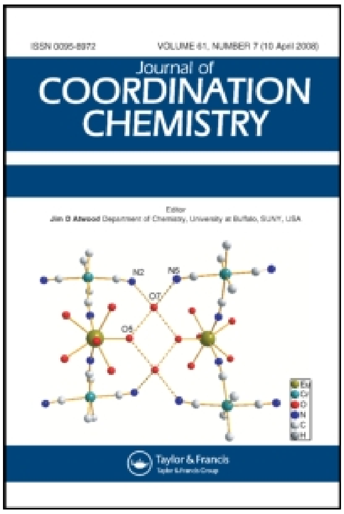

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Structural studies of some chromium and molybdenum complexes of 5,6-benzoquinoline

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Structural studies of some chromium and molybdenum complexes of 5,6-benzoquinoline

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Interaction of 5,6-benzoquinoline (BQ) with $[Cr(CO)_6]$ in air resulted in the formation of $[O_2(BQ)Cr(\mu\text{-}O)_2Cr(BQ)O_2]$ (**1**). Reaction of BQ with $[Mo(CO)_6]$ depends on the reaction conditions. In air for a short time, it gave $[(BQ)O(CO)Mo(\mu\text{-}O)_2MoO(CO)(BQ)]$ (**2**). Prolonged heating in air gave the oxo complex $[O_2Mo(\mu\text{-}o)_2MoO_2(BQ)]$ (**3**). Under reduced pressure, the reaction of BQ with $[Mo(CO)_6]$ resulted in the formation of $[Mo(CO)_5(BQ)]$ (**4**). The complexes were characterized by elemental analysis, IR, and ^1H NMR spectroscopy. The thermal properties of the complexes were investigated by thermogravimetric techniques.

Keywords: $Cr(CO)_6$; $Mo(CO)_6$; 5,6-Benzoquinoline; Azaarene derivatives

1. Introduction

Transition metal complexes of azaarene derivatives such as quinolines, isoquinoloines, quinoxalines have important uses as models for bioinorganic systems [1, 2]. Also, importance of these systems is related to facile electrochemical properties, magnetic coupling interactions and catalytic processes as well as their applications as photosensitizers [3–6].

Two dimensional NMR studies of oligonucleotide binding to three ruthenium(II) polypyridyl complexes $[Ru(Phen)_2L]^{2+}$, Phen = 1,10-phenanthroline, L = 2,3-bis(2′-pyridyl)quinoxaline (dpq) or 2,4-bis(2′-pyridyl)(6,7,8,9,-tetrahydro)phenazine, showed that they all bind in the DNA minor groove. Molecular modeling of the metal complex at the interchelation site suggested that $[Ru(Phen)_2(dpq)]^{2+}$ binds in a "head-on" fashion with the phenanthroline rings in the minor groove, with the dpq ligand inserted into the nucleotide base stack [7]. In a recent paper, the interaction of $[M(CO)_6]$, M = Cr, Mo and W, with 2-(2′-pyridyl)benzimidazole (pbiH) in the presence of 2,2′-bipyridine (bpy) giving the tetracarbonyl complexes $[M(CO)_4(pbiH)]$bpy was reported. Spectroscopic studies of these complexes indicated the presence of hydrogen

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bonding between the bpy nitrogen and the NH group of the pbiH [8]. Furthermore, reactions of $[M(CO)_6]$ with pbiH in the presence of PPh_3 gave the tricarbonyl monosubstituted derivative $[M(CO)_3(PPh_3)(pbiH)]$ [8]. In this article, the reactions of $[M(CO)_6]$, M = Cr and Mo, with 5,6-benzoquinoline (BQ) (figure 1) are reported. Complexes with interesting strucural features are isolated from such reactions depending on the reaction conditions.

2. Experimental

2.1. *Reagents*

$[M(CO)_6]$, M = Cr and Mo, were supplied by Aldrich. 5,6-Benzoquinoline was purchased from BDH. 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 dimethylsulfoxide (DMSO-d_6) using tetramethylsilane (TMS) as internal reference. 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 techniques [thermogravimetric analysis (TGA) and differential thermal analysis (DTA)] were carried out under nitrogen atmosphere with a heating rate of $10^{\circ}C\,min^{-1}$ using a Schimadzu 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 $[O_2(BQ)Cr(\mu\text{-}O)_2(BQ)O_2]$ (1). $[Cr(CO)_6]$ (0.10 g, 0.45 mmol) and BQ (0.08 g, 0.45 mmol) were mixed together in ca $25\,cm^3$ tetrahydrofuran (THF). The mixture was heated to reflux in air for 6 h. The color of the reaction mixture turned brown. The reaction mixture was left to cool and the formed solid residue was isolated by filtration. The residue was washed several times with boiling

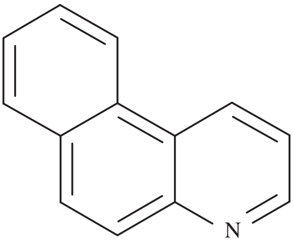


Figure 1. 5,6-Benzoquinoline (BQ).

Table 1. Elemental analyses 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	55.87	55.45	3.22	3.1	5.01	4.78	558.41	559 (p^+)
2	50.17	49.2	3.87	3.41	4.17	4.32	670.31	671 (p^+)
3	33.43	33.21	2.78	2.52	2.99	2.75	467.06	468 (p^+)
4	52.07	51.55	2.17	2.41	3.37	3.41	415.19	388 [p-CO^+]

petroleum ether and the complex was then recrystallized from hot THF to yield pale brown crystals. The complex was left to dry *in vacuo* for several hours (yield 70%).

2.3.2. Synthesis of [O(CO)(BQ)Mo(μ-O)$_2$Mo(BQ)(CO)O] (2). A mixture of [Mo(CO)$_6$] (0.13 g, 0.50 mmol) and BQ (0.09 g, 0.50 mmol) in ca 25 cm^3 THF was heated to reflux in air for 3 h. The color of the reaction mixture was brown with formation of brown precipitate. The reaction mixture was left to cool and the solid residue isolated by filtration. The residue was washed several times with boiling petroleum ether, and then recrystallized from hot THF to yield brown crystals. The complex was left to dry under vacuum for several hours (yield 63%).

2.3.3. Synthesis of [O$_2$Mo(μ-O)$_2$MoO$_2$(BQ)] (3). A similar procedure was employed as for **2** with a reaction period of 9 h. Dark brown crystals in a yield of 75% was obtained.

2.3.4. Synthesis of [Mo(CO)$_5$(BQ)] (4). A mixture of [Mo(CO)$_6$] (0.13 g, 0.5 mmol) and BQ (0.09 g, 0.5 mmol) were mixed together in a sealed tube containing ca 25 cm^3 THF. The mixture was degassed with one freeze-thaw cycle and then heated to 70°C for 10 h. The reaction mixture was cooled and the solvent was removed on a vacuum line. The residue was washed with boiling petroleum ether and then recrystallized from hot THF to yield reddish brown crystals. The complex was left to dry *in vacuo* for several hours (yield 70%).

3. Results and discussion

Reaction of [Cr(CO)$_6$] with BQ in THF in air resulted in the formation of the oxo chromium complex [O$_2$(BQ)Cr(μ-O)$_2$Cr(BQ)O$_2$] (**1**). The IR spectrum of BQ showed a characteristic band due to the C=N functional group at 1559 cm^{-1} [9]. The IR spectrum of the chromium complex (**1**) displayed a C=N band with appropriate shift due to complex formation (table 2). In addition, the IR spectrum of the complex displayed two strong bands at 821 and 755 cm^{-1} due to asymmetric and symmetric stretching frequencies of two Cr=O bonds. Furthermore, two bands at 707 and 614 cm^{-1} were assigned to two Cr–O–Cr stretching vibrations [10]. The ^{1}H NMR spectrum of the chromium(VI) complex exhibited ligand signals with the corresponding shifts to lower field (table 3). According to the spectroscopic studies, the complex may have the structure shown in figure 2.

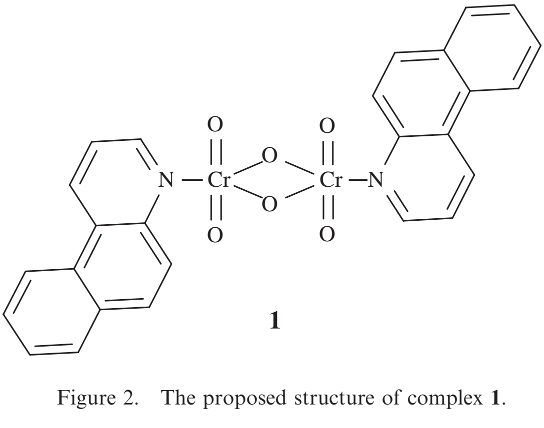
Table 2. Important IR data for the BQ and its chromium and molybdenum complexes.

Compound	IR data (cm^{-1})[a]			
	ν(C=N)	ν(C=O)	ν(M=O)	ν(M–O–M)
BQ	1569 (m)	–	–	–
1	1621 (s)	–	821 (s) 755 (s)	707 (w) 614 (m)
2	1626 (m)	1940 (vs) 1895 (m)	974 (m) 822 (m)	751 (m) 726 (m)
3	1624 (m)	–	947 (s) 908 (s) 891 (m) 822 (s)	754 (s) 708 (s)
4	1622 (m)	2071 (m) 1993 (m) 1956 (vs) 1923 (vs) 1888 (s)	–	–

[a] vs, very strong; s, strong; m, medium; w, weak.

Table 3. Important ^{1}H NMR data of BQ and its molybdenum complexes.

Compound	^{1}H NMR data (ppm)
BQ	9.21 (d), 8.95 (dd), 8.84 (d), 8.07 (m), 7.93 (d), 7.72 (m)
1	9.26 (d), 8.99 (d), 8.85 (d), 8.14 (m), 7.91 (d), 7.74 (m)
2	9.25 (d), 8.98 (d), 8.89 (d), 8.15 (m), 7.95 (d), 7.72 (m)
3	9.27 (d), 8.97 (d), 8.87 (d), 8.10 (m), 7.94 (d), 7.75 (m)
4	9.29 (d), 8.99 (d), 8.88 (d), 8.13 (m), 7.98 (d), 7.73 (m)



1

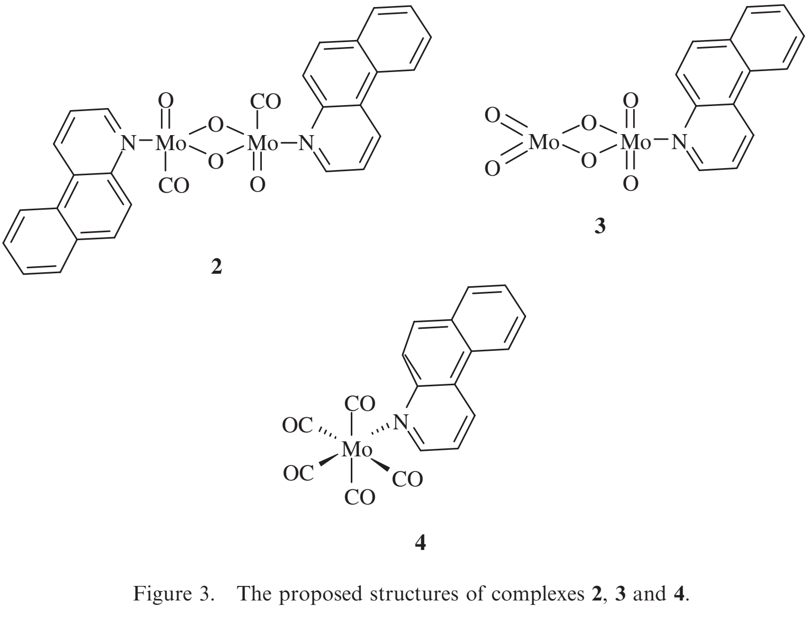
Figure 2. The proposed structure of complex **1**.

The reaction of BQ with $[Mo(CO)_6]$ was found to be dependent on the reaction conditions. In air with a short reaction time (3 h), the dicarbonyl dinuclear complex $[(BQ)O(CO)Mo(\mu\text{-}O)_2MoO(CO)(BQ)]$ (**2**) was obtained. Prolonged heating of the reaction mixture in air resulted in the formation of the dinuclear molybdenum complex $[O_2Mo(\mu\text{-}O)_2MoO_2(BQ)]$ (**3**). Under reduced pressure, reaction of BQ with $[Mo(CO)_6]$ gave the monosubstituted derivative $[Mo(CO)_5(BQ)]$ (**4**). The IR spectrum of the three complexes showed stretching frequencies due to the C=N bond of ligand with appropriate shifts (table 2). Complexes **2** and **3** also showed stretching frequencies due symmetric and asymmetric bands due to terminal (M=O) and bridged (M–O–M) bonds (table 2). However, the IR spectrum of the pentacarbonyl molybdenum complex **4** showed five CO bands in the terminal metal carbonyl region (table 2). Table 3 gives the ^{1}H NMR data for the molybdenum complexes. The proposed structures of the complexes are given in figure 3.

It was found that [Mo(CO)$_6$] reacted with BQ under reduced pressure to give the pentacarbonyl derivative **4**. Attempts to isolate the chromium analog from reaction of [Cr(CO)$_6$] and BQ under reduced pressure were unsuccessful. However, oxo chromium and molybdenum complexes were isolated from the corresponding reactions in air. The dicarbonyl oxo molybdenum complex **2** may be prepared through intermediate II in scheme 1 via dimerization. This intermediate could be generated from the pentacarbonyl derivative (intermdiate I) by reaction with oxygen. Further reaction of the dicarbonyl derivative (intermediate III) would result in the formation of dinuclear oxo complex (chromium derivative).

3.1. *Thermogravimetric analysis*

Thermal studies of the chromium and molybdenum complexes were carried out using TGA and DTA. The TGA plot of **1** displayed three resolved and well-defined decomposition steps. The first decomposition step in the temperature range 385–490 K with a net weight loss of 29.6% could be due to elimination of the ligand (table 4). The second decomposition step in the temperature range 495–673 K with a net weight loss of 19.3% was due to loss of a C_6H_4 moiety. The third decomposition step (675–900 K, 23.9%) was due to elimination of the second C_6H_4 leaving CrO_2 residue (table 4).



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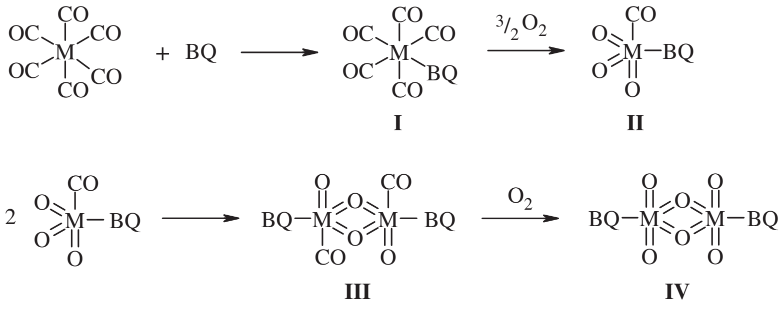
3

4

Figure 3. The proposed structures of complexes **2**, **3** and **4**.



Scheme 1. Schematic representation for complex formation.

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

Complex	Decomposition step (K)	% Weight loss	Mol. wt	Species eliminated	% Solid residue
1	385–490	29.6	393	(BQ–N)	27.2
	495–673	19.3	317	C_6H_4	
	675–900	23.9	241	C_6H_4	
2	400–660	33.3	449	(BQ–N) + 2CO	27.3
	670–1000	39.4	270	(BQ)	
3	400–620	27	341	$C_{10}H_6$	61.7
	625–925	11.3	288	C_3H_3N	
	450–590	20.2	331	3CO	30.08
	595–800	15.1	275	2CO	
	970–1150	53.48	134	$C_{11}H_9$	

The TGA plot of **2** displayed three decomposition steps in the temperature range 400–1000 K (table 4). The first decomposition step in the temperature range 400–660 K with a net weight loss of 33.3% corresponded to elimination of a BQ–N moiety and two CO groups. The second and third decomposition steps occurred in the temperature range 670–1000 K with a weight loss of 39.4% corresponding to the composition of another ligand moiety to give the residue MoO_2.

Complex **3** thermally decomposed in two well-defined steps in the temperature range 400–1000 K (table 4). The first decomposition step occurred in the temperature range 400–620 K with a net weight loss of 27% and corresponded to elimination of $C_{10}H_6$ species. The second decomposition step (625–925 K, 11.3%) was due to the elimination of C_3H_3N species leaving molybdenum metal oxide as a residue.

Complex **4** decomposed in three well-defined steps with a total mass loss of 88.78%. The first decomposition peak in the temperature range 450–590 K with a weight loss of 20.2% corresponded to the loss of three CO groups. The second decomposition step (595–800 K, 15.1%) was due to elimination of two CO groups. The third decomposition step occurred in the temperature range 970–1150 K with a weight loss of 53.48% corresponding to decomposition of $C_{11}H_9$ to leave the carbide residue $MoNC_2$.

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