

Preparation and Infrared Spectral Studies of Binuclear Molybdenum (VI) And Tungsten (VI) Complexes of Nicotinamide

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Summary: Binuclear Mo(VI) and W(VI) complexes of nicotinamide, $[M_2O_4L(OH)_4]$ (where M = Mo (VI) or W(VI) and L = nicotinamide) have been synthesized in acidic medium and characterized. The i.r. studies indicate that the coordination occurs through the pyridine ring N and N of the primary amide group. But since the complexes are binuclear, the ligand is possibly bridging in nature. Bridging also occurs through the M-O-M groups, and the complexes, have a binuclear octahedral structure.

Introduction

Nicotinamide, an essential constituent of vitamin-B complex, is well known for its clinical and biological values [1,2]. Some transition metal complexes of nicotinamide have been studied earlier by various workers, [3-6] who concluded that coordination occurs only through pyridine N. Alyaviya [7] et al., however, observed that it behaves as a bidentate ligand. The present paper describes the preparation and characterization of binuclear complexes of Mo(VI) and W(VI) with nicotinamide.

Experimental

The Mo(VI) complex was prepared by mixing the solutions of sodium molybdate and nicotinamide in 1:3 molar ratio of metal:ligand, and adjusting the pH of the solution to 3-4 by adding perchloric acid. The solution was then concentrated on electric water bath and allowed to crystallize. For the W(VI) complex, solutions of sodium tungstate and the

ligand were mixed in 1:3 molar ratio, and the pH of the solution was adjusted to 2.5 - 3.00 by adding HCl. It was then kept in an ice-cold water bath of 2-3 hours. The products were then filtered, washed thoroughly first with 50% alcohol, followed by absolute alcohol and ether and dried in a vacuum desiccator. Elemental analyses (for C, H and N) of the complexes were done at the Central Drug Research Institute, Lucknow, U.P., India. Molybdenum and tungsten were estimated gravimetrically [8] using oxine as the precipitating agent. The complexes were also heated in an air oven at 100°C for about 2 hours, but they did not show any appreciable loss in weight.

Results and Discussion

Analytical data are given below which show that in these complexes, metal: ligand ratio is 2:1, thus suggesting their binuclear nature.

(i) Mo(VI) complex

Yellow shining; crystalline, m.p. 310°C. Analysed for $[\text{Mo}_2\text{O}_4\text{L}:(\text{OH})_4]$ (where L = nicotinamide) Found: Mo, 44.0; C, 15.9; H, 2.37; N, 6.22%. Required: Mo, 43.1; C, 16.1; H, 2.24; N, 6.28%.

(ii) W(VI) complex:

White powder, m.p. 300°C. Analysed for $[\text{W}_2\text{O}_4\text{L}(\text{OH})_4]$ Found: W, 58.8; C, 11.3; H, 1.64; N, 4.45%. Required: W, 59.1; C, 11.5; H, 1.61; N, 4.49%. Both complexes are diamagnetic. The electronic spectrum [9] of the yellow Mo(VI) complex (in MgO) shows only charge transfer bands at 350, 390 and 420 (sh.) nm.

IR Studies

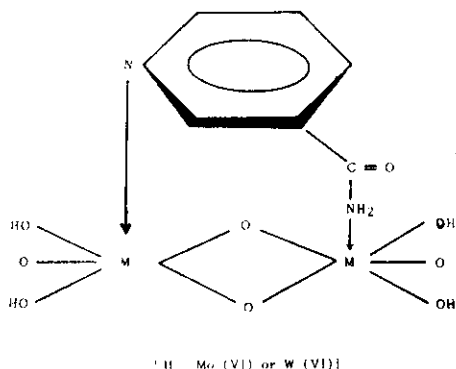
The IR spectra of nicotinamide and

its complexes were recorded in the range 4000 - 400 cm^{-1} on Perkin - Elmer model 337 spectrophotometer as KBr discs. Some important i.r. frequencies along with their assignments [10,11] are given in Table 1.

Nicotinamide is expected to give rise to characteristic i.r. frequencies for the pyridine ring and the primary amide group. In its i.r. spectrum νCH appears as a shoulder at 3050 cm^{-1} . In the metal complexes it also appears almost in the same region (3020 - 3025 cm^{-1}). The ring stretching vibrations ($\nu\text{C}=\text{C}$ and $\text{C}=\text{N}$) are observed in the ligand at 1595, 1558, 1475, and 1415 cm^{-1} , out of which the 1595 cm^{-1} band is little affected by coordination, but rest of these bands are considerably lowered in the complexes. The ring skeletal

Table-1: Characteristic I.R. frequencies of Nicotinamide and its Complexes (cm^{-1})

Nicotinamide	Mo(VI) complex	W(VI) complex	Band assignments
	3520 - 3420	3450	νOH
3325	3400 - 3200	3360 3190	νNH
3125	3150	3150	
3020	3025	3050	νCH
1666	1685	1675	$\nu\text{C}=\text{O}$ (Amide I band)
1610	1616	1620	δNH_2 (Amide II band)
1595, 1558	1600, 1545	1598, 1540	$\nu\text{C}=\text{C}$ and $\nu\text{C}=\text{N}$
1475, 1415,	1455, 1395	1455, 1400	Ring stretching + νCN (Amide group)
1200, 1118	1192, 1122	1188, 1125	νCH (in plane Ring skeletal vibration)
1026	-	-	
770, 700	782 670	790 660	δCH (out of plane)
-	940	958	$\nu\text{M}=\text{O}$
-	900	890	Bending M-OH
-	730	740	$\nu\text{M}-\text{O}-\text{M}$



and CH deformation vibrations are observed in nicotinamide at 1200, 1128, 1026, 770 and 700 cm^{-1} . In the metal complexes, the ring skeletal vibration (1026 cm^{-1}) is not observed, whereas the CH deformation vibrations appear in their usual regions with some \pm shifts in their positions. These evidences thus suggest coordination from pyridine ring N. In nicotinamide, the ν NH absorptions appear at 3325 and 3125 cm^{-1} . In the metal complexes these are observed as broad bands at 3400 - 3200 and 3150 cm^{-1} . Amide I and II bands (ν C = O and δ NH₂) are observed in the ligand at 1666 and 1610 cm^{-1} respectively. In the metal complexes these are shifted to somewhat higher frequencies (1685 - 1675, and 1620 - 1616 cm^{-1}).

The primary amides also absorb in 1420-1400 cm^{-1} region, which may be regarded as the CN stretching absorption. Thus in nicotinamide the 1415 cm^{-1} band may be considered to have contributions from both the ring stretching vibration and the ν CN of the primary amide group. In the Mo(VI) complex a broad band appears in this region (1415-1380 cm^{-1}), whereas in the W(VI) complex a sharp band is observed 1400 cm^{-1} . It may be thus concluded that in the metal

complexes, whilst the ν C=O is raised to higher frequencies, a lowering occurs in the ν CN vibration. It thus indicates coordination from nitrogen [12] of the amide group.

Besides the complexes also show ν OH frequencies [13] in 3500 - 3400 cm^{-1} region. The bending M-OH frequencies are observed at 900 cm^{-1} . The stretching ν Mo=O and ν W=O frequencies appear as usual in the same region at 940 and 958 cm^{-1} respectively. The M-O-M stretching vibrations [14,15] have been observed at 740 - 730 cm^{-1} . It may be thus concluded that in these Mo(VI) and W(VI) complexes, coordination occurs from both the pyridine N and nitrogen of the primary amide group. But since the metal:ligand ratio is 2:1, the ligand may be bridging in nature. Moreover bridging may also occur through the M-O-M bridging groups. The complexes thus appear to assume binuclear, possibly octahedral structure, the remaining coordination positions being filled by OH⁻ groups.

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