Synthesis of New Mixed-Ligand Complexes of Molybdenum (IV) and Tungsten(IV): Characterization, Structure, Thermal and Anti-microbial Studies^{*}

Festus Sunday Fabiyi¹, Friday O. Nwosu²

¹Department of Chemistry and Industrial Chemistry, Faculty of Science, Bowen University, Iwo, Nigeria

²Department of Chemistry, Faculty of Science, University of Ilorin, Ilorin, Nigeria, E-mail: nwooyef@yahoo.com

Correspondence: Festus Sunday Fabiyi, Department of Chemistry and Industrial Chemistry, Faculty of Science, Bowen University, Iwo, Nigeria. E-mail: sunfabiyi@yahoo.com or sunday.fabiyi@bowenuniversity.edu.ng

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Abstract

Six new mixed-ligand complexes of Mo(IV) and W(IV) ions have been prepared and characterized. The three new complexes of Mo(IV) ions have the molecular formulae $MoC_{12}N_2O_5H_{18}$, $MoC_{15}N_2O_5H_{22}$ and $MoC_{14}N_2O_6H_{19}$, while the W(II) ions are $WC_{12}N_2O_5H_{18}$, $WC_{15}N_2O_5H_{22}$ and $WC_{14}N_2O_6H_{19}$. The structures of the complexes were deduced from their ir, ¹H nmr, and mass spectral studies. All the complexes were found to exhibit octahedral structures. Their antimicrobial activities against some bacteria and fungi species were found to be moderate.

Keywords: 8-Hydroquinoline, amino acids, mixed ligand, metal complexes

1. Introduction

Studies of metal-complexes have become very interesting because their syntheses and chemical studies have led to exploitation of both their striking physical and chemical properties for diverse applications (Perrin *et al*, Amit *et al*).

For this reason, researches in to syntheses and studies of metal complexes with diverse applications have been growing very fast (Perrin *et al*, Wangler *et al*). In fact, the number of metal complexes that can be synthesized seems limitless. This implies that the usefulness of these complexes can result to striking applications.

Novel metal complexes can be synthesized by changing the metal ions or the coordinating ligands which may, as well, involve structural modifications, such as, number of molecules (Fabiyi *et al*), type of ligands, etc (Amit *et al*, Fabiyi *et al* and Mandegani *et al*).

Many first row transition metal ions complexes with 8-Hydroxyquinoline as the ligand, have been synthesized and reported to possess wide range of applications (Morgan *et al*, Nakamoto *et al* and Orjiekwe *et al*). A large number of metal complexes with mixed ligands have been synthesized and studied (Perrin *et al*). These group complexes have been found to have diverse usefulness, in biological processes such as enzymes activation, storage and movement of active materials. Some have been found to have anti-microbial and anti-tumor activities Mandegani *et al*, Orjiekwe *et al* and Sajadi *et al*).

Mixed ligand complexes of 8-Hydroxyquinoline and other ligands are among these reported complexes. Several first row transition metal ions mixed-ligand complexes of 8-Hydroquinone and some amino-acids have been synthesized (Fabiyi *et al*, Nakamoto *et al* and Sajadi *et al*).

However, studies on their analogues of the second row transition metal ions with these ligands are still rare. Mixed ligand metal complexes chelates are very stable Sunil *et al*, Syamal *et al* and Wanger *et al*) and established to be biologically active against pathogenic micro-organisms (Sajdi *et al*, Syamal *et al*).

Their biological roles are known to be dependent on their stabilities. Previous researches have shown that the biological activities of some biologically active ligands are significantly increased when complexed with transition metal ions (Perrin *et al*, Sunil *et al* and Wanger *et al*). In this present study, we report the synthesis, structure and thermal behavior of six new mixed-ligand complexes of molybdenum and tungsten ions with 8-hydroxyquinoline as

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primary ligand, and alanine, leucine or glutamine as secondary ligands. Their antibacterial and fungal activities were also investigated.

2. Experimental

2.1 Chemicals

Reagents of Analar grade of the chloride salts of the metal from Sigma Aldrich chemicals were used as received, without further purification. All solvents were purified by distillation using conventional method before use (Syamal *et al*).

2.2 Physicochemical Measurements

The molar conductivities of 10⁻³ M solution of the metal complexes in DMF were measured at 30 °C using Equiptronics Digital Conductivity meter Model EQ-DCM-P. The melting points were determined using Gallenkamp AZ6512 melting point apparatus. Magnetic moments were measured at room temperature (Guoy's method) with Magnetic Susceptibility Balance, model Mk1, Sherwood Scientific, Cambridge.

Infrared spectra were recorded on FTIR Spectrophotometer (IR-Prestrige 21) in the region 4500 – 400 cm⁻¹.

TGA/DTA studies were recorded on a Linesis STAPT-1000 (Pyris Diamond) thermal analyzer at a heating rate of 10 $^{\circ}$ C /min. in atmosphere of air and nitrogen at the flow rate of 50 mL min⁻¹ in the temperature range of 50 – 1000 $^{\circ}$ C.

¹H nmr sprectra were recorded on Bruker Avance 11400 NMR Spectrometer using DMSO d⁶ (spectroscopic grade) as solvent.

Electrochemical studies were carried out using EG & G Priceton Galvanostat Model 273 A.

The elemental analyses were carried out using Thermo Finnigan Elemental Analyzer (model FLASH EA-1112).

Electronic spectra were recorded in DMSO on a Shimadzu UV-1600 Spectrophotometer.

2.3 Antimicrobial Studies

The qualitative antimicrobial susceptibility tests for the complexes were carried out using agar well diffusion technique (Sunil *et al*).

Each complex (20 mg) was dissolved in 50 mL of methanol, which was used as sample solution. Sample size for all the complexes was fixed at 0.1 mL. The wells were made by scooping out agar medium with sterilized cork borer in a Petri dish which has been inoculated with the microorganisms. 0.1 mL solution of each complex was added in the wells and Petri dish was then incubated at 37 $^{\circ}$ C for 24 h in dark. Ampicillin was used as the standard antibacterial drug while the control solvent was dimethylformamide. Amphoterin B was used as the standard antifungal drug. Zone of inhibition (ZOI) produced by each complex was measured in mm.

2.4 Synthesis of the Complexes

For the preparation of (1), 50 mL of freshly prepared solution of $MoCl_4$ (0.236 g, 0.01 mol) in absolute ethanol and 20 mL of 8-hydroxyquinoline (HQ) (0.142 g, 1.00 mol) in ethanol were mixed together and stirred vigorously. The reaction mixture was then placed immediately in a boiling water bath for 15 mins with constant stirring. Then 10 mL of aqueous solution of alanine (0.005 g, 0.0125 mol) was added.



Fig.1. Proposed equation of reaction for the preparation of Mo complex with 8-hydroxyquoline and alanine The pH of the reaction solution was then adjusted to about 8.5 using ammonium solution and, then, removed from the hot water bath. The reaction mixture was further refluxed for two hours and allowed to cool to room temperature. Crystals formed after 48 hrs were removed, washed with water several times and then recrystallized twice using absolute ethanol and dried in a vacuum over phosphorous pentoxide (P_2O_5).

The remaining five complexes were prepared by same procedure using the quantities of the reactants as follows:

For (2): MoCl₄ (0.362 g, 0.24 mol.); 8-hydroxyquinoline (0.164 g, 0.24 mol.); Alanine (0.020 g, 0.026 mol.).

For (3): MoCl₄ (0.362 g, 0.24 mol.); 8-hydroxyquinoline (0.164 g, 0.24 mol.); Glutamine (0.0380 g, 0.024 mol.).

For (**4**): WCl₄ (0.424g, 0.22 mol.); 8-hydroxyquinoline (0.20 g, 0.28 mol.); Leucine (0.036 g, 0.031 mol.).

For (5): WCl₄ (0.424 g, 0.22 mol.); 8-hydroxyquinoline (0.20 g, 0.28 mol.); Alanine (0.020 g, 0.026 mol.).

For (6): WCl₄ (0.424g, 0.22 mol.); 8-hydroxyquinoline (0.20, 0.28 mol.); Glutamine (0.040 g, 0.026 mol.).

3. Results and Discussion

The physicochemical properties of the complexes are presented in Table 1. The percentage yields that obtained from the preparation of the six new complexes were appreciable as shown Table 1. Sharp melting points recorded for all the complexes indicate that the complexes were pure.

The chemical structures of all the complexes were deduced using information obtained from both their physical properties studies and spectroscopic analyses.

3.1 Molar Conductance and Magnetic Moment Measurements

The molar conductance measurements for the complexes are in the range 14.32 - 23.52 ohm⁻¹ cm² mol⁻¹. These indicate that the compounds are non-electrolytes. The magnetic moments showed that the complexes are all paramagnetic, hence, spin free d² systems. These data are presented in Table 1.

3.2 ¹H nmr

DL- alanine, L-glutamic acid were prepared in D_2O while leucine in DMSO. Doublet signal of HCN-NH appear at 4.21 ppm (Table 2). The signals observed in the spectra were assigned after careful comparison with those found in the literature (Orjiekwe *et al* and Sunil *et al*). Ist was noted that the chemical shifts of the hydroxyl and amino groups were shifted to higher fields due to deprotonation and coordination, respectively. This confirms that the two groups are involved in the coordination.

Little differences were observed in the chemical shifts of the groups that are far from the metal ion the complexes. As expected in all the complexes, the chemical shift values of the hydroxyl and amino groups are shifted to the blue region due to deprotonation and coordination, respectively.

3.3 Thermogravic Studies

Thermogravic studies of the complexes was carried out at the rate of 10 $^{\circ}$ C min⁻¹ in inert atmosphere. The first weight loss by the complexes occurred in the range 95 -182 $^{\circ}$ C which corresponds to the loss of two molecules of water. The endothermic peaks in the range 375 – 434 $^{\circ}$ C and 590 - 635 $^{\circ}$ C are indications of decompositions of the amino acid and 8-hydroxyquinone moieties. This decomposition pattern was observed in the six complexes.

3.4 I.R. Studies

Important bands from the spectra (Table 3) of the free amino acids, 8-hydroxyl quinone and the metal complexes were selected and assigned after careful comparisons with literature(Wisniewska *et al*). The 3435 cm⁻¹ stretching frequency which is rightly ascribed to vO-H band observed in the free HQ did not appear at all in all the spectra of the complexes. This is an indication that the HQ is bonded to the metal ion through the O atom of the –OH group after deprrotonation. The bands around 468 -462 and 484-480 cm⁻¹ are respectively, assigned to the stretching frequencies of vMo-N and vW-N. This is a strong indication that the HQ is coordinated to the metal ion through N atom.

As expected, there is a hypochromic shift in the wave number observed for v(C=N) in the free HQ from 1585 cm⁻¹ to 1472 cm⁻¹. This suggested that the coordination is through the tertiary nitrogen donor of HQ. The strong bands at about 1120 -1128 cm⁻¹ observed in the spectra of the complexes are assigned to the v(C=O) bands which suggests the presence of HQ moiety in the complexes with coordination through its N and O atoms (Nogueira *et al*).

The bands observed at around 3035 and 2964 cm⁻¹ are assigned as C-N asymmetrical and C-N symmetrical vibration wavelengths, respectively (Gharib *et al*). The bands shown in the regions of 610 - 602 cm⁻¹ have been assigned to Mo-O and W-O vibration wavelengths. These did not appear in the spectra of the free amino acids.

The presence of coordinated water molecules in the complexes is indicated in the ir spectra of the complexes due to the presence of weak bands in the range 1580 - 1575 cm⁻¹ which is assigned to H-O-H bending vibrations.

The v(COO) band of the free amino acids observed in the range $1605 - 1600 \text{ cm}^{-1}$ is bathochromically shifted in the complexes to around 1380 -1374 cm⁻¹. This indicated that the coordination of the COOH group to the metal ion is via O (Feng *et al*).

In-plane and out of plane deformation modes were observed at about 525 and 578 cm⁻¹, respectively in the HQ. These, however, occurred at higher wave numbers of 510 cm⁻¹ and in the range of 788 -782 cm⁻¹. This indicates that the coordination through the N of HQ with the metal ions.

3.5 Electronic Spectra Studies

One intense peak in the region 382 - 425 nm was observed in the electronic spectrum of each of the six new complexes. Each of these is assigned as charge- transfer to metal (LMCT). All the complexes also each exhibited a weak band in the region 592-644 nm and these are attributed to d –d transitions. The bands and their assignments are shown in Table 4. The spectra indicate that the geometry of the complexes is octahedral.

3.6 Mass Spectra Studies

In the mass spectra of complex (1) intense mass peaks at m/z 366, 328 and 243 were shown.

The first mass peak corresponds to the $[MoC_{12}N_2O_5H_{18}]^+$ ion and the second one proceeds by elimination of two water molecules, while the third peak corresponds to elimination of two water molecules and alanine molecular ion. The mass spectra of complexes (2), (3), (4), (5), and (6) show peaks at 408, 421, 454, 494 and 509 which correspond to their [molecular]⁺ ions peaks, respectively. These observations confirm the calculated molecular weights of the proposed structures for the compounds. The proposed typical structure of the complex is as shown in Fig. 2.



Fig.2. Proposed structure of one of the complexes

3.7 Biological Studies

All the complexes and ligands were screened for in vitro antibacterial activities against *Escherichia coli*, *Staphylococcus aureus*, *Straphytomyces viginiae* and *Staphylococcus pneumonia* and anti-fungal activities against *Candida albicans*, *Agaricus bisporus*, *Actinocorallia herbida*, *Aspergillus flavus* and *Aspergillus niger*.

The results of the antimicrobial activities of the six complexes are shown in Tables 5 and 6. All of them possess moderate biocidal properties.

4. Conclusion

This study has revealed the structure and spectroscopic properties of six new mixed-ligand complexes of Mo(IV) and W(IV) ions. All the complexes have octahedral geometry. The antimicrobial studies revealed that the complexes have moderate antimicrobial activity against some bacteria and fungi.

Table 1. Physical properties and elemental analysis of the complexes

					Analysis	% found (calculated)		
Empirical formula		Yield						µeff	λm
(formula weight)	Colour	(%)	M. Pt (°C)	N	с	н	0	(B.M.)	$(\Omega^{-1} \mathrm{cm}^2 \mathrm{mol}^{-1})$
MoC12N2O5H18	Light green	63	375-6	7.64 (7.6	i 2) 39.69	(39. 46) 4.1	91 (4.54)	4.6	8.08
(366.42)									
MoC15N2O5H22	Light green	63	375-6	6.89 (6.9	1) 6.89 (4	5.34) 5.42	(5.21)	4.8	8.22
408.42									
MoC14N3O6H19	Light green	63	375-6	9.97 (9.6	i4) 9.98 (9	9.38) 4.51	(4.14)	4.6	8.16
421.86									
WC12N2O5H18	Brownish	63	375-6	6.16 (6.3	5) 6.16 (5.98) 3.96	(4.17)	5.2	7.64
454.32									
WC15N2O5H22	Brownish	63	375-6	5.66 (5.7	8) 5.66 (5.96) 4.45	(4.84)	5.3	7.48
494.54									
WC14N3O6H19	Brownish	63	375-6	8.25 (8.3	6) 8.25 (8	3.48) 3.73	(4.01)	5.1	7.56
509.36									

Table 2. ¹HNMR spectra of the complexes

Compound	¹ HNMR (δ, ppm)
Alanine	1.69 (d, 3H, CH₃), 5.20(q, 1H, CH), 6.94(s, 1H, OH), 6.09 (s, 2H, NH₂)
Leucine	1.02 (d, 6H, CH₃), 1.52(d, 2H, CH₂), 4.44 (s, 1H, CH), 2.19 (q, 1H, CH), 8.30 s, 1 H, OH), 8.10 (s, 2H, NH₂)
Glutamine	4.20 (t, 2H, CH ₂), 5.10(q, 2H, NH ₂), 5.64(s, 1H, OH), 6.09 (s, 2H, NH ₂)
MoC12N2O5H18	1.69 (d, 3H, CH₃), 5.20(q, 1H, CH), 6.94(s, 1H, OH), 6.09 (s, 2H, NH₂)
MoC15N2O5H22	1.02 (d, 6H, CH3), 1.52(d, 2H, CH2), 4.44 (s, 1H, CH), 2.19 (q, 1H, CH), 8.30 s, 1 H, OH), 8.10 (s, 2H, NH2)
MoC14N2O6H18	4.20 (t, 2H, CH ₂), 5.10(q, 2H, NH ₂), 5.64(s, 1H, OH), 6.09 (s, 2H, NH ₂)
WC12N2O5H18	1.69 (d, 3H, CH₃), 5.20(q, 1H, CH), 6.94(s, 1H, OH), 6.09 (s, 2H, NH₂)
WC15N2O5H22	1.69 (d, 3H, CH₃), 5.20(q, 1H, CH), 6.94(s, 1H, OH), 6.09 (s, 2H, NH₂)
WC14N3O6H19	1.02 (d, 6H, CH₃), 1.52(d, 2H, CH₂), 4.44 (s, 1H, CH), 2.19 (q, 1H, CH), 8.30 s, 1 H, OH),

					Analysis %	found(ca	lculated)		
Empirical formula		Yield						_ μeff	λm
(formula weight)	Colour	(%)	M. Pt (°C)	N	С	н	0	(B.M.)	$(\Omega^{-1} \mathrm{cm}^2 \mathrm{mol}^{-1})$
MoC12N2O5H18	Light green	63	375-6	7.64 (7.62)	39.69(39.4	6) 4.91	(4.54)	4.6	8.08
(300.42) MoC15N2O5H22	Light green	63	375- 6	6.89 (6.91)	6.89 (6.34)	5.42(5.	21)	4.8	8.22
408.42 MoC14N3O6H19	Light green	63	375-6	9.97 (9.64)	9.98 (9.38)	4.51(4.	14)	4.6	8.16
421.86 WC12N2O5H18	Brownish	63	375-6	6.16 (6.35)	6.16 (5.98)	3.96(4.	17)	5.2	7.64
454.32 WC15N2O5H22	Brownish	63	375-6	5.66 (5.78)	5.66 (5.96)	4.45(4.	84)	5.3	7.48
494.54 WC14N3O6H19	Brownish	63	375 -6	8.25 (8.36)	8.25 (8.48)	3.73(4.	01)	5.1	7.56
509.36									

Table 3. Physical properties and elemental analysis of the complexes

Table 4. ¹HNMR spectra of the complexes

Compound	¹ HNMR (δ, ppm)
Alanine	1.69 (d, 3H, CH3], 5.20(q, 1H, CH), 6.94(s, 1H, OH), 6.09 (s, 2H, NH2)
Leucine	1.02 (d, 6H, CH3), 1.52(d, 2H, CH2), 4.44 (s, 1H, CH), 2.19 (q, 1H, CH), 8.30 s, 1 H, OH), 8.10 (s, 2H, NH2)
Glutamine	4.20 (t, 2H, CH ₂), 5.10(q, 2H, NH ₂), 5.64(s, 1H, OH), 6.09 (s, 2H, NH ₂)
MoC12N2O5H18	1.69 (d, 3H, CH₃), 5.20(q, 1H, CH), 6.94(s, 1H, OH), 6.09 (s, 2H, NH₂)
MoC15N2O5H22	1.02 (d, 6H, CH3), 1.52(d, 2H, CH2), 4.44 (s, 1H, CH), 2.19 (q, 1H, CH), 8.30 s, 1 H, OH), 8.10 (s, 2H, NH2)
MoC14N2O6H18	4.20 (t, 2H, CH ₂), 5.10(q, 2H, NH ₂), 5.64(s, 1H, OH), 6.09 (s, 2H, NH ₂)
8.10 (s,2H, NH ₂)	

Table 5. IR spectra of the amino acids, 8-hydroxylquinoline and the new complexes

Compound	u(OH)	u(C=N)	v(N-H)	u(C-O)	v(C=O)	u(Mo-O)	υ(W-O)	u(Mo-N)	u(W-N)
Hydroxylquinoline	3445, s	1585	-		1585, m	-	-	-	-
Alanine	3476, s		3040, m		1590, m	-	-	-	-
Leucine	3 466 , s		3042, s		1588, s	-	-	-	-
Glutamine	3 468 , s		3042, m		1586, m	-	-	-	-
MoC12N2O5H18	3306, m	1470, s	3188, m	1105, s	1610, m	622, s	638, s	464, s	482, m
MoC15N2O5H22	3314, s	1466, s	3090, s	1112, п	n 1614, s	624, m	633, m	468, m	486, s
MoC14N2O6H18	3304, s	1468, m	3086, s	1118, m	n 1616, s	626, m	640, s	466, m	488,m
WC12N2O5H18	33 06, m	1467, s	3082, m	1116, s	1612, s	622, m	642, m	462 , s	484, s
WC15N2O5H22	3318, s	1472, s	3084, s	1114, s	1618, s	620,s	636, m	464, s	485, s
WC14N3O6H19	3304, s	1470, m	3088, m	1114, m	1 6 15, s	624, s	638, s	462, s	490, m

Table 6.	Electronic	spectra	studies	data	of the	ligands	and t	the	compl	lexes
						<u> </u>				

Complex	Electronic band (cm ⁻¹)	Assignment	
HQ	51,055	π → π ⁺	
	41,200	± ב → מ	
Alanine	-	-	
Leucine	-	-	
Glutamine	-	-	
1	87,650 -86,500	$^{4}T_{1}g(F) \rightarrow ^{4}T_{1}g(P)$	
	28,450 - 28,300	$^{4}T_{1g}(F) \rightarrow ^{4}A_{2g}(F)$	
	12,700 - 12,550	$^{4}T_{1}g \rightarrow ^{4}T_{2}g(F)$	
2	87,350 -87,000	$^{4}T_{1}g(F) \rightarrow ^{4}T_{1}g(P)$	
	28,250 -27,000	${}^{4}T_{1}g(F) \rightarrow {}^{4}A_{2}g(F)$	
	12,700 - 12,550	$^{4}T_{1}g \rightarrow ^{4}T_{2}g(F)$	
4	87,350 - 86,500	$^{4}T_{1}g(F) \rightarrow ^{4}T_{1}g(P)$	
	22,350 -22,000	$^{4}T_{1g}(F) \rightarrow ^{4}A_{2g}(F)$	
	11,700 - 11,650	$^{4}T_{1}g \rightarrow ^{4}T_{2}g(F)$	
5 '	82,550 -82,300	$^{4}T_{1}g(F) \rightarrow ^{4}T_{1}g(P)$	
	22,250 -22,000	$^{4}T_{1}g(F) \rightarrow ^{4}A_{2}g(F)$	
	11,700 - 11,550	$^{4}T_{1}g \rightarrow ^{4}T_{2}g(F)$	
6	82,350 -81,900	$T_1g(F) \rightarrow T_1g(P)$	
	22,250 -22,000	$^{4}T_{1}g(F) \rightarrow ^{4}A_{2}g(F)$	
	11,500 - 11,350	$^{4}T_{1}g \rightarrow ^{4}T_{2}g(F)$	
-			

Table 7. Antibacterial activity (ZOI in mm)

Compound		Bacteria		
	S. viginiae	S. pneumonia	S. aureus	E. coli
1	12	8.5	6 .5	15.5
2	13.2	9. 2	6.5	16
3	14.8	9.5 7	7.0	16.5
4	13.5	8.8	6.5	16
5	14.3	9.5	6.5	16.8
6	14.8	10.2	7.0	17.5
HQ	7.4	4.5	2.0	4.5
Ala	3.5	2.5	0.5	1.5
Leu	3.2	2.0	0.5	0.5
Glu	2.1	2.0	0.0	0.0
Ampicillin	48	34	21.5	32
DMF	-	-	-	-

Compound		Fu	ngus	
	C. albicans	A. bispons	A. herbida	A. flavus
1	14.5	13	7	10.5
2	15	13	7.2	10.8
3	16	13.4	7.5	10.5
4	15.2	13	8	10.5
5	15.5	13	8.5	11.5
6	16.5	13.5	9	11.8
HQ	4.2	3.5	2	3.5
Ala	0.0	0.0	0.0	1.2
Leu	0.0	0.0	0.0	0.0
Glu	0.0	0.0	0.0	0.0
Amphoterin B	28	32	26	28
DMF	_	_	_	-

Table 8. Antifungal activity (ZOI in mm)

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