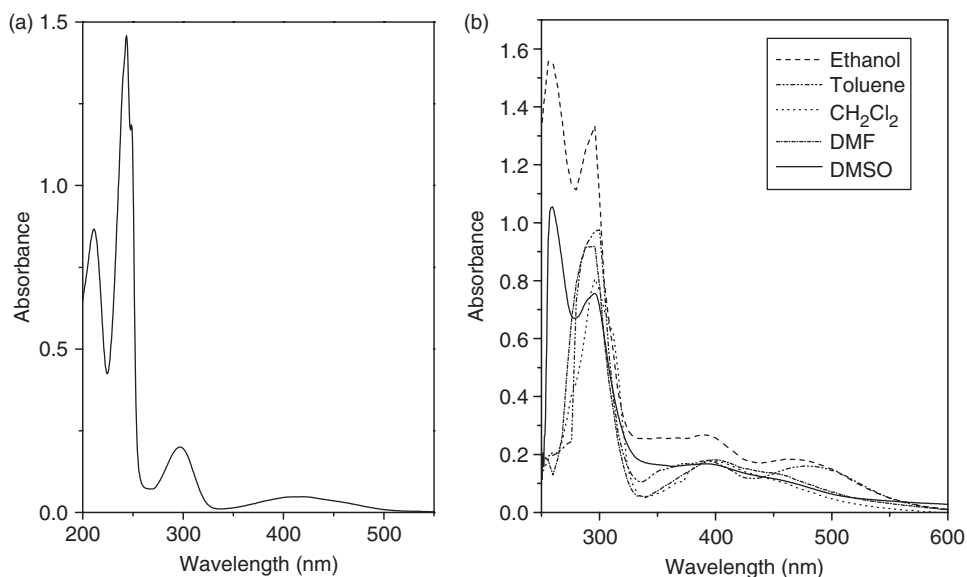
3.3. Thermogravimetric analysis

To give insight into the structure of the complexes, thermal studies were carried out using thermogravimetry (TG). The TG plot of **1** displayed two resolved and well-defined decomposition steps. The first decomposition occurred in the temperature range 65–193°C, with a net weight loss of 40.91 (41.29%), due to elimination of the five CO groups, table 4. The second decomposition step occurred in the temperature range 380.1–402.0°C with a net weight loss of 35.01 (34.31)% due to the loss of a C₈H₅N moiety to leave the residue, CrO₂ (table 4).

The TG plot of [Mo₂O₄(isatH)₂] (**3**) displayed three decomposition steps in the temperature range 145–1005°C (table 4). The first decomposition occurred in the temperature range 145–251°C with a net weight loss of 6.10% corresponding to elimination of O₂. The second decomposition peak occurred in the temperature range

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

Complex	Temperature range (°C)	% weight loss, found (Calcd)	Species eliminated	% solid residue
[Cr(CO) ₅ (isatH)]	65–193	40.91 (41.29)	5CO	CrO ₂
	380.1–402.0	35.01 (34.31)	C ₈ H ₅ N	24.77 (24.78%)
[Mo ₂ O ₄ (isatH) ₂]	145–251	6.10 (5.81)	O ₂	–
	255–536	40.23 (41.18)	Org. ligand	–
	723.4–1005	50.22 (52.36)	2MoO ₃	–
[Cr(CO) ₄ (isatH)]·bpy	118–298.2	21.37 (23.98)	4CO	CrO ₂
	297.3–387.4	60.56 (58.03)	C ₁₀ H ₈ N ₂ + C ₈ H ₅ N	18.03 (17.99%)
[Mo(CO) ₄ (isatH)]·bpy	120.6–367.7	51.61 (52.44)	4CO + bpy	–
	370.6–640.3	23.21 (22.50)	C ₈ H ₅ N	–
	720.7–839.9	24.04 (25.06)	MoO ₂	–

Figure 2. (a) UV-Vis spectrum of isatin in ethanol. (b) Absorption spectra of [Mo(CO)₄(isatH)]·bpy in different solvents.

255–536°C with a weight loss of 40.23% corresponding to decomposition of C₇H₅N to give finally the residue, MoO₃ that volatilized in the range 723.4–1005°C.

The [Cr(CO)₄(isatH)]·bipy (**4**) was found to be thermally stable up to 100°C and decomposed in two resolved steps (table 4). The first decomposition step, 118–298°C, with a net weight loss of 21.37% corresponded to elimination of four carbonyl groups. The second decomposition step (298–387°C, 60.56%) was due to the elimination of C₁₈H₁₃N₃ organic species to leave the residue, CrO₂ (18.03%).

Finally, [Mo(CO)₄(isatH)]·bipy decomposed in three well-defined steps. The first decomposition peak occurred in the temperature range 120.6–367.7°C (51.61%) and corresponded to the loss of four CO groups and bpy. The second decomposition step (370–640°C, 23.21%) was due to elimination of C₈H₅N species. The third decomposition step occurred in the temperature range 830–950°C with a weight loss of 24.04%

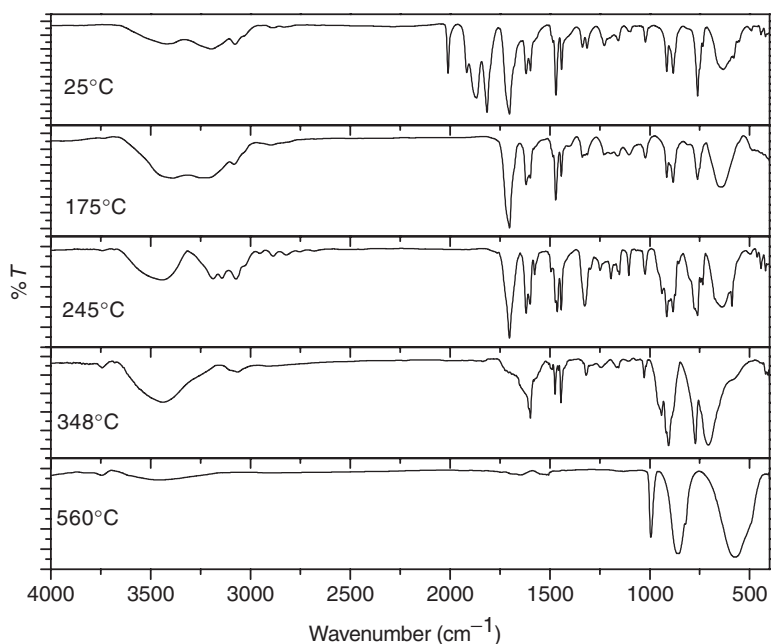


Figure 3. FTIR spectra of $[\text{Mo}(\text{CO})_4(\text{isatH})]\cdot\text{bpy}$ at different decomposition temperatures.

corresponding to decomposition of metallic oxide, MoO_2 . Furthermore, the thermal decomposition of the complex was studied by heating the complex in the air and the intermediate phases, as indicated by thermograms, were isolated and identified by percent weight and by infrared spectra, figure 3.

In conclusion, in this work the reactions between two metal carbonyls ($\text{M}=\text{Cr}$ or Mo) and isatin give complexes that depend on whether the reaction was performed in air (complexes **2** and **3**) or under reduced pressure (complex **1**). Mixed ligand complexes **4** and **5** obtained by reaction of the metal carbonyls with isatin in presence of bpy suggest that these complexes have promising CT ligands.

References

- [1] V. Glover, J.M. Halket, P.J. Watkins, A. Clone, B.L. Goodwin, M. Sandler. *J. Neurochem.*, **51**, 656 (1988).
- [2] S.K. Bhattacharya, V. Glover, I. McIntyre, G. Oxenkrug, M. Sandler. *Neurosci. Lett.*, **92**, 218 (1982).
- [3] S.K. Bhattacharya, S.K. Mitra, S.B. Acharya. *J. Psychopharmacol.*, **5**, 202 (1991).
- [4] D.A. Clarke, M.M. Hunt, R.D.W. Kemmitt. *J. Organomet. Chem.*, **175**, 303 (1979).
- [5] J.M. Law, W. Henderson, B.K. Nicholson. *J. Chem. Soc., Dalton Trans.*, 4587 (1997).
- [6] A. Lenz, K. Sünkel, W. Beck. *Z. Naturforsch., Teil B*, **51**, 1639 (1996).
- [7] C.V.R. Reddy, M.G.R. Reddy. *Indian J. Chem. Sect. A*, **33**, 233 (1994).
- [8] S.I. Al-Resayes. *Spectrosc. Lett.*, **32**, 315 (1999).
- [9] K.P. Balakrishnan, V. Krishnan. *Indian J. Chem. Sect. B*, **16A**, 83 (1976).
- [10] A.M.A. Hassaan. *Synth. React. Inorg. Met.-Org. Chem.*, **19**, 773 (1990).
- [11] A.M. Hassaan, M.A. Khalifa, A.K. Shehata. *Bull. Soc. Chim. Belg.*, **104**, 121 (1995).
- [12] A.M.A. Hassaan. *Synth. React. Inorg. Met.-Org. Chem.*, **27**, 835 (1997).
- [13] R.C. Khulbe, R.P. Singh, Y.K. Bhoon. *Trans. Met. Chem.*, **8**, 59 (1983).

- [14] B.S. Garg, P.K. Singh, S.K. Garg. *Synth. React. Inorg. Met.-Org. Chem.*, **22**, 1517 (1992).
- [15] R.M. El-Bahnasawy, E. El-Shereafy, T.I. Kashar. *J. Therm. Anal.*, **39**, 65 (1993).
- [16] B.C.S. Radovanovic, S.S. Andjekovic. *Spectrosc. Lett.*, **31**, 63 (1998).
- [17] P. Naumov, F. Anastasova. *Spectrochim. Acta*, **57A**, 469 (2001).
- [18] J.F.M. Da Silva, S.J. Garden, A.C. Pinto. *J. Braz. Chem. Soc.*, **12**, 273 (2001).
- [19] P.S. Braterman. *Metal Carbonyl Spectra*, Academic Press, London (1975).
- [20] I.A. Morkan, K. Guven, S. Özkar. *J. Organomet. Chem.*, **689**, 2319 (2004).
- [21] R.M. Buchanan, H.H. Downs, W.B. Shorthill, C.G. Pierpont, S.L. Kessel, D.N. Hendrickson. *J. Am. Chem. Soc.*, **100**, 4318 (1978).
- [22] R.M. Ramadan, W.H. Mahmoud, A.S. Attia, M.F. El-Shahat. *Spectrochim. Acta*, **49**, 117 (1993).
- [23] S.A. Ali, M.M.H. Khalil, R.M. Ramadan. *Trans. Met. Chem.*, **25**, 121 (2000).
- [24] R.S. Drago. *Physical Methods in Chemistry*, Saunders, Philadelphia (1986).
- [25] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann. *Advanced Inorganic Chemistry*, John Wiley, New York (1999).
- [26] M. Cindrić, V. Vrdoljak, N. Strukan, A. Brbot-Saranović, P. Novak, B. Kamenar. *Inorg. Chim. Acta*, **357**, 931 (2004).
- [27] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th Edn, Wiley, New York (1997).
- [28] M.M.H. Khalil, S.A. Ali, R.M. Ramadan. *Spectrochim. Acta*, **57A**, 1017 (2001).
- [29] T.B. Chenskaya, M. Berghahn, W. Kläui, J. Graf, W. Frank. *J. Mol. Struct.*, **700**, 157 (2004).