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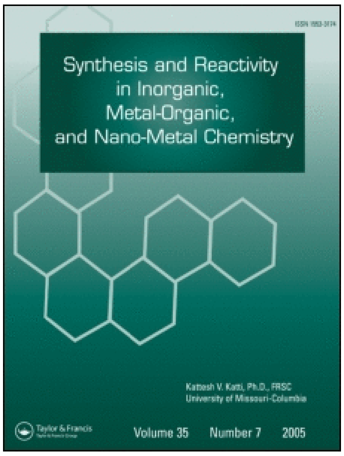

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

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Novel Chromium, Molybdenum, and Tungsten Complexes of 2-pyridylamidoxime

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Reaction of $[Cr(CO)_6]$ with 2-pyridylamidoxime (PAO) in THF under reduced pressure resulted in the formation of the tris derivative $[Cr(PAO)_3]$. The corresponding reaction in the presence of bipyridine gave the binuclear complex $[Cr_2O_4(PAO)(bpy)]$. On the other hand, reaction of $[Mo(CO)_6]$ with 2-pyridylamidoxime in air resulted in the formation of $[Mo_2O_6(PAO)_2]$, while in the presence of bipyridine, the reaction gave two isomers with molecular formula $[Mo(CO)_4(PAO)]$.bpy, where bpy form hydrogen bonds to the coordinated 2-pyridylamidoxime. Reactions of $[W(CO)_6]$ with PAO ligand in air yielded the complex $[W_2O_6(PAO)_2]$. The structures of all complexes were characterized by elemental analyses, IR, and ^{1}H NMR spectroscopy. The thermal properties of the complexes were also studied.

Keywords 2-pyridylamidoxime, chromium, complexes, hexacarbonyl, molybdenum, tungsten

INTRODUCTION

The coordination chemistry of oximes has received great attention during the last decade for their interesting properties such as the ability of the oximato group to stabilize higher oxidation states of metals.[1] Also, the application of simple metal ion/oxime systems as simple and efficient catalysts for the hydrolysis of organonitriles and the employment of oximato ligands in the synthesis of homometallic and heterometallic clusters, and coordination polymers with interesting magnetic properties were of great interest.[2–5] The coordination chemistry of various pyridyl aldoximes, (py)C(R)NOH (R = H, Me, Ph, py) with the 3d metal ions has been studied.[6–15] In addition, amidoximes and their metal complexes find a wide range of applications in technology, medicinal chemistry, and agriculture.[16]

As a bidentate ligand, $(py)C(NH_2)NOH$ incorporates the structural features of pyridine-2-carbaldehyde oxime and 2-pyridylamine, $(py)CH_2NH_2$, in a single molecule. 2-pyridylamidoxime forms stable complexes with various metal ions,[17] some of which were successfully exploited in analytical chemistry.[18] Few transition metal complexes containing the neutral ligand have been structurally characterized.[19–22] The X-ray structure of $[Cu\{(py)C(NH_2)NOH\}_2(H_2O)]Cl_2$ [19,20] shows the five-coordinate nature of the metal ion, which is bound through the heterocyclic and oxime nitrogen atoms of two trans-oriented bidentate ligands plus a H_2O molecule to give a square-based pyramidal chelate.

Our interest in studying the reactions of group 6 metal carbonyls with various nitrogen and oxygen donor ligands[23–25] has prompted us to investigate their reactions with the interesting 2-pyridylamidoxime ligand. It should be mentioned that the first structurally characterized complexes of the related compound phenyl(2-pyridyl)ketone oxime with metal carbonyl were the carbonyl compounds $[Os_3(CO)_8\{(py)C(ph)NO\}_2]$, $[Os_3(CO)_8\{(py)C(ph)NO\}\{(py)C(ph)HNH\}]$, $[Os_3H(CO)_9\{(py)C(ph)NO\}]$ and $[Os_3H(CO)_{11}\{(py)C(ph)NO\}]$ which exhibit interesting structural features.[26]

EXPERIMENTAL

$[M(CO)_6]$, M= Cr, Mo and W, and 2-pyridylamidoxime were supplied from Aldrich. All solvents were of analytical grade and were purified by distillation prior to their use.

Infrared measurements (KBr pellets) were performed on a Unicam-Mattson 1000-FTIR spectrometer. Nuclear magnetic resonance measurements were carried out on a Spectrospin-Bruker Ac 200 MHz spectrometer. Samples were dissolved in $(CD_3)_2SO$ with TMS as internal reference. Thermogravimetry analysis measurements (TG) were carried out under N_2 atmosphere at a heating rate of 10°C min^{-1} using a Shimadzu DT-50 thermal instrument. All the reported complexes were also characterized by elemental analyses (Perkin-Elmer 2400 CHN elemental analyzer) and mass spectrometry (Finnigan MAT SSQ

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TABLE 1
Elemental analysis and mass spectrometry data for the complexes

Complex	Found (Calc.)			Mass spectrometry	
	C	H	N	Mol. Wt.	*m/z*
$[Cr(PAO)_3]$	46.5 (46.6)	4.5 (4.6)	27.0 (27.1)	463.5	464 (P^+)
$[Cr_2O_4(PAO)(bpy)]$	41.5 (41.6)	3.2 (3.3)	15.1 (15.2)	461.4	462 (P^+)
$[Mo_2O_6(PAO)_2]$	25.5 (25.7)	2.5 (2.4)	14.5 (14.9)	562.3	563 (P^+)
$[Mo(CO)_4(PAO)].bpy$	47.9 (48.3)	3.0 (3.1)	15.9 (15.8)	504.3	349 $(P\text{-}bpy)^+$
$[W_2O_6(PAO)_2]$	19.3 (19.5)	1.85 (1.89)	11.34 (11.38)	738.3	722 $(P\text{-}OH)^+$

7000). Table 1 gives the elemental analysis and mass spectrometry data for the complexes.

Synthesis of $[Cr(PAO)_3]$ Complex

A solution of $[Cr(CO)_6]$ (0.10 g, 0.45 mmol) and PAO (0.06 g, 0.44 mmol) in *ca* 30 mL THF was degassed with one freeze-thaw cycle and then heated to reflux for 2 h. The reaction mixture was cooled and the formed solid was isolated by filtration. The residue was washed with hot petroleum ether (60–80°C) and then was recrystallized from hot THF to give light brown crystals. The crystals were dried *in vacuo* for several hours (yield 37%).

Synthesis of $[Cr_2O_4(PAO)(bpy)]$ Complex

A mixture of $[Cr(CO)_6]$ (0.1g, 0.45 mmol), PAO (0.06 g, 0.44 mmol) and bipyridine (0.07 g, 0.45 mmol) in *ca* 30 mL THF solvent was heated to reflux under atmospheric pressure for 6h. The solution changed from pale yellow to red and finally a scarlet red precipitate was formed. The reaction mixture was cooled and the solvent was evaporated. The residue was recrystallized from THF to give scarlet red powder (yield 35% based on Cr).

Synthesis of $[Mo_2O_6(PAO)_2]$ Complex

A mixture of $[Mo(CO)_6]$ (0.10 g, 0.38 mmol), PAO (0.053 g, 0.387 mmole) in THF (30 cm^3) were heated to reflux under atmospheric pressure for 3 h. The solution changed from pale yellow to reddish brown with the formation of reddish brown precipitate. The reaction mixture was cooled and the solvent was evaporated. The residue was washed several times by boiling petroleum ether and then recrystallized from THF. The complex was left to dry *in vacuo* for several hours (yield 61%).

Synthesis of $[Mo(CO)_4(PAO)].(bpy)$ Complex

$[Mo(CO)_6]$ (0.10 g, 0.38 mmol), PAO (0.053 g, 0.387 mmol) and bipyridine (0.05 g, 0.31 mmol) were mixed together in a sealed tube containing ~30 mL THF solvent. The mixture was degassed and heated to reflux for 2 h. The color of the solution changed from yellow to dark red. The reaction mixture was cooled and the solvent was washed several times with hot petroleum ether. Recrystallization from THF gave red powder (yield 55%).

Synthesis of $[W_2O_6(PAO)_2]$ Complex

A similar procedure was used as for $[Mo_2O_6(PAO)_2]$. The residue was recrystallized from THF to give scarlet red crystals (yield 46%). Table 1 gives the elemental analysis and mass spectrometry data for the complexes.

RESULTS AND DISCUSSION

Thermal reaction of $[Cr(CO)_6]$ and PAO ligand in THF under reduced pressure leads to the formation of a tris-derivative with molecular formula $Cr(PAO)_3$ as the major derivative. The IR spectrum of the ligand showed two bands at 3464 and 3347 cm^{-1} due to υ_{OH} and υ_{NH} stretches, as well as two strong bands at 1648 and 1590 cm^{-1} due to stretching of the C=N bonds. The ^1H NMR spectrum of the ligand exhibited two singlet signals at 5.83 and 9.91 ppm due to protons of NH_2 and OH groups, respectively, beside another three multiplets at 7.39,7.79, 8.55 ppm due to protons of pyridyamidoxime ring. The IR spectrum of the complex showed a pattern similar to that of the ligand with the corresponding shifts (Table 2). Furthermore, the spectrum displayed characteristic bands at 475 cm^{-1} assigned to the Cr-N stretching, which confirm coordination of chromium through nitrogen atoms. The ^1H NMR spectrum of $[Cr(PAO)_3]$ complex displayed a broad signal at 9.86 ppm, and this broadening could be due to intermolecular hydrogen bonding. Also, the complex showed a signal at 5.82 ppm due to the NH_2 group. On the other hand, the ^1H NMR spectrum of chromium complex showed multiplet signals at 7.77, 7.82, and 8.57 ppm due to of pyridylamidoxime rings with appropriate shift due to the complex formation. From the available spectroscopic data it can be concluded that chromium form an octahedral complex, where it is coordinated to three PAO ligands through the pyridine nitrogen and the N of the adjacent amidoxime (Figure 1).

When the reaction was carried out in the presence of bipyridine (bpy) under atmospheric pressure, a bimolecular oxo-chromium complex was obtained. Elemental analysis and mass spectrometry ($m/z = 464$) showed that it had the molecular formula $[Cr_2O_4(PAO)(bpy)]$. The IR spectrum of $[Cr_2O_4(PAO)(bpy)]$ complex showed, besides the bands due to PAO and bpy with appropriate shift, two new bands at 954 and 890 cm^{-1} due to asymmetric and symmetric frequencies

TABLE 2
The I.R. data for chromium, molybdenum, and tungsten complexes of 2-pyridylamidoxime

Complex	ν_{OH}	ν_{NH}	$\nu_{C=N}$	$\nu_{C=C}$	$\nu_{C=O}$	ν_{M-O-M}	ν_{M-N}	$N_{M=O}$	ν_{bpy}
PAO	3464 (s)	3345 (s)	1648 (s) 1590 (s)	1547 (s) 1480 (m)	—	—	—	—	—
$[Cr(PAO)_3]$	3466 (w)	3347 (w)	1640 (m) 1585 (w)	1543 (w) 1482 (m)	—	—	475 (w)	—	—
$[Cr_2O_4(PAO)(bpy)]$	3466 (s)	3348 (s)	1638 (s) 1589 (m)	1549 (s) 1481 (m)	—	652 (w)	—	954 (m) 890 (m)	712 (w)
$[Mo_2O_6(PAO)_2]$	3467 (m)	3348 (m)	1692 (s) 1587 (m)	1459 (m) 1432 (m)	—	667 (w)	483 (sh)	943 (s) 905 (s)	—
$[Mo(CO)_4(PAO)]$.bpy	3317 (w)	3194 (w)	1640 (m) 1592 (m)	1547 (m) 1467 (m)	2009 (m) 1918 (m) 1872 (s) 1816 (s)	—	445 (w)	—	671 (w)
$[W_2O_6(PAO)_2]$	34420 (w)	3399 (w)	1688 (s) 1655 (m)	1542 (w) 1459 (w)	—	651 (w)	486 (w)	961 (m) 885 (m)	—

[a]S, strong; m, medium; w, weak; sh, shoulder.

of two terminal Cr=O bonds. On the other hand, the IR spectrum of the chromium complex displayed characteristic bands at 712 and 652 cm^{-1} due to in-plan ring deformation band of bpy and stretches of the Cr−O−Cr bonds, respectively (Table 2). Therefore, according to the spectroscopic observations, it was expected that each chromium atom would have a +4 formal oxidation state. Magnetic susceptibility determination of the solid $[Cr_2O_4(PAO)(bpy)]$ at 293K showed that the complex has an effective magnetic moments (μ_{eff}) of 2.31 B.M. The μ_{eff} value for the $[Cr_2O_4(PAO)(bpy)]$ complex is lower than the spin-only value for two unpaired electrons.

Therefore, it can be concluded that both pyridylamidoxime and bipyridine were involved in coordination. The chromium moieties in the complex may exist in a square pyramidal environment with the pyridylamidoxime ligand bound to one chromium atom through the nitrogen atoms of pyridyl and oxime groups, while the bipyridine coordinated to the other chromium. Two oxygen atoms as well as two bridged oxygen atoms are also involved in coordination as shown in Figure 2. It can be proposed that during the reaction of $[Cr(CO_6]$ with dpy and PAO, $[Cr(CO)_4dpy]$ and $[Cr(CO)_4(PAO)]$ were formed in the first stage and with longer reaction time, in presence of oxygen, the proposed complex $[Cr_2O_4(PAO)(bpy)]$ was formed. Trials to get a single crystals for x-ray cryxtallography had failed.

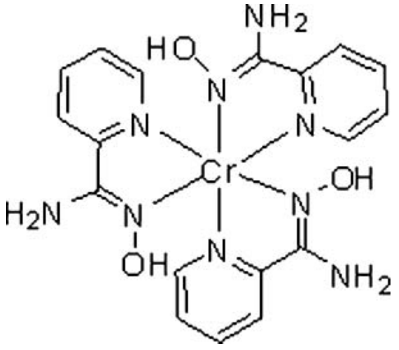

FIG. 1. The proposed structure of $[Cr(PAO)_3]$ complex.

It was found[27] that treatment of a white slurry of $[Cr(CO)_6]$ in MeCN/H_2O (1:1 v/v) with three equivalents of solid dipyridyloxime, $(py)_2CNOH$ (pyridyl group instead of NH_2 group in pyridylamidoxime) resulted in a pale yellow suspension, which – upon refluxing for 5 days – turned to a brown solution due to slow oxidation of Cr^0 under aerobic conditions. The brown solution soon deposited brownish red crystals of the dichromium(II,II) complex $[Cr_2\{(py)_2CNO\}_4].2H_2O$. The two high-spin Cr(II) atoms are doubly bridged by two oximate ligands, while a chelating $(py)_2CNO^-$ ion completes distorted trigonal bipyramidal coordination at each metal center. The dimers are stabilized by intramolecular stacking interactions between the terminal $(py)_2CNO^-$ ligands.

Thermal reactions of 2-pyridylamidoxime with $[Mo(CO)_6]$ in THF gave only one product. The elemental analysis and mass spectrometry ($m/z = 563$) confirmed the molecular formula $[Mo_2O_6(PAO)_2]$ for the complex. The IR spectrum of the complex exhibited the characteristic bands of the 2-pyridylamidoxime ligand with the corresponding shifts due to complex formation (Table 2). The infrared spectrum of

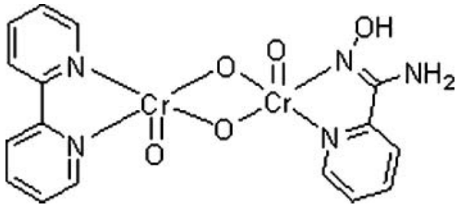

FIG. 2. The proposed structure of $[Cr_2O_4(PAO)(bpy)]$ complex.

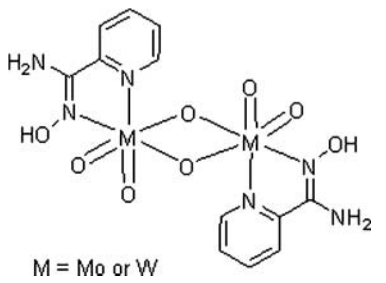

FIG. 3. The proposed structure of $[MO_4(PAO)_2]$ complex, M = Mo or W.

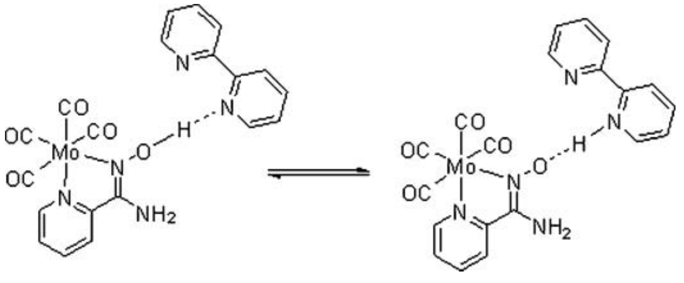

FIG. 4. The proposed structure of $[Mo(CO)_4(PAO)]$.bpy complex.

the molybdenum complex also displayed non-ligand bands at 483 cm^{-1} and 667 due to Mo—N, Mo—O—Mo, respectively. Also, two stretching bands were observed at 943 and 905 cm^{-1} due to symmetric and asymmetric frequencies of two terminal cis Mo=O bonds.[28] This has been found to be common for Mo=O bonds reported for a *cis* MoO_2 fragment of a dimeric structures having the Mo_2O_6 core.[29–31] Many complexes having the Mo_2O_6 or Mo_2O_5 cores have been recently reported, where molybdenum atoms bonded to a *cis* dioxo group and the two Mo atoms were bridged by one or two oxygen atoms.[29,32]

The ^1H NMR spectrum of the complex displayed singlet signals at 5.81 and 9.90 ppm due to the NH_2 and OH protons, respectively. The $[Mo_2O_6(PAO)_2]$ complex exhibited multiplets at 7.60, 7.97, 8.62 ppm due to the pyridine ring of PAO ligand with shifts due to complex formation. Therefore, from the spectroscopic data, it can be concluded that the complex might have molybdenum species existing in an octahedral environment that coordinated to PAO ligand through the nitrogen atoms. Also, each molybdenum atom attached to two oxygen atoms in cis positions as well as two bridged oxygen atoms with the metal in d^0 state (Figure 3).

Heating a mixture of $[Mo(CO)_6]$ and PAO ligand in the presence of bipyridine in THF resulted in the formation of $[Mo(CO)_4(PAO)]$.bpy complex. The IR spectrum of the complex showed a pattern similar to that of ligands with the corresponding shifts (Table 2). Furthermore,, the IR spectrum showed a pattern of CO stretching frequencies due to four CO groups in the terminal metal carbonyl region (Table 2). IR spectrum of the complex 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 PAO ligand occupying two equatorial positions.[28] The IR spectrum of the complex showed shift of the OH group comparing to that in the free ligand (Table 2). The elemental analysis and mass spectra of the complexes (Table 2) revealed the presence of bpy. Therefore, the bonding of bpy to the complexes $[Mo(CO)_4(PAO)]$ was probably through hydrogen bonding between the nitrogen of the bipyridine and the O–H group of the PAO part (Figure 4). The [1]HNMR spectrum of the molybdenum complex displayed two broad signals at 9.89 and 5.82 ppm, due to the protons of the OH and NH_2 groups of PAO, beside a new singlet signal at 8.98 ppm, which did not belong to PAO and bpy. The broadening of the signals of OH group and the presence of the new signal suggest the presence of O—H···N hydrogen bonding. In addition, the ^1H NMR spectrum of the complex showed multiplets due to the pyridylamidoxime and bipyridine moieties, which confirmed the proposed structure of the complex. Such arrangement of $[M(CO)_4L]$.bpy, where L = istain[33] or 2—(2′-pyridyl)benzimidazole[25] have been reported.

$[W(CO)_6]$ reacted with the PAO ligand alone or in the presence of bpy to give a complex with the molecular formula $[W_2O_6(PAO)_2]$. The IR spectrum of the complex displayed a pattern similar to that of $[Mo_2O_6(PAO)_2]$ suggesting a similar structure of the two complexes (Table 2). In addition, two non-ligand bands at 961 and 885 cm^{-1} due to symmetric and asymmetric frequencies of two terminal cis W=O bonds, appeared in the spectrum. The infrared spectrum of the tungsten complex also showed characteristic bands at 486 and 651 cm^{-1} due to W—N, W—O—W bonds. The ^1H NMR spectrum of $[W_2O_6(PAO)_2]$ complex is similar to that of $[Mo_2O_6(PAO)_2]$ complex, which confirmed that the two complexes might have the same structure (Figure 3). It should be mentioned that while bpy did not participate in the coordination with tungsten or co-crystallized with it, bpy co-crystallized with the molybdenum complex due to hydrogen bonding between the OH(POA) and N(bpy) moieties, while bpy coordinated directly to Cr in the $[Cr_2O_4(PAO)(bpy)]$ complex.

Thermogravimetric Analysis

In order to gain more insight into structure of the complexes, the thermal studies of the complexes were carried out using thermogravimetric (TG) techniques. The TG plot of $[Cr(PAO)_3]$ complex displayed four resolved and well defined decomposition steps. The first decomposition step occurred in the temperature range (74–205°C) with a net weight loss 33.26% corresponding to elimination of $(C_6H_7N_3O + H_2O)$ species. The second decomposition step (205–329°C), with net weight loss of 19.87% was due to elimination of $C_5H_3N_2$ moiety. The third decomposition step occurred in the temperature range (329–426°C) with a net weight loss of 14.03% due to elimination of C_4H_2N2 species. The fourth decomposition step occurred in the temperature range (426–477°C) with a net weight loss

TABLE 3
Thermal data for chromium, molybdenum, and tungsten complexes of 2-pyridylamidoxime

Molecular formula	Mol. wt.	Decomp. temp. (°C)	Weight loss (%)	Mass loss found (calc.)	Eliminated species	Solid decomp. product (%)
[$C_{18}H_{21}N_9O_3Cr$]	463.5	74–205	33.26	153.90 (154)	$C_6H_7N_3O + H_2O$	11.33 Cr
		205–329	19.87	91.55 (91)	$C_5H_3N_2$	
		329–426	14.03	64.31 (65)	C_4H_2N2	
		426–477	21.59	100.78 (100)	$C_3H_6N_2O$	
[$C_{16}H_{15}N_5O_5Cr_2$]	461.4	74–160	3.90	17.94 (18)	H_2O	32.48 (32.97) Cr_2O_3
		160–240	25.09	120.72 (119)	$C_6H_5N_3$	
		240–433	21.24	96.76 (94)	C_5H_4NO	
		433–533	16.74	77.50 (77)	C_5H_4N	
[$C_{12}H_{14}N_6O_8Mo_2$]	562.3	115–233	29.93	168.28 (169)	$C_6H_7N_3O + O_2$	43.27 Mo_2O_3
		233–453	12.58	70.76 (69)	C_4H_7N	
		453–667	14.30	80.4 (84)	$C_2N_2O_2$	
[$C_{20}H_{15}N_5O_5Mo$]	502.3	122–200	31.24	157.05 (156)	$C_{10}H_8N_2$	—
		200–308	10.76	54.23 (56)	2CO	
		309–469	14.52	73.94 (73)	NH_3+2CO	
		470–634	3.83	19.23(18)	H_2O	
		650–1038	39.68	199.3 (200)	$MoC_6H_4N_2$	
[$C_{12}H_{14}N_6O_8W_2$]	738.3	74–293	27.24	204.73 (201)	$C_6H_7N_3O + 2O_2$	49.85 2W
		293–587	9.21	68.56 (68)	C_4H_6N	
		587–930	13.68	101 (100)	$C_2N_2O_2$	

of 21.59% due to elimination of $C_3H_6N_2O$ species to leave Cr metal as a residue.

The [Cr_2O_4(PAO)(bpy)] complex displayed four resolved and well defined decomposition steps. The first, at 74–160°C with a net weight loss of 3.90%, was ascribed to elimination of a water molecule. The second decomposition step occurred in the temperature range (160–24°C) with a net weight loss 27.09% due to the loss of $C_6H_5N_3$ species. The third decomposition step occurred in the temperature range (240–433°C) with a net weight loss of 21.24% due to elimination of C_5H_4NO species. The fourth decomposition step (433–533°C, 16.74%) was due to elimination of C_5H_4N species leaving Cr_2O_3 as a residue (Table 3).

The [$Mo_2O_6(PAO)_2$] complex was found to decompose in three well-defined steps in the temperature range (115–667°C) (Table 3). The first decomposition step occurs at 115–233°C with a net weight loss of 29.93% corresponding to elimination of (PAO) + O_2 species. The second decomposition step (233–453°C, 12.58%) was due to elimination of C_4H_7N species. The third decomposition step occurred in the temperature range 453–667°C with a net weight loss of 14.30% probably due to elimination of a $C_2N_2O_2$ moiety to leave Mo_2O_3 as a residue.

The TG plot of [$Mo(CO)_4$(PAO)].bpy displayed five successive decomposition steps. The first two decomposition steps were overlapped and occurred in the temperature ranges 122–308°C, with a net weight loss of 42.24%, were ascribed to elimination of bipyridine $C_{10}H_8N_2$ and 2CO species (Table 3). In a similar complex [$Mo(CO)_4$(isatH)].bpy the elimination of the bipyridine molecule occurred in the temperature range of 120–367°C.[33] The third decomposition step (309–469°C, 14.52%) was due to the elimination of 2CO and H_2O species. The fourth decomposition step occurred in the temperature range (470–634^{0}C) with a net weight loss of 3.83% due to the loss of H_2O molecule. The fifth step (650–1038^{0}C) had a net weight loss of 39.68% and corresponded to the decomposition and volatilization of the rest of the compound.

The [$W_2O_6(PAO)_2$] complex was found to decompose like the molybdenum analog, in three steps within the temperature range (74–830°C). The first decomposition step occurs at (74–293°C) with a net weight loss of 27.24% corresponding to elimination of (PAO) with $2O_2$ species. The second decomposition step occurred in the temperature range (293–587°C) with a net weight loss 9.21% probably due to elimination of C_4H_6N species. The third decomposition step (587–830°C, 13.68%) was due to elimination of a $C_2N_2O_2$ moiety to leave 2W as a residue.

CONCLUSION

Five new complexes were isolated from the reaction of group 6 metal carbonyls with 2-pyridylamidoxime (PAO) alone or in the presence of dpy. The resulted complexes revealed that the product depends on the reaction time and the reaction condition. The tris derivative [$Cr(PAO)_3$], resulted from the reaction of [$Cr(CO)_6$] with PAO under reduced pressure, while the binuclear ternary complex [Cr_2O_4(PAO)(bpy)], resulted in the presence of bpy under atmospheric pressure.

On the other hand, reaction of [M(CO)$_6$], M=Mo or W with 2-pyridylamidoxime under atmospheric pressure resulted in the formation of [M$_2$O$_6$(PAO)$_2$]. When the last reactions were carried out in the presence of bipyridine, [Mo(CO)$_4$(PAO)].bpy and [W$_2$O$_6$(PAO)$_2$] complexes were isolated. The bands in the IR spectra of the complexes revealed appropriate shifts due to complex formation. The thermogravimetric studies of the complexes showed multistep decompositions.

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