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# Reaction of Anti-Tubercular Isonicotinic Acid Hydrazide Drug with Chlorides of Niobium (V) and Tantalum (V)

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## ABSTRACT

The reaction products of niobium (V) and tantalum (V) Chlorides with anti-Tubercular isonicotinic acid hydrazide drug are isolated and their structures are deduced using elemental analysis, conductivity measurements, magnetic susceptibility, IR and UV-vis Spectral studies. All metal derivatives were seven-coordinated having Pentagonal bipyramidal structure and isonicotinic acid hydrazide drug acts as bidentate NO donor. Metal-ligand vibrations in far-IR Spectra of complexes are analyzed and tentatively assigned.

**Keywords:** Niobium, Tantalum, Isonicotinic acid, Isoniazide.

## INTRODUCTION

A part of our studies on reaction between anti-Tubercular isonicotinic acid hydrazide drug with low-valent [1] and high valent [2] metal ions. We have studied reactions involving the niobium (V) and Tantalum (V) Chlorides. The formation of O-abstraction products by $MCl_5$(M=Nb/Ta) above room temperature was also observed leading to the formation of solid products. The different solid products in different reaction conditions were isolated with coordination number seven having Pentagonal bipyramidal structure. The ligand-bridged and chloro-bridged structures were observed and deduced using various physico-chemical measurements.

## MATERIALS AND METHODS

All the reagents were AR grade or CP grade. $MX_5$ (M = Nb/Ta: X=Cl) (Aldrich) and isonicotinic acid hydrazide (E.Merch) were commercial products of the highest purity available. All complexes were prepared using a general method taking $MX_5$ and ligand in different molar ratios in $CCl_4$:$CH_3OH$ (1:1) solvents adopting our previous method [3].

Elemental analysis was performed by micro-analysis division, RSIC, CDRI, Lucknow. IR Spectra of ligands and complexes were recorded on a Perkin-Elmer model- 577 Spectrophotometer in the range of 4000-200 $cm^{-1}$ as KBr pellets. The electronic spectra were recorded with Ziess (Jena) Model of automatic recording system. Magnetic measurements were made on Gouy balance using Hg $[CO\ (SCN)_4]$ as calibrant. The molar conductance of complexes ($10^{-3}$M) were measured in DMF using Wiss- Wekstatter Weitheim obb type LBR conductivity meter. Niobium and tantalum was determined gravimetrically as pentaoxide and chloride as silver chloride.

## RESULTS AND DISCUSSION

The reaction between $MCl_5$ and isonicotinic acid hydrazide in $CCl_4$ : MeOH (1:1) yielded various products given in table 1. The reaction between them is exothermic and the nature of products formed was dependent on the stoichiometry of reacting species, pH value of reaction mixture and temperature. At room temperature no evidences for the formation of O-abstraction products were found. In all the reactions of $MCl_5$ an addition compound was probably first formed after which HCl(g) was liberated. All niobium (V) complexes showed slight paramagnetism between 0.37 - .53 BM which is in agreement with results reported earlier [4]. The products did not melt but were decomposed to blue black mass in all cases in the temperature range 235-250ºC due to reduction of Nb (V) to blue Nb (III) and Ta (V) to black Ta (III) by ligand [5]. The molar conductance in DMF ($10^{-3}$M) were observed between 20-32. $ohm^{-1}cm^2mol^{-1}$ suggested their non electrolyte nature [6]. However, molar conductance of $[TaL_3Cl]$ Cl (S.No. 4) was 89.72 $ohm^{-1}cm^2mol^{-1}$ indicating as 1:1 electrolytes [7]. The similar orientation of ligand about the metal ion was indicated having same formula type.

Electronic spectra of complexes exhibit strong band in the region 28170-27625 cm$^{-1}$ due to charge transfer besides the ligand bands. However, no absorption is observed above 25000 cm$^{-1}$ indicating d$^{o}$- configuration of Nb (V) and Ta (V) complexes.

**IR Spectra**

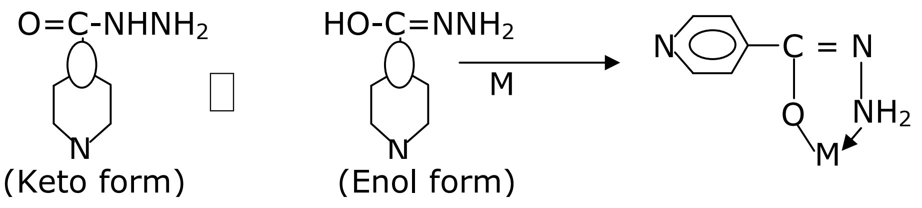
The characteristic IR bands at 3400 cm$^{-1}$, 3310 cm$^{-1}$, 3210 cm$^{-1}$, 1680 cm$^{-1}$, 1560 cm$^{-1}$ in the spectrum of ligand are assigned to $\upsilon NH_2$, $\upsilon_{asym}(NH)$, $\upsilon_{sym}(NH)$, amide band I and amide band II respectively. The $\upsilon NH_2$ of free ligand red shift to lower frequency 100 cm$^{-1}$ on coordination indicating bonding of ligand through amino nitrogen of hydrazine residue[1, 2]. The red shift (25-30 cm$^{-1}$) of band observed at 1640 cm$^{-1}$ due to $NH_2$ deformation associated with OCN bending on complexation also support the formation of M-N bond. The pronounced shifting of $\upsilon$C-N + $\upsilon$N-H frequency by 30-35 cm$^{-1}$ towards lower frequency in complexes as compared to free ligand also supports involvement of amino nitrogen of the ligand in coordination. New bands at 503 cm$^{-1}$, 524 cm$^{-1}$ & 480 cm$^{-1}$ $\upsilon$Nb-N and at 546 cm$^{-1}$, 510 cm$^{-1}$ and 450 cm$^{-1}$ $\upsilon$Ta-N in far- IR Spectra of complexes also support formation of metal-N bond[8].

Table-1: Analytical and physical data of complexes

| S. No. | Compound (pH, color) | % analysis : Calcd/ (Found) | | | | | ∧m ohm$^{-1}$ cm$^{2}$ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|
| | | C | H | N | Cl | M | |
| 1 | [NbOL$_3$] (7, Faint Pink) | 56.69<br>(56.82) | 4.72<br>(4.83) | 33.07<br>(33.32) | - | 24.41<br>(24.50) | 31.48 |
| 2 | [TaOL$_3$].2CH$_3$OH (7, Brown) | 35.87<br>(36.21) | 3.88<br>(3.43) | 18.40<br>(19.90) | - | 27.05<br>(27.11) | 32.43 |
| 3 | [NbL$_3$Cl]Cl (7.5, Pale yellow) | 37.76<br>(37.72) | 3.14<br>(3.66) | 22.02<br>(22.01) | 12.41<br>(12.50) | 16.25<br>(16.12) | 73.60 |
| 4 | [TaL$_3$Cl]Cl (7.5, Yellow) | 32.72<br>(32.83) | 2.72<br>(2.71) | 19.09<br>(19.32) | 10.75<br>(10.80) | 27.42<br>(27.50) | 89.72 |
| 5 | [Ta$_2$(LH)(H$_2$O)Cl$_{10}$] (6, Orange) | 7.62<br>(7.37) | 1.80<br>(1.67) | 2.40<br>(2.38) | 37.60<br>(36.82) | 38.34<br>(38.50) | 23.02 |
| 6 | [Ta$_2$(LH)(NCS)$_2$Cl$_8$(CH$_3$OH)$_2$] (6, Yellow) | 12.46<br>(12.26) | 1.55<br>(1.77) | 7.26<br>(7.54) | 29.49<br>(29.50) | 37.59<br>(37.62) | 20.3 |
| 7 | [Ta$_2$(LH)Cl$_{10}$(CH$_3$OH)$_2$] (6, Brown) | 10.45<br>(10.42) | 1.63<br>(1.56) | 4.57<br>(4.62) | 38.67<br>(38.71) | 39.43<br>(39.50) | 21.20 |
| 8 | [Nb$_2$(LH)(H$_2$O)$_2$Cl$_{10}$] (6, Orange Yellow) | 10.08<br>(10.11) | 1.54<br>(1.62) | 5.88<br>(5.87) | 49.71<br>(49.75) | 26.05<br>(26.11) | 22.32 |

(Where, LH = $C_6H_7N_3O$)

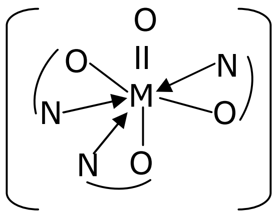
The $\upsilon$CO of the ligand observed at 1680 cm$^{-1}$ as strong band red shift to lower frequency (35-40 cm$^{-1}$) on complexation indicating bonding through carbonyl oxygen atom which decreases CO bond order and increase in CN bond order substantiated by splitting of band at 1255 cm$^{-1}$ into two component (1195-1210cm$^{-1}$) and (1380-1390cm$^{-1}$) in the spectra of complexes (S. No. 5, 6, 7 & 8). The formation of M-O is indicated by the replacement of hydrogen atom of OH group of the enolic form (amidol system) of the ligand in other complexes (S. No. 1, 2, 3, 4).



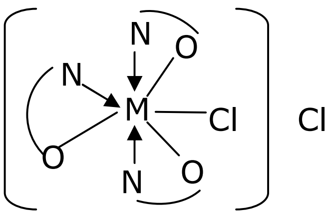
The ʋC-N observed at 1490 cm$^{-1}$ in free ligand shifted to 1500-1515 cm$^{-1}$ on comlexation which suggest enol form seemed more prominent at high pH values where replacement of hydrogen atom or deprotonation appeared easier. New non-ligand bands around 370- 415 cm$^{-1}$ supports the form of Metal-O bond [9].

The ʋCN, ʋCS and δNCS frequencies observed at 2045 cm$^{-1}$, 785cm$^{-1}$ and 490 cm$^{-1}$ confirms the N-bonded isothiocyanate ion [10] in corresponding complex (S. No. 6). The presence of strong absorption in the 850-950 cm$^{-1}$ region also confirms the existence of M= O species in OXO- complexes (S.No. 1 and 2) [11]. New bands between 340-345 cm$^{-1}$ in niobium (V) complexes and at 460-465 cm$^{-1}$ in tantalum (V) complexes in far IR Spectra are assigned due to metal-Cl stretching mode [12]. Such bands are not present in OXO-complexes (S.No. 1 and 2). The bridging chloride group vibration in complexes is generally observed around 200 cm$^{-1}$ [13]. The new bands at 250 and 283cm$^{-1}$ in far IR spectra does not ruled out the possibility of bridging chlorido group. The decrease of ʋC-O (alcoholic) stretch of MeOH from 1034cm$^{-1}$ to lower energy by 45-70cm$^{-1}$ in complexes (S. No.6 and 7) indicate the involvement of the O atom of MeOH towards coordination[14].

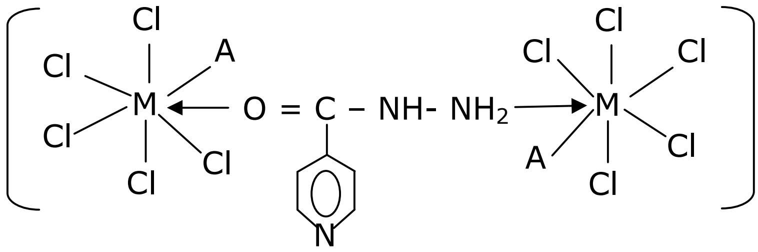
Thus, on the basis of analytical data (Table-1), valence requirements and the infrared spectral studies, it is proposed that the ligand behaves as bidentate and structure of complexes may be deduced as:



(Str. of S. No. 1 & 1, M= Nb/Ta)



(Str. of S. No. 3 & 4, M= Nb/Ta)



(A = $H_2O$; $CH_3OH$; NCS; M = Mb/Ta)
(Strs. of S. No. 5 and 8)
Fig.-1

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