

## Complexes of Niobium(V) and Tantalum(V) Halides with Dinitriles. I. Malononitrile and Succinonitrile

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Complexes of niobium(V) and tantalum(V) halides with malononitrile and succinonitrile have been prepared and characterized. Two types of complexes having stoichiometry  $MX_5 \cdot L(1:1)$  and  $2MX_5 \cdot L(2:1)$  [where  $M = Nb$  or  $Ta$ ;  $X = Cl$  or  $Br$  and  $L =$  dinitrile] have been isolated. Conductivity measurements in acetonitrile have shown that they are virtually non-ionic in this solvent. Infrared spectra of these complexes show the absence of  $\pi$ -bonding. In the case of succinonitrile complexes, trans conformers have been stabilized in 2:1 complexes, while in 1:1 complexes gauche conformation is assumed. Studies have also been made in the low-frequency infrared region ( $600$ - $250\text{ cm}^{-1}$ ) to determine the possible coordination number of the metal in the two types of complexes.

### Introduction

Complexes of niobium(V) and tantalum(V) halides with a variety of nitrogen containing ligands have been reported in literature,<sup>1-11</sup> the ligands being either monodentates or chelating bidentates. Among the lesser studied nitrogen containing bidentate ligands, organic dinitriles are considered to be potentially bridging in nature. The reactions of group(IV) metal halides with several dinitriles have shown that under different experimental conditions, complexes with metal-ligand ratios 1:1, 1:2 and 2:1 could be obtained.<sup>12,13</sup> It was observed that the dinitriles act as chelating as well as bridging ligands depending upon the number of methylene groups in the ligand separating the two nitrile ends. Also, in the case of dinitrile

complexes of  $Cu^{I}$ ,<sup>14</sup>  $Ag^I$ ,<sup>15</sup>  $Co^{II}$ ,  $Ni^{II}$ ,  $Zn^{II}$ ,<sup>16</sup>  $SnCl_4$ ,<sup>17</sup>  $TiCl_3$ ,<sup>18</sup> and  $MoOCl_3$ ,<sup>19</sup> it has been shown that dinitriles act only as bridging ligands between two metal atoms. Although the likelihood of chelation in this type of ligands cannot be completely ruled out, it can best be prevented by choosing dinitriles with short carbon chains. The present work has been taken up with the view to synthesize and study such bridged complexes of niobium(V) and tantalum(V) halides using such short chain dinitriles, malononitrile and succinonitrile. Moreover, it was also of interest to study which of the rotational conformers in succinonitrile would be stabilized on complex formation. Although oxygen- and sulphur-containing ligands such as 1,4-dioxan and 1,4-thioxan are potentially bridging ligands, their reactions with niobium(V) and tantalum(V) halides led to the formation of 1:1 monomeric complexes.<sup>20</sup>

In this communication, we report the formation of the complexes of niobium(V) and tantalum(V) chlorides and bromides with malononitrile and succinonitrile. With both halides two types of complexes,  $MX_5 \cdot L$  and  $2MX_5 \cdot L$  [where  $L$  is the dinitrile], have been isolated and studied.

### Experimental Section

**Materials and methods.** The pentahalides of niobium and tantalum were prepared and purified as reported earlier.<sup>21</sup> The dinitriles were purified by repeated sublimation *in vacuo*. All the solvents were of AnalaR grade. They were dried over appropriate drying agents and freshly distilled through a packed column before use.

All operations were carried out in an inert atmosphere dry box which was continuously flushed with dry nitrogen and maintained dry by means of phosphorus(V) oxide. The general procedure for the preparation of the complexes was the same as reported in our earlier communication.<sup>21</sup> The ligand was dissolved in methylene chloride while the metal halide was dissolved either in methylene chloride or suspended in

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carbon tetrachloride for carrying out the reaction. While synthesizing 2:1 complexes it was always preferable to start with a solution of the metal halide in methylene chloride to which the ligand dissolved in the same solvent was added slowly. The complexes obtained as fine powders were filtered and washed with a mixture of methylene chloride/carbon tetrachloride. The products thus obtained were dried *in vacuo* for several hours. Typical examples for the preparation of 1:1 and 2:1 complexes are described below:

**Niobium(V) chloride: succinonitrile (1:1).** Succinonitrile (0.582 g; 7.27 m moles) dissolved in about 8 ml of methylene chloride was added to niobium(V) chloride (1.95 g; 7.22 m moles) suspended in about 40 ml of carbon tetrachloride. The yellow coloured suspension of the metal halide immediately started changing and a light yellow compound started separating out. The contents were stirred for four hours, filtered, washed thoroughly with a mixture of methylene chloride and carbon tetrachloride and dried *in vacuo* for 5-6 hours.

**Niobium(V) chloride: succinonitrile (2:1).** Succinonitrile (0.384 g; 4.79 m moles) dissolved in about 5 ml of methylene chloride was added to niobium(V) chloride (2.65 g; 9.81 m moles) dissolved in about 30 ml of methylene chloride. The yellow coloured solution of the metal halide immediately started changing and a light yellow solid started separating out. The contents were stirred for about 5 hours, filtered, washed with methylene chloride and dried for 5-6 hours *in vacuo*.

**Analysis.** The complexes were analysed for metal and halide as reported earlier.<sup>21</sup> The nitrogen content was determined by micro-analysis.

**Melting points.** Melting points were determined in sealed capillaries.

**Infrared spectra.** The infrared spectra were recorded as Nujol Mulls on a Perkin-Elmer spectrophotometer model 21 using sodium chloride optics. The low frequency infrared spectra were recorded using CsBr optics.

**Conductivity.** The molar conductance of the complexes in acetonitrile was measured in a specially designed cell using Industrial Instrument Conductivity Bridge Model RC-16B2 at 30°. The acetonitrile used in these measurements was purified by repeated fractional distillation over phosphorus(V) oxide.

**Magnetic susceptibility.** Magnetic measurements were made at room temperature by the Gouy technique. AnalaR grade ferrous ammonium sulphate was used for calibration of the tube. The measurements were made at different field strengths.

**X-ray.** The X-ray powder diffraction photographs were obtained with filtered  $\text{CuK}\alpha$ -radiation using a Debye-Scherrer 114.83 mm camera. The specimens were taken in about 0.3 mm quartz capillaries which were filled inside the dry box.

## Results and Discussion

The reactions of niobium(V) and tantalum(V) chlorides and bromides with malononitrile and succinonitrile have led to the formation of two types of complexes  $\text{MX}_5\cdot\text{L}$  and  $2\text{MX}_5\cdot\text{L}$  (Table I), when nearly stoichiometric amounts of ligand were added to the solution or suspension of the metal halide in the solvent. The complexes obtained were extremely sensitive to atmospheric moisture and changed their colour on slight exposure. They were highly soluble in acetonitrile but were only sparingly soluble in methylene chloride and chloroform. They were insoluble in carbon tetrachloride and benzene. The complexes have no definite melting point but turn dark between 120-205° in sealed capillaries. All attempts to prepare complexes with stoichiometry 1:2 failed. The use of excess ligand over the halide resulted in the formation of only 1:1 complexes.

The conductance measurements on the  $10^{-3}$  molar solutions of these complexes in acetonitrile gave values between 19-30  $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$  (Table II). This is in contrast to the value of 150-160  $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$  found for typical 1:1 electrolytes in the same solvent.<sup>7</sup> The conductivity of the complexes of niobium(V) chloride with succinonitrile (1:1 and 2:1)

Table I. Analytical results.

Complex	Colour	Analysis			Calculated %			Stoichiometry
		Found % Metal	Found % Halogen	Found % Nitrogen	Metal	Halogen	Nitrogen	
$\text{NbCl}_5 \cdot (\text{CH}_2)(\text{CN})_2$	Light yellow	27.2	51.9	7.6	27.6	52.7	8.3	1:1
$2\text{NbCl}_5 \cdot (\text{CH}_2)(\text{CN})_2$	Light yellow	30.9	57.5	5.2	30.6	58.4	4.6	2:1
$\text{NbBr}_5 \cdot (\text{CH}_2)(\text{CN})_2$	Red	17.3	70.6	4.6	17.7	71.5	5.0	1:1
$2\text{NbBr}_5 \cdot (\text{CH}_2)(\text{CN})_2$	Red	17.4	75.6	2.8	16.6	76.0	2.7	2:1
$\text{TaCl}_5 \cdot (\text{CH}_2)(\text{CN})_2$	White	42.6	39.9	6.8	42.6	41.8	6.6	1:1
$2\text{TaCl}_5 \cdot (\text{CH}_2)(\text{CN})_2$	White	46.7	44.8	3.5	46.2	45.3	3.6	2:1
$\text{TaBr}_5 \cdot (\text{CH}_2)(\text{CN})_2$	Yellow	28.4	59.1	4.0	28.0	61.8	4.3	1:1
$2\text{TaBr}_5 \cdot (\text{CH}_2)(\text{CN})_2$	Yellow	30.1	64.4	2.5	29.5	65.1	2.3	2:1
$\text{NbCl}_5 \cdot (\text{CH}_2)_2(\text{CN})_2$	Light yellow	26.1	49.2	7.4	26.5	50.6	8.0	1:1
$2\text{NbCl}_5 \cdot (\text{CH}_2)_2(\text{CN})_2$	Light yellow	29.5	55.4	4.6	29.9	57.1	4.5	2:1
$\text{NbBr}_5 \cdot (\text{CH}_2)_2(\text{CN})_2$	Red	16.7	69.4	4.7	16.2	69.8	4.9	1:1
$2\text{NbBr}_5 \cdot (\text{CH}_2)_2(\text{CN})_2$	Red	17.1	74.0	3.5	17.4	75.0	2.6	2:1
$\text{TaCl}_5 \cdot (\text{CH}_2)_2(\text{CN})_2$	White	42.6	39.2	6.1	41.3	40.4	6.4	1:1
$2\text{TaCl}_5 \cdot (\text{CH}_2)_2(\text{CN})_2$	White	45.7	44.0	3.5	45.4	44.5	3.5	2:1
$\text{TaBr}_5 \cdot (\text{CH}_2)_2(\text{CN})_2$	Yellow	28.0	59.8	4.7	27.4	60.5	4.3	1:1
$2\text{TaBr}_5 \cdot (\text{CH}_2)_2(\text{CN})_2$	Yellow	29.4	64.1	2.2	29.2	64.4	2.3	2:1

**Table II.** Infrared and molar conductance results.

Compound	Infrared vibrations cm <sup>-1</sup>		Molar conductance <sup>a</sup>
	$\nu(\text{C}\equiv\text{N})$	$+\Delta\nu(\text{C}\equiv\text{N})$	
NbCl <sub>5</sub> .L <sub>M</sub>	2275	—	—
NbCl <sub>5</sub> .L <sub>M</sub>	2320	45	27.0
2NbCl <sub>5</sub> .L <sub>M</sub>	2335	60	30.0
NbBr <sub>5</sub> .L <sub>M</sub>	2315	40	—
2NbBr <sub>5</sub> .L <sub>M</sub>	2326	51	—
TaCl <sub>5</sub> .L <sub>M</sub>	2317	42	25.5
2TaCl <sub>5</sub> .L <sub>M</sub>	2323	48	25.5
TaBr <sub>5</sub> .L <sub>M</sub>	2327	52	27.0
2TaBr <sub>5</sub> .L <sub>M</sub>	2322	47	28.7
NC(CH <sub>2</sub> ) <sub>2</sub> CN(L <sub>S</sub> )	2262	—	—
NbCl <sub>5</sub> .L <sub>S</sub>	2303	41	18.0
2NbCl <sub>5</sub> .L <sub>S</sub>	2313	51	24.0
NbBr <sub>5</sub> .L <sub>S</sub>	2304	42	—
2NbBr <sub>5</sub> .L <sub>S</sub>	2302	40	—
TaCl <sub>5</sub> .L <sub>S</sub>	2304	42	19.1
2TaCl <sub>5</sub> .L <sub>S</sub>	2313	51	23.0
TaBr <sub>5</sub> .L <sub>S</sub>	2296	34	27.0
2TaBr <sub>5</sub> .L <sub>S</sub>	2292	30	28.7

<sup>a</sup> 10<sup>-3</sup>M solution in acetonitrile (ohm<sup>-1</sup>cm<sup>2</sup>mole<sup>-1</sup>); monomeric species assumed.

**Table III.** X-ray powder data for niobium(V) and tantalum(V) chloride complexes.

NbCl <sub>5</sub> .(CH <sub>2</sub> ) <sub>2</sub> (CN) <sub>2</sub>		TaCl <sub>5</sub> .(CH <sub>2</sub> ) <sub>2</sub> (CN) <sub>2</sub>		2NbCl <sub>5</sub> .(CH <sub>2</sub> ) <sub>2</sub> (CN) <sub>2</sub>		2TaCl <sub>5</sub> .(CH <sub>2</sub> ) <sub>2</sub> (CN) <sub>2</sub>	
d, A°	I	d, A°	I	d, A°	I	d, A°	I
9.3093	vs	9.4841	vs	7.8860	s	6.2152	s
5.4213	w	8.2105	s	6.0055	s	5.6265	s
4.8808	m	5.6353	ms	4.8808	s	4.9069	s
3.7308	m	4.9279	vs	4.2104	s	4.0450	ms
3.2491	ms	3.6926	ms	3.8420	m	3.4630	m
3.1512	ms	3.2520	m	2.7207	w	3.1507	m
2.7719	s	3.1345	m	2.5959	m	2.8666	m
2.4939	m	2.7719	m	2.1118	vw	2.4342	w
2.1560	m	2.4964	m	1.7554	w	2.3122	w
2.0074	w	2.1572	s			2.1584	w
		2.0133	w			1.9801	m
		1.9227	s			1.8971	m
		1.6958	w			1.8284	m
		1.6737	w			1.7554	w
						1.7098	w
						1.6536	w
						1.6072	w

s = strong, m = medium, w = weak, v = very.

and malononitrile (2:1) was also determined as a function of concentration. The molar conductances of NbCl<sub>5</sub>.succinonitrile, 2NbCl<sub>5</sub>.succinonitrile and 2NbCl<sub>5</sub>.malononitrile were 5 to 12 ohm<sup>-1</sup>cm<sup>2</sup>mole<sup>-1</sup> at 10<sup>-2</sup>M rising only slightly to 18 to 32 ohm<sup>-1</sup>cm<sup>2</sup>mole<sup>-1</sup> at 10<sup>-3</sup>M. The small rise of conductivity on dilution could result from trace impurities in the solvent. The other possibility may be dissociation of the complex. However, the conductivity data clearly suggest that the complexes are non-electrolytes in acetonitrile.

It is known that nitrogen containing ligands e.g., nitriles, pyridine, etc., reduce the metal halide to a lower valence state on complexation.<sup>5,6,12</sup> However, in the case of mononitrile complexes with niobium(V) and tantalum(V) halides no reduction was observed.<sup>7</sup> The magnetic susceptibility measurements were carried out on tantalum(V) chloride: succinonitrile 1:1 and 2:1 complexes and the values obtained were [TaCl<sub>5</sub>.(CH<sub>2</sub>)<sub>2</sub>(CN)<sub>2</sub>],  $\chi'$  Ta =  $-16.4 \times 10^{-6}$  c.g.s. units; [2TaCl<sub>5</sub>.(CH<sub>2</sub>)<sub>2</sub>(CN)<sub>2</sub>],  $\chi'$  Ta =  $31 \times 10^{-6}$

c.g.s. units, thus showing that the compounds were diamagnetic as expected for d<sup>0</sup> niobium(V) and tantalum(V) compounds. The oxidation state titration with ceric ammonium sulphate as oxidant also confirmed that in these complexes the metals are in +5 oxidation state.

The partial X-ray powder diffraction patterns together with the visually estimated intensities for four of the complexes of this series are listed in Table III. The poor powder patterns made it difficult to interpret the data. It is seen that niobium(V) chloride:succinonitrile 1:1 and the corresponding tantalum complex have somewhat similar patterns, but it is not possible to decide whether or not they are definitely isomorphous. The powder pattern of niobium(V) chloride:succinonitrile (2:1) and its tantalum analog differ widely. It appears that the crystals of these complexes possess low symmetry.

*Infrared spectra.* Theoretically an organic nitrile can coordinate to a metal atom either through the lone pair of electrons on nitrogen or through the  $\pi$ -

electrons from the CN triple bond. The position of the CN stretching frequency in the infrared spectra of the complexes has been utilized in the elucidation of the bonding mode of the nitrile group on coordination. It is known that in the N-bonded complexes, the CN stretching mode is almost always shifted to higher frequency<sup>12,22-27</sup> while in the case of  $\pi$ -bonded complexes the shift is towards the lower frequency region.<sup>28,29</sup> In the case of dinitriles also, coordination of the nitrile group to the metal atom from both sites is known to occur.<sup>18,19,30,31</sup>

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In all the complexes studied, we have observed that nitrile stretching frequency has shifted (30-60  $\text{cm}^{-1}$ ) to higher frequencies as compared to that of the free ligand (Table II). There is no absorption band in the region 2200-1500  $\text{cm}^{-1}$ , thus confirming that the dinitriles are not bonded through the  $\pi$ -electrons of the CN group. Similar observations were also made earlier in the case of niobium(V) and tantalum(V) halide complexes with mononitriles.<sup>7</sup> The absorption spectra of the complexes recorded as Nujol mulls show a strong band near 2300  $\text{cm}^{-1}$  and a weak shoulder in the region of the free nitrile stretching frequency in the case of 1:1 complexes. However, when these spectra were taken in solution (methylene chloride), only a single absorption peak was observed. The quantitative intensity measurements of spectra in Nujol and solution (methylene chloride) for some of the complexes ruled out that the weak shoulder could be due to the uncoordinated nitrile in the complex. Therefore it is concluded that both nitrile groups in the dinitrile are taking part in the bonding.

*Rotational isomers of succinonitrile.* The infrared spectra of the succinonitrile complexes of niobium(V) and tantalum(V) halides have been useful in showing the stabilization of a particular isomeric form in both 1:1 and 2:1 complexes. The infrared spectrum of succinonitrile was studied by Fitzgerald and Janz<sup>32</sup> and later by Matsubara<sup>33</sup> who showed that the spectroscopically identifiable, *gauche* and *trans* isomers exist in the liquid as well as in the solid state above  $-43.7^\circ$ . When succinonitrile was frozen below this temperature crystallization occurred exclusively in the *gauche* form. It was found that below  $-43.7^\circ$ , sharp and pronounced changes occurred in the spectrum of succinonitrile and considerable spectral simplification took place. The absorption bands at or near 1270, 917, 760 and 530  $\text{cm}^{-1}$  disappeared below  $-43.7^\circ$  and therefore these bands were assigned to the *trans* isomer. The infrared studies of the  $\text{Cu}^1$  complex,  $[\text{Cu}[(\text{CH}_2)_2(\text{CN})_2]_2\text{NO}_3]$ <sup>33</sup> showed that the ligand was stabilized in the *gauche* form only. This has been substantiated also by x-ray crystal structure data.<sup>14</sup> In the case of  $[\text{TiCl}_4(\text{CH}_2)_2(\text{CN})_2]$ <sup>18</sup> and  $[\text{MoOCl}_3(\text{CH}_2)_2(\text{CN})_2]$ <sup>19</sup> complexes, the infrared data have been interpreted in favour of stabilization of the ligand in the *trans* form. The *trans* conformer of succinonitrile has also been reported for  $[\text{Ag}[(\text{CH}_2)_2(\text{CN})_2]_2\text{ClO}_4]$ ,  $[\text{Ag}[(\text{CH}_2)_2(\text{CN})_2]_2\text{BF}_4]$ ,  $[\text{AgNO}_3(\text{CH}_2)_2(\text{CN})_2]$  and  $[[\text{AgNO}_3]_2(\text{CH}_2)_2(\text{CN})_2]$  by Kubota and coworkers<sup>34</sup> and the crystal structure of the latter compound verifies the assignment.<sup>35</sup>

In our studies, we have also observed that a considerable spectra simplification on complex formation with succinonitrile takes place. The observed bands in the infrared spectra of niobium(V) and tantalum(V) chloride complexes with succinonitrile for both 1:1 and 2:1 stoichiometry are tabulated (Table IV) along with the infrared data of succinonitrile and some of its complexes reported earlier by other workers. Ab-

sorption bands at 1255, 931 and 748  $\text{cm}^{-1}$  appear in the spectrum of  $[2\text{NbCl}_5(\text{CH}_2)_2(\text{CN})_2]$  and at 1254, 937 and 752  $\text{cm}^{-1}$  in that of  $[2\text{TaCl}_5(\text{CH}_2)_2(\text{CN})_2]$ . The  $\text{CH}_2$  twisting mode in the free ligand at 1197  $\text{cm}^{-1}$  assigned in the *trans* isomer<sup>32,33</sup> has shifted to 1186 and 1187  $\text{cm}^{-1}$  in the above 2:1 complexes. The absorption pattern is characteristic of the *trans* isomer and therefore it is proposed that succinonitrile assumes *trans* configuration in these complexes. Also the close similarity of the infrared spectra of the 2:1 complexes with those of  $[\text{TiCl}_4(\text{CH}_2)_2(\text{CN})_2]$ <sup>18</sup> (*trans*) and  $[\text{MoOCl}_3(\text{CH}_2)_2(\text{CN})_2]$ <sup>19</sup> (*trans*) support this view (Table IV).

In the case of 1:1 complexes with succinonitrile the characteristic absorption bands assigned to *trans* conformers do not appear in the infrared spectra of these complexes. The intense absorption bands at 963 and 999  $\text{cm}^{-1}$  in the spectrum of succinonitrile particularly characteristic of the *gauche* conformation<sup>33</sup> appear in the spectra of 1:1 complexes although slightly shifted. Therefore it is concluded that the succinonitrile assumes *gauche* conformation in these complexes. A comparison of the frequencies in the spectra of the 1:1 complexes with those of  $[\text{Cu}[(\text{CH}_2)_2(\text{CN})_2]_2\text{NO}_3]$ <sup>33</sup> (*gauche*) and succinonitrile at  $-50^\circ$  (*gauche*) (Table IV) confirms our conclusions.

*Low-frequency infrared spectra.* Absorption bands in the low-frequency region (650-250  $\text{cm}^{-1}$ ) for niobium(V) and tantalum(V) chloride complexes with succinonitrile are shown in Table V. It is observed that in the case of 1:1 complexes two bands at 606 and  $\sim 485$   $\text{cm}^{-1}$  appear, which are characteristic of *gauche* conformation. This further supports the view that in 1:1 complexes the ligand succinonitrile is being stabilized in the *gauche* form. The absence of these bands and appearance of a very weak band at 535  $\text{cm}^{-1}$  in the spectra of the 2:1 complexes supports our interpretation that the ligand succinonitrile is *trans* oriented in these compounds.<sup>33</sup>

It is known that the  $\nu(\text{M-X})$  bands are strong and broad. In the case of  $[2\text{TaCl}_5(\text{CH}_2)_2(\text{CN})_2]$  four strong bands appear in the region 386-338  $\text{cm}^{-1}$ , while in  $[\text{TaCl}_5(\text{CH}_2)_2(\text{CN})_2]$  similar bands appear in the region 360-296  $\text{cm}^{-1}$ . This shows a general trend of shifting to lower frequencies as one goes from 2:1 to 1:1 complexes. In the case of niobium(V) chloride complexes, the number of  $\nu(\text{M-X})$  bands are comparatively less because of poor resolution. In all the four complexes one medium intensity band appears in the region 420-403  $\text{cm}^{-1}$ . This band seems to be the shifted  $\text{C-C}\equiv\text{N}$  bonding mode which appears at  $\sim 385$   $\text{cm}^{-1}$  in the free ligand.<sup>33</sup> Similar observations have been made in the case of gallium trihalide complexes of acetonitrile.<sup>35</sup> In addition, several very weak absorption bands which appear in the lower frequency region were difficult to assign.

*Proposed structure: 2:1 complexes.* Since infrared spectra of these complexes have shown that both the nitrile groups in the dinitrile are N-bonded, the only possible mode of bonding in the case of 2:1 complexes would be where one ligand molecule bridges two metal halide molecules.

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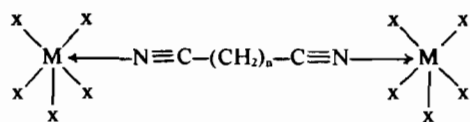
**Table IV.** Infrared spectra ( $\text{cm}^{-1}$ ) of succinonitrile(L) and its complexes.

60° <sup>a</sup> Liquid	Solid <sup>b</sup> -50°	$\text{CuL}_2 \cdot \text{NO}_3$ <sup>b</sup>	$\text{TiCl}_4 \cdot \text{L}$ <sup>c</sup>	$\text{MoOCl}_4 \cdot \text{L}$ <sup>d</sup>	$\text{NbCl}_5 \cdot \text{L}$ <sup>e</sup>	$2\text{NbCl}_5 \cdot \text{L}$ <sup>e</sup>	$\text{TaCl}_5 \cdot \text{L}$ <sup>e</sup>	$2\text{TaCl}_5 \cdot \text{L}$ <sup>e</sup>	Gauche $\text{C}_2$	Trans $\text{C}_2$
2985vs 2965vs	2994m 2959w								B-C-H str AC-H str	$\text{A}_g\text{C-Hstr}$ $\text{B}_g\text{C-Hstr}$
2255vs	2257s 1431vs	2283ms	2293s	2302s	2303s 2262w,sh	2313ms	2313vs 2262w,sh	2324vs	C-N-M C-Nstr	C-N-M C-Nstr
1425vs 1338s	1414vs 1332s	1418ms 1310vs	1417w	1416w	1402m 1312w,sh 1307w	1408w	1408w 1323w 1309w	1412w	$\text{ACH}_2\text{bend}$ $\text{BCH}_2\text{bend}$ $\text{BCH}_2\text{wag}$	$\text{B}_g\text{CH}_2\text{bend}$
1270m 1230s 1197m 1025w 1002vs 962vs 917s 818s 762s 610vs 530w	1225s 1189m 1032m 999vs 963vs 820s 810ms	1242m 1202ms 1021m 1010w 966m 826ms 813mw	1267s 1198s	1262m 1196m	1212vw 1016vw 993s 952s	1255ms 1186ms	992m 955m	1254s 1187w	$\text{ACH}_2\text{wag}$ $\text{ACH}_2\text{twist}$ AC-Cstr BC-CNstr ACH <sub>2</sub> rock	$\text{B}_g\text{CH}_2\text{wag}$ $\text{A}_g\text{CH}_2\text{twist}$
			938s	940s	823ms	931s	826m	937s	BCH <sub>2</sub> rock AC-CNstr	$\text{B}_g\text{C-CNstr}$
			754s	758s		816w 748ms		752s	BC-Ccbend	$\text{A}_g\text{CH}_2\text{rock}$
			538s		606w	535w	606m	535w		$\text{B}_g\text{C-Ccbend}$

<sup>a</sup> Ref. 32. <sup>b</sup> Ref. 33. <sup>c</sup> Ref. 18. <sup>d</sup> Ref. 19. <sup>e</sup> Present work. s = strong, m = medium, w = weak, sh = shoulder, v = very.

**Table V.** Far-infrared absorption bands in some succinonitrile complexes.

Complex	ligand bands	$\nu(\text{M-X})$ bands	Unassigned bands
$[\text{NbCl}_5 \cdot (\text{CH}_2)_2(\text{CN})_2]$ $[\text{TaCl}_5 \cdot (\text{CH}_2)_2(\text{CN})_2]$	606w, 483w, 413m 606m, 485m, 403s	362vs br 360vs br, 337s br 309s br, 296s 390s br, 356s br	304vw, 297vw, 269vw 287sh, 272w
$[2\text{NbCl}_5 \cdot (\text{CH}_2)_2(\text{CN})_2]$ $[2\text{TaCl}_5 \cdot (\text{CH}_2)_2(\text{CN})_2]$	535vw, 420m 535w, 408s, 370s	386s sh, 356vs br 346s, 338vs	288vw, 260w 307w, 300w, 270w, 264w

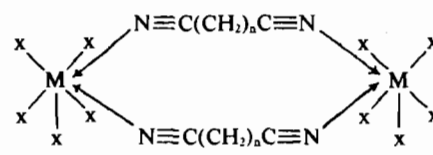


In such a structure both the metal atoms exhibit the usual coordination number of six.

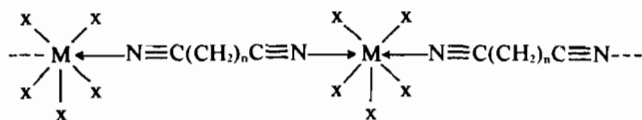
**1:1 complexes.** In this stoichiometry, where again both the nitrile groups of the dinitrile are N-bonded, two structural possibilities exist. The dinitrile may behave as a chelating ligand or act as a bridging ligand, each nitrile group forming a bond with two adjacent metal halides. In both cases, the coordination number of the metal atom will be seven.

X-ray crystallographic studies have shown that in the N-bonded complexes of mononitriles  $[\text{BF}_3 \cdot \text{CH}_3\text{CN}]^{37}$ ,  $[\text{PdCl}_2 \cdot 2\text{C}_3\text{H}_5\text{CN}]^{38}$  and also the dinitrile complex  $[\text{Cu}\{(\text{CH}_2)_2(\text{CN})_2\}_2\text{NO}_3]^{14}$ , a linear C-C-N-M linkage exists in the solid complexes. It is assumed that such a linear arrangement of atoms will be maintained in the complexes under study since chelation by the 'short chained' dinitriles is ruled out due to the steric restrictions.

It would be reasonable to conclude that in the 1:1 complexes also the dinitriles act only as bridging ligands. This leads us to propose two possible structures for these complexes:



Structure I



Structure II

Structure I is a dimer and somewhat analogous to that observed in the case of  $\text{Cu}^I$  complex  $[\text{Cu}\{(\text{CH}_2)_2(\text{CN})_2\}_2\text{NO}_3]^{14,33}$  with a polymeric structure. In structure II, the dinitrile is bridging two adjacent metal halides in a polymeric chain. The polymer could be linear or cyclic. Structure I can be considered as a special case of this polymeric structure.

Monomeric complexes of niobium(V) and tantalum(V) halides with mononitriles reported earlier<sup>7</sup> have definite melting points and are soluble in common organic solvents. In contrast, the solubility data and non-melting nature of the dinitrile complexes in the present study may be interpreted in favour of a polymeric structure. Such polymeric structures have been proposed by several workers in case of metal halide complexes with dinitriles.<sup>17-19</sup>

In 1:1 complexes of  $\text{TiCl}_4$ ,  $\text{SnCl}_4^{18}$  and  $\text{MoOCl}_3^{19}$

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with succinonitrile, it was also observed that the ligand was *trans* oriented. The stabilization of *trans* conformation of succinonitrile in these complexes favoured their linear polymeric structure. It has been shown that in the case of the 1:1 complexes under study, succinonitrile assumes the *gauche* conformation similar to  $[\text{Cu}[(\text{CH}_2)_2(\text{CN})_2]_2\text{NO}_3]$ <sup>33</sup> complex. Although linear polymeric structure for such an orientation cannot be ruled out, this particular configuration would favour structure I. However, in the absence of x-ray data, discussion of the structure of these complexes is purely speculative.

In the present study, the 1:1 complexes are believed to be seven coordinated. Although the complexes of niobium(V) and tantalum(V) halides are generally six coordinated, there are some cases where coordination number seven for these metals has been obtained.<sup>9,39</sup> Further evidence for coordination number seven in the present case is obtained from the position of metal-halogen stretching modes in the low-frequency infrared region. Several authors<sup>9,40,41</sup> have interpreted the possible coordination number of the central metal atom from the positions of  $\nu(\text{M-X})$  bands. Since

bond lengths are expected to increase as coordination number of the metal atom increases, it is expected that  $\nu(\text{M-X})$  bands would appear at different positions in 2:1 and 1:1 complexes. The highest frequency  $\nu(\text{M-X})$  bands in  $[2\text{NbCl}_5 \cdot (\text{CH}_2)_2(\text{CN})_2]$  and  $[\text{NbCl}_5 \cdot (\text{CH}_2)_2(\text{CN})_2]$  appear at 390 and 362  $\text{cm}^{-1}$ , respectively and in the case of  $[2\text{TaCl}_5 \cdot (\text{CH}_2)_2(\text{CN})_2]$  and  $[\text{TaCl}_5 \cdot (\text{CH}_2)_2(\text{CN})_2]$  at 386 and 360  $\text{cm}^{-1}$ , respectively. Both niobium(V) and tantalum(V) chlorides are dimeric in the solid state and therefore have coordination number six.<sup>42</sup> The highest frequency,  $\nu(\text{M-X})$  bands in these pentachlorides have been reported at 398 and 388  $\text{cm}^{-1}$  respectively.<sup>43</sup> The spectral data therefore would support that the 2:1 complexes are six coordinated while the 1:1 complexes are seven coordinated.

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