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Synthesis and Characterization of Niobium(V) and Tantalum(V) Complexes with Neutral Schiff Bases as Ligands

K. YAMANOUCHI and S. YAMADA
Institute of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka 560, Japan
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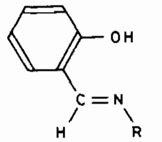
The reactions of niobium and tantalum pentachlorides and oxotrichlorobis(triphenylphosphine oxide)niobium(V) with N-arylsalicylaldimines, abbreviated as (Sal-R)H, have yielded new niobium(V) and tantalum(V) complexes of the following three types: (1) $MCl_3(OR')_2[(Sal\text{-}R)H]$; (2)$\{M(NCS)_2(OC_2H_5)_2[(Sal\text{-}R)H]\}_2O$; (3) $NbOCl_3[(Sal\text{-}R)H]_2$ ($M = Nb, Ta$; $R' = CH_3, C_2H_5$). They are light-yellow to yellow–orange, air-stable crystalline materials and are decomposed rapidly in solutions. On the basis of physical measurements, it is postulated that these complexes assume a six-coordinate structure involving the neutral Schiff base, which is coordinated as a unidentate ligand through an oxygen atom. Possible structures of these complexes are discussed mainly on the basis of pmr and infrared spectra.

Introduction

Although numerous papers have been published about transition metal complexes of N-substituted salicylaldimines, [1,2]most of these studies have dealt with those complexes in which the Schiff bases in their deprotonated form are bound with a metal ion as bidentate ligands. However, there are known only a small number of complexes, which contain neutral molecules of N-substituted salicylaldimines (I, abbreviated as (Sal-R)H) as ligands.



I

abbreviated as (Sal-R)H

Dioxotungsten(VI) complexes with neutral Schiff bases were reported in a previous paper concerning the synthesis and properties of Group VI transition metal complexes with various Schiff bases.[3] In these compounds, the neutral molecules of N-arylsalicylaldimines were concluded to be coordinated as unidentate ligands through their oxygen atom. In the course of the studies on the Schiff base complexes of Group V transition elements, it has been found that a new series of niobium(V) and tantalum(V) complexes, synthesized by the reactions of niobium and tantalum pentachlorides and oxotrichlorobis(triphenylphosphine oxide)niobium(V) with N-arylsalicylaldimines, afford additional examples of complexes with neutral Schiff base molecules as ligands. The present paper describes their synthesis and characterization. Although some other niobium and tantalum compounds involving deprotonated or neutral Schiff bases were reported previously,[4–6] no detailed and systematic studies about these compounds have been carried out.

Experimental

Materials

Niobium and tantalum pentachlorides, obtained commercially, were used without further purification. All the solvents were dried by the standard procedures and distilled before use. Potassium thiocyanate was stored over phosphorus pentoxide, and N-arylsalicylaldimines, obtained from salicylaldehyde and arylamines in methanol, were recrystallized from ethanol and stored over phosphorus pentoxide. All the preparative manipulations were carried out in a dry atmosphere.

Trichlorodialkoxo(N-arylsalicylaldimine)niobium(V)

Niobium pentachloride (5 g, 0.018 mol) and an equimolar amount of the appropriate N-arylsalicylaldimine were weighed out into a 100 ml round-bottom flask in a dry box. Either methanol (*ca.* 40 ml) or ethanol (*ca.* 30 ml) was added gradually at room temperature. Hydrogen chloride gas was liberated with evolution of heat during the addition of the alcohol. Then the mixture was heated with stirring under reflux for about 30 min, until the solution, initially bright red, became deep red. The resulting solution was filtered to remove residual solid and the filtrate was allowed to stand at room temperature for a few days. Yellow to yellow–orange microcrystals were filtered off, washed with a small amount of alcohol, and dried *in vacuo*. A further precipitate was obtained, when the mother liquor was evaporated *in vacuo* to 10–15 ml and allowed to stand at room temperature for several days.

Trichlorodialkoxo(N-arylsalicylaldimine)tantalum(V)

These compounds were prepared by a method similar to that for the corresponding niobium(V) derivatives, except that tantalum pentachloride was employed instead of niobium pentachloride. The desired compounds were obtained as yellow to light yellow microcrystals.

These compounds in the solid state are stable to the atmosphere. They are soluble in acetone, acetonitrile, nitromethane, methylene dichloride and chloroform, but decomposition occurs quickly to give a white to pale yellow precipitate. They are almost insoluble in cool alcohol, considerably soluble in hot alcohol, and highly soluble in dimethylformamide and dimethylsulphoxide, although decomposition takes place.

μ-Oxobis[diisothiocyanatodiethoxo(N-p-methylphenylsalicylaldimine)niobium(V)]

Ethanol (50 ml) was added dropwise at room temperature to a mixture of niobium pentachloride (5 g, 0.018 mol) and N-*p*-methylphenylsalicylaldimine (3.9 g, 0.018 mol). After vigorous evolution of hydrogen chloride gas, a clear, deep orange solution resulted. The solution was heated under reflux for 30 min, followed by addition of potassium thiocyanate (9 g, 0.092 mol). Immediately a precipitate of potassium chloride separated out. After refluxing was continued for another 1 hr, the mixture was allowed to cool to room temperature and the potassium chloride was removed by filtration. The resulting red solution was concentrated to about 15 ml and again filtered to remove a small amount of potassium chloride formed in the solution. The filtrate was diluted with ethanol (20 ml) and allowed to stand at room temperature for a few days. Bright yellow microcrystals were collected by filtration, washed with a small amount of ethanol, and dried *in vacuo*.

μ-Oxobis[diisothiocyanatodiethoxo(N-p-methylphenylsalicylaldimine)tantalum(V)]

This compound was prepared by the same procedure as that for the above niobium(V) derivative, except that tantalum pentachloride was used in place of niobium pentachloride. The desired compound was isolated as bright yellow microcrystals.

The two complexes of this type in the solid state are fairly stable to the atmosphere. They are similar in solubility to the compounds described above, although decomposition takes place much more rapidly in the solutions.

Oxotrichlorobis(triphenylphosphine oxide)niobium(V)

This compound was prepared from niobium pentachloride and triphenylphosphine oxide according to the literature, except that acetone was employed instead of methylene dichloride as the solvent.[7,8] Recrystallization of the product from methylen dichloride–acetone yielded white crystals of the desired compound (yield 75%). *Anal.* Found: C, 56.21; H, 3.94%. Calcd. for $C_{36}H_{30}O_3P_2Cl_3Nb$: C, 56.02; H, 3.92%. Infrared bands (cm^{-1}): $\nu(Nb = O)$ 937; $\nu(P = O)$ 1122, 1160sh, 1168.

The corresponding tantalum(V) derivative was reported previously.[7] However, our attempt to isolate pure crystals of the desired compound by the method of the literature has not been successful.

Oxotrichlorobis(N-arylsalicylaldimine)niobium(V)

To a solution of oxotrichlorobis(triphenylphosphine oxide)niobium(V) (0.005 mol) in methylene dichloride (50 ml) was added the appropriate N-arylsalicylaldimine (0.011 mol). The mixture was heated with stirring under reflux for about 1 hr. Yellow microcrystals formed in the solution were filtered off, while the solution was hot, washed several times with methylene dichloride and dried *in vacuo*.

In the solid state, the complexes of this type are stable to the atmosphere. They are almost insoluble in common organic solvents, and considerably soluble in dimethylformamide and dimethylsulphoxide, although they undergo decomposition fairly fast.

In the above mentioned preparations, it was difficult to find a satisfactory method of recrystallization because of spontaneous decomposition in solution, but these three types of complexes are crystalline and found to be reasonably pure. Analytical data of these compounds are shown in Table I with their melting points.

All these compounds melt over a fairly wide temperature range after turning slightly darker, though sintering takes place in some cases. Some compounds were found to be charred without melting, when gradually heated. The most reliable data which are reproducible, therefore, were obtained in the following way. After temperature was raised comparatively fast to about 15°C below the melting point or the sintering point anticipated by preliminary measurements, the specimen was heated very slowly until it finally melted.

Measurements

Magnetic susceptibilities were measured at room temperature by the Gouy method. The compounds proved to be diamagnetic. Conductivities were obtained using a Toa Model CM-IDB conductivity bridge and a calibrated Toa Electronics CG-201 PL cell at 25°C.

TABLE I. Analytical Data, Melting Points and Molar Conductivities of Niobium(V) and Tantalum(V) Complexes.

Compound	Melting Point[a] °C		Analyses, %			Conductivity[e] ohm^{-1} cm^2 mol^{-1}		
			C	H	N	DMF[f] [g]	[h]	Parent Alcohol
$NbCl_3(OCH_3)_2[(Sal\text{-}ph)H]$	256–258	Found	39.48	3.70	3.05	42	67	320[i]
		Calcd	39.28	3.74	3.06			
$NbCl_3(OCH_3)_2[(Sal\text{-}p\text{-}CH_3\text{-}ph)H]$	230–232[b]	Found	40.56	4.13	3.00	43	72	321[i]
		Calcd	40.66	4.05	2.96			
$NbCl_3(OC_2H_5)[(Sal\text{-}p\text{-}CH_3\text{-}ph)H]$	132–135	Found	43.15	4.65	2.85	35	73	119[j]
		Calcd	43.18	4.63	2.80			
$TaCl_3(OCH_3)_2[(Sal\text{-}ph)H]$	184–187[c]	Found	33.19	3.26	2.58	43	73	323[i]
		Calcd	32.96	3.14	2.56			
$TaCl_3(OCH_3)_2[(Sal\text{-}p\text{-}CH_3\text{-}ph)H]$	182–185[d]	Found	33.92	3.35	2.42	42	68	317[i]
		Calcd	34.28	3.42	2.50			
$TaCl_3(OC_2H_5)_2[(Sal\text{-}p\text{-}CH_3\text{-}ph)H]$	135–138	Found	36.71	3.94	2.35	32	70	118[j]
		Calcd	36.73	3.94	2.38			
$\{Nb(NCS)_2(OC_2H_5)_2[(Sal\text{-}p\text{-}CH_3\text{-}ph)H]\}_2O$	163–165	Found	46.15	4.46	8.10	100	108	–
		Calcd	46.33	4.47	8.11			
$\{Ta(NCS)_2(OC_2H_5)_2[(Sal\text{-}p\text{-}CH_3\text{-}ph)H]\}_2O$	167–170	Found	39.25	3.77	6.83	97	110	–
		Calcd	39.61	3.82	6.93			
$NbOCl_3[(Sal\text{-}ph)H]_2$	207–210	Found	50.95	3.64	4.47	47	72	–
		Calcd	51.21	3.64	4.60			
$NbOCl_3[(Sal\text{-}p\text{-}CH_3\text{-}ph)H]_2$	213–215	Found	52.54	4.12	4.51	48	74	–
		Calcd	52.73	4.11	4.39			

[a] See also the Experimental in the text. Sintering point, °C: b, 177; c, 178; d, 176. [e] 10^{-3} *M* solutions with respect to metal ion. The values are conductivities per mol of metal ion. [f] Abbreviation of dimethylformamide. [g] The molar conductivity of a fresh solution 2–3 min after preparation. [h] The molar conductivity of a solution after 1 hr. [i] The molar conductivity in methanol. [j] The molar conductivity in ethanol.

Infrared spectra were determined in nujol and hexachlorobutadiene mulls with a Hitachi EPI-S2 spectrophotometer in the range 4000–650 cm^{-1} and a Hitachi EPI-L spectrophotometer in the range 700–200 cm^{-1}. Proton magnetic resonance spectra in deuterated dimethylsulphoxide were recorded on a Varian Model A-60 spectrometer using tetramethylsilane as an internal reference. X-ray powder diffraction patterns were obtained with a Toshiba ADX-101 diffractometer equipped with a Geiger Müller counter using nickel filtered Cu-K$_\alpha$ radiation.

Since all the compounds undergo decomposition on dissolution, measurements in solutions were repeated with the utmost care to ensure their reliability. In the cases of thiocyanato derivatives, decomposition proceeded to an enormous extent, even with fresh solutions, for example, a few minutes after preparation.

Results and Discussion

Niobium(V) and tantalum(V) complexes of the following three types have been synthesized in the present work: (1) $MCl_3(OR')_2[(Sal\text{-}R)H]$; (2) $\{M(NCS)_2(OC_2H_5)_2[(Sal\text{-}p\text{-}CH_3\text{-}ph)H]\}_2O$; (3) $NbOCl_3[(Sal\text{-}R)H]_2$ (M = Nb, Ta; R = ph, *p*-CH$_3$-ph; R′ = CH$_3$, C$_2$H$_5$). These formulations involving the neutral N-arylsalicylaldimines agree closely with analytical data of the compounds, as shown in Table I. Any attempt to deprotonate the neutral Schiff base in these complexes with bases such as pyridine, triethylamine and potassium alkoxide, has not been successful with these complexes.

Trichlorodialkoxo-N-arylsalicylaldimineniobium(V) and -tantalum(V)

Niobium(V) and tantalum(V) pentachlorides react with N-arylsalicylaldimines in methanol or ethanol to produce alkoxo complexes with the neutral Schiff base coordinated, $MCl_3(OR')_2[(Sal\text{-}R)H]$. The colour of the niobium and methoxo derivatives is deeper than that of the analogous tantalum and ethoxo derivatives, respectively. Niobium(V) and tantalum(V) complexes, $NbCl_3(OCH_3)_2[(Sal\text{-}p\text{-}CH_3\text{-}ph)H]$ and $TaCl_3(OCH_3)_2[(Sal\text{-}p\text{-}CH_3\text{-}ph)H]$, are isomorphous, showing strongly similar X-ray powder diffraction patterns.

Molar conductivities in dimethylformamide and in the parent alcohols are presented in Table I. In the alcohols, the compounds give values corresponding to 1:3 electrolytes. Previous studies have shown that the values for 1:3 electrolytes in methanol and in ethanol are in the range 290–350 ohm^{-1}cm^2 and 120 ohm^{-1}cm^2, respectively.[9] These values indicate that the extensive replacement of the coordinated chloride ions by the alcohol molecules may occur on dissolution, as observed earlier for related β-diketone complexes of niobium(V) and tantalum(V).[10] In dimethylformamide, however, the values obtained with fresh solutions, about 2–3 minutes after preparation, are in the range 32–43 ohm^{-1}cm^2. These values are intermediate between 1:1 electrolytes and non-electrolytes, since 1:1 electrolytes are expected to show values in the range 65–90 ohm^{-1}cm^{-2} in dimethylformamide. The conductivity increases rapidly with time at the initial stage to reach the value of 60 ohm^{-1}cm^2 after 15–20 min and then increases slowly to give values in the range 90 to 110 ohm^{-1}cm^2 after 24 hr. In view of the change in conductivity, it is likely that the complexes of this type are originally non-electrolytes, rapid replacement of one alkoxo group by a solvent molecule taking place in the solutions, followed by further replacement of the other alkoxo group. This interpretation is corroborated by pmr studies, which will be discussed below.

In Table II, main infrared bands of the complexes of this type are given with tentative assignments. These compounds exhibit strong bands in the ranges 1050 to 1150 cm^{-1} and 530–590 cm^{-1}, which may tentatively be assigned to ν(C–O) and ν(M–O) of the coordinated alkoxo group, respectively. Very intense, broad bands, which are attributed to ν(M–Cl), are also found in the region 280–340 cm^{-1}. According to the criteria proposed previously,[11–14] these values seem to indicate the presence of the terminal alkoxo and chloro groups. In complexes containing the bridging groups, the corresponding bands are expected to appear at lower frequencies. An intense band occurs at about 1640 cm^{-1}, which is slightly higher in frequency than those due to ν(C–N) in complexes with deprotonated bidentate N-arylsalicylaldiminate or the free ligand. A similar band was observed previously with $CoCl_2[(Sal\text{-}R)H]_2$,[15] $FeCl_3[(Sal\text{-}R)H]_2$,[16] $SnCl_4[(Sal\text{-}R)H]_2$[17] and $WO_2Cl_2[(Sal\text{-}R)H]_2$[3] and has been considered as characteristic of the complexes involving N-arylsalicylaldimine molecules. Another characteristic band of medium intensity occurs at about 3150 cm^{-1}, which may be due to intramolecular hydrogen bonding of the coordinated Schiff base. In $WO_2Cl_2[(Sal\text{-}R)H]_2$, the corresponding band was found at about 3050 cm^{-1}.

Since solvolysis takes place very quickly, the pmr spectra in the region due to alkoxo groups could not be determined with significant accuracy, even with fresh solutions. The most reliable spectra, which were obtained with $NbCl_3(OC_2H_5)_2[(Sal\text{-}p\text{-}CH_3\text{-}ph)H]$, are shown in Figure 1. The CH=N signal appears as a singlet in the range 9.10–9.25 ppm, at slightly lower

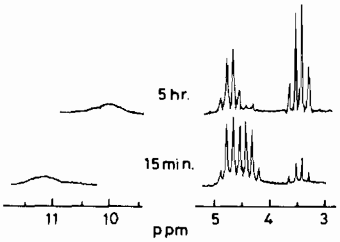


Figure 1. Pmr spectra of $NbCl_3(OC_2H_5)_2[(Sal\text{-}p\text{-}CH_3\text{-}ph)H]$ in deuterated dimethylsulphoxide.

TABLE II. Main IR and FIR Spectra of Niobium(V) and Tantalum(V) Complexes of the Type $MCl_3(OR')_2[(Sal\text{-}R)H]$ (ν: cm^{-1}).

M	R′	R	ν(O···H···N)	ν(C=N)	ν(C–O)	ν(M–OR′)	ν(M–Cl)
Nb	CH_3	ph	3140	1639	1110 1075	563	333 322
Nb	CH_3	p-CH_3-ph	3140	1640	1097 1065	561	337 325
Nb	C_2H_5	p-CH_3-ph	3160	1642	1113 1090 1075 1052	592 555	326 313
Ta	CH_3	ph	3150	1640	1140 1125, sh 1100	557 545 533	307 291 282
Ta	CH_3	p-CH_3-ph	3150	1643	1158 1125 1093	548 542, sh 533	306 291 282
Ta	C_2H_5	p-CH_3-ph	3180	1642	1130 1100 1080, sh 1068	586	304 299

fields compared with that of the free Schiff bases. A broad singlet, which is due presumably to the O· ·H· ·N resonance, occurs in the range 10.0–13.5 ppm, being shifted progressively toward higher fields with time, as seen from Figure 1. These pmr spectra, together with the infrared spectra, may afford evidence of the presence of the coordinated neutral Schiff base in these compounds. They also exhibit proton resonances due to coordinated alkoxo groups at about 4.5 ppm for the methoxo derivatives and in the range 4.2–5.0 ppm (multiplet) for the ethoxo derivatives, in addition to those arising from decomposed species at lower fields. In the spectrum of the fresh solution of $NbCl_3(OC_2H_5)_2$-$[(Sal$-p-CH_3-$ph)H]$, for example, two overlapping quartets of approximately equal intensity, which are due to the OCH_2 protons of the coordinated ethoxo groups, occur at 4.70 and 4.36 ppm, although an additional quartet is found at 3.46 ppm, which may be attributed to the OCH_2 protons of the decomposed species. The higher field part of the quartets at 4.2–5.0 ppm, due to the coordinated ethoxo group, decreases gradually in intensity with time, while the quartet at 3.46 ppm, due to the decomposed species, increases in intensity.

Since the possibility of bridged alkoxo groups is excluded by infrared spectra, the above observation probably implics the presence of two distinguishable terminal ethoxo groups, one of which is much more susceptible to solvolysis, in agreement with the conductivity data. The information so far available indicates that the compounds of this type are monomers containing a neutral Schiff base, three terminal chloride ions and two non-equivalent alkoxo groups.

Various structures may be proposed for these complexes, depending upon the mode of coordination of the neutral Schiff base. If the neutral Schiff base were coordinated to a metal ion as a bidentate ligand in the keto-amine form,[15–17] the metal ion would achieve seven-coordination in the complexes of this type and eight-coordination in the complexes of type (3), $NbOCl_3[(Sal\text{-}R)H]_2$, which will be discussed later. This structure, therefore, may be less probable. Although several niobium(V) and tantalum(V) complexes with coordination number exceeding six were reported previously, octahedral arrangement is preferred in most cases.[18,19] Moreover, the highest coordination number so far observed of niobium(V) is seven in the complexes with the Nb=O group.[20]

It may thus be more reasonable to assume that the complexes obtained in this work may have six-coordinate structures containing the neutral Schiff base, which is coordinated to a metal ion as a unidentate ligand through the oxygen atom, as postulated previously for $WO_2Cl_2[(Sal\text{-}R)H]_2$.[3] In corroboration of this argument seems to be the structure of the bis(salicylaldehyde)ethylenediimine adduct with dimethyldichlorotin(IV), in which the neutral Schiff base containing four donor atoms is coordinated to tin(IV) ions as a bidentate ligand through their oxygen atoms bridging two Me_2SnCl_2 units.[21]

μ-Oxo-bis[diisothiocyanatodiethoxo(N-p-methylphenylsalicylaldimine)niobium(V)] and -tantalum(V)]

It should be noted that a similar procedure to that in the above mentioned chloroderivatives, except for the addition of potassium thiocyanate, yields complexes of the type $\{M(NCS)_2(OC_2H_5)_2[(Sal$-$p$-$CH_3$-$ph)H]\}_2O$, instead of the thiocyanato analogues of type (1), the chloro derivatives. The reason for the difference in the reaction products between the chloro and the thiocyanato derivatives is not clarified in the present work. However, a trace amount of water, which most probably originates in hygroscopic potassium thiocyanate, may play a role in this reaction.

As shown in Table I, these compounds give conductance of about 100 $ohm^{-1}cm^2$ in dimethylformamide, even with the fresh solutions, a few minutes after dissolution. The values, which are almost unchanged with time, correspond to values intermediate between those for 1:1 and 1:2 electrolytes. The present data, therefore, indicate that these compounds are dissociated in solution. It was not possible to measure conductivity in ethanol because of too low solubility.

The complexes show pmr resonances due to the free Schiff base and the decomposed species, although very weak signals, possibly due to the OCH_2 protons of the coordinated alkoxo groups, occur in the range 4.2–4.9 ppm. The pmr and conductivity data show that remarkable solvolysis of the coordinated alkoxo

TABLE III. Main IR and FIR Spectra of Niobium(V) and Tantalum(V) Complexes of the Type $\{M(NCS)_2(OC_2H_5)_2[(Sal$-$p$-$CH_3$-$ph)H]\}_2O$ (ν: cm^{-1}).

M	ν(O···H···N)	ν(C=N)	ν(C–O)	ν(M–OR′)	ν(M–O–M)	ν(CN)	δ(NCS)
Nb	3050	1635	1110 1095,sh 1060	586	710	2050 2020 2000,sh	490 482
Ta	3050	1636	1120 1105,sh 1075	565	760	2050 2030 1995,sh	492 482

TABLE IV. Main IR and FIR Spectra of Niobium(V) Complexes of the Type $NbOCl_3[(Sal\text{-}R)H]_2$ (ν: cm^{-1}).

R	$\nu(O\cdots H\cdots N)$	$\nu(C{=}N)$	$\nu(Nb{=}O)$	$\nu(Nb{-}Cl)$
ph	3050, 3120	1633	940	317
p-CH_3-ph	3050, 3140	1635	936	318, 305

groups and Schiff base molecules takes place on dissolution.

Table III shows main infrared bands of the complexes of this type with tentative assignment. Similarly to the complexes of type (1), they exhibit characteristic bands of the coordinated neutral Schiff base at about 1635 and 3050 cm^{-1}. Intense bands due to $\nu(C{-}O)$ and $\nu(M{-}O)$ of the terminal alkoxo groups appear in the expected regions. A strong, broad band is observed at 760 and 710 cm^{-1} for the niobium and tantalum derivatives, respectively. In this region, characteristic bands attributed to $\nu(M{-}O{-}M)$ are known to appear.[22–24] Taking analytical results into account, these bands suggest the presence of a bridging M–O–M group in the complexes of this type.

Infrared data may also be used to determine the mode of coordination of the thiocyanato group in these complexes. On the basis of $\nu(CN)$ and $\nu(NCS)$ bands and the criteria previously established,[25,26] it is concluded that the thiocyanato groups in these complexes are coordinated to a metal ion through the nitrogen atom. This conclusion is consistent with the results of other niobium(V) and tantalum(V) complexes with thiocyanate ions coordinated.[25,27] Bands $\nu(CS)$ are masked by strong bands due to the neutral Schiff base occurring in the region near 800 cm^{-1}.

Based on the data discussed above, it seems likely that the complexes of this type may assume a binuclear structure, in which an oxygen atom acts as a bridge and makes up a six-coordinate configuration around a metal ion, together with two alkoxo groups, two N-bonded thiocyanate groups and a unidentate Schiff base. Unfortunately, the lability of these complexes in solution did not allow determination of molecular weight.

Oxotrichlorobis(N-arylsalicylaldimine)niobium(V)

It was reported in the literature[4] that oxotrichloro-(N-arylsalicylaldimine)niobium(V) complexes, $NbOCl_3[(Sal\text{-}R)H]$ (R being ph and p-CH_3-ph) were synthesized by a method using niobium(V) oxotrichloride as a starting material. Repeating the same procedure, we were not able to confirm these results. On the contrary, treatment of oxotrichlorobis(triphenylphosphine oxide)niobium(V) with N-arylsalicylaldimines yielded only oxo complexes of the type $NbOCl_3[(Sal\text{-}R)H]_2$ in the present work. Any attempt to prepare $NbOCl_3[(Sal\text{-}R)H]$ type complexes by similar and other methods under various reaction conditions has not been successful so far. It may be interesting to remember that the two methods, starting from dioxodichlorobis-(triphenylphosphine oxide)tungsten(VI) and from dioxotungsten(VI) dichloride, yielded only $WO_2Cl_2[(Sal\text{-}R)H]_2$.[3]

Molar conductivity of the complexes of this type in dimethylformamide, as shown in Table I, exhibits the same behaviour as that of the complexes of type (1). This indicates that these compounds are originally non-electrolytes, although replacement of coordinated chloride ions by the solvent molecules occurs in solution.

As shown in Table IV, these complexes display characteristic infrared bands at about 1635 cm^{-1} and 3050, 3150 cm^{-1}, which are assigned to $\nu(C{=}N)$ and $\nu(O\cdots H\cdots N)$ of the neutral Schiff base, respectively. Intense, broad bands, assigned to $\nu(Nb{-}Cl)$, occur near 320 cm^{-1}. These values suggest the absence of the bridging chloride ion. In addition, another characteristic band is observed at about 940 cm^{-1}, which may be ascribed to $\nu(Nb{=}O)$, but no absorption band corresponding to $\nu(Nb{-}O{-}Nb)$ appears in the expected region.

In the pmr spectrum of $NbOCl_3[(Sal\text{-}p\text{-}CH_3\text{-}ph)H]_2$, the CH=N and the $O\cdots H\cdots N$ resonances appear as a sharp singlet at 9.12 ppm and as a broad singlet with a maximum at 11.8 ppm, respectively. It may be concluded that two neutral Schiff bases are equivalent in this case, in contrast to the related dimethylsulphoxide complex, $NbOCl_3(DMSO)_2$, in which two coordinated dimethylsulphoxide molecules are non-equivalent.[28]

From the information available, it seems very likely that the complexes of this type are monomers, in which a niobium(V) ion achieves six-coordination with an oxygen atom, three chloride ions, and two unidentate neutral Schiff bases. The most probable structure may be either of the two structures with one chloride ion *trans* to the oxygen atom of an Nb=O group.

The definitive conclusion about the structures of the complexes of these three types as well as the mode of coordination of the neutral Schiff bases, however, must await X-ray studies.

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