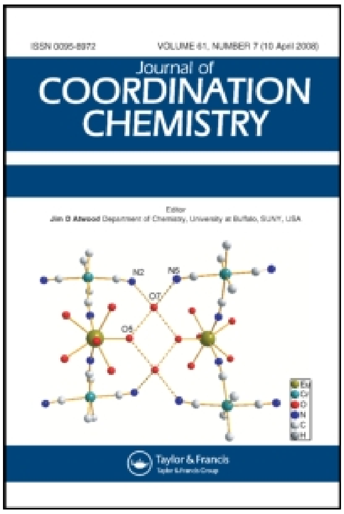

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Synthesis and spectroscopic studies of some new metal carbonyl derivatives of 1-(2-pyridylazo)-2-naphthol

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Synthesis and spectroscopic studies of some new metal carbonyl derivatives of 1-(2-pyridylazo)-2-naphthol

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Interaction of 1-(2-pyridylazo)-2-naphthol (PAN) with [$Mo(CO)_6$] in air resulted in formation of the tricarbonyl oxo-complex [$Mo(O)(CO)_3(PAN)$], **1**. The dicarbonyl complex [$Ru(CO)_2(PAN)$], **3**, was obtained from the reaction of [$Ru_3(CO)_{12}$] with PAN. In presence of triphenyl phosphine (PPh_3), the reaction of PAN with either $Mo(CO)_6$ or $Ru_3(CO)_{12}$ gave [$Mo(CO)_3(PAN)(PPh_3)$], **2**, and [$Ru(CO)_2(PAN)(PPh_3)$], **4**. All the complexes were characterized by elemental analysis, mass spectrometry, IR, and NMR spectroscopy. The thermal properties of the complexes were also investigated by thermogravimetry.

Keywords: ^1H NMR spectra; Ruthenium; Molybdenum; Metal carbonyl; 1-(2-Pyridylazo)-2-naphthol; IR spectra; Thermogravimetry

1. Introduction

Carbonyl derivatives of transition metals are useful intermediates in the synthesis of important coordination compounds [1–4] and have applications in catalysis of epoxidation, carbonylation, hydrogenation, and hydroformylation [5–8]. Molybdenum complexes also catalyze nitrogen fixation in plants by some microorganisms [9]. Many metal carbonyl derivatives are used in photochemical, photochromic, and thermochromic processes [10]. Pyridines and their azo derivatives have biological and pharmaceutical importance [11, 12]. Oxidation–reduction of pyridine derivatives play important roles in biological activity [13]. These derivatives are characterized by their antiviral, antifungal, antioxidant, antithyroid, and diuretic action [14]. Some pyridine complexes act as active catalysts for olefin polymerization [15]. Azo pyridine derivatives are used in manufacture of inks and dyes [16].

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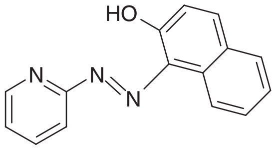


Scheme 1. PAN.

Biological and industrial interest in transition metal carbonyl derivatives of azo pyridines have prompted us to investigate the reactions of [$Mo(CO)_6$] and [$Ru_3(CO)_{12}$] with 1-(2-pyridylazo)-2-naphthol (PAN), scheme 1. The reactions were carried out in air with either PAN alone or in presence of triphenyl phosphine (PPh_3). PAN is different from our previous Schiff-base ligands [1–4], containing azo and naphthol groups which change the electronic structure. This ligand is expected to coordinate from its N donor sites making it a soft ligand. For example, from previous work, the change from chrysenequinone to chrysenequinonemonoxime led to different products with $M(CO)_6$ under similar conditions [17, 18].

2. Experimental

2.1. *Reagents*

[$Mo(CO)_6$] and [$Ru_3(CO)_{12}$], PAN, and PPh_3 were supplied by Fluka. All chemicals were of analytical reagent grade and used without purification.

2.2. *Instrumentation*

Infrared measurements (KBr pellets) were carried out on a Unicam-Mattson 1000 FT-IR spectrometer. Electronic absorption spectra were measured on a Unicam UV2-300 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. 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. Thermogravimetric (TG) 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 analyses and mass spectrometry data of the complexes.

2.3. *Synthesis of [Mo(O)(CO)$_3$(PAN)] (1)*

[$Mo(CO)_6$] (0.10 g, 0.38 mmol) and PAN (0.09 g, 0.38 mmol) were mixed in THF (ca. 30 cm^3) and heated to reflux in air for 4 h giving a brown solution. The reaction mixture was cooled and the solvent evaporated under vacuum. The solid residue was washed several times with boiling petroleum ether (60–80), recrystallized from hot THF to yield brown crystals and dried under vacuum for several hours (yield 88%).

Table 1. Elemental analysis and mass spectrometry data for the complexes.

				Mass spectrometry	
Complex	C% Found (Calcd)	H% Found (Calcd)	N% Found (Calcd)	Molecular weight	*m*/*z*[a]
$Mo(O)(CO)_3(PAN)$	48.3 (48.6)	2.8 (2.5)	9.1 (9.4)	445.25	385(11.3), 387(7.0), 388(12.1), 389(12.7), 390(7.3), 391(18.4), 393(7.3): $[P-2CO]^+$
$Mo(CO)_3(PAN)(PPh_3)$	62.3 (62.5)	3.9 (3.8)	6.3 (6.1)	691.63	631(7.7), 633(4.9), 634(8.3), 635(8.7), 636(5.0), 637(12.6), 639(4.9): $[P-2CO]^+$
$Ru(CO)_2(PAN)$	50.5 (50.3)	2.8 (2.7)	10.6 (10.3)	406.28	373(1.8), 375(0.6), 376(4.2), 377(4.1), 378(5.7), 379(10.5), 381(6.2): $[P-CO]^+$
$Ru(CO)_2(PAN)(PPh_3)$	62.8 (63.0)	3.9 (3.7)	6.1 (6.3)	667.66	634(1.4), 636(0.5), 637(3.3), 638(3.2), 639(4.4), 640(8.1), 642(4.9): $[P-CO]^+$

Note: [a]Intensity of peak between parenthesis relative to the most abundant peak, PAN, $m/z = 249$ (100).

2.4. *Synthesis of [Mo(CO)₃(PAN)(PPh₃)] (2)*

A mixture of $[Mo(CO)_6]$ (0.10 g, 0.38 mmol), PAN (0.09 g, 0.38 mmol) and PPh_3 (0.1 g, 0.38 mmol) in THF (ca. 30 cm^3) was heated to reflux in air for 7 h. Brown solid was separated and purified by recrystallization from hot THF (yield 65%).

2.5. *Synthesis of [Ru(CO)₂(PAN)] (3)*

$[Ru_3(CO)_{12}]$ (0.032 g, 0.05 mmol) and PAN (0.037 g, 0.15 mmol) were mixed in THF (ca. 30 cm^3) and heated to reflux in air for 10 h. A violet solid was collected by filtration. The solid was washed several times with hot petroleum ether (60–80) and then recrystallized from hot ethanol giving fine violet crystals (yield 75%).

2.6. *Synthesis of [Ru(CO)₂(PAN)(PPh₃)] (4)*

A mixture of $[Ru_3(CO)_{12}]$ (0.032 g, 0.05 mmol), PAN (0.037 g, 0.15 mmol) and PPh_3 (0.04 g, 0.15 mmol) in THF (ca. 30 cm^3) was heated to reflux in air for 3 h. A brown solid obtained was collected and recrystallized from hot ethanol (yield 80%).

3. Results and discussion

3.1. *IR and NMR studies*

Reaction of $[Mo(CO)_6]$ with PAN in THF in air gave the tricarbonyl oxo complex $[Mo(O)(CO)_3(PAN)]$, **1**. The IR spectrum of the free ligand showed characteristic bands due to its functional groups (table 2) [19–22]. The IR spectrum of the molybdenum complex, **1**, (Supplementary Material) displayed the ligand characteristic bands with the appropriate shifts due to complex formation (table 2). The IR spectrum showed a small shift in the ν(OH) and no shift in ν(C–O) frequencies to those of the free ligand (table 2). The presence of OH in **1** was confirmed by the ^{1}H NMR spectroscopy (table 3). These results indicate that OH was not involved in coordination. Complex **1** showed that the in-plane ring deformation bands, δ(Py), and the stretching frequency of the C=N of the pyridyl moiety shifted to lower frequencies indicating coordination of PAN to molybdenum through its pyridyl nitrogen, table 2 [20]. The shift of the ν(N=N) (1384 cm^{-1}) on complexation revealed involvement of the azo-nitrogen in coordination (table 2) [22]. IR spectrum of **1** also exhibited three strong vibrations in the terminal metal carbonyl range at 2068, 2019, and 1984 cm^{-1} [19]. The number and pattern of these bands suggests the *fac* structure as shown in scheme 2. Moreover, the IR spectrum

Table 2. Important IR data for PAN and its molybdenum and ruthenium complexes.

	IR data (cm^{-1})^a						
Compound	ν(OH)	ν(C=O)	ν(C=N) (Py)	ν(N=N)	ν (C–O)	δ(Py)	$\gamma_{C–H}$ (PPh$_3$)
PAN	3419(m)	–	1566(s)	1436(m)	1142(m)	624(m)	–
PPh$_3$	–	–	–	–	–	–	1474(m) 1430(m) 745(s) 694(s) 493(m)
Mo(O)(CO)$_3$(PAN)^b	3400(m)	2068(s) 2019(s) 1984(s)	1560(s)	1384(m)	1142(m)	607(m)	–
Mo(CO)$_3$(PAN)(PPh$_3$)^c	3420(m)	2070(m) 1925(s) 1889(m)	1563(m)	1359(m)	1140(m)	582(m)	750(m) 693(m) 501(m)
Ru(CO)$_2$(PAN)^d	3380(m)	2047(s) 1972(s)	1548(s)	1347(m)	1138(m)	565(m)	–
Ru(CO)$_2$(PAN)(PPh$_3$)^e	3423(m)	1965(s)	1543(m)	1345(m)	1141(m)	559(m)	747(m) 695(m) 518(m)

Note: ^{a}s, strong; m, medium; w, weak.
^{b}The ν(Mo–N): 495 and 413 cm^{-1}; ν(Mo=O): 893 cm^{-1}.
^{c}The ν(Mo–N): 520 and 411 cm^{-1}.
^{d}The ν(Ru–N): 449 and 419 cm^{-1}; ν(Ru–O): 562 cm^{-1}.
^{e}The ν(Ru–N): 457 and 422 cm^{-1}; ν(Ru–O): 589 cm^{-1}.

Table 3. ^{1}H NMR data of PAN and its molybdenum and ruthenium complexes.

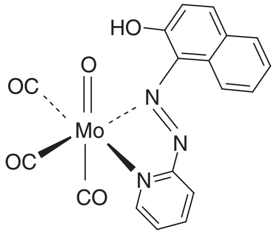
Compound	^{1}H NMR data (ppm)
PAN	15.67 (s, OH), 8.40–7.92 (m, py), 7.65–6.65 (m, Ph)
Mo(O)(CO)$_3$(PAN)	10.21 (s, OH), 8.42–8.2 (m, py), 8.07–6.75 (m, Ph)
Mo(CO)$_3$(PAN)(PPh$_3$)	15.68 (s, OH), 8.41–7.90 (m, py), 7.71–6.67 (m, Ph)
Ru(CO)$_2$(PAN)	13.28 (s, OH), 12.96 (s, OH), 12.48 (s, OH), 8.77–8.36 (m, py), 8.13–6.69 (m, Ph)
Ru(CO)$_2$(PAN)(PPh$_3$)	7.68–7.57 (m, py), 7.53–7.46 (m, py), 7.45–7.24 (m, Ph)

of the complex displayed a strong band at 893 cm^{-1} due to ν(Mo=O) stretching vibration. Terminal Mo=O bonds are usually in the range 900–950 cm^{-1} [1, 23]. That **1** is at lower frequency may be due to *trans* effect of the CO [19].

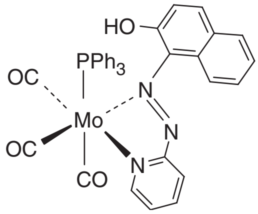
In the far IR spectrum of **1**, nonligand bands at 495 and 413 cm^{-1} due to Mo–N bonds provided further evidence for bonding of azo and pyridyl nitrogens to molybdenum [20, 24]. Although molybdenum carbonyl derivatives containing oxo groups are rare, a few papers report such complexes [18, 25, 26]. Magnetic studies of **1** indicate diamagnetism.

Reaction of $[Mo(CO)_6]$ with PAN in presence of PPh_3, resulted in $[Mo(CO)_3(PAN)(PPh_3)]$, **2**. The mass spectrum of **2** gave a molecular ion peak at $m/z = 636$ corresponding to $[P\text{-}2CO]^+$ (table 1). The IR spectrum of the complex displayed the PAN and PPh_3 characteristic bands with the appropriate shifts indicating the formation of a mixed ligand complex (table 2). Furthermore, the IR spectrum of **2** displayed nonligand bands at 2070, 1925 and 1889 cm^{-1} with a shoulder at 1870 cm^{-1}. The IR spectrum of the complex also showed a stretching frequency due to OH at 3420 cm^{-1} without significant shift with respect to that of ligand, suggesting that the OH group is not involved in coordination. The uncoordinated OH was also confirmed by ^{1}H NMR studies (table 3) where OH is a singlet at 15.68 ppm (free PAN at 15.67 ppm). The lower shifts in ν(N=N) and δ(Py) in the IR spectrum of **2** indicate binding of PAN to molybdenum via azo and pyridyl nitrogens (table 2). In the far IR spectrum of **2**, nonligand bands were observed at 520 and 411 cm^{-1} due to Mo–N bonds [24]. The IR spectrum of **2** showed no vibrational frequencies due to Mo=O; scheme 3 represents the proposed structure of **2**.

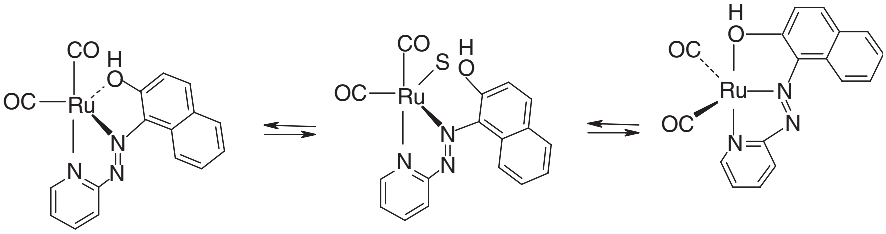
Interaction of $[Ru_3(CO)_{12}]$ with PAN gave $[Ru(CO)_2(PAN)]$, **3**. The IR spectrum displayed the ligand characteristic bands with shifts due to complex formation (table 2). Strong bands in the terminal carbonyl region at 2047 and 1972 cm^{-1} are due to



Scheme 2. The proposed structure of $[Mo(O)(CO)_3(PAN)]$ (**1**).



Scheme 3. The proposed structure of $[Mo(CO)_3(PAN)(PPh_3)]$ (**2**).



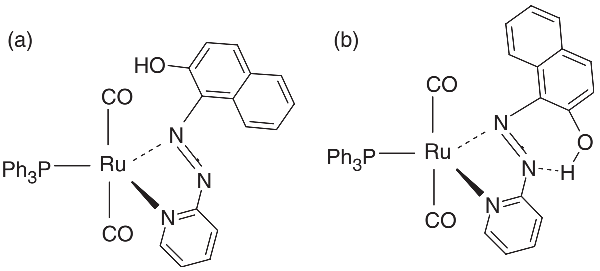
I II III

Scheme 4. The proposed structures of the three isomers of [Ru(CO)$_2$(PAN)] (**3**). S is referred to DMSO.

stretching frequencies of two CO groups in a *cis* position [19]. The IR spectrum of **3** also showed a strong and broad band at 3380 cm^{-1} due to a stretching of an OH. The shift in the ν(OH) frequency with respect to that of ligand indicated coordination of ruthenium to PAN through its OH group without proton displacement (table 2) [20]. The presence of the OH group in the complex was also confirmed by the ^{1}H NMR spectroscopy (table 3). Lower shifts observed in the stretching frequency of C=N group of the pyridyl ring at 1548 cm^{-1} and the bending frequency, δ(Py), at 565 cm^{-1} indicated bonding of PAN to ruthenium via its pyridyl nitrogen. Furthermore, the IR spectrum of the complex showed that N=N was shifted to lower frequency suggesting azo coordination to the metal (table 2). Moreover, the IR spectrum of **3** displayed nonligand bands at 562 cm^{-1} due to ν(Ru–O) and two bands at 449 and 419 cm^{-1} for ν(Ru–N).

Besides ligand signals with appropriate shifts (8.77–8.36 and 8.13–6.69 ppm corresponding to the pyridyl and phenyl rings, respectively), the ^{1}H NMR spectrum of the complex in DMSO showed three broad signals at 13.28, 12.96, and 12.48 ppm with a relative ratio 1 : 4 : 4 and a total integration intensity of one proton (Supplementary Material). Addition of D$_2$O resulted in the disappearance of these signals, indicating that they correspond to the OH. The presence of three broad OH signals indicated that the complex persists in three isomeric forms (scheme 4). The lower field signal (13.28 ppm) with the least relative intensity could be due to isomer **II**, the one with nonbonded OH group. (This 16e isomer could be stabilized by DMSO). The other two signals with equivalent ratio correspond to **I** and **III**. This is confirmed from the ^{13}C NMR spectrum of the complex which displayed four CO signals with equal intensity at 177.72, 164.95, 159.66, and 157.89 ppm due to isomers **I** and **III** (Supplementary Material). Isomer **II** could not be detected from the spectrum. That the ^{13}C signals occur at higher field than normal could be from the presence of nitrogen donors in the other coordination sites. Scheme 4 gives the proposed structures of the three isomers of **3**.

Interaction of [Ru$_3$(CO)$_{12}$] with PAN in presence of PPh$_3$ resulted in the formation of a reddish-brown [Ru(CO)$_2$(PAN)(PPh$_3$)], **4**. The IR spectrum of the solid complex showed the ligand bands with the proper shifts due to complex formation with ν(OH) at 3423 cm^{-1} without significant shift (table 2), indicating uncoordinated OH [scheme 5(a)]. The ^{1}H NMR spectrum in DMSO showed no signals corresponding to hydroxyl hydrogen (table 3), probably due to some type of inter- and intra-hydrogen bonding with the oxygen and nitrogens of the ligand [scheme 5(b)]. The exchange rate of hydrogen between oxygen and nitrogen atoms could be very fast and lead to the collapse of the signal [27–29]. Furthermore, the IR spectrum showed a very strong band



Scheme 5. The proposed structure of [Ru(CO)$_2$(PAN)(PPh$_3$)]: (a) solid state structure; (b) structure in solution (DMSO).

Table 4. UV-vis data for PAN and its molybdenum and ruthenium complexes in ethanol.

Compound	λ nm
PAN	226, 304, 462
Mo(O)(CO)$_3$(PAN)	228, 290, 335
Mo(CO)$_2$(PAN)(PPh$_3$)	225, 347(sh), 464
Ru(CO)$_2$(PAN)	240, 280, 340(sh)
Ru(CO)$_2$(PAN)(PPh$_3$)	212, 225, 443

in the terminal metal carbonyl range at 1965 cm^{-1}, which could correspond to two CO groups in *trans* positions. Furthermore, the lower frequency shifts observed in the C=N stretching frequency of the pyridyl ring, the bending frequency, δ(Py), and ν(N=N) (table 2) indicated bonding of PAN to ruthenium through both the pyridyl nitrogen and the azo group. In addition, the IR spectrum of **4** displayed nonligand bands at 589, 457, and 422 cm^{-1} due to ν(Ru–O) and ν(Ru–N) frequencies, respectively.

3.2. *UV-vis studies*

Electronic absorption spectra of PAN and its complexes were investigated in ethanol (table 4). Absorption bands were observed for PAN at 226 and 304 nm due to π–π* and n–π* transitions, respectively. The electronic absorption spectra displayed a third band at 462 nm, which could be due to a charge transfer transition. In the UV-vis spectra, on going from ligand to complex, the π–π* and n–π* electronic transition band showed shifts with considerable change in absorbance. These observations are consistent with complex formation (table 4). In addition, the four complexes exhibited absorption bands at 335–464 nm that could be due to metal-to-ligand charge transfer transitions [2, 30, 31].

3.3. *TG analysis*

In order to give more insight into the structure of the complexes, thermal studies on the solid complexes using TG and differential thermogravimetric (DTG) techniques were performed [32].

Table 5. Thermal analysis data for PAN and its molybdenum and ruthenium complexes.

Complex	Decomposition step, K	% Weight loss	Mol. wt.	Species eliminated	% Solid residue
$Mo(C_{18}H_{11}N_3O_5)$	300–484	12.58	56.02	2CO	MoO
	484–996	62.28	277.29	$2NO + C_{16}H_{11}N$	
$Mo(C_{36}H_{26}N_3O_4P)$	341–466	12.15	84.03	3CO	MoO
	466–723	24.33	168.28	$N_2 + C_{10}H_{20}$	
	723–809	4.48	30.99	P	
	809–1273	42.84	296.31	$C_{23}H_6N$	
$Ru(C_{17}H_{11}N_3O_3)$	341–491	6.89	28.01	CO	Ru O
	491–682	38.92	158.16	$NO + C_9H_6N$	
	682–886	25.38	103.12	C_7H_5N	
$Ru(C_{35}H_{25}N_3O_3P)$	364–496	8.39	56.01	2CO	Ru O
	496–700	53.82	359.35	$C_{23}H_{10}N_3P$	
	700–882	20.25	135.23	$C_{10}H_{15}$	

The TG and DTG plots of $Mo(O)(CO)_3PAN$ [$MoC_{18}H_{11}N_3O_5$; M. wt. = 445.26] exhibited three decomposition steps. The first from 300–484 K, with a net weight loss of 12.58%, is probably due to elimination of two CO, table 5. The second and third steps occurred in the temperature range 484–996 K with a net weight loss of 62.28%, consistent with elimination of ($2NO + C_{16}H_{11}N$), to give finally MoO (table 5).

The TG and DTG plots of $Mo(CO)_3(PAN)(PPh_3)$ [$Mo(C_{36}H_{26}N_3O_4P)$; M. wt. = 691.63] exhibited six decomposition steps in the temperature range 341–1273 K. The first and second steps occurred in the temperature range 341–466 K, the third from 466–723 K, the fourth from 723–809 K and the fifth and sixth steps in the temperature range 809–1273 K, to give MoO (table 5).

Thermal studies of the ruthenium complex, $Ru(CO)_2(PAN)$, were carried out using thermogravimetry. The TG plot of $Ru(CO)_2(PAN)$ [$RuC_{17}H_{11}N_3O_3$; M. wt. = 406.40] showed three well defined and nonoverlapping steps in the 341–886 K range (listed in table 5).

The TG plot of $Ru(CO)_2(PAN)(PPh_3)$ [$Ru(C_{35}H_{25}N_3O_3P)$; M. wt. = 667.66] showed three-step decomposition. The first at 364–496 K with a net weight loss of 8.39% corresponds to elimination of 2CO [32]. The second decomposition peak (496–700 K) showed a net weight loss of 53.82% (table 5) and the third at 700–882 K gave RuO (table 5).

4. Conclusion

1-(2-Pyridylazo)-2-naphthol is an important substance in biological and pharmaceutical fields. Reactions of molybdenum and ruthenium carbonyls with PAN yielded the carbonyl derivatives [$Mo(O)(CO)_3(PAN)$] and [$Ru(CO)_2(PAN)$]. In presence of PPh_3 the reactions gave [$Mo(CO)_3(PAN)(PPh_3)$] and [$Ru(CO)_2(PAN)(PPh_3)$].

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