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Characterization of Isothiocyanato Niobates(V) Isolated from Solutions for the Spectrophotometric Determination of Niobium

B. Tamhina and C. Djordjević

Laboratory of Analytical Chemistry, Faculty of Science, University of Zagreb,
41000 Zagreb, Croatia, Yugoslavia

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From aqueous solutions containing niobium(V), sulphuric acid and an excess of thiocyanate, under the conditions for the spectrophotometric determination of niobium, the compounds $[(C_6H_5)_4P]_2[NbO(NCS)_5]$, $[(C_6H_5)_4As]_2[NbO(NCS)_5]$ and $[(C_2H_5)_4N]_2[NbO(NCS)_5]$ were isolated either by crystallization or by extraction with diethyl ether and evaporation of the extracts. $(C_2H_2N_2S_3)_2H[Nb(NCS)_6]$ was isolated from an ether extract only. The compounds have been characterised by analytical data, infrared spectra, magnetic and conductivity measurements. In all the compounds the thiocyanate groups bond through the nitrogen atom.

INTRODUCTION

A method based on the niobium—thiocyanate reaction is frequently recommended for the spectrophotometric determination of small amounts of niobium.

Many papers have been presented about this procedure but only a few of the authors have discussed the possible mechanism of the reaction, giving only the niobium—thiocyanate ratio and proposing the composition of the thiocyanate-niobium complex¹⁻⁹. Some of these authors claim that more than one thiocyanato niobium complex species is formed. Complexes of niobium have not been isolated in solid state under the conditions obtaining at the spectrophotometric determination.

Several solid niobium thiocyanate complexes have been isolated¹⁰⁻¹⁵. These complexes were prepared from niobium pentachloride by the reaction with alkali thiocyanates (in stoichiometric ratio) in water-free acetonitrile under special conditions. In these isolated complexes nitrogen bonded thiocyanate groups are present.

In our studies^{16,17} of the analytical procedure for niobium determination we produced evidence for the presence of $[Nb(NCS)_6]^-$ and $[NbO(NCS)_5]^{2-}$ anions and isoperthiocyanic acid.

From aqueous solutions and ether extracts, imitating the conditions obtaining at the spectrophotometric determination of niobium, $(C_2H_2N_2S_3)_2H[Nb(NCS)_6]$, $[(C_6H_5)_4P]_2[NbO(NCS)_5]$, $[(C_6H_5)_4As]_2[NbO(NCS)_5]$ and $[(C_2H_5)_4N]_2[NbO(NCS)_5]$ were isolated.

These complexes are the first isothiocyanate-niobates isolated in solid state from aqueous solutions and ether extracts under conditions obtaining at the spectrophotometric determination of niobium.

EXPERIMENTAL

Reagents

All chemicals used were of analytical grade. Niobium solutions (about 0.01 M) were prepared in sulphuric acid (1 : 1). Nb_2O_5 was fused with KHSO_4 in a platinum crucible. The melt was extracted with hot 10% oxalic acid solution. The niobium was precipitated with ammonia and was centrifuged and washed three times with 2% ammonium chloride solution and once with distilled water. The freshly precipitated niobium hydroxide was then dissolved in sulphuric acid (1 : 1). Ether was purified by treatment with FeSO_4 and by distillation.

Preparation of $(\text{C}_2\text{H}_2\text{N}_2\text{S}_3)_2\text{H} [\text{Nb}(\text{NCS})_6]$

Potassium thiocyanate solution (20%, 500 ml) was added to the 0.01 M niobium (V) solution (200 ml) and the mixture shaken 5 times with 50 ml portions of diethyl ether; the extracts were separately investigated. From these ether extracts we have obtained the red crystalline compound, $(\text{C}_2\text{H}_2\text{N}_2\text{S}_3)_2\text{H} [\text{Nb}(\text{NCS})_6]$ and the yellow crystalline compound, $\text{C}_2\text{H}_2\text{N}_2\text{S}_3$.^{16,17} A tedious process is necessary to obtain the red crystals free from isoperthiocyanic acid, because yellow $\text{C}_2\text{H}_2\text{N}_2\text{S}_3$ crystallizes from ether first, then a mixture of yellow and red crystals is obtained, and finally only isoperthiocyanic acid remains in the ether solution. Only by fractional crystallization is it possible to control the middle step of the evaporation process, when a crop of pure red crystals is obtained. The crystals have to be separated immediately from the mother liquor. The best yield of red crystals is obtained from the first ether extract; the last extracts give only yellow isoperthiocyanic acid. The red crystals are washed with carbon tetrachloride and kept in a dry atmosphere.

Preparation of $[(\text{C}_6\text{H}_5)_4\text{P}]_2 [\text{NbO}(\text{NCS})_5]$, $[(\text{C}_6\text{H}_5)_4\text{As}]_2 [\text{NbO}(\text{NCS})_5]$ and $[(\text{C}_2\text{H}_5)_4\text{N}]_2 [\text{NbO}(\text{NCS})_5]$

To the ether extract of the aqueous solution (obtained as above) 2.5 g of tetraphenylphosphonium chloride, 3 g tetraphenylarsonium chloride, or 2 g tetraethylammonium chloride are added. Yellow crystals precipitate immediately. The same compounds, in powder form, are obtained by adding the reagents to the aqueous solution.

Analytical procedures

About 40 mg of sample were decomposed in a Kjeldahl flask with conc. sulphuric acid (1 ml), to which 4 or 5 drops of conc. nitric acid were added. The procedure was repeated three times. The solution was transferred with 5% oxalic acid solution (25 ml) to a beaker, diluted to 50 ml, and niobium was precipitated by the tannin method.¹⁸ Niobium was also determined in $(\text{C}_2\text{H}_2\text{N}_2\text{S}_3)_2\text{H} [\text{Nb}(\text{NCS})_6]$ directly by decomposing the compound in a platinum crucible with concentrated ammonia solution (0.5 ml), gentle heating of the reaction mixture, and evaporating to dryness. The residue was carefully burned and then ignited at 950 °C and weighed as Nb_2O_5 . Thiocyanates were determined by two different methods. About 40 mg of sample was decomposed with hot water. The $\text{Nb}_2\text{O}_5 \times \text{H}_2\text{O}$ precipitate was filtered off, and the thiocyanate in solution was determined by potentiometric titration with 0.05 M NaOH or by titration with 0.05 M AgNO_3 by the Volhard method.

Phosphorus was determined by the molybdate method¹⁹ after decomposition of the sample with conc. sulphuric and nitric acids.

Arsenic was determined by titration with 0.05 M $\text{Na}_2\text{S}_2\text{O}_3$ ²⁰ after decomposition of the sample with conc. sulphuric and nitric acids. Carbon, hydrogen, nitrogen and sulphur were determined by standard microanalytical methods. The analytical results are collected in Table I.

TABLE I
Analytical data

Compound	%	C	H	N	S	As	P	Nb	NCS
$(C_2H_2N_2S_3)_2H[Nb(NCS)_6]$	calc'd.	16.2	0.7	18.9	51.8			12.5	46.9
	found	16.1	1.0	18.8	51.8			12.4	46.7
$[(C_6H_5)_4P]_2[NbO(NCS)_5]$	calc'd.	59.0	3.7	6.5	14.9		5.8	8.6	26.9
	found	59.0	4.1	6.6	14.5		5.2	8.2	26.5
$[(C_6H_5)_4As]_2[NbO(NCS)_5]$	calc'd.	54.6	3.5	6.0	13.8	12.9		8.0	25.0
	found	54.4	3.6	6.1	13.5	12.5		7.8	24.6
$[(C_2H_5)_4N]_2[NbO(NCS)_5]$	calc'd.	38.4	6.1	14.9	24.3			14.0	44.0
	found	38.9	6.9	15.0	23.9			13.7	43.5

Physical measurements

Infrared spectra were recorded on Perkin Elmer IR spectrophotometers Models 221 and 551 in the region 4000—250 cm^{-1} .

X-Ray measurements were taken with CuK_α radiation on a Unicam S 25 Camera, with a Ni-filter.

The magnetic susceptibility was measured at room temperature by the Gouy method. The niobium complexes described are diamagnetic.

Molar conductances in CH_3NO_2 were determined at 25 $^\circ\text{C}$, at a concentration of 10^{-3} M, with a specific conductance of the solvent $\leq 6.38 \times 10^{-6}$ $\text{ohm}^{-1} \text{cm}^2$.

RESULTS AND DISCUSSION

The complexes $[(\text{C}_6\text{H}_5)_4\text{P}]_2[\text{NbO}(\text{NCS})_5]$, $[(\text{C}_6\text{H}_5)_4\text{As}]_2[\text{NbO}(\text{NCS})_5]$ and $[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{NbO}(\text{NCS})_5]$ were isolated in powder form by precipitation, but were crystalline when obtained from ether extracts. The salts are isomorphous. They are 2 : 1 electrolytes in CH_3NO_2 , soluble in acetone and hydrolysed by hot water.

The hexathiocyanatoniobate was isolated only from ether extract, by fractional crystallization. It is a crystalline compound, and hydrolysed in water and several other solvents. Properties of these complexes are given in Table II.

Metal-thiocyanate complexes have been extensively investigated in order to solve the interesting problem of whether the thiocyanate group is bonded to the metal through the nitrogen atom ($\text{M}-\text{NCS}$), through the sulphur atom ($\text{M}-\text{SCN}$), or through both by bridging ($\text{M}-\text{NCS}-\text{M}$)²¹⁻²⁶. The infrared spectrum of the free thiocyanate ion in aqueous solution has three fundamental modes: C—N stretching frequency at 2060 cm^{-1} , NCS bending frequency at 470 cm^{-1} and C—S stretching frequency at 749 cm^{-1} .²⁷ The change of these fundamental modes in thiocyanato complexes shows how the thiocyanate group is bonded to the metal.

It has been found that metals classified by Ahrland, Chatt and Davies²⁸ as class (a) are generally bonded to the nitrogen atom, whereas class (b) metals are bonded to the sulphur atom.²³ Presence of other organic ligands can influence the bond type of the thiocyanate group to the metal.²⁹

The relevant frequencies in the infrared spectrum are given in Table III.

For the complexes, absorption in the C—N stretching region is resolved into two strong maxima. The first appears as a sharp band around 2100 cm^{-1} , followed by a broad, strong absorption between 2060 and 1980 cm^{-1} , showing

TABLE II
Properties of niobium complexes with thiocyanate

Complex	Colour	M. p./ $^\circ\text{C}$ (dec.)	Molar conductivity in CH_3NO_2 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$
$(\text{C}_2\text{H}_2\text{N}_2\text{S}_3)_2\text{H}[\text{Nb}(\text{NCS})_6]$	red	98—162	—
$[(\text{C}_6\text{H}_5)_4\text{P}]_2[\text{NbO}(\text{NCS})_5]$	yellow	261—265	173
$[(\text{C}_6\text{H}_5)_4\text{As}]_2[\text{NbO}(\text{NCS})_5]$	dark yellow	258—261	173
$[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{NbO}(\text{NCS})_5]$	yellow	228—235	175

TABLE III
 Characteristic group frequencies/cm⁻¹ in the infrared spectrum

Complex	ν_{C-N}	ν_{C-S}	δ_{N-C-S}	$\nu_{Nb=O}$	ν_{Nb-N}
$(C_2H_2N_2S_3)_2H[Nb(NCS)_6]$	2100 s { 2060 sh 2010 vs 1980 vs }	910 m { 900 s 880 s }	{ 490 m 480 m }	—	300 s br
$[(C_6H_5)_4P]_2[NbO(NCS)_5]$	2085 s { 2040 s 2015 s br }	885 m	{ 485 m 495 m }	935 s	300 s br
$[(C_6H_5)_4As]_2[NbO(NCS)_5]$	2085 s { 2040 s 2015 s br }	885 m	{ 485 m 495 m }	935 s	300 s br
$[(C_2H_5)_4N]_2[NbO(NCS)_5]$	2085 s { 2040 s 2015 s br }	885 m	{ 485 m 495 m }	935 s	300 s br

some distinct peaks. According to previous investigations, the positions of these stretching frequencies indicate the presence of nitrogen-bonded thiocyanate groups, as the sulphur-bonded and bridging groups would show absorption at higher frequencies.^{21,24}

The frequency of the C—S stretching was found to give a criterion for distinguishing between sulphur-bonded and nitrogen-bonded thiocyanate groups, higher frequency occurring for the nitrogen-bonded thiocyanate.²³⁻²⁵ A single C—S band is another indication that terminal nitrogen-bonded thiocyanate groups are present in the $[\text{NbO}(\text{NCS})_5]^{2-}$ anions. Complex $(\text{C}_2\text{H}_2\text{N}_2\text{S}_3)_2\text{H}[\text{Nb}(\text{NCS})_6]$ contains two molecules of isoperthiocyanic acid, $(\text{C}_2\text{H}_2\text{N}_2\text{S}_3)$ per hexathiocyanatoniobate group. $\text{C}_2\text{H}_2\text{N}_2\text{S}_3$ is a yellow, crystalline compound³⁰ formed in acid media by thiocyanate polymerization. The band for the C—S bond present in isoperthiocyanic acid interferes with the thiocyanato bands in the infrared spectrum and therefore for $(\text{C}_2\text{H}_2\text{N}_2\text{S}_3)_2\text{H}[\text{Nb}(\text{NCS})_6]$ there are three absorption frequencies (Table III). The other group vibrations of $\text{C}_2\text{H}_2\text{N}_2\text{S}_3$ do not interfere with the thiocyanate bands.³¹

It had previously been noted that the NCS bending mode can be used to characterize the bond type,^{23,26} giving a band at $450\text{--}490\text{ cm}^{-1}$ for *N*-thiocyanates and a band at $400\text{--}440\text{ cm}^{-1}$ for *S*-thiocyanates. The NCS bending vibrations at $490\text{--}480\text{ cm}^{-1}$ showed *N*-bonding thiocyanate in all the compounds isolated.

In all the compounds studied there are strong Nb—N stretching bands at 300 cm^{-1} and in oxopentaisothiocyantoniobates there are strong Nb=O bands at 935 cm^{-1} .

The isolated oxapentaisothiocyantoniobates(V) contain octahedrally coordinated niobium. This is proved by the crystal structure of one of our isolated oxopentaisothiocyantoniobates(V), $[(\text{C}_6\text{H}_5)_4\text{As}]_2[\text{NbO}(\text{NCS})_5]$. In the anion of $[(\text{C}_6\text{H}_5)_4\text{As}]_2[\text{NbO}(\text{NCS})_5]$ the equatorial apices of the octahedron are occupied by four nitrogen atoms from four thiocyanate groups at a mean distance of 2.09 \AA , the fifth position is occupied by the oxo-oxygen at 1.70 \AA , while the sixth position (*trans* to the oxo-oxygen) at 2.27 \AA belongs to the nitrogen atom from the fifth thiocyanate group.³² The hexaisothiocyantoniobate(V) contains two molecules of isoperthiocyanic acid but the structure of this complex is uncertain because it is not known whether the isoperthiocyanic acid molecules in this complex are coordinated to the niobium, but if they are, the question still remains, by which donor atom.

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SAŽETAK

Karakterizacija izotiocijanatonioбата(V) izoliranih iz otopina za spektrofotometrijsko određivanje niobija

B. Tamhina i C. Djordjević

Iz vodene sumporno-kisele otopine niobija i iz eterskog ekstrakta te otopine pod uvjetima za spektrofotometrijsko određivanje niobija izolirani su kompleksi $[(C_6H_5)_4P]_2[NbO(NCS)_5]$, $[(C_6H_5)_4As]_2[NbO(NCS)_5]$ i $[(C_2H_5)_4N]_2[NbO(NCS)_5]$. Spoj $(C_2H_5N_2S_3)_2H[Nb(NCS)_6]$ izoliran je samo iz eterskog ekstrakta. Izolirani spojevi karakterizirani su kemijskom analizom, mjerenjem magnetizma i vodljivosti te infracrvenim spektrima. U svima izoliranim spojevima tiocijanatna skupina vezana je preko dušika.

PRIRODOSLOVNO-MATEMATIČKI FAKULTET, ZAGREB
ZAVOD ZA ANALITIČKU KEMIJU
41000 ZAGREB

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