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Synthesis of Niobium Pentachloride Complexes with 1,5-Diaryl-Substituted 2,4-Dithiobiurets and 1,5-Diaryl-Substituted 2-Thiobiurets and Their Semiconducting Properties

K. P. Srivastava, G. P. Srivastava,[†] S. K. Arya,[*] and K. L. Madhok
Chemistry Group, Birla Institute of Technology and Science, Pilani (Rajasthan) 333 031, India

In tetrahydrofuran medium, niobium pentachloride forms complex compounds with 1,5-diaryl-substituted 2,4-dithiobiurets (DSDTB) and 1,5-diaryl-substituted 2-thiobiuret (DSTB) having general formula $NbCl_5L$, where L is a molecule of bidentate ligand. The complex compounds have been characterized on the basis of elemental analysis, molar conductance, magnetic susceptibility, infrared spectral studies, and electrical conductivity measurements. Coordination through sulfur atoms in the case of diaryl dithiobiurets and coordination through sulfur and oxygen atoms in the case of diaryl thiobiurets have been proposed for these complexes, and their band gaps have been found in the range 1.09–1.47 eV.

Introduction

Complexes of niobium pentachloride with acetophenone and benzophenone formed moisture-sensitive complexes of type $NbCl_5L$ (*1*). The carbonyl stretching frequency was lower in complexes indicating coordination through oxygen of acetophenone and benzophenone. Gadd and Fowles (*2*) prepared 2,2′-bipyridyl complexes of Nb(V) in methyl cyanide and observed the formation of 1:1 complexes. The infrared spectra and magnetic measurements showed that the complexes are diamagnetic. 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. Parasher and Tandon (*6*) have reported hexa- and octacoordinated Schiff base complexes of Nb(V). Later Biradar et al. (*7*) reported coordination number 7 for some Schiff base complexes of niobium.

Semiconducting properties of several other metal (Cu(II), Co(II), Ni(II), and Pt(II)) phthalocyanin complexes (*8*) have been reported. Their activation energies, E_a, have been found to be in the range 0.75–0.90 eV (*9*, *10*). The etioporphyrin and its complexes of Cu(II), Ni(II), and Mg(II) have E_a in the range of 0.9–1.0 eV (*11*).

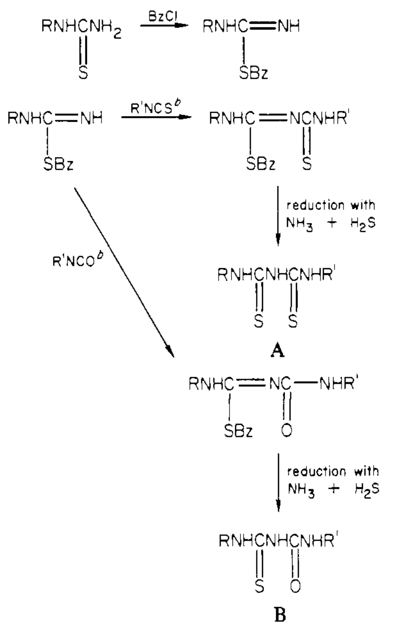
A careful survey of literature shows that almost no work has been done on the complex formation of 1,5-disubstituted 2,4-dithiobiurets and 1,5-disubstituted 2-thiobiurets with niobium pentachloride. The present paper deals with the isolation and characterization of complex compounds of niobium pentachloride with DSDTB and DSTB.

Experimental Section

All chemicals used were of BDH AnalaR or E. Merck "GR" reagent. Alcohol, ether, chloroform, and dimethylformamide were distilled before use. Niobium pentachloride of Fluka Grade was used.

The ligands 1,5-diphenyl-2,4-dithiobiuret (DPDTB), 1,5-diphenyl-2-thiobiuret (DPTB), 1,5-di-*o*-tolyl-2,4-dithiobiuret (D-*o*-TDTB), 1,5-di-*p*-tolyl-2,4-dithiobiuret (D-*p*-TDTB), 1-phenyl-5-*p*-tolyl-2,4-dithiobiuret (P-*p*-TDTB), 1-phenyl-5-*o*-tolyl-2,4-dithiobiuret (P-*o*-TDTB), 1-phenyl-5-*o*-tolylthiobiuret (P-*o*-TTB) and 1-phenyl-5-*p*-tolylthiobiuret (P-*p*-TTB) were prepared by the method of Dixit (*12*) and purified by crystallization from ethanol. A general method of preparation of lignds is summarized in Scheme I. Purity of these ligands was checked by sharp melting point and elemental analysis.

Scheme I[a]



[a] A = 1,5-diaryl-substituted 2,4-dithiobiuret; B = 1,5-diaryl-substituted 2-thiobiuret; R,R′ = phenyl, *o*-tolyl, *p*-tolyl; and Bz = benzyl. [b] Mustard oils were prepared by the method described by Vogel, A. I. "Practical Organic Chemistry", 3rd ed., Longmans Green and Co., London, 1962.

General Method of Preparation and Analysis of Complexes

To a solution (0.01 M) of niobium pentachloride in tetrahydrofuran, ligand was added in slight excess (mole ratio 1:1.3) in the same solvent with vigorous shaking, and sufficient time was allowed for the precipitate to settle. The flask containing the reaction mixture was kept at 5–10 °C. The complex thus settled was filtered, washed with either chloroform or tetrahydrofuran and then with dry ether, and finally dried under vacuum. All the preparations were carried out in a drybox in the absence of moisture.

A weighed quantity of the complex was fused with a 1:1 mixture of sodium peroxide and sodium carbonate in nickel crucibles. The fused mass was extracted with water and then neutralized with nitric acid. Hydrated niobium pentoxide precipitated by adding ammonium hydroxide while the pH was maintained between 7 and 8. The precipitate was filtered, washed with hot water, ignited and weighed. In the filtrate,

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[†] Physics group.

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Table I. IR Spectral Peaks of Ligands (cm^{-1})[a]

no.	compd	N-H str	N-H bend	N-H bend + ν[(C-N) + (C=S)] str	ν(C=S)	C=S str	C=O str
1	DPDTB	3120 m	1615 m	1480 m	1250 s	750 s	
2	DPTB	3230 s	1600 s	1435 m	1227 s	745 m	1710 s
3	D-*o*-TDTB	3215 m	1625 s	1502 s	1260 m	750 s	
4	D-*p*-TDTB	3160 m	1625 m	1455 m	1255 m	795 w	
5	P-*o*-TDTB	3235 m	1615 m	1450 b	1240 s	725 m	
6	P-*p*-TDTB	3225 s	1600 s	1465 m	1240 m	770 w	
7	P-*o*-TTB	3250 s	1620 s	1450 s	1245 s,b	755 s	1715 m
8	P-*p*-TTB	3196 m	1620 s	1460 m	1295 m	795 m	1715 s

[a] Key: w = weak; m = medium; s = strong; b = broad.

Table II. IR Spectral Peaks of Complexes (cm^{-1})[a]

compd	N-H str	N-H bend	N-H bend + ν[(C-N) + (C=S)] str	ν(C=S)	C=S str	C=O stretch
$NbCl_5$DPDTB	3170 b	1590 m	1450 b	1237 m	780 w	
$NbCl_5$DPTB	3050 b	1577 m	1425 m	1200 b 1275 w	743 b	1642 m
$NbCl_5$D-*o*-TDTB		1600 m	1550 b	1240 m	740 m	
$NbCl_5$D-*p*-TDTB		1615 m	1450 m	1220 s	730 m	
$NbCl_5$P-*o*-TDTB		1585 m	1415 m	1210 m	750 w	
$NbCl_5$P-*p*-TDTB		1615 m	1460 m	1200 b	700 w	
$NbCl_5$P-*o*-TTB		1625 s	1480 m	1225 s	725 b	1710 s
$NbCl_5$P-*p*-TTB	3125 m	1610 s	1475 m	1240 m	760 w	1640 m

[a] Key: s = strong; m = medium; w = weak; b = broad.

Table III. Molar Conductance, Magnetic Susceptibility Band Gaps, and Seebeck Coefficients of the $NbCl_5$ Complexes

		molar conductance in DMF				
no.	formula	concn × 10^{-2} M	λ_m, cm^2 mol^{-1} Ω^{-1}	magnetic susceptibility $\chi \times 10^{-5}$	E_g, eV	$\mu V/°C$
1	$NbCl_5$DPDTB	0.10	80.66	−0.299	1.41	+376
2	$NbCl_5$DPTB	0.10	87.16	−0.294	1.34	+212
3	$NbCl_5$D-*o*-TDTB	0.099	91.52	−0.352	1.34	−285
4	$NbCl_5$D-*p*-TDTB	0.098	85.07	−0.298	1.15	+450
5	$NbCl_5$P-*o*-TDTN		insoluble	−0.373	1.25	+146
6	$NbCl_5$P-*p*-TDTB	0.12	93.22	−0.481	1.58	+180
7	$NbCl_5$P-*o*-TTB	0.10	92.44	−0.543	1.13	−178
8	$NbCl_5$P-*p*-TTB		insoluble	−0.429	1.09	−240

chloride and sulfur were estimated by standard methods (*13*). The obtained percentage values of these elements are in good agreement with calculated ones for 1:1 complexes. (Anal. Calcd for $NbCl_5$DPDTB: Nb, 16.64; S, 11.48; Cl, 31.84. Found: Nb, 16.89; S, 11.85; Cl, 32.06. Calcd for $NbCl_5$DPTB: Nb, 17.18; S, 5.91; Cl, 32.78. Found: Nb, 17.32; S, 6.12; Cl, 33.00. Calcd for $NbCl_5$D-*o*-TDTB: Nb, 15.88; S, 10.92; Cl, 30.31. Found: Nb, 16.14; S, 11.10; Cl, 30.45. Calcd for $NbCl_5$D-*p*-TDTB: Nb, 15.88; S, 10.92; Cl, 30.31. Found: Nb, 16.20; S, 11.15; Cl, 30.52. Calcd for $NbCl_5$P-*o*-TDTB: Nb, 16.28; S, 11.18; Cl, 32.45. Found: Nb, 16.42; S, 11.38; Cl, 32.64. Calcd for $NbCl_5$P-*p*-TDTB: Nb, 16.28; S, 11.18; Cl, 32.45. Found: Nb, 16.38; S, 11.38; Cl, 32.70. Calcd for $NbCl_5$P-*o*-TTB: Nb, 16.74; S, 5.76; Cl, 31.96. Found: Nb, 16.96; S, 5.92; Cl, 32.28. Calcd for $NbCl_5$P-*p*-TTB: Nb, 16.74; S, 5.76; Cl, 31.96. Found: Nb, 17.04; S, 5.96; Cl, 32.20.) Melting points of these compounds were determined in open capillary tubes on a Unimelt temperature apparatus and are uncorrected.

The magnetic measurements of these complexes were carried out on a Guoy balance at room temperature by using field strength of about 4.5 × 10^3 G. The sample tube was calibrated with mercury tetrathiocyanate cobaltate.

The infrared spectra of the ligand and complex compounds were recorded by the KBr pellet technique on a Perkin-Elmer grating infrared spectrophotometer, Model 237-B. The spectra are complicated and difficult to interpret; however, only those peaks that could be assigned with reasonable certainity are recorded in Tables I and II.

Molar conductances of the complexes were determined in *N,N*-dimethylformamide at a concentration of about 10^{-2} M, with conductivity meter type LBR of Wissenschaftlich technisch, Werkstattn, Germany, using a dip type cell. The results are reported in Table III.

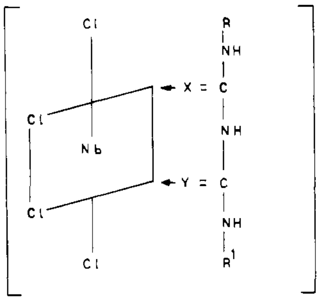
The electrical conductivities (σ) of the complexes were measured in the temperature range 30–150 °C in the form of cylindrical pellets by employing a conductivity cell and Digital Picoammeter (ESA 813 Electronics Corp. of India Limited).

The Seebeck coefficients (α) of the complexes were measured by using a d.c. microvoltameter (Philips GM 6020) (cf. Table III).

Results and Discussions

The analytical data indicate the metal–ligand ratio 1:1 which corresponds to the general empirical formula $NbCl_5L$. The molar conductance values (80.66–93.22 Ω^{-1}) in freshly distilled *N,N*-dimethylformanide indicate the 1:1 electrolytic nature of the complexes (*14*). The negative values of magnetic susceptibility (−0.294 × 10^{-5} to −0.543 × 10^{-5}) suggest that complexes are diamagnetic. From Tables I and II it can be observed that there is no considerable change in N–H stretching and bending vibrations, but considerable increases in intensity and frequency of C═S stretching frequencies (15–45 cm^{-1}) in DPDTB, D-*o*-TDTB, D-*p*-TDTB, P-*o*-TDTB, and *p*-TPDTB, complexes are indicative of coordination through sulfur. The medium-intensity band in the region 1710–1715 cm^{-1} of C═O stretching in thiobiuret is shifted to 1640–1710 cm^{-1} (~75 cm^{-1}) lower upon coordination.

It is thus concluded that the complexes of $NbCl_5$ have octahedral configuration, with donation through two sulfur atoms in dithiobiuret ligands and through sulfur and oxygen in thiobiuret ligands. The complexes so formed can be represented by structure I, having d^2sp^3 hybridization.



I: $NbCl_5$ complexes of 1,5-disubstituted 2,4-dithiobiurets and 2-thiobiurets

FOR :–

$[NbCl_4 . DPDTB]Cl$; X = S; Y = S; R = $-C_6H_5$; $R^1 = -C_6H_5$

$[NbCl_4 . P\text{-}oTDTB]Cl$; X = S; Y = S; R = $-C_6H_5$; $R^1 = -C_6H_4\underset{\text{ortho}}{(CH_3)}$

$[NbCl_4 . P\text{-}pTDTB]Cl$; X = S; Y = S; R = $-C_6H_5$; $R^1 = -C_6H_4\underset{\text{para}}{(CH_3)}$

$[NbCl_4 . D\text{-}oTDTB]Cl$; X = S; Y = S; R = $-C_6H_4\underset{\text{ortho}}{(CH_3)}$; $R^1 = -C_6H_4\underset{\text{ortho}}{(CH_3)}$

$[NbCl_4\ D\text{-}pTDTB]Cl$; X = S; Y = S; R = $-C_6H_4\underset{\text{para}}{(CH_3)}$; $R^1 = -C_6H_4\underset{\text{para}}{(CH_3)}$

$[NbCl_4 . DPTB]Cl$; X = S; Y = O; R = $-C_6H_5$; $R^1 = -C_6H_5$

$[NbCl_4 . P\text{-}oTTB]Cl$; X = S; Y = O; R = $-C_6H_5$; $R^1 = -C_6H_4\underset{\text{ortho}}{(CH_3)}$

$[NbCl_4\ P\text{-}pTTB]Cl$; X = S; Y = O; R = $-C_6H_5\underset{\text{para}}{(CH_3)}$; $R^1 - -C_6H_5$

Semiconducting Properties of Complexes

In Figure 1 the logarithm of electrical conductivity (σ) of $NbCl_5D$-*p*-TDTB against the reciprocal of temperature (T) in K is shown. The band gaps, E_g, for the conduction process were calculated by using the equation (*15*)

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

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

The electrical conductivities of DSDTB complexes and DSTB 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 conductivity range of the semiconductors as given by Kittel (*16*) it is observed that DSDTB and DSTB complexes are good semiconductors with band gaps ranging from 1.09 to 1.47 eV (Table III). It is also observed that complexes having a substituent at para positions in the ligands have more conductivity than in the case of substituents at the ortho position.

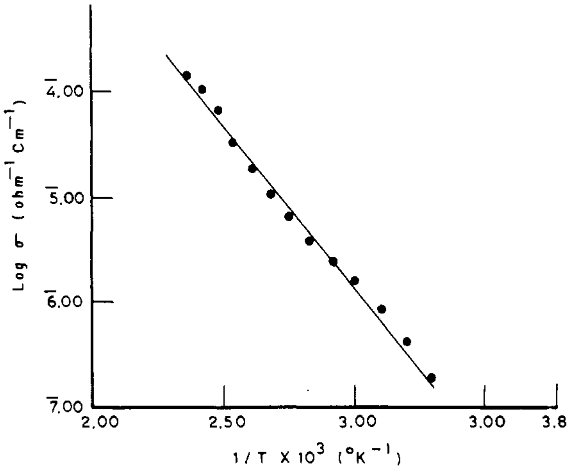


Figure 1. Plot of log σ vs. $1/T$ for $NbCl_5D$-*p*-TDTB.

The Seebeck coefficient (α) measurements in these complexes showed that D-*o*-TDTB, P-*o*-TTB, and P-*p*-TTB complexes are n-type semiconductors (negative α) and DPDTB, DPTB, D-*p*-TDTB, P-*o*-TDTB, and P-*p*-TDTB complexes to be p-type semiconductors (positive α) as shown in Table III.

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