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ONE-DIMENSIONAL COMPOUNDS—II. HALOGEN OXIDATION OF THE PLANAR MACROCYCLIC Ni(II) COMPLEX, $Ni(C_{18}H_{14}N_4)$[1]

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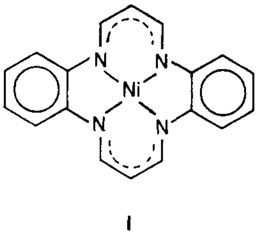
Abstract—Oxidation of the planar four-coordinate complex $Ni(C_{18}H_{14}N_4)$ with halogens (bromine and iodine) results in the formation of new complexes of $Ni(C_{18}H_{14}N_4)I_{1.57}$ and $Ni(C_{18}H_{14}N_4)Br_{2.43}$ stoichiometry. They all form semiconducting solids with specific conductivity 4.4×10^{-3} ohm^{-1}cm^{-1} for $Ni(C_{18}H_{14}N_4)I_{1.57}$ and 1.3×10^{-5} ohm^{-1}cm^{-1} for $Ni(C_{18}H_{14}N_4)Br_{2.43}$. These compounds were characterized by elemental analyses and spectroscopic means; resonance Raman studies on $Ni(C_{18}H_{14}N_4)I_{1.57}$ indicate that iodine is present as I_3^-; EPR studies show an essentially ligand based character of the odd electron, thus the conductive path of these materials may involve π–π and perhaps d–π overlap.

INTRODUCTION

Recently the mixed valence and partially oxidized chain inorganic complexes which have a number of anisotropic properties associated with the one-dimensionality have been vigorously studied[2, 3]. Most of these one-dimensional complexes have contained infinite stacks of closely packed planar molecules and a nonintegral formal oxidation of the constituents, i.e. $K_2Pt(CN)_4X_{0.3} \cdot 3H_2O$ ($X = Cl$, Br)[4], $NiPcI_x$(Pc = phthalocyanine, $x = 0.56$, 1.0, and 1.74)[5], Ni(omtbp)I_x (omtbp = octamethyltetrabenzoporphyrin, $x = 1.05$ and 2.91)[6] $Ni(dpg)_2I_x$ (dpg = diphenylglyoximato, $x = 1.02$)[7, 8] and $Ni(opd)_2I_x$ (opd = *o*-phenylenediimine, $x = 0.97$, 2.57, and 5.79)[1].

One plausible approach for obtaining partially oxidized chain inorganic complexes is the halogen oxidation of the planar macrocyclic Ni(II) complex $Ni(C_{18}H_{14}N_4)$, **I**.



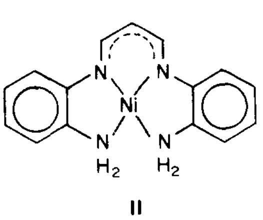
I

The reasons are the following: (1) The planar complex $Ni(C_{18}H_{14}N_4)$ has a stack packing structure with the average interplanar separation of 3.26 Å[9] comparable to the interplanar separations in $Ni(dmg)_2$ (3.25 Å)[10] NiPc (3.24 Å)[11] and $Ni(opd)_2$ (3.3 Å)[12]. The weak interactions of π–π and/or d–π orbitals of adjacent stacked $Ni(C_{18}H_{14}N_4)$ molecules have been proposed to account for the observed differences in the solid state and solution spectra[9]. (2) Iodine would be an especially advantageous oxidant because of the high stability of I_3^- in nonpolar environments and because of the ability of I_3^- to be accommodated in channels in one-dimensional lattices. In this paper we present the preparations, characterizations and conductivities of the new complexes from halogen oxidation of planar macrocyclic Ni(II) complex $Ni(C_{18}H_{14}N_4)$.

EXPERIMENTAL

Bromine water, iodine, Ni(II) acetate, *o*-phenylene-diamine, 1,1,3,3-tetramethoxypropane and common solvents were obtained commercially without further purification. Elemental analyses are reported as obtained from Chun-Shan Institute of Science and Technology. IR spectra (KBr) were recorded on a Perkin Elmer 137 spectrometer. X-Ray powder diffraction data were obtained on a Toshiba ADP-301 diffractometer. Raman spectra were taken as KBr pellet with rotating disc and 5145 Å excitation. Electronic spectra were recorded on a Cary 14 or Beckman DG-B spectrometer. EPR data were obtained with a Varian E9 spectrometer. Electric conductivity measurements were performed on pellets pressed at 400 ψ of dimension about 1 mm using a locally designed two-electrode apparatus.

Preparation of materials. $Ni(C_{18}H_{14}N_4)$, I.[13]. A 4 ml (24.36 m moles) of 1,1,3,3-tetramethoxypropane was added to a solution of 3.03 g (12.18 m moles) of nickel acetate tetrahydrate and 2.63 g (24.36 m moles) of *o*-phenylenediamine in 250 ml of water. This mixture was refluxed for 4 hr. Within the first hour, the orange brown uncyclic complex, **II**, was precipitated. A longer refluxing resulted in the formation of cyclic product I as a deep pink-red precipitate. The product was collected by filtration, washed with water, and vacuum dried. The yield of this analytically pure product was 90%. *Anal.* Calc: C, 62.80; H, 4.08; N, 16.32. Found: C, 62.24; H, 4.52; N, 15.82%.



II

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$Ni(C_{18}H_{14}N_4)I_{1.57}$. A solution of 3.1 g (12.18 m moles) of iodine in 80 ml acetone was added to a slurry of 0.7 g (2.03 m moles) of $Ni(C_{18}H_{14}N_4)$ in 200 ml acetone. After 24 hr stirring, the original pink-red powder was transformed into a black powder which was collected by filtration, washed with acetone, and vacuum dried. *Anal.* Calc: C, 40.41; H, 2.62; I, 37.33. Found: C, 40.06; H, 3.06; I, 37.38.

$Ni(C_{18}H_{14}N_4)Br_{2.43}$. 80 ml of 3% bromine water was added to a slurry of 0.7 g (2.03 m moles) of $Ni(C_{18}H_{14}N_4)$ in 200 ml acetone. After 24 hr stirring, the pink-red powder was transformed into brown powder which was collected by filtration, washed with acetone, and vacuum dried. *Anal.* Calc: C, 40.02; H, 2.59; Br, 36.02. Found: C, 40.26; H, 3.08; Br, 36.27.

Removal of I_2 from $Ni(C_{18}H_{14}N_4)I_{1.57}$. 0.1636 g of $Ni(C_{18}H_{14}N_4)I_{1.57}$ was heated at 100°C under vacuum (about 1 mm Hg) for 1 hr. A residue of 0.1067 g was resulted. The substance which was trapped by liquid nitrogen was identified as iodine by the electronic spectrum ($\nu_{max} = 363$ nm). The loss of the weight of 0.057 g corresponds to the amount of iodine (theoretical value 0.059 g).

RESULT AND DISCUSSION

The synthesis of $Ni(C_{18}H_{14}N_4)$, I, was carried out by refluxing an aqueous solution of *o*-phenylenediamine, 1,1,3,3-tetramethoxypropane, and nickel acetate (2:2:1) according to the method of Dolphin[13]. The product was characterized by elemental analysis, IR, and electronic spectra.

The oxidation of pink-red complex $Ni(C_{18}H_{14}N_4)$ by iodine results in a black solid with a stoichiometry $Ni(C_{18}H_{14}N_4)I_{1.57}$. The stoichiometry was evaluated for different batches of preparations and numerous elemental analyses. Although other stoichiometries $Ni(C_{18}H_{14}N_4)I_x$ ($x < 1.57$) can be obtained by using a lesser amount of I_2, but the spectroscopic evidence (IR spectra and X-ray powder pattern) indicate that these complexes are the mixtures of $Ni(C_{18}H_{14}N_4)$ and $Ni(C_{18}H_{14}N_4)I_{1.57}$. $Ni(C_{18}H_{14}N_4)I_{1.57}$ is stable in solid state for months, but iodine can be removed by warming the solid *in vacuo*. Thus the oxidation reaction is reversible. The analogues were observed in the case of $NiPcI_x$[5] and $Ni(dpg)_2I$[14].

Similarly, the oxidation of $Ni(C_{18}H_{14}N_4)$ by bromine gives a brown solid with stoichiometry $Ni(C_{18}H_{14}N_4)Br_{2.43}$. The compound is stable in solid phase, and bromine can't be removed by warming the solid (up to 180°C) *in vacuo*.

The X-ray powder patterns of the unoxidized material, $Ni(C_{18}H_{14}N_4)$, indicate it is polymorphic. Both forms, which appear as pink-red crystals and have identical IR spectra and have been oxidized by Br_2 to give identical product. X-Ray powder patterns which are present in Table 1 indicate they have different structures and form A appears to be identical with that on which Goedken[9] performed a single crystal structure determination. Iodine oxidation of $Ni(C_{18}H_{14}N_4)$ results in an amorphous solid which does not diffract X-rays but the product obtained from bromine oxidation of $Ni(C_{18}H_{14}N_4)$ does give an X-ray powder pattern (Table 1).

The forms of the halogen in the complexes are of considerable interest. The resonance Raman spectrum of $Ni(C_{18}H_{14}N_4)I_{1.57}$ taken with a rotating disc sample and 5145 Å Ar^+ laser excitation clearly reveals the resonance-enhanced totally symmetric $I\text{-}I\text{-}I^-$ stretch at 108 cm^{-1} and the expected overtone at 215 cm^{-1} [15] (Fig. 1). No I_2 ($\nu = 210$–180 cm^{-1}) is found. So the iodine is present as I_3^-.

The IR spectra of $Ni(C_{18}H_{14}N_4)$, $Ni(C_{18}H_{14}N_4)I_{1.57}$, and $Ni(C_{18}H_{14}N_4)Br_{2.43}$ are slightly different. They are presented in Fig. 2. The characteristic absorptions of $Ni(C_{18}H_{14}N_4)I_{1.57}$ are at 1000 and 1220 cm^{-1}, and of $Ni(C_{18}H_{14}N_4)Br_{2.43}$ at 1230 cm^{-1}. These absorptions are not observed in the spectrum of parent compound, $Ni(C_{18}H_{14}N_4)$.

All complexes are intensely colored in the solid and solution phases. The electronic spectra of these complexes are given in Table 2. These spectra are dominated by intense charge transfer bands in the visible and UV portions of the spectra.

The samples of $Ni(C_{18}H_{14}N_4)I_{1.57}$ and $Ni(C_{18}H_{14}N_4)Br_{2.43}$ in the solid state yield EPR signals which are not observed in the parent compound $Ni(C_{18}H_{14}N_4)$. The signals give *g* values near the free-electron value (2.0023), with about 30G width, may indicate an essentially ligand based character of the odd electron.

The structure of unoxidized $Ni(C_{18}H_{14}N_4)$ has a stack

Table 1. X-Ray powder pattern data for $Ni(C_{18}H_{14}N_4)$ and $Ni(C_{18}H_{14}N_4)Br_{2.43}$

$Ni(C_{18}H_{14}N_4)$		$Ni(C_{18}H_{14}N_4)Br_{2.43}$
form A	form B	
9.025(100)[a, b]	9.118(100)[a]	10.915(69)[a]
6.970(82)	8.845(68)	10.048(34)
6.067(10)	6.151(70)	6.151(10)
5.717(38)	5.471(10)	5.405(12)
4.901(19)	5.096(7)	5.155(12)
4.647(47)	4.874(13)	4.230(57)
4.152(48)	4.353(31)	3.969(21)
3.850(63)	4.040(8)	3.290(100)
3.708(10)	3.834(27)	3.164(20)
3.480(20)	3.633(7)	
	3.427(6)	
	3.278(34)	
	3.008(10)	

a. Filtered Cu-K_α radiation was used, peak was reported as d in Å, relative intensity in parentheses.

b. The powder pattern is consistent with following cell parameters[9]: a= 19.456Å, b= 5.228Å, c= 14.868Å, β= 112.28°

Table 2. The electronic spectra and conductivity parameters for $Ni(C_{18}H_{14}N_4)X_y$.

Compound	Electronic Absorptions in DMSO[a]	Room Temp Conductivity ($ohm^{-1}cm^{-1}$)
$Ni(C_{18}H_{14}N_4)$	500(3400); 466(3800); 426(25600); 403(13400)	$< 1 \times 10^{-10}$
$Ni(C_{18}H_{14}N_4)I_{1.57}$	518(5800); 430(15100)	4.4×10^{-3}
$Ni(C_{18}H_{14}N_4)Br_{2.43}$	525(3760); 439(14900); 426(12600,sh); 412(9800,sh)	1.3×10^{-5}

a. Absorption in nm, extinction coefficient in parentheses, sh=shoulder.

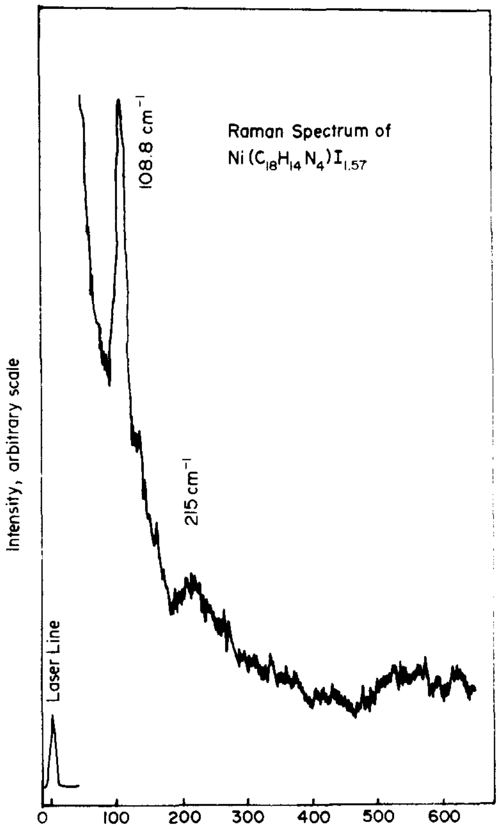

Fig. 1. Raman spectrum of $Ni(C_{18}H_{14}N_4)I_{1.57}$.

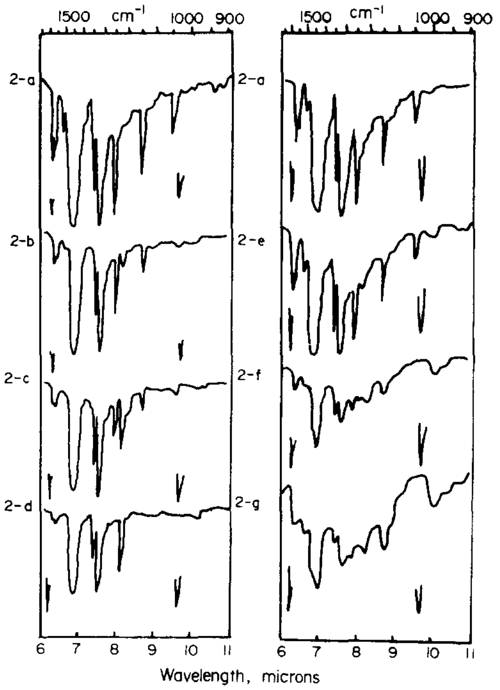

Fig. 2. IR spectra of $Ni(C_{18}H_{14}N_4)X_y$: (a) $y = 0$; (b) $X = Br$, $y \sim 0.3$; (c) $X = Br$, $y \sim 0.7$; (d) $X = Br$, $y = 2.43$; (e) $X = I$, $y \sim 0.8$; (f), (g) $X = I$, $y = 1.57$.

packing structure with a long Ni-Ni distance, 5.23 Å. However the solid state spectrum of $Ni(C_{18}H_{14}N_4)$ is different from its solution spectrum. This suggests d(metal)-π(ligand) or π–π(ligand) interactions between adjacent molecules in the solid state. The halogen oxidations of $Ni(C_{18}H_{14}N_4)$ produce the "hole" on the ligand-center and induce the conductive path which results the conductivity of these materials. As shown in Table 2, the pressed pellet conductivity of $Ni(C_{18}H_{14}N_4)I_{1.57}$ is higher than those of $Ni(opd)_2Ni(edt)_2$ (edt = ethylenedithiolato) ($1.7 \times 10^{-3}\,\Omega^{-1}\,cm^{-1}$)[16], $Ni(dpg)_2I$ ($1.1 \times 10^{-2}\,\Omega^{-1}\,cm^{-1}$)[17], and $C_{34}H_{18}I_{1.52}$ ($C_{34}H_{18}$ = isoviolanthrene) ($1.7 \times 10^{-3}\,\Omega^{-1}\,cm^{-1}$)[18], but smaller than the values of $NiPcI_x$ ($7 \times 10^{-1}\,\Omega^{-1}\,cm^{-1}$)[5].

The results shown above indicate that iodine oxidation of stack-packing d^8 complexes can be used to synthesize one-dimensional conducting materials. In order to understand the electronic and conductive properties of these complexes, further structural studies are still in progress.

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