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Synthesis, Characterization and Antimicrobial Investigation of Three New Mo (VI) Mixed Ligand Complexes

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Authors' contributions

This work was carried out in collaboration between all authors. Author FKC and AK performed the experimental study, wrote the protocol and wrote the first draft of the manuscript. Author MAA managed the analyses of the study. Author MSI designed the study and author MKEZ supervised all the work. All authors read and approved the final manuscript.

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ABSTRACT

Three new Mo(VI) peroxo complexes $[MoO(O_2)(Val)_2(IQ)_2]$, $[MoO(O_2)(Val)_2(2\text{-Apy})]$ and $K[MoO(O_2)(Val)_2(8\text{-HQ})]$, where Val = Valine, 2-Apy = 2-Aminopyridine, IQ = Isoquinoline, and 8-HQ = 8-Hydroxyquinoline were prepared and characterized by elemental analysis, conductivity, magnetic measurements, IR and ^1H NMR spectroscopy. The complexes exhibited a high to moderate activity against some gram-positive and gram-negative bacteria. The MIC test showed that the $K[MoO(O_2)(Val)_2(8\text{-HQ})]$ complex was more potent against all the bacteria tested than the other two complexes.

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Keywords: Mo (VI) peroxo complexes; mixed complex; biological activity.

1. INTRODUCTION

Mixed-ligand peroxo complexes of transition metals belong to an important class of reactive intermediates in catalytic oxidations and are quite likely to play a substantial role as an active centre in biological processes involving dioxygen species [1]. Molybdenum peroxo amino acid complexes contain three biologically important components: peroxo group, amino acid, and Mo(VI) ion. Consequently, they are of interest in biochemistry due to their catalytic properties like some other molybdenum peroxides [2,3].

Peroxo complexes of Mo(VI) have been known for a long time [4-7], and their catalytic activity has been a topic of considerable interest [8–12]. Since dioxygen, hydrogen peroxide, or alkyl hydroperoxides are not prone to spontaneous oxygen transfer to olefins to yield the corresponding epoxides, efforts have been made during the last three decades to selective activation of these oxidizing agents. Only in the case of ethylene, direct epoxidation using dioxygen has been successfully applied in a technical- scale process. Higher epoxides cannot be synthesized in this way because of selective oxidation, therefore, they are usually obtained by the reaction of an olefin with an activated peroxide compound. Mechanistic details of the activation steps involved herein have also been a subject of experimental and theoretical studies since the works of Filatov, et al. [13] who investigated the reaction between olefins and percarboxylic acids.

In a continuation of our previous publications [14-16] we herein report the synthesis, structural assessment, and antimicrobial activity of three new Mo (VI) peroxo complexes containing valine as a primary ligand and heterocyclic amines as secondary ligands.

2. SYNTHESIS AND STRUCTURAL ASSESSMENT OF THE COMPLEXES

Three new Mo(VI) peroxo complexes $[MoO(O_2)(Val)_2(IQ)_2]$ (1), $[MoO(O_2)(Val)_2(2\text{-Apy})]$ (2) and $K[MoO(O_2)(Val)_2(8\text{-HQ})]$ (3), where, Val = Valine, IQ = Isoquinoline, and 8-HQ = 8-Hydroxyquinoline were prepared.

2.1 Experimental and Physical Measurements

All the reagents and chemicals used were reagent grade and used as supplied. Weighing was performed on a Mettler PM-200 electronic balance. Conductivity measurements were carried out using a WPACMS 35 conductivity meter and a dip-cell with platinized electrodes for DMSO solution. The melting or decomposition points of all the prepared metal complexes were measured in an electrothermal melting point apparatus (model AZ6512). Magnetic measurements were performed using a Sherwood Scientific Magnetic Susceptibility Balance. The IR spectra were recorded on a Shimadzu FTIR-8400 spectrophotometer in the range 4000–400 cm^{-1} for KBr disks. The UV-Vis spectra of the complexes in DMSO have measured on a Nicolet evolution 300 UV-Visible spectrophotometer. The ^1H NMR spectra were obtained on a Bruker 400 Ultrashield spectrometer in DMSO-d_6 and $CDCl_3$ at the Analytical Research Division, BCSIR Laboratories, Dhaka (Bangladesh). Analyses for carbon, hydrogen, and nitrogen were carried out on PerkinElmer 2400 Series II CHNS/O Elemental Analyzer at the Okayama University (Japan). The metal analysis of the complexes was done by conventional metal estimation method (treating the sample with conc. H_2SO_4, conc. HNO_3 and $HClO_4$ followed by evaporation to dryness and complexometric titration from distilled water solution).

2.2 Synthesis of Complexes 1–3 (General Procedure)

Molybdic acid (1.5 g, 0.0 mol) in 30% H_2O_2 (50 mL) was heated with constant stirring for about 36 hours, cooled and filtered to obtain a clear solution. The solution was mixed carefully with a solution of the secondary ligand in ethanol (40 mL) and a solution of valine in 30mL of aqueous KOH under slow continuous stirring, and the resulting solution was reduced to 50 mL under heating (refluxing temperature). The precipitate that formed was filtered off, washed with water and ethanol, and was dried over P_4O_{10} in a vacuum desiccator.

Complex $[MoO(O_2)(Val)_2(IQ)_2]$ (IQ = isoquinoline) (1). Yield 51%, colorless solid, mp 258°C, IR spectrum (KBr), v(N-H) 3329 cm^{-1}, v(C=O) 1662 cm^{-1}, v(C-O) 1546 cm^{-1}, v(M-O) 982 cm^{-1}, v(M-N) 419 cm^{-1}, v(O-O) 827 cm^{-1}, v( ) 650 cm^{-1}, 530cm^{-1}. Anal. Found, %: C 52.74, H 5.28, N 9.99, Mo 15.02. Calculated for $C_{28}H_{34}MoN_4O_7$, %: C 52.83, H 54.34, N 10.06, Mo 15.09.

Complex [MoO(O_2)(Val)$_2$(2-Apy)] (2-Apy = 2-aminopyridine) (2). Yield 59%, colorless solid, mp 258°C, IR spectrum (KBr), ν(N-H) 3229 cm^{-1}, ν(C=O) 1636 cm^{-1}, ν(C-O) 1548 cm^{-1}, ν(M-O) 948 cm^{-1}, ν(M-N) 402 cm^{-1}, ν(O-O) 838 cm^{-1}, ν(M$\overset{O}{\underset{O}{}}$) 630 cm^{-1}, 541 cm^{-1} . Anal. Found, %: C 47.81, H 5.00, N 12.01, Mo 18.45. Calculated for $C_{15}H_{26}MoN_4O_7$, %: C 47.89, H 5.06, N 12.10, Mo 18.51.

Complex K [MoO(O_2)(Val)$_2$(8-HQ)] (8-HQ = 8-hydroxyqionoline) (3). Yield 63%, colorless solid, mp 322°C, IR spectrum (KBr), ν(N-H) 3329 cm^{-1}, ν(C=O) 1662 cm^{-1}, ν(C-O) 1546 cm^{-1}, ν(M-O) 982 cm^{-1}, ν(M-N) 419 cm^{-1}, ν(O-O) 827 cm^{-1}, ν(M$\overset{O}{\underset{O}{}}$) 650 cm^{-1}, 530cm^{-1} . Anal. Found, %: C 42.85, H 4.98, N 7.88, Mo 18.35. Calculated for $C_{19}H_{26}MoN_3O_8K$, %: C 42.92, H 5.06, N 7.95, Mo 18.41.

The elemental analyses are in good agreement with the proposed empirical formulas of the prepared complexes. The structures of complexes **1**–**3** were proposed on the basis of their conductivity and magnetic moment measurements (Table 2) and electronic spectral data. The molar conductances of 10^{-3} M solutions of the complexes in DMSO indicate that complexes **1** and **2** are non-electrolytes, whereas complex **3** is electrolyte. The effective magnetic moments of Mo(VI) complexes **1**–**3** vary from 0.910 to 0.321 B.M., indicating that the complexes are paramagnetic in nature. The UV-vis spectra of the complexes show bands between 158 and 512 nm which are due to charge ligand to metal charge transfer band.

The IR spectra of complexes display ν(C=O) bands at 1608-1676 cm^{-1} and ν(C-O) bands at 1531-1574 cm^{-1}, which is significantly lower than the respective frequencies for amino acids (~1690-1586 cm^{-1}). This suggests coordination of the amino acid (valine) in complexes **1**–**3** through its carboxylate anion. The ν(M-O) modes appear in the range 907–966 cm^{-1}. The presence of M–N bonds in the complexes is confirmed by the appearance of ν(M-N) modes at 405 to 419 cm^{-1} [17–19]. The ν(N-H) modes are observed in the range 3128–3438 cm^{-1}. The metal peroxo group in complexes **1**–**3** gives rise to three IR-active vibrational modes: ν (O–O) at 813–852 cm^{-1}, ν_s (Mo–O) at 502–542 cm^{-1}, and ν_{as} (Mo–O) at 630– 671 cm^{-1} [17].

The ^{1}H NMR spectrum was measured for the complex K[MoO(O)$_2$(Val)$_2$(8-HQ)] only. Comparison of the ^{1}H NMR spectra of free 8-hydroxyquinoline [18] and the complex K[MoO(O)$_2$(Val)$_2$(8-HQ)] shows than that the signals of C-2 and C-7 in the complex are strongly shifted downfield due to the complexation with Mo(VI) [9.14 (s, 1H, Ar-H), 8.42 (s, 1H, m Ar-H), 7.82-7.78 (m, 4H, Ar-H), 7.57-7.51 (m, 4H, Ar-H),]. While the other 8-hydroxyquinoline protons signals also change their positions and coupling patterns. Similarly, the valine protons signals shift from their original positions after complexation [(d, 1H, *J* = 6.4, CH), 3.22-3.11 (m, 1H, CH), 1.33 (d, 6H *J* = 6.4, 2 × CH_3).] [19]. As follows from the integral intensities and heights of proton signals, the complexation of Mo(VI) involves two valine and one 8-hydroxyquinoline molecules.

Thus, the above spectral evidence coupled with magnetic data, IR data, UV-vis data, physiochemical properties allows us to propose the following structure for the complex K[MoO(O_2)(Val)$_2$(8-HQ)] (Fig. 1):

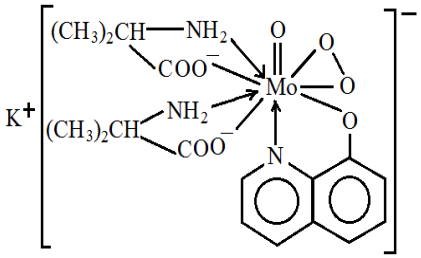

Fig. 1. Structure of the complex K[MoO(O_2)(Val)$_2$(8-HQ)]

The disc diffusion method for in vitro antimicrobial assay was used for screening a primary selection of the compounds as a therapeutic agent [20]. Antimicrobial activities of the test samples are expressed by measuring the zone of inhibition observed around the area. The results revealed that the complexes are more microbial toxic than the free metal ions or ligands. All the complexes of metals under investigation for molybdenum (VI) showed more or fewer activities against the four pathogenic bacteria tested. From the zone of inhibition, it is observed that all the complexes of molybdenum (VI) exhibited greater susceptibilities towards all the bacteria used (Table 1). The results also revealed that the complex K[MoO(O_2)(Val)$_2$(8-HQ)] (3) showed strong activity against both the Gram positive and Gram negative bacteria than the other complexes, indicating the higher zone of inhibition (Table 1).

Table 1. Antibacterial activity of Mo (VI) complexes 1–3

Complex no.	Minimum inhibition concentration, µg/mL			
	***P. auriginosa* (-ve)**	***S. β-haemolyticus* (+ve)**	***E. coli* (-ve)**	***B. subtilis* (-ve)**
1	32	32	32	32
2	32	64	32	32
3	64	64	64	32

Table 2. Antifungal activity of Mo (VI) complexes 1–3

Complex no.	Diameter of inhibition zone, mm (200 µg/disc)		
	A. niger	***A. fumigatus***	***A. flarus***
1	11	12	12
2	12	12	13
3	14	14	16

The results of the antifungal activity of the complexes are recorded in Table 2. From the zone of inhibition, it is observed that all the complexes of molybdenum (VI) showed significant activity towards all the fungi used. The highest antifungal activity was shown in the complex K[$MoO(O_2)(Val)_2$(8-HQ)] (3) against *A. flarus* and (16 mm) while the complex [$MoO(O_2)(Val)_2(IQ)_2$] (1) showed the lowest activity against *A. niger* (11 mm).

3. CONCLUSION

In this paper, we have explored the synthesis and coordination chemistry of three complexes. The IR spectral analysis indicated that N and O atoms are coordinated to central metal atom. Magnetic moment, UV-Vis and ^{1}H NMR analysis confirmed the proposed structure of metal complexes as shown in Figure-1. Biological activity revealed that the metal complexes have excellent antimicrobial activity.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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