

ONE-DIMENSIONAL COMPOUNDS—I

IODINE OXIDATION OF BIS(ORTHOPHENYLENEDIIMINE) COMPLEXES OF NICKEL(II)

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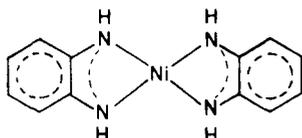
(Received 30 August 1978; in revised form 2 January 1979)

Abstract—Oxidation of $\text{Ni}(\text{opd})_2$ (opd = *o*-phenylenediimine) with iodine results in the formation of a series of new complexes of $\text{Ni}(\text{opd})_2\text{I}_x$ ($x = 0.97, 2.57$ and 5.79) stoichiometry. These compounds were characterized by elemental analyses and spectroscopic means; they all form semiconducting solids with specific conductivity of 10^{-7} – $10^{-4}\Omega^{-1}\text{cm}^{-1}$.

INTRODUCTION

In recent years there has been a great interest in mixed-valent and partially oxidized chain inorganic complexes due to the observation of a variety of anisotropic properties associated with the one-dimensionality of the system [1, 2]. Most of the one-dimensional complexes studied to date have contained infinite stacks of closely packed planar molecules and a nonintegral formal oxidation of the constituents, i.e. $\text{K}_2\text{Pt}(\text{CN})_x\text{X}_{0.3}\cdot 3\text{H}_2\text{O}$ ($X = \text{Cl}, \text{Br}$) [3], NiPcI_x (Pc = phthalocyanine, $x = 0.56, 1.0$, and 1.74) [4], $\text{Ni}(\text{omtbp})\text{I}_x$ (omtbp = octamethyl-tetrabenzoporphyrin, $x = 1.05$ and 2.91) [5], and $\text{Ni}(\text{dpg})_2\text{I}_x$ (dpg = diphenylglyoximate, $x = 1.02$) [6, 7].

Iodine oxidation of bis(*o*-phenylenediimine) complex of Ni(II), I, was reported to yield only dark iodide complex of $\text{Ni}(\text{opd})_2\text{I}$ by Balch and Holm [8]. Miles and



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Wilson [9] synthesized the semiconducting salts from bis(*o*-phenylenediimine) nickel and related cations with several bis(1,2-dithiolato) metal anions. In this paper we present the preparation and characterization of a series of new complexes from iodine oxidation of the bis(*o*-phenylenediimine) complex of Ni(II).

EXPERIMENTAL

Ammonia water, bromine water, nickel(II) chloride, *o*-phenylenediimine, acetone, methanol, and tetrahydrofuran were obtained commercially without further purification. Elemental analyses are reported as obtained from Chun-Shan Institute of Science and Technology. Each sample was analysed at least twice and the average is reported. X-Ray powder diffraction data were obtained on a Toshiba ADP-301 diffractometer. IR spectra (KBr) were recorded on a Perkin-Elmer 137 spectrometer. 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 psi of dimension about 1 mm using locally designed two-electrode apparatus.

Preparation of materials. $\text{Ni}(\text{opd})_2$ [8, 9] (opd = $\text{C}_6\text{H}_4(\text{NH})_2$). A solution of 10 g of nickel chloride hexahydrate in 30 ml of water and 30 ml of concentrate aqueous ammonia was added to a solution of 6 g of *o*-phenylenediimine in 800 ml warm water. This mixture was stirred in an open beaker for 24 hr. A deep blue precipitate formed and was collected by filtration, washed with water, acetone and dried. The yield of this crude product was 70%. Purification was accomplished by soxhlet extraction using acetone. The first extracts of a greenish color were discarded. Once a deep blue extract was obtained, the extraction was allowed to proceed for several days. Fine crystals, ranging in surface color from deep blue to metallic greenish gold, formed during the extraction. These were collected, washed with acetone and vacuum dried. The yield of these fine crystals was 10%.

$\text{Ni}(\text{opd})_2\text{I}_{0.97}$ [8]. A solution of 0.343 g (2.70 mg-atoms) of iodine in 70 ml acetone was added slowly to a slurry of 0.665 g (2.45 m mole) of $\text{Ni}(\text{opd})_2$ in 80 ml acetone. After 20 hr of stirring, the original deep blue crystals were transformed into a brown-black powder which was collected by filtration, washed with acetone, and vacuum dried. *Anal. Calc.*: C, 36.50; H, 3.04; I, 31.32. *Found*: C, 36.00(9); H, 3.21(5); I, 30.89(4).

$\text{Ni}(\text{opd})_2\text{I}_{2.57}$. A solution of 1.56 g (12.25 gm-atoms) of iodine in 80 ml of acetone was added slowly to a slurry of 0.665 g (2.45 m mole) of $\text{Ni}(\text{opd})_2$ in 70 ml of acetone. After 3 hr of stirring, the original deep blue crystals were transformed into black powder which was collected by filtration, washed with acetone twice, and vacuum dried. *Anal. Calc.*: C, 24.11; H, 2.01; I, 54.62. *Found*: C, 24.58(4); H, 1.90(9); I, 55.70(14).

$\text{Ni}(\text{opd})_2\text{I}_{5.79}$. A solution of 3.12 g (24.5 mg-atoms) of iodine in 130 ml of THF was added slowly to a slurry of 0.665 g (2.45 m mole) of $\text{Ni}(\text{opd})_2$ in 70 ml of THF. After 1 hr of stirring, the original deep blue crystals were transformed into a gray black powder which was collected by filtration, washed with acetone twice, and vacuum dried. *Anal. Calc.*: C, 14.31; H, 1.19; I, 73.06. *Found*: C, 14.36(19); H, 1.46(5); I, 73.35(13).

$\text{Ni}(\text{opd})_2$ reacted with bromine. A solution of 10 ml (2.14 m mole) of bromine water was added slowly to a slurry of 0.542 g (2 m mole) of $\text{Ni}(\text{opd})_2$ in 50 ml of acetone. After 3 hr of stirring, the deep blue crystals were transformed into a black powder which was collected by filtration, washed with acetone, and vacuum dried. The elemental analysis was done with non-reproducible data. The ratios of C, H, N vary in each analysis.

RESULTS AND DISCUSSION

Careful evaluation of the elemental analysis data revealed that in addition to the previously described formally stoichiometric 1:1 I/Ni $\text{Ni}(\text{opd})_2\text{I}$ [8], a series of non-stoichiometric complexes can be isolated. A maximum I/Ni ratio of 5.79 was observed. This stoichiometry was confirmed by different batches of preparations and four times of elemental analyses. A slightly excess of

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iodine was used to prepare those complexes, i.e. I/Ni ratio of 1.1 for $\text{Ni}(\text{opd})_2\text{I}_{0.97}$, 5.0 for $\text{Ni}(\text{opd})_2\text{I}_{2.57}$, and 10 for $\text{Ni}(\text{opd})_2\text{I}_{5.79}$. Their extremely low solubility and low stability in solution rendered purification difficult. All complexes are stable in solid phase for months. Oxidation of $\text{Ni}(\text{opd})_2$ with large excess of iodine or equivalent amount of bromine led to the decomposition of $\text{Ni}(\text{opd})_2$. The decomposed products which were brown to black in color, did not diffract X-ray well and had poorly resolved IR spectra were not pursued.

It was reported [9, 10] that neutral bis(*o*-phenylenedimine) nickel(II) was polymorphic, one crystalline form appearing to be dark green and the other gold. Both forms, which have identical IR spectra, have been isolated. X-Ray powder patterns which are presented in Table 1 indicate the dark green form and gold form have different structures and the former appears to be identical with that on which Hall and Soderberg performed a single crystal structure determination [10]. Because of identical *d* for several peaks, samples of both forms prepared may appear to be impure or have cell constants which result in same *d* values.

Iodine oxidation of dark green form of $\text{Ni}(\text{opd})_2$ were characterized by X-ray powder diffraction. All appear to have different structures, to be homogeneous in nature, most of all, they are not mixtures of $\text{Ni}(\text{opd})_2$ and $\text{Ni}(\text{opd})_2\text{I}_{\text{max}}$.

The IR spectra of this series of the complexes vary significantly. All exhibit a N-H stretch at 3250 cm^{-1} , and C=C, C=N stretches in the $1400\text{--}1600\text{ cm}^{-1}$ region. The characteristic region of these compounds is 740--

900 cm^{-1} , the tentative assignment of those bands is out of plane bending of phenylene C-H. The unoxidized form of $\text{Ni}(\text{opd})_2$ has a strong absorption at $730, 745\text{ cm}^{-1}$, where $\text{Ni}(\text{opd})_2\text{I}_{0.97}$ at 790 cm^{-1} , $\text{Ni}(\text{opd})_2\text{I}_{2.57}$ at 770 cm^{-1} , and $\text{Ni}(\text{opd})_2\text{I}_{5.79}$ at $820, 870\text{ cm}^{-1}$. Samples prepared from I/N ratio of 0.5, 2.0, or 6.0 have IR absorptions which are characteristics of $\text{Ni}(\text{opd})_2$ and $\text{Ni}(\text{opd})_2\text{I}_{0.97}$, $\text{Ni}(\text{opd})_2\text{I}_{2.57}$ and $\text{Ni}(\text{opd})_2\text{I}_{5.79}$ respectively. This again indicates the homogeneity of the nonstoichiometric complexes, $\text{Ni}(\text{opd})_2\text{I}_x$ ($x = 0.97, 2.57, \text{ and } 5.79$).

All complexes are intensely colored in the solid and solution phases. The electronic spectra of $\text{Ni}(\text{opd})_2\text{I}_x$ are given in Table 2. These spectra are dominated by intense charge transfer bands in the visible and UV portions of the spectra. No detailed assignment will be made due to the overlap of ligand field and charge transfer absorptions.

All of the samples including unoxidized $\text{Ni}(\text{opd})_2$ yield EPR signals at solid state. The signals of *g* values near the free-electron value (2.0023) with about 25 G width may indicate an essentially ligand based character of the odd electron. The signal of neutral complex, $\text{Ni}(\text{opd})_2$, is not understood and may be due to a small impurity of the cationic species. It should be noted that a large number of diamagnetic phthalocyanine, including Ni phthalocyanine, give sharp isotropic signals. The origin of these "radical" is still not well known [11].

The structure of unoxidized $\text{Ni}(\text{opd})_2$ has a stack packing structure with a long Ni-Ni distance, 4.65 \AA . However the solid state spectrum of $\text{Ni}(\text{opd})_2$ is different

Table 1. X-Ray powder pattern data for $\text{Ni}(\text{opd})_2\text{I}_x$

$\text{Ni}(\text{opd})_2$ Darkgreen	$\text{Ni}(\text{opd})_2$ Gold form	$\text{Ni}(\text{opd})_2\text{I}_{0.97}$	$\text{Ni}(\text{opd})_2\text{I}_{2.57}$	$\text{Ni}(\text{opd})_2\text{I}_{5.79}$
12.804(100) ^{a, b}	12.804(100) ^a	10.276(100) ^a	12.621(65) ^a	9.403(100) ^a
6.414(12)	6.460(28)	6.191(42)	9.403(18)	7.400(17)
4.597(16)	5.826(17)	5.275(25)	8.187(20)	5.536(16)
4.309(40)	4.620(35)	5.094(20)	5.244(42)	4.980(65)
4.208(39)	4.330(45)	4.620(58)	4.718(100)	4.482(60)
3.737(50)	4.228(32)	4.189(22)	4.020(85)	4.112(15)
3.676(25)	3.737(50)	4.075(90)	3.932(60)	4.038(15)
3.588(12)	3.588(42)	3.800(20)	3.768(46)	3.438(77)
3.119(16)	3.425(10)	3.676(16)	3.207(22)	3.325(45)
3.057(6)	3.207(9)	3.588(38)	3.163(8)	3.253(10)
2.939(6)	3.119(42)	3.451(85)	3.057(22)	2.997(50)
2.391(25)	3.057(16)	3.400(35)	2.939(9)	2.948(26)
2.022(13)	2.958(23)	3.207(14)	2.562(8)	2.920(50)
1.980(20)	2.391(14)	3.077(7)	2.514(9)	2.487(30)
1.774(8)	2.297(13)	2.997(18)	2.195(10)	2.441(20)
1.745(9)	2.253(14)	2.902(12)	1.972(8)	2.379(6)
1.721(8)	2.226(5)	2.839(10)		2.314(18)
	2.150(5)	2.745(20)		2.269(7)
	2.022(5)	2.534(20)		2.231(12)
	1.980(5)	2.253(12)		2.150(32)
	1.844(6)	2.221(14)		2.066(17)
	1.777(5)	2.031(12)		1.777(12)
		1.997(14)		

a. Filtered Cu-K α radiation was used, peak was reported as *d* in \AA , relative intensity in parentheses.

b. The powder pattern is consistent with following cell parameters [10]: $a = 5.845, b = 7.485, c = 25.27, \alpha = \gamma = 90^\circ, \beta = 90^\circ 10'$.

Table 2. The electronic spectra and conductivity parameters for Ni(opd)₂I_x

Compound	Electronic Absorptions in DMSO	Room Temp Conductivity $\Omega^{-1}\text{cm}^{-1}$
Ni(opd) ₂	782(4450, sh) ^a ; 732(5900); 645(3250); 560(1700, sh); 510(1550); 445(1600, sh); 415(1700).	1×10^{-8}
Ni(cpdp) ₂ I _{0.97}	785(37500); 645(7500); 510(6950); 385(8725); 345(9950).	7×10^{-7}
Ni(opd) ₂ I _{2.57}	488(1700, sh); 435(4300, sh); 388(5025).	4×10^{-5}
Ni(opd) ₂ I _{5.79}	707(16000) ^b ; 368(48000).	1×10^{-7}

a. Absorption in nm, extinction coefficient in parentheses. sh = shoulder.
b. Acetone as solvent.

from its solution spectrum[9]. This suggests $d(\text{metal})-\pi(\text{ligand})$ or $\pi-\pi(\text{ligand})$ interactions between adjacent molecules in the solid state. The iodine oxidation of Ni(opd)₂ may produce the "hole" either on metal- or ligand-centers and induce the conductive path which results the conductivity of these materials. As shown in Table 2, the pressed pellet conductivities of Ni(opd)₂I_x are comparable to those of Ni(opd)₂·Ni(edt)₂ (edt = ethylenedithiolato) ($1.7 \times 10^{-3} \Omega^{-1}\text{cm}^{-1}$)⁹, Ni(dpg)₂I[12], and others[1].

The results of this study demonstrate the iodine oxidation of square planar d^8 complexes with highly unsaturated ligand is a viable synthetic route to highly conducting mixed valence materials. Further structural studies are in progress and necessary for (i) elucidating the form of the halogen (i.e. I₂, I⁻, I₃⁻ or I₅⁻) in these complexes, (ii) understanding of the electronic and conductive properties of these materials.

Acknowledgement—The authors wish to express their sincere gratitude to Prof. K. H. Houg for his help of X-ray powder patterns measurements and Dr. L. P. Hwang for obtaining EPR

spectra. The work was supported by the National Science Council of the Republic of China, to which thanks are due.

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