Thermal and Spectral Studies of Peroxo Complexes of Molybdenum(VI) and Tungsten(VI) with Benzimidazole Derivatives†

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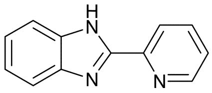
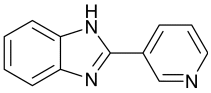
Synthesis, spectral and thermal studies of diperoxo complexes of molybdenum(VI) and tungsten(VI) with 2-(2-pyridyl)-benzimidazole, 2-(3-pyridyl)benzimidazole and 2,6-bis(benzimidazol-2-yl)pyridine are reported.

As molybdenum and tungsten are biologically important metals, the various aspects of the chemistry of molybdenum(VI) and tungsten(VI) peroxo complexes with organic ligands have been of considerable interest.[1,2] These complexes serve as reactive intermediates in the catalytic oxidation of organic substrates.[3] They are also important in biological processes involving oxidation or conversion of dioxygen species.[4] In addition, these complexes have also been used as potential precursors for molybdenum and tungsten complexes in various oxidation states.[5]

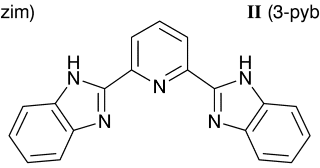
Djordjevic *et al.*[6] were the first to report on peroxo complexes of the biologically important ligand imidazole with molybdenum. Recently we have extended this study to 2-(2-hydroxyphenyl)benzimidazole, where we have isolated and studied its molybdenum(VI) and tungsten(VI) peroxo complexes.[5c] These complexes were further transformed into the corresponding stable monoxo $[MO]^{2+}$ and dioxo $[MO_2]^{2+}$ species. In the present investigation we describe the isolation, spectral and thermal studies of some diperoxo complexes of molybdenum(VI) and tungsten(VI) with the biologically important ligands **I**, **II** and **III**.



I (2-pybzim)



II (3-pybzim)



III (bzimpy)

Results and Discussion

The non-isolable peroxo species,[7] prepared *in situ* by stirring MoO_3 or $WO_3 \cdot H_2O$ with an excess of 30% H_2O_2, readily react with ligands **I**–**III** to give the corresponding peroxo complexes **1**–**6**, respectively. All these complexes are crystalline in nature, white to light yellow in colour and sparingly soluble in methanol and ethanol while highly soluble in dimethylformamide and dimethyl sulfoxide (except for the molybdenum complex of 2-pybzim). Analytical data suggest a $[MO(O_2)_2L]$ ($M = Mo$ or W) stoichiometry when L = 2-pybzim and 3-pybzim but a $[\{MO(O_2)_2\}_3L_2]$ stoichiometry when L is bzimpy. The complexes are non-electrolytes in dimethylformamide solution. They are stable and do not explode on heating but decompose at 210–240 °C.

Spectral Studies.—The IR spectra of the complexes exhibit three IR active vibrational modes, at ~560, 650 and 870 cm^{-1} which are assigned to the symmetric $\overline{\mathrm{O{-}M{-}O}}$ stretch (ν_2), the antisymmetric $\overline{\mathrm{O{-}M{-}O}}$ stretch (ν_3) and the O–O intra-stretching (ν_1) mode, respectively.[8] The presence of these bands owing to the metal-peroxo group (local C_2 symmetry) confirms the η^2-coordination of the peroxo group. In addition, they display the diagnostic $\nu(M{=}O)$ band at 926–962 cm^{-1} (ref. 9).

The N–H stretching and bending vibrations of the ligands, ~3100 and 1450 cm^{-1}, remain either unperturbed or undergo a slight shift towards lower wavenumber in the complexes, suggesting that the NH proton remains attached at the N1 position.[10] The presence of a sharp band at ~1600 cm^{-1} owing to $\nu(C{=}N)$ (ring) vibration in the complexes, indicates the bonding of N_2 with the metal ions. Such $\nu(C{=}N)$ (ring) vibration in free ligands appears as a weak band at a relatively higher position. The comparison of bands owing to $\nu(C{=}N)$ (pyridine moiety) of the ligands and complexes is somewhat difficult owing to appearance of this band along with the bands of the tertiary nitrogen of the benzimidazole residue. However, the appearance of a band at 1017–1039 cm^{-1} owing to ring breathing mode of the pyridine moiety, which is at 20–35 cm^{-1} higher wavenumbers than the free ligands, indicates the coordination of pyridinic nitrogen.[11]

The ^1H NMR spectra of the ligands exhibit a singlet at 13.10–13.15 ppm and several multiplets in the 6.80–8.95 ppm region owing to –NH and aromatic protons, respectively. 3-pybzim displays an additional singlet at 9.35 ppm owing to a proton of the pyridine moiety. All the aromatic proton signals are also observed at nearly identical positions in the complexes. However, the signal due to –NH proton of the benzimidazole moiety could not be located. This proton either resonates along with aromatic protons or appears beyond 15 ppm. Mohanty *et al.*[12] have also not observed this signal in mononuclear $[MoO_2L(im)]$ (LH_2 = Schiff base ligands, im = imidazole) complexes in the 0–15 ppm range.

The UV-VIS spectra of the complexes display an intense band centred at 290–305 nm, which can be assigned to the π–π^* transition arising from the benzimidazole residue of the coordinated ligand;[13] such a band usually occurs at higher energy in the free ligand. In addition, they show a poorly resolved broad absorption between 325 and 365 nm. A very low molar absorptivity assigns this to the peroxo-metal charge transfer (LMCT) band.[14]

Thermal Study.—The main features of the TGA curves are the loss of two peroxo groups at two different temperature ranges in the complexes of neutral bidentate ligands, while there is an overlapping temperature in the complexes with a neutral tridentate ligand. Djordjevic *et al.*[14] have observed the ready loss of one peroxide in the complex $[MoO(O_2)_2(nicH)(H_2O)]$ (nicH = protonated nicotinic acid). A similar intermediate may also be proposed here for complexes **1**–**4** after intermolecular loss of O_2. After the total

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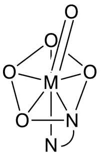
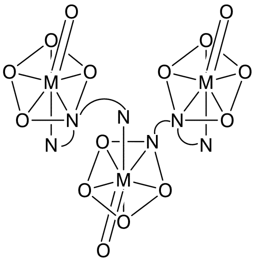
loss of peroxo groups, the organic moiety decomposes further with increasing temperature. Although decomposed fragments of the ligand could not be approximated owing to continuous weight loss, the complete decomposition of the ligands occurs at ~650 °C in all complexes.

From the physico-chemical and spectral evidence discussed above, complexes **1**–**4** (*i.e.* those obtained with a neutral bidentate ligand) are proposed to be mononuclear pentagonal bipyramidal (**IV**) while complexes **5** and **6** (*i.e.* those obtained with a neutral tridentate ligand) are thought to be trinuclear, each having a pentagonal bipyramidal structure (**V**). Two different environments around the central metal ion in trinuclear complexes, as proposed here, might have caused the decomposition of its peroxo groups at different temperatures and thus show a continuous loss of peroxo groups in their thermograms. Thus the proposed structures are supported by the thermolytic pattern. A pentagonal structure has been confirmed by X-ray crystallography in diperoxo complexes of molybdenum(VI) and tungsten(VI) having bi- and tridentate ligands.[2c,7]



IV



V

Experimental

All chemicals used were of A.R. grade. 2-(2-Pyridyl)benzimidazole and 2,6-bis(benzimidazol-2-yl)pyridine were prepared by the literature methods.[15]

The electronic spectra were recorded in dimethylformamide (DMF) on a Shimadzu UV-300 dual recording spectrophotometer while IR spectra were run as Nujol mulls on a Perkin-Elmer model 1620 FT-IR spectrophotometer. The ^{1}H NMR spectra were obtained in $(CD_3)_2SO$ using Bruker WH-90 and WH-200 spectrometers. Chemical shifts (ppm) are reported relative to tetramethylsilane. Conductivity measurements were carried out in DMF solutions (0.001 mol dm^{-3}) of the complexes using a Biochem model DC-808 digital conductivity bridge calibrated with potassium chloride solution. A laboratory built instrument was used to record thermograms of the complexes. All measurements were carried out in a quartz cup under a static air atmosphere.

Synthesis.—2-(3-*pyridyl*)*benzimidazole* (3-*pybzim*).—*o*-Phenylenediamine (2.16 g, 20 mmol) and nicotinic acid (2.46 g, 20 mmol) were mixed in syrupy orthophosphoric acid 950 ml). The reaction mixture was heated at 240–250 °C for 4 h with occasional shaking and the coloured melt so obtained was poured into one litre of chilled water with vigorous stirring. After 2 h, the brownish solid that precipitated was collected by filtration. This was treated with 200 ml of 15% sodium carbonate solution, filtered off and washed with water. Finally, recrystallization from ethanol–water (3:2) resulted in a white solid in 30% yield. (decomp. 240 °C). (Found: C, 73.6; H, 4.7. $C_{12}H_9N_3$ requires C, 73.8, H. 4.6%); δ_H 13.15 (s, NH), 7.25 (m), 7.65 (m), 8.45 (d), 8.70 (d), 9.35 (s, aryl).

[$MO(O_2)_2L$] ($M = Mo$ *or* W).—A solution of peroxomolybdic acid or peroxotungstic acid was prepared by stirring MoO_3 (0.15 g, 1 mmol) or $WO_3{\cdot}H_2O$ (0.25 g, 1 mmol), respectively, in 30% H_2O_2 (12 ml) for 15 h at ~40 °C and the solution filtered. This solution was added to a hot ethanolic solution (15 ml) of ligand (1 mmol) with stirring. The reaction mixture was stirred, along with cooling in an ice-bath. After 2 h the separated solid was filtered off, washed with water–ethanol (1:3 v/v) and dried *in vacuo*.

[$MoO(O_2)_2$(2-*pybzim*)] **1**.—Yield: 60%. (Found: C, 39.1; H, 2.7; N, 11.1. $C_{12}H_9MoN_3O_5$ requires C, 38.8; H, 2.4; N, 11.3%); ν_{max}/cm^{-1} 1604 (C=N, C=C), 1021 (py ring breath), 1954 (Mo=O), 863 (O–O), 682 (MoO_2 antisym), 578 (MoO_2 sym).

[$WO(O_2)_2$(2-*pybzim*)] **2**.—Yield: 65%. (Found: C, 31.2; H, 2.1; N, 9.3. $C_{12}H_9N_3O_5W$ requires C, 31.4; H, 2.0; N, 9.2%); ν_{max}/cm^{-1} 1601 (C=N, C=C), 1017 (py ring breath), 955 (W=O), 838 (O–O), 644 (WO_2 antisym), 516 (WO_2 sym); δ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}), 365 (1120), 300 (18400); δ_H 7.30–8.30 (m, aryl); Λ_M/Ω^{-1} cm^2 mol^{-1}, 4.5.

[$MoO(O_2)_2$(3-*pybzim*)] **3**.—Yield: 70%. (Found: C, 38.6; H, 2.6; N, 11.2. $C_{12}H_9MoN_3O_5$ requires C, 38.8; H, 2.4; N, 11.3%); ν_{max}/cm^{-1} 1635, 1614 (C=N, C=C), 1039 (py ring breath), 958 (Mo=O), 884 (O–O), 661 (MoO_2 antisym), 564 (MoO_2 sym); δ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}), 325 (990), 298 (15400); δ_H 7.40–8.95 (m, aryl), 9.35 (s, aryl); Λ_M/Ω^{-1} cm^2 mol^{-1}, 6.0.

[$WO(O_2)_2$(3-*pybzim*)] **4**.—Yield: 60%. (Found: C, 31.5; H, 2.3; N, 9.1. $C_{12}H_9N_3O_5W$ requires C, 31.4; H, 2.0; N, 9.2%); ν_{max}/cm^{-1} 1628, 1603 (C=N, C=C), 1030 (py ring breath), 926 (W=O), 835 (O–O), 640 (WO_2 antisym), 532 (WO_2 sym); δ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}), 355 (880), 305 (14700); δ_H 7.30–8.75 (m, aryl), 9.35 (s, aryl); Λ_M/Ω^{-1} cm^2 mol^{-1}, 5.8.

[$\{MO(O_2)_2\}_3L_2$] ($M = Mo$ *or* W).—These complexes were prepared in the same way as described above, using peroxomolybdic acid or peroxotungstic acid (1.5 mmol) and the ligand (1 mmol).

[$\{MoO(O_2)_2\}_3$(*bzimpy*)$_2$] **5**.—Yield: 53%. (Found: C, 39.9; H, 2.5; N, 12.2. $C_{38}H_{26}Mo_3N_{10}O_{15}$ requires C, 39.6; H, 2.3; N, 12.2%); ν_{max}/cm^{-1} 1625, 1596 (C=N, C=C), 1035 (py ring breath), 962 (Mo=O), 877 (O–O), 652 (MoO_2 antisym), 542 (MoO_2 sym); λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}), 335 (1230), 290 (15800); δ_H 7.35–8.45 (m, aryl); Λ_M/Ω^{-1} cm^2 mol^{-1}, 7.2.

[$\{WO(O_2)_2\}_3$(*bzimpy*)] **6**.—Yield: 62%. (Found: C, 32.5; H, 2.1; N, 9.7. $C_{38}H_{26}N_{10}O_{15}W_3$ requires C, 32.3; H, 1.8; N, 9.9%); ν_{max}/cm^{-1} 1619, 1597 (C=N, C=C), 1033 (py ring breath), 954 (W=O), 835 (O–O), 648 (WO_2 antisym), 559 (WO_2 sym); λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}), 360 (1470), 300 (16000); δ_H 7.35–8.40 (m, aryl); Λ_M/Ω^{-1} cm^2 mol^{-1}, 6.9.

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