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Some Dioxo-metal (V & VI) Complexes of Anti-tubercular Isonicotinic Acid Hydrazide

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Metal complexes of anti-tubercular isonicotinic acid hydrazide drug with VO_2^+, MoO_2^{2+} and WO_2^{2+} have been prepared and their structures elucidated by various physico-chemical studies. The ligand acts as neutral bidentate with VO_2^+ and neutral monodentate with MoO_2^{2+} and WO_2^{2+}. Infrared spectra suggests *cis*-dioxo structure for VO_2^+ and WO_2^{2+} but *trans* dioxo group is present in MoO_2^{2+} complexes.

INTRODUCTION

Isonicotinic acid hydrazide is a very common and useful antitubercular drug in human tuberculosis. The extensive clinical investigations have been reported in literature by several workers.[1–4] The present paper describes various physico-chemical investigations of some metal chelates of this drug with dioxo-cations such as VO_2^+, MoO_2^{2+} and WO_2^{2+}. Tentative structure and mode of metal-ligand bonding have been tentatively assigned.

EXPERIMENTAL

All chemicals used in the present work were of CP grade. INH was obtained from Koch-light Laboratories, Ltd., Coinbrook Bucks, England and used after recrystallisation. The complexes were prepared adopting the following general procedure.

A calculated amount (0.01 mole) of $NaVO_3$, Na_2MoO_4 or Na_2WO_4 was dissolved in dil. HCl (*ca.* 20 ml) by warming and filtered hot. The filtrate was mixed with methanolic solution of INH (0.02 mole). The pH of the mixture was fixed as desired using dil. HCl, dil. NaOH or NH_4OH. The mixture was stirred for 2 h in a covered beaker with a magnetic stirrer at 100°C. The mixture was then concentrated to *ca.* 10 ml by evaporation and allowed to stand overnight. The coloured metal complexes separated were filtered, washed with methanol and dried in vacuum over anhydrous calcium chloride. The micro-analytical and physical data of complexes have been presented in Table 1.

RESULTS AND DISCUSSION

Isonicotinic acid hydrazide forms high melting, non-hygroscopic and air-

TABLE 1

ANALYTICAL, PHYSICAL AND ELECTRONIC SPECTRAL DATA OF METAL COMPLEXES

Compounds	pH of isolation	Colour/ (m.pt. °C)	Molar Conductance (Ω^{-1} cm^2 mole^{-1})	Elemental analysis, Found/(calc.) %				Electronic spectral band position (nm) and assignment L → M (CT)
				M	C	H	N	
$[VO_2(INH)(H_2O)Cl]\cdot 3H_2O$	6	Grey (>300)	10.2	15.56 (15.54)	22.11 (21.95)	4.50 (4.57)	12.98 (12.80)	275
$[MoO_2(OH)_2(INH)_2]\cdot 3H_2O$	7	Black (>300)	6.3	19.59 (19.59)	29.48 (29.38)	4.02 (4.08)	17.82 (17.14)	270
$[MoO_2(OH)_2(INH)_2]$	7	Grey (>300)	8.2	22.00 (22.01)	33.32 (33.02)	3.60 (3.62)	19.50 (19.26)	270
$Na[MoO_2(OH)_3(INH)]\cdot 3H_2O$	8	Heavy blue (>300)	45.6	21.86 (21.81)	32.80 (32.72)	3.00 (2.90)	19.20 (19.00)	272
$[MoO_2Cl_2(INH)_2]$	6	Light brown (>300)	6.2	20.19 (20.29)	30.32 (30.44)	2.95 (2.95)	17.21 (17.75)	270
$NH_4[MoO_2(OH)_3(INH)]\cdot 4H_2O$	8	Grey (>300)	42.3	25.58 (25.87)	19.42 (19.40)	4.40 (4.58)	11.30 (11.32)	270
$[WO_2(OH)_2(INH)_2]$	7	Cream (>300)	6.2	35.32 (35.11)	27.58 (27.48)	3.01 (3.05)	16.20 (16.00)	270
$Na[WO_2Cl_3(INH)]\cdot 2H_2O$	6	Cream (>300)	47.5	38.01 (38.00)	15.01 (14.93)	1.44 (1.45)	8.5 (8.71)	269

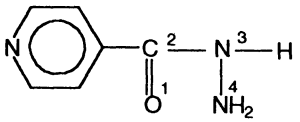
stable solid with VO_2^+, MoO_2^{2+} and WO_2^{2+} species. All are diamagnetic as expected for d°-complexes and insoluble in common organic solvents such as methanol, ethanol, benzene, nitrobenzene and acetone. However, fair solubility was attributed in DMF and all were non-electrolyte in this solvent except $Na[MoO_2(OH)_3(INH)]\cdot 3H_2O$, $NH_4[MoO_2(OH)_3(INH)]\cdot 4H_2O$ and $Na[WO_2Cl_3(INH)]\cdot 2H_2O$. Molar conductance values of these anionic complexes suggest their 1 : 1 elecrolytic nature[5]. Moreover, the low molar conductance value may be probably due to bulky anion.

All the complexes display very strong absorption band at 275 nm (VO_2^+), 270–272 nm (MoO_2^{2+}) and 269–270 nm (WO_2^{2+}) in electronic spectra assigned to L → M charge transfer bands. However, no absorption band is observed between 400 to 750 nm which supports their d°-electronic configuration.

IR Spectra

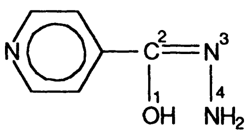
In order to identify the mode of bonding in the complexes, IR spectra of the ligand and the complexes were compared. Three medium intensity bands at 3400, 3310 and 3210 cm^{-1} in the spectrum of the ligand assigned to $\nu(NH_2)$, $\nu_{asym}(NH)$ and $\nu_{sym}(NH)$ are red shifted about 100 cm^{-1} in all complexes suggesting bonding of ligand through amino nitrogen atom of hydrazine residue[6]. The bonding through amino nitrogen atom is further supported by the change in position of strong band at 1420 cm^{-1} ($\nu(C{-}N) + \nu(N{-}N)$) to lower frequency (15–20 cm^{-1}) due to increase of CN bond order having bonding through amino nitrogen atom. The red shift of band at 1640 cm^{-1} due to NH_2 deformation associated with OCN bending on coordination also supports bonding of ligand through amino nitrogen atom.

The $\nu(CO)$ of the ligand observed at 1680 cm^{-1} as stong band blue shift on coordination to MoO_2^{2+} (1730 ± 5 cm^{-1}), WO_2^{2+} (1715 ± 5 cm^{-1}) species indicating the absence of bonding through carbonyl oxygen. However, this band undergoes red shift to lower frequency about 20 cm^{-1} on coordination to VO_2^+-ion suggesting formation of vanadium-oxygen bond. The formation of metal-oxygen bond is assumed through keto-form (II) and not through enol form (III) on the basis of $\nu(C{-}N)$ band observed at 1490 cm^{-1} in the spectrum of ligand shifts to 1500 cm^{-1} in the spectrum of VO_2^+-complex. Thus, form I seems to be more prominent for coordination than form II at low pH where deprotonation or replacement of H-atom is difficult.



Keto form

I



Enol form

II

The two non-ligand bands at *ca.* 980 and 820 cm^{-1} in VO_2^+-complexes[7] and at *ca*, 985 & 920 cm^{-1} in WO_2^{2+} -complexes[8] assigned to metal-oxygen multiple bond stretching modes of *cis*-dioxo group. However, one strong band at *ca.* 960 cm^{-1} in MoO_2^{2+}-complexes suggests two oxygen atoms are *trans* in MoO_2^{2+} species[9].

The strong broad band between 3700–3460 cm^{-1} in hydroxo complexes assigned to ν(OH) and at 790 cm^{-1} assigned to M-OH bending[10]. New bands at 450 and 390 cm^{-1} in VO_2^+ complex, at 500 and 460 cm^{-1} in MoO_2^{2+} complex and at 410 and 390 cm^{-1} in WO_2^{2+}-complexes assigned to metal-oxygen stretching modes. Metal-nitrogen stretching modes are observed at 500–525 cm^{-1} in WO_2^{2+}, at 510 and 530 cm^{-1} in MoO_2^{2+} and 590 cm^{-1} in VO_2^+.

On the basis of the above evidences, it has been concluded the INH acts as neutral bidentate ligand with VO_2^+ and monodentate netural legand with $MoO_2^{2+}$and WO_2^{2+} species.

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