Indian Journal of Chemistry
Vol. 23A, September 1984, pp. 783-784

Synthesis of Thiocyanato Derivatives of Niobium(V) & Tantalum(V) Isopropoxides

B L GORSI & R C MEHROTRA*

Department of Chemistry, University of Rajasthan, Jaipur 302 004

Received 1 *August* 1983; *revised and accepted* 16 *April* 1984

Reactions of acetyl isothiocyanate with isopropoxides of Nb(V) and Ta(V) give products of the type $M(OPr^i)_{5-n}(NCS)_n$ (where M = Nb, Ta; $n = 1$ to 4). Molecular weights and IR spectra of these derivatives reveal that mono- and di-thiocyanato derivatives are dimeric.

Synthesis and characterisation of halide and cyanide derivatives of Nb(V) and Ta(V) alkoxides have been reported earlier from our laboratory[1,2]. As an extension of these works, the thiocyanato derivatives of these metal isopropoxides have now been prepared.

The reactions of metal isopropoxides with acetyl isothiocyanate under strictly anhydrous condition are exothermic and proceed smoothly upto 1:4 molar ratios of the reactants (metal isopropoxide-acetyl isothiocyanate) in cyclohexane:

$$M(OPr^i)_5 + nCH_3CONCS \rightarrow M(OPr^i)_{5-n}(NCS)_n + nCH_3COOPr^i$$

(where M = Nb or Ta; n = 1 to 4)

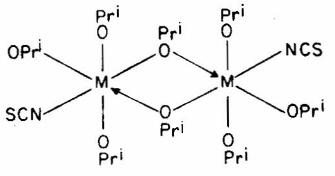
The ester produced is continuously fractionated off azeotropically with cyclohexane. The compounds obtained are listed in Table 1.

The reaction of niobium(V) isopropoxide with acetyl isothiocyanate in the molar ratio 1:5 always resulted in the formation of an insoluble oxy-derivative having the composition, $NbO(NCS)_3.CH_3COOPr^i$. These observations are in close conformity with those of Mehrotra and Kapoor[1] who reported the formation of oxy-halide derivatives, $NbOX_3.CH_3COOPr^i$ (where X = Cl,Br) in the reactions of niobium(V) alkoxides with acetyl halides.

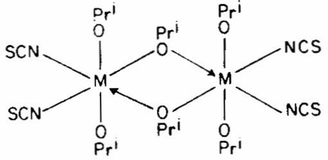
Neither an oxy-compound nor a pentathiocyanato derivative is formed when $Ta(OPr^i)_5$ reacts with acetyl isothiocyanate in 1:5 molar ratio; in this reaction only 1:4 product, $Ta(OPr^i)(NCS)_4$ is obtained.

Ebullioscopic molecular weight determinations of these isothiocyanato derivatives in benzene show that mono- and di- thiocyanato derivatives of Nb(V) and Ta(V) isopropoxides are dimeric. The molecular weights of tri- and tetra-thiocyanato derivatives could not be determined because of their insolubility in common organic solvents.

In view of the well known tendency of alkoxy bridge formation in metal alkoxides in general, the dimeric mono- and di- thiocyanato derivatives of Nb(V) and Ta(V) isopropoxides can be represented as **1** and **2**, respectively.



(1)



(2)

The IR spectra of the mono- and di- thiocyanato derivatives of Nb(V) and Ta(V) isopropoxides in KBr exhibit νCN(2055 ± 5 cm^{-1}) and νCS(805 ± 5, 855 ± 5 cm^{-1}), indicating that these derivatives have N-bonded terminal thiocyanate group[3-5]. In addition, a band of medium intensity in some of the derivatives at 725 ± 5 cm^{-1}, is indicative of S-bonded terminal thiocyanate group[3,4,6]. Appearance of bands at 725 ± 5 and 805 ± 5,855 ± 5 cm^{-1} in some of these derivatives is indicative of mixed mode of linkage (N-bonded or S-bonded) of the thiocyanate groups[6,7]. The absence of bands at 725 ± 5 cm^{-1} in other derivatives like $Nb(OPr^i)_4(NCS)$, $Nb(OPr^i)(NCS)_4$, $NbO(NCS)_3.CH_3COOPr^i$ may be because of its much lower intensity. Thiocyanate groups in the Nb(V) and Ta(V) isopropoxide having the stoichiometries 1:3 or 1:4 gave complicated IR spectra. Splitting of the bands has been observed in νCN as well as νCS modes.

Further, the bands in the regions 970-1055 and 560-680 cm^{-1} in the IR spectra of the derivatives have been ascribed to the νC-O (alkoxy) and νM-O respectively.

The dimeric structures of mono- and di- thiocyanato derivatives of Nb(V) and Ta(V) isopropoxides can, therefore, be explained with alkoxy bridging having isomeric mixtures of N-bonded and S-bonded terminal thiocyanate groups.

Reaction of $Nb(OPr^i)_5$ with CH_3CONCS in 1:1 *molar ratio*

To a solution of $Nb(OPr^i)_5$ (2.05 g) in cyclohexane (50 ml), CH_3CONCS (0.55 g) was added and the

Table 1—Reactions of Niobium and Tantalum Isopropoxides with Acetylisothiocyanate

Reactants (g)	Molar ratio	Product	Found(Calc) (%)		Mol.wt found (calc)
			Metal	Nitrogen	
$Nb(OPr^i)_5 + CH_3CONCS$	1:1	$Nb(OPr^i)_4(NCS)$	24.63	3.73	795
(2.09) (0.53)		(Yellow crystalline solid)	(24.01)	(3.61)	(387)
$Nb(OPr^i)_5 + CH_3CONCS$	1:2	$Nb(OPr^i)_3(NCS)_2$	23.90	7.03	804
(1.87) (0.95)		(Yellow semisolid)	(24.07)	(7.25)	(384)
$Nb(OPr^i)_5 + CH_3CNCS$	1:3	$Nb(OPr^i)_2(NCS)_3$	24.02	10.75	—
(1.92) (1.45)		(Reddish semisolid)	(24.13)	(10.91)	
$Nb(OPr^i)_5 + CH_3CONCS$	1:4	$Nb(OPr^i)(NCS)_4$	24.10	14.47	—
(1.79) (1.86)		(Reddish semisolid)	(24.20)	(14.58)	
$Nb(OPr^i)_5 + CH_3CONCS$	1:5	$NbO(NCS)_3.CH_3COOPr^i$	24.32	11.61	—
(2.35) (3.07)		(Reddish semisolid)	(24.13)	(10.91)	
$Ta(OPr^i)_5 + CH_3CONCS$	1:1	$Ta(OPr^i)_4(NCS)$	38.17	3.05	1003
(2.54) (0.54)		(White crystalline solid)	(38.09)	(2.94)	(475)
$Ta(OPr^i)_5 + CH_3CONCS$	1:2	$Ta(OPr^i)_3(NCS)_2$	38.43	6.10	1007
(3.25) (1.38)		(Brown viscous)	(38.17)	(5.90)	(474)
$Ta(OPr^i)_5 + CH_3CONCS$	1:3	$Ta(OPr^i)_2(NCS)_3$	38.18	8.64	—
(2.41) (1.53)		(Brown viscous)	(38.25)	(8.89)	
$Ta(OPr^i)_5 + CH_3CONCS$	1:4	$Ta(OPr^i)(NCS)_4$	38.38	11.79	—
(2.42) (2.05)		(Brown semisolid)	(38.34)	(11.86)	
$Ta(OPr^i)_5 + CH_3CONCS$	1:5	$Ta(OPr^i)(NCS)_4$	38.30	12.17	—
(2.33) (2.47)		(Brown semisolid)	(38.34)	(11.86)	

reaction mixture was refluxed for 30 min and the ester formed was continuously fractionated off azeotropically. The remaining solvent was removed under reduced pressure and the product dried for 5 hr at 60° under reduced pressure (1 mm of Hg). A yellow crystalline solid was obtained.

The products obtained by the reactions of Nb(V) and Ta(V) isopropoxides with CH_3CONCS are given in Table 1.

References

1 Mehrotra R C & Kapoor P N, *J lesscommon Metals*, **10** (1966) 348.
2 Gorsi B L, Kapoor P N & Mehrotra R C, *Indian J Chem*, **14A** (1976) 406.
3 Mitchell P C H & Williams R J P, *J chem Soc*, (1960) 1912.
4 Schmidtke H H & Garthoff D, *Helv chim Acta*, **50** (1967) 1631.
5 Burmeister J L, *Inorg Chem*, **3** (1964) 919.
6 Lewis J, Nyholm R S & Smith P W, *J chem Soc*, (1961) 4590.
7 Meek D W, Nicpon P E & Meek V I, *J Am chem Soc*, **92** (1970).
8 Gorsi B L & Mehrotra R C, *Indian J Chem*, **15A** (1977) 1199.