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Synthesis and Structural Studies on Niobium(V) Chloride Complexes of N,N′-(substituted) Formamidino-N″-(substituted) Carbamides and Thiocarbamides and their Semiconducting Properties

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In tetrahydrofuran media, niobium pentachloride forms complex compounds with N,N′-diarylsubstituted formamidino-N″-arylsubstituted carbamides (DSFSC), thiocarbamides (DSFSTC) and N-benzoylsubstituted formamidino N′-arylsubstituted carbamides (BSFSC) and thiocarbamides (BSFSTC) having the general formula $NbCl_5L$, where L is a bidentate ligand. The complex compounds have been characterized on the basis of elemental analysis, molar conductance, magnetic susceptibility measurements and infrared, ultraviolet spectral studies. The ligands when oxidised with iodine undergo ring closure to 3-5-diarylamino-1,2,4-thiadiazolidines and 3,5-diarylamino-1,2,4-diazolidines while the complexes are not susceptible to oxidation. The band gaps of complexes have been found in the range 1.09–1.4 ev.

Introduction

Complexes of the type $NbCl_5L$ are known for L-acetophenone [1] and 2,2′-bipyridyl [2]. The carbonyl frequency was lower in the complexes, indicating coordination through oxygen of acetophenone and benzophenone. Complexes of Nb(V) with a wide range of Schiff bases containing a variety of donor sites have been reported [3–5]. It has been observed that in almost all of the complexes the coordination number of niobium is 7. Hexa and octacoordinated complexes of Nb(V) were reported by Parasher and Tandon [6]. This author has already reported the complexes of Nb(V) Mo(V), Mo(VI) with bidentate ligands having sulphur, oxygen and nitrogen donors [7–11]. The present paper describes the physicochemical studies of Nb(V) chloride with the title ligands.

Experimental

The ligands N,N′-diphenylformamidino N″-phenylcarbamide (DPFPC), N,N′-diphenylformamidino-N″-phenylthiocarbamide (DPFPTC),N,N′-diphenylformamidino-N″-orthotolylthiocarbamide (DPF.*o*-TTC), N,N′-diarylformamidino-N″- paratolylthiocarbamide (DPF.*p*-TTC), N-benzoylformamidino-N′-phenylcarbamide (BFPC), N-benzoylformamidino N′-phenylthiocarbamide (BFPTC), N-benzoylformamidino-N′-orthotolylthiocarbamide (BF.*o*-TTC), N-benzoylformamidino-N′-paratolylthiocarbamides (BF.*p*-TTC) were prepared and purified as described earlier [7]. To a solution (0.01 *M*) of niobium pentachloride in tetrahydrofuran, ligand was added in slight excess (mol ratio 1:1:3) in the same solvent with vigorous shaking, and sufficient time was allowed for the resulting precipitate to settle. The flask containg the reaction mixture was kept at 5–10 °C. The complex thus settled was filtered, washed with chloroform and then with ether, and finally dried under vacuum. All the preparations were carried out in a dry box in the absence of moisture. Niobium was estimated as Nb_2O_5. Chloride and sulphur were estimated by standard methods [12]. The obtained percentage values of these elements are in good agreement with calculated ones for 1:1 complexes. Melting points of these complexes were determined in open capillary tubes on a Unimelt temperature apparatus and are uncorrected.

The magnetic measurements of these compounds were determined on a Gouy balance at room temperature by using a field strength of about 4.5×10^3 G.

The infrared spectra of the ligands and complexes were recorded by a KBr pellet technique on a Perkin-Elmer Grating Infrared Spectrophotometer model 237-B. Molar conductances of the complex compounds were determined in freshly distilled N,N′-dimethylformamide at a concentration of about 10 *M* with a conductivity meter type LBR (Wissenschaftliche Technische Werkstätten Germany) using a dip type cell. The results are reported in tables I–II.

Studies on oxidation of ligands and their complexes were carried out with iodine solution in tetrahydrofuran using calomel and platinum electrodes. 20 ml of *M*/500 solution in THF of ligand was titrated with *M*/50 iodine solution in THF. The

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TABLE I. Molar Conductance, Magnetic Susceptibility, Band Gaps and Seebeck Coefficients of Nb(V) complexes.

Formula	Molar Conductance in DMF		Magnetic Susceptibility $(\chi) \times 10^{-5}$	E_g, ev	α $\mu V/°C$
	Concentration $\times 10^{-2}$ *M*	λ_m, cm^2 mol Ω^{-1}			
$NbCl_5$DPFPTC	0.10	82.66	−0.299	1.41	+375
$NbCl_5$DPFPC	0.10	86.16	−0.294	1.33	+210
$NbCl_5$DPF.*o*-TTC	0.099	90.52	−0.352	1.34	+285
$NbCl_5$DPF.*p*-TTC	0.099	85.00	−0.295	1.15	+450
$NbCl_5$BFPTC	0.10	87.00	−0.295	1.24	+147
$NbCl_5$BFPC	0.10	83.80	−0.297	1.57	+180
$NbCl_5$BF.*o*-TTC	0.098	84.20	−0.308	1.13	−178
$NbCl_5$BF.*p*-TTC	0.10	86.50	−0.310	1.09	+241

TABLE II. I.R. Spectral Data of Ligands and their Nb(V) Chloride Chelates (in cm^{-1}).[a]

	=NH Stretch	C=O Stretch	N–H Stretch	C–H Stretch	C–N Str. + N–H bend + (C=S) bend	(C=S) Stretch	C=S Stretch
DPFPTC	3385s	–	1641vw	1540s	1441vw	1225m	729m
$NbCl_5$DPFPTC	3280mb	–	1635s	1585s	1485s	1225m	720m
DPFPC	3400s	1735w	1640m	1582m	1460m	1260m	–
$NbCl_5$DPFPC	–	1722w	1630m	1500m	1470w	1222m	–
DPF.*o*-TTC	3402s	–	1660m	1540m	1439s	1270m	760b
$NbCl_5$DPF.*o*-TTC	–	–	1648s	1552m	1405s	1258m	740m
DPF.*p*-TTC	3400s	–	1600s	1566m	1441m	1220m	756m
$NbCl_5$DPF.*p*-TTC	–	–	1625w	1575m	1460w	1205b	745m
BFPTC	3400s	1700m	1680s	1550s	1413s	1227s	716w
$NbCl_5$BFPTC	3300m	1700m	1630s	1595m	1480w	1215m	700m
BFPC	3360s	1725m	1685s	1550m	1440s	1280w	–
$NbCl_5$BFPC	–	1715w	1635vw	1590m	1440ms	1255ms	–
BF.*o*-TTC	3400ms	1698m	1625b	1525w	1400m	1175w	750m
$NbCl_5$BF.*o*-TTC	3300	1698m	1630m	1575w	1400m	1150ws	732w
BF.*p*-TTC	3400s	1700m	1625s	1563s	1440m	1282s	799w
$NbCl_5$BF.*o*-TTC	3250m	1722m	1620m	1570m	1445w	1266m	780w

[a] s = strong, m = medium, b = broad, w = weak.

results of these studies are recorded in Tables III and IV. Absorption spectra of Nb(V) chloride complexes and ligands were measured by the standard method using a Perkin-Elmer UV–VIS spectrophotometer, model 139. Ethanol and methanol were distilled before use. Transition energy E_T and oscillatory strength (f) were calculated by the standard method [13].

The electrical conductivities (σ) of the complexes were measured in the temperature range 30–150 °C in the form of cylindrical pallets by employing a conductivity cell and Digital Picoammeter (ESA 813 Electronics Corp. of India Ltd).

The Seebeck Coefficients (α) of the complexes were measured by using a d.e. microroltameter (Phillips GM 6020) (*cf.* Table I).

Results and Discussions

The analytical results indicate a metal–ligand ratio of 1:1, which corresponds to the general empirical formula $NbCl_5L$. The molar conductance values (82.66–90.52 Ω^{-1}) in freshly distilled DMF indicate the 1:1 electrolyte nature of the complexes [14]. The negative values of magnetic susceptibility (-0.294 to -0.352×10^{-5}) suggest that the complexes are diamagnetic. The UV spectra of ligands show bands around 240–265 nm in methanol and ethanol, which are shifted to 305–350 nm in the complexes. This shift is attributed to the fact that during complex formation, the energy level is lowered due to stabilization of the excited state.

TABLE III. Potentiometric Titrations of Ligands with Iodine in THF.

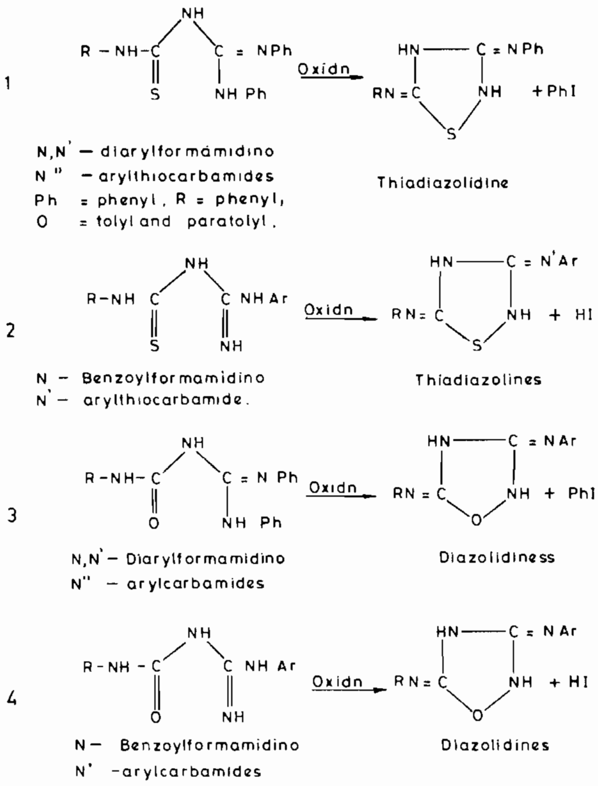
Volume of iodine in ml	EMPF of DPFPTC (in mv)	EMF of DPFPC (in mv)	EMF of DPF.*o*-TTC (in mv)	EMF of DPF.*p*-TTC (in mv)	EMF of BFPTC (in mv)	EMF of BFPC (in mv)	EMF of BF.*o*-TTC (in mv)	EMF of BF.*p*-TTC (in mv)
0.50	225	222	245	210	215	217	228	232
1.00	238	235	250	215	218	219	240	244
1.20	245	242	250	218	223	225	245	249
1.40	247	246	253	222	230	232	249	253
1.60	251	250	257	226	233	236	260	265
1.80	260	258	255	232	250	254	277	279
1.90	275	273	290	245	271	274	295	298
2.00	293	290	315	270	294	296	322	325
2.10	315	310	355	295	320	326	345	348
2.20	347	344	375	335	352	355	365	366
2.30	370	367	385	350	360	362	388	398
2.40	380	378	390	360	365	368	398	402
2.60	388	385	394	365	372	375	398	406
2.80	392	390	398	368	376	379	402	407
3.00	396	392	400	370	380	387	404	409
3.20	400	394	404	373	384	389	407	410
3.40	495	395	407	375	387	392	409	411
3.60	408	400	409	375	390	395	411	413
3.80	410	405	412	377	391	396	414	414
4.00	411	406	418	378	392	397	415	414

TABLE IV. Potentiometric Titrations of Nb(V) Chloride Complexes with Iodine in THF.

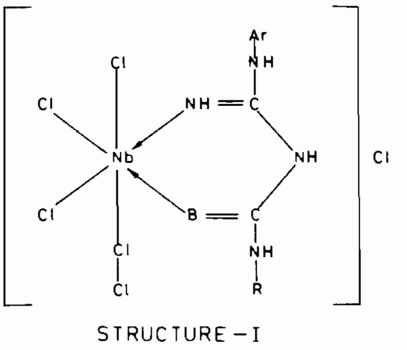
Volume of iodine in ml	EMF of $NbCl_5$ DPFPTC in mv	EMF of $NbCl_5$ DPFPC in mv	EMF of $NbCl_5$ DPF.*o*-TTC in mv	EMF of $NbCl_5$ DPF.*p*-TTC in mv	EMF of $NbCl_5$ BFPTC in mv	EMF of $NbCl_5$ BF.*o*-TTC in mv	EMF of $NbCl_5$ BF.*o*-TTC in mv	EMF of $NbCl_5$ BF.*p*-TTC in mv
0.5	542	530	544	506	540	532	539	541
1.0	538	525	540	507	539	532	538	541
1.2	535	522	543	508	537	531	539	541
1.4	531	522	544	503	540	528	541	540
1.6	529	519	550	502	540	527	540	540
1.8	528	520	548	504	542	528	538	539
2.0	528	517	545	505	537	529	537	539
2.2	530	521	545	506	533	530	536	541
2.4	531	516	543	507	542	531	535	538
2.6	531	520	544	511	541	526	541	539
2.8	530	519	545	509	541	527	539	537
3.0	529	520	545	502	540	530	537	540
3.5	528	523	545	501	537	529	538	541
4.0	528	512	546	505	535	530	537	540

On examination of the infrared spectra of the ligands and their metal chelates it can be seen that these ligands exhibit a C=O stretching band of medium intensity in the region 1698–1735 cm^{-1}, which is stronger than the usual ketone C=O bond [15]. On chelation with the metal the carbonyl absorption peak is shifted to a lower frequency (10–15 cm^{-1}) of comparatively weak intensity. As there is almost no change in the benzoylic carbonyl frequencies on complexation, the benzoylic C=O group cannot be considered as a site for coordination. A peak at 1400–1485 cm^{-1} is due to a mixed band of (C–N) stretch, N–H bend and C=S bend. The strong bands at 3355–3400 cm^{-1} in the case of DSFSTC and DSFSC are attributed to N–H stretching of secondary amines (=NH). In complexes this peak is either missing or a broad peak covering a range of 3300–3272 cm^{-1} of comparatively low intensity is obtained. The broad nature of the peak suggests that bonding between metal and ligands is strong. The infrared spectra of ligands show that BFPTC, BF.*o*-TTC, DPFPTC, DPFP-TTC, and DPF.*o*-TTC exhibit a C=S band of medium intensity at 716–799 cm^{-1} which is lowered (9–20 cm^{-1}) on complexation. All these observations show that coordination in the case of BFPTC, BF.*o*-TTC, BF.*p*-TTC, DPFPTC, DPF.*o*-TTC and DPF.*p*-TTC is through sulphur and nitrogen (of =NH), while in the case of BFPC and DPFPC complexes the coordination is through oxygen and nitrogen.

Potentiometric titrations of the ligands against iodine in THF (Table III) indicate that an equimolar amount of iodine is consumed in the oxidation reaction. It is due to the oxidation of the ligands to related thiazoles [16], (reactions 1–4).

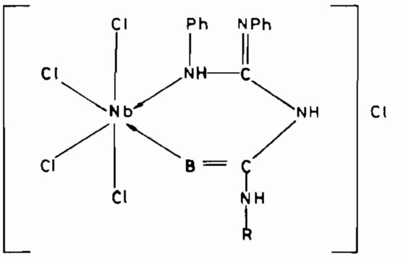


On titrating the Nb(V) chloride chelates with iodine, effectively constant values of potential are obtained (Table IV), indicating that the complexes are not being oxidized by iodine. This may be due to the fact that the sulphur and oxygen atoms are already bonded to the metal in the metal chloride complexes and are not free to form the thiols (which are susceptible to oxidation and consequently cyclization). All these observations show that coordination in the case of DPFPTC, DPF.*o*-TTC, DPF.*p*-TTC, BFPTC, BF.*o*-TTC and BF.*p*-TTC is through nitrogen and sulphur, while in the case of DPFPC and BFPC complexes the coordination is through oxygen and nitrogen atoms. On the basis of these observations the complexes so formed can be represented by the following structure I & II.



STRUCTURE – I

$NbCl_5$, BFPTC, R = $-C_6H_5$, Ar' = $-C_6H_5CO$, B = S
$NbCl_5$, BFO.TTC, R = $-C_6H_4(CH_3)$, Ar = $-C_6H_5CO$, B = S
$NbCl_5$, BFpTTC, R = $-C_6H_5(CH_3)$, Ar = $-C_6H_5CO$, B = S
$NbCl_5$, BFPC R = $-C_6H_5$ Ar = $-C_6H_5CO$ B = O



STRUCTUR – II

$NbCl_5$. DPFPC, R = $-C_6H_5$, Ph = $-C_6H_5$, B = O
$NbCl_5$. DPFPTC, R = $-C_6H_5$, Ph = $-C_6H_5$, B = S
$NbCl_5$. DPFPTC, R = $-C_6H_4(CH_3)$, Ph = $-C_6H_5$, B = S
$NbCl_5$. DPF.pTTC, R = $-C_6H_4(CH_3)$, Ph = $-C_6H_5$, B = S

Semiconducting Properties of Complexes

In Fig. 1 the logarithm of electrical conductivity (σ) of the $NbCl_5 \cdot$DPF.*p*-TTC against the reciprocal of temperature (T) in K is shown. The band gaps Eg

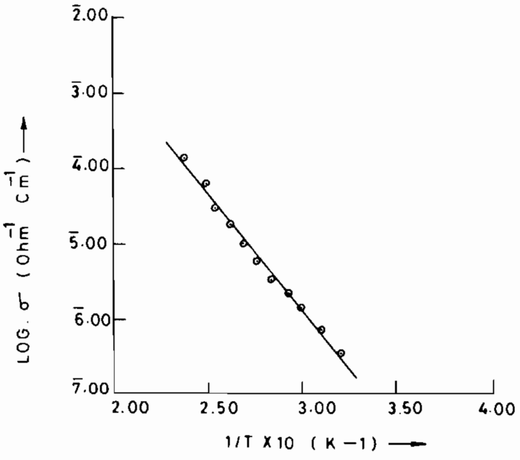


Fig. 1. Plot of σ vs. 1/T for $NbCl_5$DPF.*p*-TTC.

for the conduction process were calculated by using the equation [17]:

$$\sigma = \sigma_0 e^{-E_g/2KT}$$

where σ is conductivity at T °K, σ_0 is a constant, and K is Boltzmann's constant. The slopes of log σ *vs.* 1/T straightlines were accurately determined by using the least squares method.

The electrical conductivities of the complexes are in the ranges $10^{-8} - 10^{-5}$ and 10^{-7}–10^{-4} Ω^{-1} cm^{-1}. On comparison of these ranges with the electrical conductivities range of the semiconductors as given by Kittel [18] it is observed that DPFPTC and DPFPC complexes are good semiconductors with band gaps ranging from 1.09 to 1.40 ev (Table I). It is also observed that the complexes having a substituent at *para* positions in the ligands have more conductivity than the case of substituents at the *ortho* positions.

The Seebeck coefficients (α) measurements in these complexes showed that complexes are n-type semiconductors (negative α) and DPFPTC, DPFPC DPF.*o*-TTC, DPF.*p*-TTC BFPC, BFPTC, BF.*o*-TTC and BF.*p*-TTC complexes to be p-type semiconductors (positive α) as shown in the Table.

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References

1 C. D. Jordjevic and V. Katovic, *J. Less Common Met., 21*, 325 (1970).
2 G. W. A. Fowles and K. F. Gadd, *J. Chem. Soc. A*, 2232 (1970).
3 Ya Yu Chang and I. A. Savich, *Vestn, Misk. Univ. Khim., 15*, 40 (1960).
4 A. V. Lapitskii, Ya Yu Chang and I. A. Savich, *Russ. J. Inorg. Chem., 37*, 333 (1967).
5 L. V. Orlovo, A. D. Garnovaskii, O. A. Osipov and O. A. Raevskii, *Zh. Obshch. Khim., 37*, 1787 (1967).
6 P. Parasher and J. P. Tandon, *Z. Naturforsch. B, 25*, 32 (1970).
7 K. P. Srivastava, G. P. Srivastava, S. K. Arya and K. L. Madhok, *J. Chem. & Eng. Data, 25*, 173 (1980).
8 K. P. Srivastava and K. L. Madhok, *J. Chem. & Eng. Data, 23*, 256 (1978).
9 K. P. Srivastava and K. L. Mahok, *J. Inorg. Nucl. Chem., 40*, 1821 (1978).
10 K. P. Srivastava and K. L. Madhok, *Indian J. Chem., 16A*, 990 (1978).
11 K. P. Srivastava and K. L. Madhok, *Chemical Era, XIV*, 188 (1978).
12 A. I. Vogel, "Quantitative Inorganic Analysis", 2nd Ed., Longmans Green, London (1961).
13 C. N. R. Rao, 'Chemical Applications of Ultraviolet and Visible Spectroscopy', Butterworth, London, p. 14 (1967).
14 W. J. Geary, *Coordination Chem. Rev., 7*, 81 (1971).
15 F. Scheinmann, 'Nuclear Magnetic Resonance and Infrared Spectroscopy', Vol. I, p. 178, Pergamon Press, Oxford, New York (1970).
16 S. N. Dixit, *J. Indian Chem. Soc., 38*, 221 (1961).
17 A. C. Wert and W. R. Thomas, 'Physics of Solids', McGraw–Hill, Tokyo (1970).
18 C. Kittel, 'Introduction to Solid State Physics', 4th Ed., Ester Private, New Delhi (1974).