

valence AO's, which are different due to the differences in electronegativity and principal quantum number. Therefore, it seems reasonable that other heteroatomic Zintl anions with large differences in their periodic positions might also have a significant ionic component. In a further study<sup>40</sup> we will show that ionic effects are important in understanding the electronic and molecular structure of the  $Tl_2Te_2^{2-}$  anion.

(40) Axe, F. U.; Marynick, D. S., work in progress.

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## Nickel, Cobalt, and Copper Complexes of *o*-Benzenediselenolate: Synthesis and Structural and Magnetic Properties<sup>1</sup>

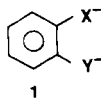
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The *o*-benzenediselenolate ( $bds^{2-}$ , **1b**) ligand is conveniently prepared by sodium borohydride reduction of poly(*o*-phenylene diselenide), which was readily synthesized from *o*-dibromobenzene and sodium diselenide. The  $bds^{2-}$  species was characterized by reaction with thiophosgene to give the known 4,5-benzo-1,3-diselenole-2-thione (**3**) and with the chlorides of nickel, cobalt, and copper to give new diselenolenes isolated as tetra-*n*-butylammonium salts. The new complexes were characterized by elemental analysis, cyclic voltammetry, electronic spectra, static magnetic susceptibility, electron spin resonance (ESR) spectroscopy, and X-ray diffraction, and, where possible, the properties of the  $bds$  complexes were compared to those of the sulfur analogue ( $bdt^{2-}$ , **1a**) or the mixed-sulfur-selenium analogue (**1c**). The intense features of the electronic spectra of the three  $bds$  complexes are observed at energies lower than those reported for the  $bdt$  complexes. The magnetic moments of the Ni- and Co- $bds$  complexes are 1.94 and 3.43  $\mu_B$ , respectively; both are slightly larger than those reported for the  $bdt$  analogues. Polycrystalline samples of the  $Ni(bds)_2^-$  complex have axial ESR signals, and the principal components of the  $g$  tensor are reported. The temperature dependence of the  $g$  values and differential scanning calorimetry provide evidence for a phase transition near 167 K. The ESR spectra of polycrystalline samples of  $Co(bds)_2^-$  at low temperatures reveal the half-field resonance, which indicates that the electronic ground state is a triplet. The principal components of the  $g$  tensors for the Ni- and Co- $bds$  complexes are larger than for the corresponding  $bdt$  complexes, indicating a larger spin-orbit interaction in the heavier chalcogen systems.  $(n-C_4H_9)_4N^+Ni(bds)_2^-$ ,  $C_{28}H_{44}NSe_4Ni$ , is an orthorhombic crystal of space group  $Pbc2_1$  with  $a = 9.904$  (3) Å,  $b = 16.954$  (5) Å,  $c = 19.106$  (6) Å,  $V = 3208.1$  Å<sup>3</sup>, and  $Z = 4$ . The structure was solved by Patterson and difference-Fourier syntheses and reveals a mixed-stack array of cation and anion, precluding cooperative magnetic interactions, as observed in the Curie law behavior of the susceptibility and in the resolved anisotropic  $g$ -tensor ESR spectral envelope. X-ray photographic studies reveal that the Co and Cu  $bds$  complexes are isomorphous to the Ni complex.

### Introduction

This work reports our experimental studies to date of the nickel, cobalt, and copper complexes of *o*-benzenediselenolate (**1b**,  $bds^{2-}$ ).



**1**  
a, X = Y = S; b, X = Y = Se; c, X = S, Y = Se

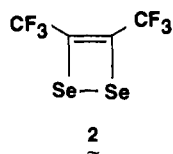
The electrochemical, spectral, magnetic, and crystallographic properties of these new materials are compared to those of their known<sup>4,5</sup> sulfur analogues (**1a**,  $bdt^{2-}$ ), and the consequences of the presence of the heavier chalcogen are discussed. Our convenient synthetic approach to  $bds^{2-}$  was facilitated by an extension of a pattern of chemistry that has proved useful for the synthesis of a variety of both molecular and polymeric organoselenium and -tellurium materials.<sup>1a,b,6</sup> Theoretical studies inquiring into the orbital origin of the spectral and magnetic properties of these materials are presented elsewhere.<sup>1c</sup>

Metal complexes of 1,2-dithiolenes<sup>7</sup> have attracted attention for over two decades as a result of properties such as multistage electron transfer, trigonal-prismatic coordination, novel electronic structures, and, more recently,<sup>8</sup> their solid-state electrical and magnetic properties. While hundreds of metal complexes of 1,2-dithiolenes have been prepared and characterized, relatively few examples of 1,2-diselenolenes are known, and several metal complexes of mixed-sulfur-selenium ligands, including **1c**, have been described.<sup>9</sup>

- (1) Preliminary accounts of portions of this work were presented at: (a) 4th International Conference on the Organic Chemistry of Selenium and Tellurium, Birmingham, U.K., July 25-29, 1983. (b) 35th Southeastern Regional Meeting of the American Chemical Society, Charlotte, NC, Nov 9-11, 1983; Symposium on Solid State Chemistry, Paper 205. (c) International Conference on the Physics and Chemistry of Low Dimensional Synthetic Metals, Abano Terme, Italy, June 17-22, 1984. (d) 188th National Meeting of the American Chemical Society, Philadelphia, PA, Aug 26-31, 1984; Paper ORGN 251. (e) 1984 International Chemical Congress of Pacific Basin Society, Honolulu, HI, Dec 16-22, 1984. (f) Yamada Conference XV in Physics and Chemistry of Quasi-One-Dimensional Conductors, Lake Kawaguchi, Japan, May 26-30, 1986.
- (2) (a) GTE Laboratories Inc. (b) University of Missouri—St. Louis. (c) Cranfield Institute of Technology. (d) Brandeis University.
- (3) (a) 1982 Industrial Undergraduate Research Participant at GTE Laboratories, from Eastern Nazarene College, Quincy, MA 02170. (b) National Science Foundation Industrial Research Participation Program at GTE Laboratories, Summers, 1981-1983; permanent address: Department of Chemistry, Eastern Nazarene College, Quincy, MA 02170.

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In 1970, Davison and Shaw<sup>10</sup> prepared bis(trifluoromethyl)-1,2-diselenetene (**2**) and converted it, via metal carbonyls, to several four- and six-coordinate transition-metal complexes, which were characterized. A structural study<sup>11</sup> of the tris complex



of **2** with molybdenum revealed trigonal-prismatic coordination. A charge-transfer salt was prepared from tetrathiafulvalene and the copper complex of **2**, and its magnetic properties were studied as an example of a system showing a spin-Peierls transition.<sup>12</sup> The Ni and Pt complexes of **2** interact with tetramethyltetraselenafulvalene to give conductive solids that have phase transitions which enhance the conductivity.<sup>13</sup> New procedures for the preparation of methyl- and CF<sub>3</sub>-substituted diselenolenes have been recently reported.<sup>14</sup> An initial description of the preparation of diselenolenes from C<sub>2</sub>Se<sub>5</sub><sup>2-</sup> has appeared.<sup>15</sup>

In contrast to these approaches<sup>10,14,15</sup> several recent reports of the synthesis of metal 1,2-diselenolenes have described less direct methods. There have been two reports<sup>16-18</sup> of 1,2-diselenolene formation via insertion of selenium into a carbon-metal bond, one of which involves formation of a Zr-bds complex.<sup>17</sup> Bolinger and Rauchfuss<sup>18</sup> have reported the addition of activated acetylenes to Cp<sub>2</sub>Ti-pentaselelide complexes. Lewis acids accomplished the conversion of a Rh-CSe<sub>2</sub> complex to a diselenolene.<sup>19</sup> In the present work, new metal diselenolenes were prepared by reaction of bds<sup>2-</sup> with metal chlorides.

## Experimental Section

**General Procedures.** Melting points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Electronic spectra were recorded in dichloromethane solution on a Varian Cary 17 spectrophotometer. Cyclic voltammetry was performed with a Princeton Applied Research Model 173 potentiostat and Model 175 programmer and a Hewlett-Packard 7046A recorder. Measurements were performed in acetonitrile solution with 0.10 M tetraethylammonium perchlorate as support electrolyte and a saturated calomel reference electrode (SCE). Substrate concentrations were 10<sup>-3</sup> M. Static magnetic susceptibility measurements were made on 30-mg samples by using the Faraday technique in the temperature range 20–300 K.

**ESR Spectra.** The measurements were performed on a Varian E-12 spectrometer equipped with a dual cavity using techniques that have been previously described in detail.<sup>20,21</sup> The values of the principal components of the *g* tensors were obtained from the polycrystalline ESR spectra by the method described by Kneubuhl.<sup>22</sup> Spectral simulations using the

**Table I.** Elemental Analysis of (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N<sup>+</sup> Complexes of bds

metal	MP, °C (dec)		% C	% H	% N	% Se	% M
Ni	192 dec	calcd	43.72	5.77	1.82	41.06	7.63
		found	43.21	5.26	1.81	40.00	7.29
Co	196–205 dec	calcd	43.71	5.76	1.82	41.05	7.66
		found	42.66	5.52	1.81	40.66	8.09
Cu	191–194 dec	calcd	43.45	5.73	1.81	40.80	8.21
		found	43.13	5.63	1.71	41.21	8.09

values of the principal components so obtained and the simulation program developed by Jones et al.<sup>23</sup> for a few representative spectra confirmed the applicability of Kneubuhl's method.

A Varian V-4540 temperature controller provided for sample temperature change within ±1 K over the range 120–300 K. The sample temperature was measured by means of a copper-constantan thermocouple placed inside the variable-temperature Dewar and alongside the sample. The 77 K points were measured with a finger Dewar that was inserted into the ESR cavity. The measurements at temperatures below 77 K were made with a modified Air Products Liquid Transfer Cryo-Tip refrigerator, Model LT-3-110. The sample temperature was measured with a chromel vs. gold–0.07% iron thermocouple placed alongside the sample.

**Reaction of *o*-Dibromobenzene with Sodium Diselenide.** To a sodium diselenide reagent, prepared under argon at ca. 100 °C from selenium (15.79 g, 0.2 mol) and sodium (4.60 g, 0.2 mol) in DMF (200 mL), was added *o*-dibromobenzene (23.6 g, 12.1 mL, 0.1 mol). The bath temperature was increased to ca. 140 °C and the mixture kept there for 40 h. The reaction mixture was diluted with an equal volume of methanol, poured into brine (1000 mL), washed with water, sodium sulfide solution, water, and tetrahydrofuran (THF), and vacuum-dried to give a brown solid: mp 117–124 °C (dec); 4.69 g (26% yield). This solid showed infrared absorption at, inter alia, 740 and 285 cm<sup>-1</sup>, and X-ray diffraction showed it to be amorphous except for the presence of small amounts of elemental Se. Anal. Calcd for (C<sub>6</sub>H<sub>4</sub>Se<sub>2</sub>)<sub>x</sub>: C, 30.79; H, 1.72; Se, 67.48. Found: C, 26.21; H, 1.60; Se, 68.91; Br, 2.63. The observed analysis corresponds to C<sub>6.0</sub>H<sub>4.36</sub>Se<sub>2.40</sub>Br<sub>0.09</sub>.

Evaporation of the THF extracts typically gave 1–2 g of an oligomeric material, mp 103–107 °C (dec), whose infrared spectrum was indistinguishable from that of the polymer.

**Conversion of Poly(*o*-diselenobenzene) to 4,5-Benzo-1,3-diselenole-2-thione (**3**).** Solid sodium borohydride (less than 0.50 g) was added to a magnetically stirred suspension of poly(*o*-diselenobenzene) (0.262 g, 1.14 mmol) in methanol (10 mL) and tetrahydrofuran (10 mL) at 0 °C until a homogeneous solution was observed. At this stage, acetone (5 mL) was added, followed by thiophosgene (0.15 g, 1.2 mmol). The reaction mixture was filtered and the filtrate evaporated. The residue was mixed with brine and extracted with dichloromethane. This solution was dried over sodium sulfate and evaporated to give a yellow-orange solid, 195 mg. This solid was recrystallized from 1:4 v/v benzene-hexane to give **3**: 73 mg (23% yield); mp 148–150 °C (lit.<sup>24</sup> mp 147–148 °C).

**Preparation of Tetra-*n*-butylammonium Metal Bis(benzene-1,2-diselenolates).** Solid NaBH<sub>4</sub> (less than 0.50 g) was added to a suspension of poly(*o*-diselenobenzene) (0.468 g, 2 mmol) in methanol (10 mL) at 0 °C until solution occurred. To the solution was added NiCl<sub>2</sub>·6H<sub>2</sub>O (0.238 g, 1 mmol) in methanol (10 mL), and after 1 h at 0 °C, tetra-*n*-butylammonium bromide (0.322 g, 1 mmol) in methanol (10 mL) was added. The mixture was allowed to stir to room temperature over 1 h, to give a black precipitate, 0.563 g (73% yield). Recrystallization was accomplished from a mixture of methylene chloride and absolute ethanol to give dark reflective crystals, mp 192 °C (dec). The X-ray powder diffraction of these crystals reveals the following *d* spacings (Å): 9.58, 8.45, 7.76, 6.86, 5.34, 4.90, 4.36, 4.14, 3.88, and 3.54. These spacings are similar to those reported<sup>4</sup> for the analogous sulfur compound, suggesting a related crystal structure.

The yields for the preparation of the Co and Cu complexes are 80% and 65%, respectively. Table I lists the elemental analyses for the complexes and their decomposition temperatures.

Precession photographs of single crystals of the Co and Cu complexes revealed that their structures are isomorphous with that of the Ni complex described below. X-ray powder diffraction of samples of the Cu complex reveals them to be a mixture of at least two solid phases.

The intense features of the absorption spectra are as follows: ( $\nu_{\max}$ , cm<sup>-1</sup> (log  $\epsilon$ ): Ni(bds)<sub>2</sub><sup>-</sup>, 10 360 (3.51), 11 800 (3.63), 25 600 (3.71),

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**Table II.** Data for the X-ray Diffraction Study of  $[(C_4H_9)_4N][Ni(C_6H_4Se_2)_2]$ 

(A) Crystal Data at 21 (1) °C	
cryst syst: orthorhombic	$Z = 4$
space group: $Pbc2_1$ ( $C_{2v}^5$ , No. 29) <sup>a</sup>	cryst size: $0.05 \times 0.25 \times 0.40$ mm
$a = 9.904$ (3) Å	$\mu = 55.0$ cm <sup>-1</sup> (Mo $K\alpha$ )
$b = 16.954$ (5) Å	fw: 769.3
$c = 19.106$ (6) Å	$\rho_{obsd} = 1.59$ (1) <sup>b</sup> g cm <sup>-3</sup>
$V = 3208.1$ Å <sup>3</sup>	$\rho_{calcd} = 1.59$ g cm <sup>-3</sup>
cell const detern: 12 pairs $\pm(hkl)$ and refined $2\theta$ , $\omega$ , $\chi$ values in the range $20 \leq  2\theta  \leq 22^\circ$ ( $\lambda(\text{Mo } K\alpha) = 0.71073$ Å)	
(B) Measurement of Intensity Data	
radiation: Mo $K\alpha$ , graphite monochromator	
reflecons measd: $+h,+k,+l$ (to $2\theta = 42^\circ$ )	
scan type, speed: $\theta-2\theta$ , 1.95–5.33°/min	
scan range: sym, $[1.6 + \Delta(\alpha_2 - \alpha_1)]^\circ$	
no. of reflecons measd: 1798	
std reflecons: 500, 060, 0, 0, 10 measd after each 50 reflecons; variation $\leq \pm 3\sigma(I)$ for each	
abs cor: empirical, normalized transmission factors 0.506–1.000	
statistical information: $R_s = 0.047$	
(C) Solution and Refinement, with 1029 Data for which $F > 3.92\sigma(F)$	
weighting of reflecons: as before, <sup>c</sup> $p = 0.035$	
soln: Patterson, difference Fourier, routine	
refinement: <sup>d</sup> full-matrix least squares, with anisotropic temp factors for Se, Ni atoms and isotropic temp factors for C, N atoms;	
$R = 0.0645$ , $R_w = 0.0678$ , SDU = 1.29	
structure factor calcn (all 1798 reflections): $R = 0.134$ ; $R_w = 0.077$	
final difference map: 2 peaks, 0.56 and 0.50 e Å <sup>-3</sup> , near Se;	
other peaks random and $\leq 0.4$ e Å <sup>-3</sup>	

<sup>a</sup> Equivalent positions:  $(x, y, z)$ ;  $(x, 1/2 - y, 1/2 + z)$ ;  $(\bar{x}, 1/2 + y, z)$ ;  $(\bar{x}, \bar{y}, 1/2 + z)$ . This is a nonstandard setting of space group  $Pca2_1$ .  
<sup>b</sup> Measured by neutral buoyancy in  $CCl_4-C_2H_4Br_2$ .  
<sup>c</sup> Foxman, B. M.; Mazurek, H. *Inorg. Chem.* **1979**, *18*, 113 and references therein.  
<sup>d</sup>  $R_s = \sum \sigma(|F_o|) / \sum |F_o|$ .  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ . SDU =  $\{\sum w[|F_o| - |F_c|]^2 / (m - n)\}^{1/2}$ , where  $m$  (=1029) is the number of observations and  $n$  (=161) is the number of parameters. For the structure of opposite polarity refinement as above resulted in  $R = 0.0653$ ,  $R_w = 0.0685$ .

33 670 (3.77); Co(bds)<sub>2</sub><sup>-</sup>, 12 510 (3.04), 13 800 (3.30), 14 720 (3.20), 17 680 (3.20), 25 320 (3.85), 29 430 (3.91); Cu(bds)<sub>2</sub><sup>-</sup>, 24 530 (4.28), 31 670 (3.66). These data reveal that the bds complexes absorb at slightly lower energies than their bdt analogues.<sup>4</sup>

**Collection and Reduction of Diffraction Data.** Single crystals of  $(n-C_4H_9)_4N^+Ni(bds)_2^-$  suitable for structural determination were obtained from methylene chloride-ethanol solution, as described above.

Laue photographs and a preliminary X-ray photographic study indicated the crystals to be of acceptable quality. From both the appearance of photographs and a preliminary diffractometric study, it was apparent that little data at angles greater than  $2\theta(\text{Mo } K\alpha) > 42^\circ$  would be "observable". Although a number of crystals were examined, all appeared to have the above diffraction properties. (The Wilson plot temperature factor for the crystals used in the data collection was 5.5 Å<sup>2</sup>.) The precision of the structure analysis is thus limited by the relatively low diffraction quality of the crystals. This is reflected in the high standard deviations of positional parameters, bond lengths, and angles. Nevertheless, the stereochemistries of the anion and cation are well-defined, as is their relationship to one another in the crystal structure. The crystal was then transferred to a Supper No. 455 goniometer and optically centered on a Syntex P2<sub>1</sub> diffractometer. Operations were performed as described previously.<sup>25</sup> The analytical scattering factors of Cromer and Waber were used; real and imaginary components of anomalous scattering for Co and Cl were included in the calculations.<sup>26</sup> Systematic absences ( $k = 2n + 1$  for  $hk0$ ;  $l = 2n + 1$  for  $h0l$ ) indicated space group  $Pbc2_1$  or  $Pbcm$ ; the former choice was suggested by intensity statistics and the appearance of the Patterson function and was confirmed by the structure analysis. Details of the structure analysis, in outline form, are presented in Table II. Atomic coordinates for all atoms appear in Table III.

**Table III.** Atomic Coordinates for  $[(C_4H_9)_4N][Ni(C_6H_4Se_2)_2]^{a,b}$ 

atom	x	y	z	U, Å <sup>2</sup>
Se(1)	0.0010 (3)	0.5912 (2)	0.7424 <sup>c</sup>	0.076 (2)
Se(2)	0.2093 (4)	0.5234 (3)	0.8607 (3)	0.098 (3)
Se(3)	0.2408 (4)	0.6060 (2)	0.6365 (3)	0.084 (3)
Se(4)	0.4470 (3)	0.5380 (2)	0.7555 (3)	0.086 (3)
Ni	0.2263 (4)	0.5677 (3)	0.7489 (4)	0.063 (3)
N	0.206 (2)	0.3056 (14)	0.6343 (15)	0.067 (8)
C(1)	-0.068 (3)	0.558 (2)	0.826 (2)	0.070 (11)
C(2)	-0.212 (4)	0.556 (2)	0.841 (2)	0.094 (13)
C(3)	-0.254 (4)	0.535 (2)	0.908 (2)	0.089 (11)
C(4)	-0.166 (4)	0.505 (3)	0.959 (2)	0.116 (15)
C(5)	-0.025 (4)	0.507 (2)	0.944 (2)	0.108 (14)
C(6)	0.019 (3)	0.531 (2)	0.878 (2)	0.078 (11)
C(7)	0.432 (3)	0.585 (2)	0.616 (2)	0.082 (12)
C(8)	0.469 (4)	0.600 (2)	0.543 (2)	0.099 (13)
C(9)	0.607 (4)	0.581 (2)	0.527 (2)	0.088 (11)
C(10)	0.694 (4)	0.557 (2)	0.579 (2)	0.106 (14)
C(11)	0.655 (4)	0.546 (2)	0.650 (2)	0.090 (12)
C(12)	0.512 (4)	0.562 (3)	0.667 (2)	0.111 (15)
C(13)	0.157 (3)	0.244 (2)	0.583 (2)	0.065 (10)
C(14)	0.088 (3)	0.281 (2)	0.520 (2)	0.088 (12)
C(15)	0.038 (4)	0.206 (2)	0.479 (2)	0.100 (14)
C(16)	-0.020 (5)	0.232 (3)	0.407 (3)	0.16 (2)
C(17)	0.263 (3)	0.264 (2)	0.700 (2)	0.075 (11)
C(18)	0.331 (3)	0.308 (2)	0.756 (2)	0.097 (11)
C(19)	0.382 (4)	0.249 (4)	0.815 (3)	0.15 (2)
C(20)	0.451 (5)	0.297 (3)	0.867 (3)	0.17 (2)
C(21)	0.101 (3)	0.365 (2)	0.658 (2)	0.077 (11)
C(22)	-0.018 (3)	0.315 (2)	0.700 (2)	0.086 (12)
C(23)	-0.130 (5)	0.375 (3)	0.713 (2)	0.14 (2)
C(24)	-0.259 (4)	0.337 (3)	0.748 (3)	0.15 (2)
C(25)	0.315 (3)	0.361 (2)	0.600 (2)	0.081 (11)
C(26)	0.436 (4)	0.308 (2)	0.574 (2)	0.095 (12)
C(27)	0.538 (4)	0.371 (3)	0.543 (2)	0.120 (15)
C(28)	0.670 (4)	0.325 (2)	0.521 (2)	0.102 (13)

<sup>a</sup> Numbers in parentheses in this and subsequent tables indicate uncertainties in the least significant digit. <sup>b</sup> For Ni and Se atoms,  $U = U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$ . <sup>c</sup> Parameter fixed in space group  $Pbc2_1$ .

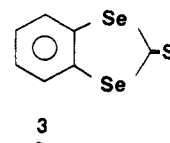
**Table IV.** Reduction Potentials (V vs. SCE) for  $ML_2^- \rightleftharpoons ML_2^{2-}$ 

M	L = bdt <sup>a</sup>	L = Ie <sup>a</sup>	L = bds <sup>b</sup>
Ni	-0.55	-0.53	-0.47
Co	-0.88	-0.90	-0.92
Cu	-0.64	-0.70	-0.75

<sup>a</sup> From ref 9. <sup>b</sup> Present work.

## Results and Discussion

**Synthesis.** While a straightforward, albeit time-consuming, approach to bds<sup>2-</sup> has been described,<sup>24</sup> our method takes advantage of the direct route to selenium and tellurium polymers previously developed<sup>6</sup> and the observation that the facile reduction of diselenides by  $NaBH_4$ <sup>27</sup> may be extended to polymers. Sodium diselenide easily reacts with *o*-dibromobenzene in DMF at 140 °C to give a useful yield of poly(*o*-diselenobenzene). This polymer, which may be stored at room temperature for well over 1 year, is readily reduced by excess  $NaBH_4$  in methanol to bds<sup>2-</sup>, which we have characterized by conversion to the known<sup>24</sup> 4,5-benzo-1,3-diselenole-2-thione (**3**) using thiophosgene. Metal chlorides

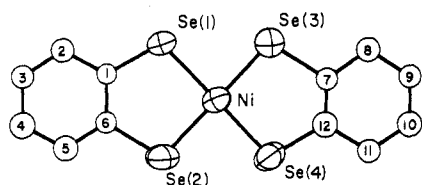


of Ni, Co, and Cu were reacted with bds<sup>2-</sup>, and the products were crystallized in good yield as the tetra-*n*-butylammonium salts of monoanions analogously to the earlier<sup>4</sup> bdt<sup>2-</sup> work.

The decomposition temperatures of these new complexes, listed in Table I, are higher than these reported<sup>4</sup> for their sulfur ana-

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**Figure 1.** Molecular structure and labeling scheme (showing 50% probability ellipsoids for atoms refined with anisotropic temperature factors; 37.5% boundary spheres for atoms refined with isotropic temperature factors) for  $[(C_4H_9)_4N][Ni(C_6H_4Se_2)_2]$ .

**Table V.** Selected Bond Distances (Å) and Angles (deg) for  $[(C_4H_9)_4N][Ni(C_6H_4Se_2)_2]$

Ni–Se(1)	2.270 (5)	C(2)–C(3)	1.39 (6)
Ni–Se(2)	2.270 (9)	C(3)–C(4)	1.40 (6)
Ni–Se(3)	2.249 (9)	C(4)–C(5)	1.42 (6)
Ni–Se(4)	2.247 (5)	C(5)–C(6)	1.40 (6)
Se(1)–C(1)	1.83 (3)	C(7)–C(8)	1.47 (6)
Se(2)–C(6)	1.92 (3)	C(7)–C(12)	1.31 (6)
Se(3)–C(7)	1.96 (3)	C(8)–C(9)	1.44 (5)
Se(4)–C(12)	1.86 (4)	C(9)–C(10)	1.37 (6)
C(1)–C(2)	1.45 (5)	C(10)–C(11)	1.42 (6)
C(1)–C(6)	1.39 (5)	C(11)–C(12)	1.48 (6)
Se(1)–Ni–Se(2)	92.1 (2)	Ni–Se(4)–C(12)	103.6 (14)
Se(1)–Ni–Se(3)	87.7 (2)	C(2)–C(1)–Se(1)	123 (3)
Se(1)–Ni–Se(4)	177.2 (3)	C(6)–C(1)–Se(1)	119 (3)
Se(2)–Ni–Se(3)	177.4 (3)	Se(2)–C(6)–C(1)	121 (3)
Se(2)–Ni–Se(4)	86.9 (3)	Se(2)–C(6)–C(5)	116 (3)
Se(3)–Ni–Se(4)	93.2 (3)	C(8)–C(7)–Se(3)	113 (3)
Ni–Se(1)–C(1)	105.6 (11)	C(12)–C(7)–Se(3)	119 (3)
Ni–Se(2)–C(6)	102.1 (11)	Se(4)–C(12)–C(7)	122 (3)
Ni–Se(3)–C(7)	101.4 (11)	Se(4)–C(12)–C(11)	119 (3)

logues. Davison and Shaw<sup>10</sup> noted that the complexes of **2** that they prepared were much less stable than their dithiolene analogues.

**Electrochemistry.** The redox properties of the new complexes were probed by cyclic voltammetry, and the observed reversible reduction potentials are given in Table IV along with those for the bdt and **1c** systems. While the  $Ni(bds)_2^-$  complex is reduced at a slightly lower potential than that of bdt and **1c**, the Co and Cu complexes are reduced at slightly higher potentials than the related systems.

The  $Ni(bds)_2^-$  complex also exhibited an additional quasi-reversible process, possibly related to  $Ni(bds)_2^0$ . At a sweep rate of 100 mV s<sup>-1</sup>, an anodic peak was observed at +0.2 V and a cathodic peak was noted at +0.38 V.

**Crystal and Molecular Structure of  $(n-C_4H_9)_4N^+Ni(bds)_2^-$ .** The molecular structure of the complex anion is shown in Figure 1. Bond distances in the 1,2-diselenolate anion (Table V) are similar to those observed<sup>17a</sup> in  $(n^5-t-BuC_5H_4)_2ZrSe_2C_6H_4$ , while the chelate ring angles in the present case reflect the smaller "bite" required by the Ni atom. The Ni–Se distances appear to be normal; the range (2.247–2.270 Å) is shorter than that observed in four-membered ring systems, such as nickel(II) diethyldiselenocarbamate,<sup>28</sup> 2.317 (2) Å. The  $NiSe_4$  fragment is approximately planar, with Ni 0.045 (5) Å out of the plane; the  $C_6H_4$  fragments are bent away from this plane at an average of 6.5°. In the structure of the related anion,  $Ni(bdt)_2^-$ , two independent anions both possess crystallographic  $C_i$  symmetry and are thus planar;<sup>29</sup> angles subtended at Ni, S, and Se are quite similar in the  $S_2$  and  $Se_2$  analogues.

The crystal structure (Figure 2) shows that the anions are well-isolated from one another by the tetrabutylammonium cations; this is consistent with the observed magnetic susceptibility data and ESR measurements. Accordingly, the shortest Se–Se contact is 5.57 Å, and the shortest intermolecular contact to Ni is 4.04 Å, to C(21) on the tetrabutylammonium cation. There are no

**Table VI.** Principal Components of the *g* Tensors at  $T = 300$  K for  $(n-Bu)_4N^+Ni(bds)_2^-$  and Related Compounds

<i>g</i>	ligands		
	bdt <sup>a</sup>	mixed S/Se <sup>b</sup>	bds <sup>a</sup>
<i>g</i> <sub>1</sub>	2.1204	2.228	2.1723
<i>g</i> <sub>2</sub>	2.1087	2.086	2.1723
<i>g</i> <sub>3</sub>	2.0271	2.034	2.0765
$\langle g \rangle$	2.0854	2.116	2.1404

<sup>a</sup> This work. <sup>b</sup> Reference 9a.

**Table VII.** Linear Least-Squares Analysis of the Isotropic *g* Values for Ni- and Co(bdt)<sub>2</sub><sup>-</sup> and Ni- and Co(bds)<sub>2</sub><sup>-</sup><sup>a</sup>

metal	$\langle g \rangle_0$	<i>b</i>
Ni	2.0703	0.3235
Co	2.0706	0.2700

<sup>a</sup> Spin-orbit interaction energies ( $S_0$ ) = 0.050 and 0.22 eV for sulfur and selenium, respectively.

**Table VIII.** Atomic Spin-Orbit Interaction Contributions to the Isotropic *g* Values for Ni- and Co(bdt)<sub>2</sub><sup>-</sup> and Ni- and Co(bds)<sub>2</sub><sup>-</sup>

metal	$\Delta g$ from metal	$\Delta g$ from 4 S	$\Delta g$ from 4 Se
Ni	0.0680	0.0151	0.0701
Co	0.0683	0.0135	0.0594

intermolecular Ni–Se contacts at distances less than 6.0 Å.

**Magnetic Properties. (a) Static Susceptibility.** The magnetic moments of the Co- and  $Ni(bds)_2^-$  complexes are 3.43 and 1.94  $\mu_B$ , respectively, corresponding to two and one unpaired electrons. The moments of the analogous bdt complexes are 3.27 and 1.83  $\mu_B$ , respectively.<sup>4</sup> The Cu complex of bds is diamagnetic, analogous to its bdt analogue.<sup>4</sup> The Ni and Co complexes of bds follow Curie's law over the temperature range studied.

**(b) Electron Spin Resonance (ESR) of  $Ni(bds)_2^-$  and  $Ni(bdt)_2^-$ .** Polycrystalline samples of the tetra-*n*-butylammonium salts of  $Ni(bds)_2^-$  and  $Ni(bdt)_2^-$  were studied by ESR over the temperature range of 77–300 K. The 300 K spectra are displayed in Figure 3. For the bds salt, the *g* tensor and the ESR spectral envelopes of polycrystalline samples demonstrate that it possesses axial symmetry over the entire temperature range of the study. However, between 150 and 160 K, there is an abrupt change in the value of the perpendicular component of the *g* tensor over the same temperature range.

The change in value of the perpendicular component of the *g* tensor of  $Ni(bds)_2^-$ , shown in Figure 4, is not reflected by a corresponding change in the static magnetic susceptibility. It is, however, independent of the solvent mixture from which the complex is crystallized. The data shown in Figure 4 are independent of whether  $CH_2Cl_2-C_2H_5OH$ ,  $CH_2Cl_2-CH_3OH$ , or  $ClCH_2CH_2Cl$  is the crystallizing medium. This point is of interest in connection with apparent phase transitions induced by the presence of the solvent of crystallization.<sup>30</sup> Differential scanning calorimetry of the complex reveals a transition at 167 K with a heat of transition equal to 1.09 kJ mol<sup>-1</sup>. The freezing point of ethanol is 156 K, in the range of the *g*-tensor change in Figure 4. Certain TCNQ salts prepared in acetonitrile exhibit transitions at 229 K (the melting point of acetonitrile) but reveal no transition when crystallized from other solvents.<sup>30</sup> On the basis of our results, we conclude that the  $(n-Bu)_4N^+Ni(bds)_2^-$  salt undergoes a phase transition in this temperature range that is not related to solvent melting. Low-temperature X-ray studies are planned to study this conclusion.

Table VI compares the values of the principal components of the *g* tensor of  $(n-C_4H_9)_4N^+Ni(bds)_2^-$  and  $(n-C_4H_9)_4N^+Ni(bdt)_2^-$  with those of a nickel salt prepared from a mixed-sulfur–selenium ligand. The isotropic *g* values in Table VI can be analyzed as shown in Figure 5, which shows the isotropic *g* value for the three

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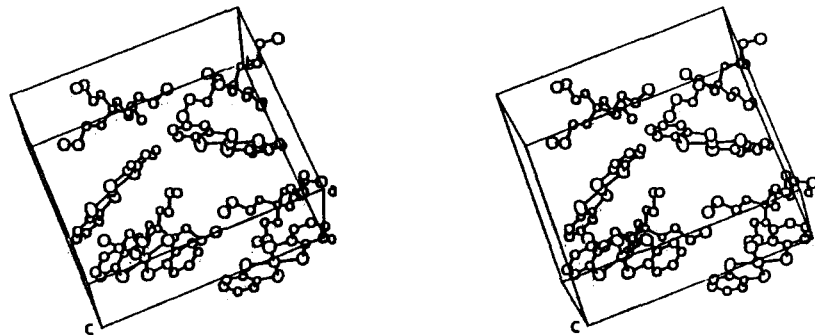


Figure 2. Perspective view of the unit cell contents of  $[(C_4H_9)_4N][Ni(C_6H_4Se_2)_2]$ .



Figure 3. ESR spectral envelopes (300 K) of polycrystalline  $(C_4H_9)_4N^+Ni(bds)_2^-$  (A) and  $(C_4H_9)_4N^+Ni(bdt)_2^-$  (B). The spectra are shown in the correct magnetic field relationship, i.e., the field increases left to right.

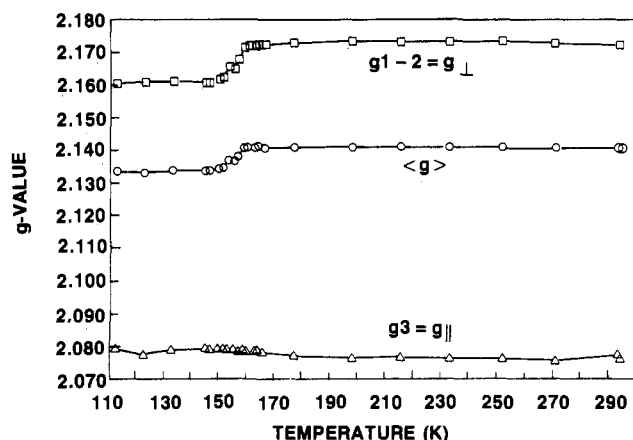


Figure 4. Plot of the  $g$  tensors vs. temperature (K) for polycrystalline  $Ni(bds)_2^-$ .

nickel complexes described in Table VI plotted against the mean spin-orbit interaction parameter of the chalcogen atoms in the complex. An analysis of these data can be made by using eq 1.

$$g = g_0 + b \cdot S_0 \quad (1)$$

In this equation,  $g_0$  is the isotropic  $g$  value for the homologue for which the chalcogen atoms have spin-orbit interaction energies equal to zero,  $b$  is the slope, and  $S_0$  is the mean spin-orbit interaction energy of the chalcogen atoms of the appropriate salt. The results are shown in Table VII. This analysis also allows one to estimate the contribution to the isotropic  $g$  tensor from the spin-orbit interaction energy due to the presence of the nickel ion in the salt, which is approximately the difference between  $g_0$  and the free-electron  $g$  value. The value so obtained is shown in Table VIII.

(c) ESR of  $Co(bds)_2^-$  and  $Co(bdt)_2^-$ . Polycrystalline samples of the tetra-*n*-butylammonium salts of  $Co(bds)_2^-$  and  $Co(bdt)_2^-$  were studied by ESR over the temperature ranges of 10–300 and 77–300 K, respectively. Both salts possess orthorhombic  $g$  tensors. The temperature range over which the  $Co(bds)_2^-$  salt could be accurately studied was limited. Thus, the temperature dependence of its  $g$  tensor could not be determined. However, the  $Co(bdt)_2^-$  salt has a slightly temperature dependent  $g$  tensor. The values of the principal components of the  $g$  tensor for the cobalt  $bds$  and  $bdt$  salts are shown in Table VI.

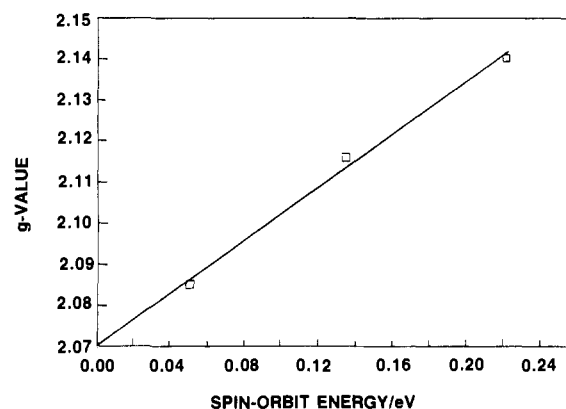


Figure 5. Plot of the isotropic  $g$  values for the  $Ni(ligand)_2^-$  series vs. the spin-orbit interaction energies for the respective chalcogen atoms in the ligand.

Table IX. Principal Components of the  $g$  Tensors for  $(n-Bu)_4N^+Co(bdt)_2^-$  and  $Co(bds)_2^-$

$g$	ligands	
	$bdt^a$	$bds^{b,c}$
$g_1$	2.1942	2.246
$g_2$	2.0445	2.096
$g_3$	2.0136	2.045
$\langle g \rangle$	2.0841	2.130

<sup>a</sup> Temperature 300 K. <sup>b</sup> Temperature 10 K. <sup>c</sup> The  $\Delta m = 2$  transition occurs at  $H_{hf} = 1547$  G ( $H_{ff} = 3119$  G) for  $\nu = 9.298$  GHz.

The same analysis of the  $g$  values for the cobalt salts as for the nickel salts can be performed. The results are shown in Tables VII and VIII. We do not believe there is any significance to the observation that the Co and Ni intercepts shown in Table VI and the  $\Delta g$ 's due to the metal atom shown in Table VII are essentially equal. We note the Co complex possesses a triplet ground state that has two electrons distributed over two molecular orbitals, whereas the Ni complex has one electron in one molecular orbital. However, this point, among others, is being investigated theoretically and will be reported at a later date.

Also observed at low temperatures for  $Co(bds)_2^-$  is a half-field resonance ( $\Delta m = 2$ ) at 1547 G ( $H_{ff} = 3119$  G). This is in agreement with the static magnetic susceptibility measurements, which show that the electronic ground state is a triplet. A half-field resonance was not observed for  $Co(bdt)_2^-$ . The analysis of de Groot and van der Waals<sup>31</sup> allows one to estimate the value of  $D$ , the spin-spin dipolar coupling parameter, and hence the mean separation of the two electrons that form the triplet state from the knowledge of the value of the magnetic field at which the half-field ( $H_{hf}$ ) resonance occurs relative to the value at which the full-field ( $H_{ff}$ ) resonance occurs. This analysis yields a value for  $D^*$  of  $0.039$  cm<sup>-1</sup> ( $\sim 341$  G) and hence a mean separation of

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**Table X.** Comparison of Ratios of Magnetic Moments to Ratios of Squares of Isotropic  $g$  Values for Isoelectronic Transition-Metal Complexes

metal	$\mu(\text{bds})/\mu(\text{bdt})$	$[(g)(\text{bds})/g(\text{bdt})]^2$
Co	1.049	1.045
Ni	1.060	1.053

4.3 ( $\pm 0.5$ ) Å. The significance of this observation lies in the fact that the unpaired electron density cannot be primarily on the transition-metal atom (i.e., the Co) alone or distributed over the entire complex, including the organic ligands, but rather primarily distributed over the transition metal and the four chalcogen atoms.

The  $g$  tensors, which are summarized in Table IX, show that the electronic ground states of the cobalt complexes do not arise from orbitally degenerate states (i.e., from states possessing E-type symmetry) because the  $g$  tensors are orthorhombic.

(d) **General Observations.** The magnetic moment varies as the square of the isotropic  $g$  value. Thus, it is of interest to compare the ratios of the magnetic moments of isoelectronic pairs of complexes (e.g.,  $\text{Ni}(\text{bds})_2^-$  and  $\text{Ni}(\text{bdt})_2^-$ )<sup>4</sup> with the ratio of the

square of their respective isotropic  $g$  values taken from Tables VI and IX. The results are shown in Table X. The agreement is quite good.

ESR studies and the static magnetic susceptibility data on  $\text{Co}(\text{bds})_2^-$  and  $\text{Ni}(\text{bds})_2^-$  clearly indicate that there is no cooperative magnetic interaction between paramagnetic spin sites in either complex (i.e., each spin state acts independently of all of its neighbors). This is consistent with the observed crystal structure of these complexes, in which each magnetic entity is physically rather far from its nearest neighbor.

**Registry No.** 3, 87143-01-9; **1b**, 107658-47-9; (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N<sup>+</sup>Ni(bds)<sub>2</sub><sup>-</sup>, 96030-04-5; (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N<sup>+</sup>Co(bds)<sub>2</sub><sup>-</sup>, 96030-06-7; (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N<sup>+</sup>Cu(bds)<sub>2</sub><sup>-</sup>, 96042-48-7; (*n*-Bu)<sub>4</sub>N<sup>+</sup>Ni(bdt)<sub>2</sub><sup>-</sup>, 15077-51-7; (*n*-Bu)<sub>4</sub>N<sup>+</sup>Co(bdt)<sub>2</sub><sup>-</sup>, 15186-37-5; (*o*-C<sub>6</sub>H<sub>4</sub>Se)<sub>x</sub>, 107658-48-0; *o*-dibromobenzene, 583-53-9; sodium diselenide, 39775-49-0; thiophosgene, 463-71-8.

**Supplementary Material Available:** Tables SI–SIII, listing thermal parameters, nonessential bond lengths and angles, and least-squares planes, and a figure showing the geometry and labeling scheme for the tetrabutylammonium ion (4 pages); a table of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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## Extended X-ray Absorption Fine Structure (EXAFS) Studies of a Soluble Chevrel Phase

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The structure of the one-dimensional chains within  $\text{Li}_2\text{Mo}_6\text{Se}_6$  in propylene carbonate solution was investigated by means of extended X-ray absorption fine structure (EXAFS) spectroscopy and compared to that of the crystalline  $\text{M}_2\text{Mo}_6\text{Se}_6$  ( $\text{M} = \text{Li, In, Tl}$ ) phases. The Fourier-transformed Mo K-edge EXAFS displays three peaks at  $r' = 2.4, 3.5,$  and  $4.2$  Å ( $r'$  = distance uncorrected for phase shift), while the Fourier-transformed Se K-edge EXAFS exhibits four peaks at  $r' = 2.3, 3.5, 4.3,$  and  $4.9$  Å. The Mo EXAFS was modeled with a theoretical single-electron single-scattering EXAFS equation using a total of five backscattering pairs, and the Se EXAFS was fit with a total of six backscattering pairs. The similarity of the solution- and solid-phase EXAFS spectra of  $\text{Li}_2\text{Mo}_6\text{Se}_6$  indicates that the bulk of the Mo and Se atoms in solution experience an environment indistinguishable from that within the solid phase; this is consistent with retention of, essentially, unaltered  $(\text{Mo}_3\text{Se}_3)_\infty^{\text{I}}$  strands in solution.

Polynuclear  $\text{Mo}^{\text{II}}\text{-Y}$  ( $\text{Y} = \text{S, Se}$ ) clusters have been the object of much study in recent years, with most attention focused on the Chevrel phases  $(\text{Mo}_6\text{Y}_8)^{n-}$ ,  $n = 0, 2$  because of their intriguing superconductivity properties.<sup>2</sup> In the search for novel superconductors in the  $\text{Mo}^{\text{II}}\text{-chalcogenide}$  system, new clusters formed by the linear confacial condensation of discrete  $\text{Mo}_6$  octahedra were discovered.<sup>3</sup> These cluster compounds are often difficult to characterize, both physically and structurally, due to their amorphous nature and insolubility. EXAFS has proved useful in initially characterizing the most recalcitrant of these compounds. EXAFS characterization of the one-dimensional chains observed in  $\text{M}_2\text{Mo}_6\text{Se}_6$  solid phases and its recently reported solution phase<sup>4</sup> was initiated to assess structural modifications within the chains resulting from interchain interactions and crystal-packing forces.

Transmission electron microscopy (TEM) results<sup>4</sup> suggest that in  $10^{-3}\text{--}10^{-4}$  M solutions the linear chains of  $(\text{Mo}_3\text{Se}_3)_\infty^{\text{I}}$  form bundles that are roughly 20 Å in diameter and 10 μm in length. We report herein the first Mo and Se K-edge EXAFS of the solubilized phase and its comparison with the EXAFS of the corresponding solid phases of the one-dimensional chains within  $\text{M}_2\text{Mo}_6\text{Se}_6$  ( $\text{M} = \text{Li, In, Tl}$ ). Because of the large number of coordination shells within 5 Å of the source atom and the large number of components of each coordination shell, the EXAFS of the extended cluster compounds proved difficult to analyze. The demonstration that the spectra are tractable to analysis and an examination of *intra-* and *interchain* interactions in the crystalline and solution phases is of importance to an understanding of these low-dimensional materials.

### Experimental Section

Samples of solid  $\text{Tl}_2\text{Mo}_6\text{Se}_6$ ,  $\text{In}_2\text{Mo}_6\text{Se}_6$ , and  $\text{Li}_2\text{Mo}_6\text{Se}_6$  and solutions of  $\text{Li}_2\text{Mo}_6\text{Se}_6$  dissolved in propylene carbonate ( $\text{Li}_2\text{Mo}_6\text{Se}_6/\text{PC}$ ; ca. 0.01 *m*) were prepared as described.<sup>5</sup> The samples are air-stable except for  $\text{Li}_2\text{Mo}_6\text{Se}_6$  and its solutions, which were handled under an  $\text{N}_2$  atmosphere. Mo and Se K-edge (19.999 and 12.652 keV, respectively) absorption spectra were recorded in transmission mode at room temperature at the Cornell High Energy Synchrotron Source (CHESS). The K-edge absorption spectra of  $\text{Li}_2\text{Mo}_6\text{Se}_6$  and  $\text{Li}_2\text{Mo}_6\text{Se}_6/\text{PC}$ , which are typical for the compounds studied, are shown in Figures 1 and 2.

The data reduction procedure for the compounds studied here is similar to that reported previously by us.<sup>6-8</sup> The EXAFS analysis utilized

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