

**Figure 4.** Plot of experimental values of  $\text{MoO}_2(\text{Et}_2\text{NCS}_2)_2$  vs. predicted values from the computer fits for four different initial concentrations: ( $\diamond$ )  $9.5 \times 10^{-5}$  M; ( $\square$ )  $5.7 \times 10^{-5}$  M; ( $\triangle$ )  $4.5 \times 10^{-5}$  M,  $I_0 = 3.2 \times 10^{-9}$  einstein; ( $\circ$ )  $6.5 \times 10^{-5}$  M,  $I_0 = 5.4 \times 10^{-9}$  einstein.

signals ( $^1g_{\text{iso}} = 1.978$ ,  $^1a_{\text{iso}} = 37$  G;  $^2g_{\text{iso}} = 1.966$ ,  $^2a_{\text{iso}} = 39$  G;  $^3g_{\text{iso}} = 1.953$ ,  $^3a_{\text{iso}} = 41$  G). These signals are stable over

hours in degassed solution. Ultraviolet and infrared spectroscopy indicates that  $\text{MoO}_2(\text{Et}_2\text{NCS}_2)_2$  reacts with  $\text{Et}_2\text{NCS}_2\text{H}$  to form  $\text{Mo}_2\text{O}_3(\text{Et}_2\text{NCS}_2)_4$  in moderate yields. The ESR of the reaction mixture shows two Mo(V) signals at  $g_{\text{iso}} = 1.965$ ,  $a_{\text{iso}} = 39$  G and  $g_{\text{iso}} = 1.977$ ,  $a_{\text{iso}} = 37$  G.

On the basis of the above results we postulate that at low temperatures hydrogen atom abstraction from either solvent or other ligands becomes competitive with other possible ligand radical reactions.

### Conclusions

We have demonstrated for the first time the ability of a Mo(VI) complex of the very common form  $\text{MoO}_2\text{L}_2$  to do redox photochemistry. The primary photostep can be assumed to be thermodynamically uphill since step 3 must be included in the ultimate mechanism. The driving force toward decomposition appears to be the stability of  $(\text{Et}_2\text{NCS}_2)_2$ . The radical chain mechanism provides an efficient kinetic pathway to the final products. The RK4 method is a useful way for the kineticist to eliminate possible reaction steps.

**Acknowledgment.** We thank Mr. Reuel Van Atta for experimental assistance, Mr. Howard Wagenblast of the Mellon Institute for EDAX and X-ray diffraction results, and Professor Patrick M. McCurry for helpful discussions. Financial support of the Office of Basic Energy Sciences, Department of Energy, is gratefully acknowledged.

Registry No. 1, 18078-69-8.

Contribution from the Department of Chemistry, Northeastern University, Boston, Massachusetts 02115

## Thiocyanate-Bridged Transition-Metal Polymers. 3. Structure and Low-Temperature Magnetic Properties of $\text{Ni}(\text{bpy})(\text{NCS})_2$ : An Infinite-Chain Ferromagnetic Insulator

BRUCE W. DOCKUM and WILLIAM MICHAEL REIFF\*

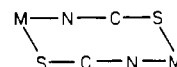
Received October 12, 1981

The new compound  $\text{Ni}(\text{bpy})(\text{NCS})_2$  (bpy = 2,2'-bipyridine) has been prepared by the stepwise thermolytic decomposition of  $\text{Ni}(\text{bpy})_3(\text{NCS})_2 \cdot 3\text{H}_2\text{O}$  with  $\text{Ni}(\text{bpy})_2(\text{NCS})_2$  as an intermediate product. Studies by optical and infrared spectroscopy indicate that  $\text{Ni}(\text{bpy})(\text{NCS})_2$  is a polymer with six-coordinate metal centers and bridging thiocyanate anions. The structure is proposed to have either zigzag or helical chains each containing stepwise, metal-thiocyanate bridging groups. Variable-temperature magnetic susceptibility measurements in a field of 1.69 kG show the presence of relatively strong ferromagnetic interactions, i.e., a rapid increase in the moment until a maximum value of  $8.4 \mu_B$  is obtained at  $\sim 3.5$  K. The susceptibility exhibits a very rapid rise until  $\sim 2$  K at which it levels off. From the susceptibility behavior, it is shown that  $\text{Ni}(\text{bpy})(\text{NCS})_2$  orders as a ferromagnet with  $T_c = 3.5$  K.

### Introduction

In previous articles,<sup>1-4</sup> we have reported the structural and magnetic properties for some first transition-metal series diimine compounds having the empirical formula  $\text{M}(\text{bpy})(\text{NCS})_2$  (M is divalent Fe, Co, Mn, and Cu; bpy = 2,2'-bipyridine). X-ray powder patterns of each system have revealed

structural isomorphism between the manganese, iron, and cobalt compounds and a different pattern for  $\text{Cu}(\text{bpy})(\text{NCS})_2$ .<sup>5</sup> The available spectral data including optical, infrared, EPR, and Mössbauer spectroscopy indicate that  $\text{Fe}(\text{bpy})(\text{NCS})_2$ <sup>2,4</sup> and its Mn and Co analogues<sup>3</sup> are polymers in which all the thiocyanate groups are bridging forming zigzag chains of stepwise, near-orthogonal



bridging groups. The structure of these compounds is believed

- (1) W. M. Reiff, H. Wong, B. Dockum, T. Brennan, and C. Cheng, *Inorg. Chim. Acta.*, **30**, 69 (1978).
- (2) W. M. Reiff, B. Dockum, C. Torardi, H. Wong, and S. Foner, paper presented at the 168th National Meeting of the American Chemical Society, Atlantic City, NJ, Sept 1974, No. 82.
- (3) B. W. Dockum and W. M. Reiff, paper presented at the Second Joint Conference of the CIC and ACS, Montreal, Canada, May 1977, No. 9.
- (4) B. W. Dockum and W. M. Reiff, *Inorg. Chem.*, **21**, 391, 1406 (1982).

- (5) B. W. Dockum, Ph.D. Dissertation, Department of Chemistry, Northeastern University, Boston, MA, 1977.

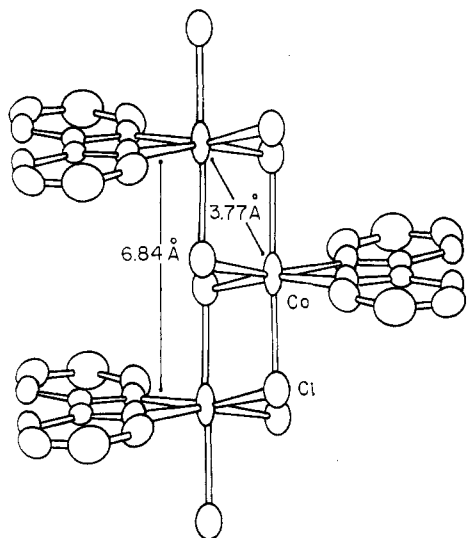
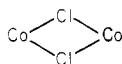


Figure 1. Basic structure of  $\text{Co}(\text{bpy})\text{Cl}_2$  as determined from X-ray diffraction study.

to be similar to that recently determined for  $\text{Co}(\text{bpy})\text{Cl}_2$  in a single-crystal study save for the more complex three-atom bridging groups<sup>6</sup> (Figure 1). The latter groups



are found to be stepwise and near orthogonal. From a Mössbauer spectroscopy study between 130 and 200 K,<sup>4</sup>  $\text{Fe}(\text{bpy})(\text{NCS})_2$  is found to undergo a structural phase transition believed to be similar in nature of the  $\alpha \rightarrow \gamma$  polymer displacement transition of the linear-chain  $\text{Co}(\text{py})_2\text{Cl}_2$  that occurs at 154 K.<sup>7,8</sup> For  $\text{Fe}(\text{bpy})(\text{NCS})_2$ , the transition is the result of changes in the metal-thiocyanate bridging framework from a symmetric to an asymmetric form with decreasing temperature. The presence of a similar phase transition for  $\text{Mn}(\text{bpy})(\text{NCS})_2$  and  $\text{Co}(\text{bpy})(\text{NCS})_2$  was not observed.<sup>3</sup> In contrast, the structure of  $\text{Cu}(\text{bpy})(\text{NCS})_2$  has been proposed to be similar to that for  $\text{Cu}(\text{en})(\text{NCS})_2$  ( $\text{en}$  = ethylenediamine).<sup>1</sup> The structure of the latter compound consists of double "ladderlike" chains containing two types of copper atoms bridged by half the available thiocyanate anions through unusual tricoordinate sulfur atoms.<sup>9</sup>

We have found that the magnetic-exchange behavior for metal monodiiimine polymers is quite variable depending on the nature of the bridging halide or pseudohalide. For example,  $\text{Fe}(\text{bpy})(\text{NCS})_2$  shows evidence of low-dimensional antiferromagnetic exchange as implied by the presence of a maximum in  $\chi_M$  at  $\sim 18$  K and a negative  $\theta$  value. However, there is no evidence of cooperative, 3-D antiferromagnetic ordering to as low as 1.5 K. The magnetic behavior for the analogous manganese and cobalt compounds,<sup>3</sup> similar to  $\text{Fe}(\text{bpy})(\text{NCS})_2$ , shows the presence of antiferromagnetic exchange. In contrast,  $\text{Fe}(\text{bpy})\text{Cl}_2$ <sup>10,11</sup> and its phenanthroline

Table I. Elemental Analysis of the Nickel Compounds

compd	calcd			obsd		
	% C	% H	% N	% C	% H	% N
$\text{Ni}(\text{bpy})_2(\text{NCS})_2$	54.23	3.31	17.25	54.27	3.24	17.30
$\text{Ni}(\text{bpy})(\text{NCS})_2$	43.53	2.44	16.92	43.36	2.34	16.81
$\text{Ni}(\text{py})_2(\text{NCS})_2$	43.27	3.03	16.82	43.59	3.60	15.93

analogue,  $\text{Fe}(\text{phen})\text{Cl}_2$ ,<sup>10,12</sup> are insulating 3-D ferromagnets with Curie temperatures ( $T_C$ ) of  $\sim 3.8$  and 4.5 K, respectively. In preliminary reports of the magnetic properties of the monodiiimine halides,  $\text{Co}(\text{bpy})\text{Cl}_2$ <sup>5</sup> and  $\text{Mn}(\text{bpy})\text{Cl}_2$ <sup>13</sup> ferro-magnetic ordering was also observed. Both  $\text{Cu}(\text{bpy})\text{Cl}_2$  and the corresponding thiocyanate exhibit relatively weak anti-ferromagnetic exchange interactions.

During the preparation and characterization of the preceding monobipyridyl thiocyanate polymers,  $\text{Ni}(\text{bpy})(\text{NCS})_2$  was prepared. X-ray powder studies of  $\text{Ni}(\text{bpy})(\text{NCS})_2$  indicate that the powder pattern of  $\text{Ni}(\text{bpy})(\text{NCS})_2$  is different from those for the Mn, Fe, and Co monobipyridyl analogues and  $\text{Cu}(\text{bpy})(\text{NCS})_2$  is different from those for the Mn, Fe, and Co monobipyridyl analogues and  $\text{Ni}(\text{bpy})(\text{NCS})_2$ , indicating a different space group and possibly a structure different from the latter systems. In this investigation, we present the details of further spectroscopic and magnetic characterization of  $\text{Ni}(\text{bpy})(\text{NCS})_2$ , whose existence, to our knowledge, has not been previously reported.

### Experimental Section

The metal salts used for the preparation were reagent grade and were used without further purification. The ligands used for the preparation were obtained from the following sources: 2,2'-bipyridine, Columbia Organic Chemical Co., Inc.; 2,9-dimethyl-1,10-phenanthroline hemihydrate, Aldrich Chemical Co., Inc.; pyridine, J. T. Baker Chemical Co. They were not further purified before use. The chemical analyses were performed by Galbraith Laboratories, Knoxville, TN. The results of elemental analysis for all compounds, except where noted, are presented in Table I.

**Synthesis of  $\text{Ni}(\text{bpy})(\text{NCS})_2$ .**  $\text{Ni}(\text{bpy})(\text{NCS})_2$  was prepared by the high-vacuum thermolysis of  $\text{Ni}(\text{bpy})_3(\text{NCS})_2 \cdot 3\text{H}_2\text{O}$  (pink), which loses water and 1 mol of 2,2'-bipyridine to form a product that analyzed to be  $\text{Ni}(\text{bpy})_2(\text{NCS})_2$  (light green). The second mole of bipyridine is lost between 230 and 240 °C, forming a more intensely colored green product,  $\text{Ni}(\text{bpy})(\text{NCS})_2$ . For both steps of the thermolysis, the heating was stopped when the difference between the actual and theoretical bipyridine weight loss was  $\pm 3$  mg.

The starting material  $\text{Ni}(\text{bpy})_3(\text{NCS})_2 \cdot 3\text{H}_2\text{O}$  was prepared with the method of Morgan and Burstall.<sup>14</sup>

**$\text{Ni}(\text{py})_2(\text{NCS})_2$ .** This compound as well as the subsequent dimethylphenanthroline complexes were prepared for comparative optical spectra studies. The compound was prepared from the following method. Anhydrous nickel chloride ( $\text{NiCl}_2$ ; 2.5812 g, 19.91 mmol) was mixed with 50 mL of absolute methanol to form a slurry which was heated to dissolve as much  $\text{NiCl}_2$  as possible. A potassium thiocyanate ( $\text{KNCS}$ ; 3.9126 g, 40.26 mmol) solution in 50 mL of absolute methanol was added to the still hot  $\text{NiCl}_2$  slurry. The heating of the resulting mixture was continued in order to reduce the volume by half and saturate it with nickel salt. After the mixture was filtered to remove KCl and undissolved nickel salts, a 10-mL pyridine (1.5479 g, 19.56 mmol) solution in absolute methanol was added slowly to the green nickel thiocyanate solution with stirring. The resulting mixture turned blue in color, and no precipitate formed after 10 min. It was necessary to reduce the volume of the mixture in order to obtain a precipitate. After the precipitate was filtered off, the mother liquid was cooled in ice to see if more product could be recovered. After 15 min, more solid was retrieved; it was filtered and was added to the original product. The precipitate was washed three times with

- (6) W. M. Reiff, H. Wong, G. Eisman, W. Rode, and B. Foxman, paper presented at the 179th National Meeting of the American Chemical Society, Houston, March 1980, No. 22.
- (7) P. J. Clarke and H. J. Milledge, *Acta Crystallogr., Sect. B*, **B31**, 1543 (1975).
- (8) P. J. Clarke and H. J. Milledge, *Acta Crystallogr., Sect. B*, **B31**, 1554 (1975).
- (9) J. Garaj, M. Dunaj-Jurco, and O. Lindgren, *Collect. Czech. Chem. Commun.*, **36**, 3863 (1971).
- (10) W. M. Reiff, B. Dockum, C. Torardi, S. Foner, R. B. Frankel, and M. A. Weber, "Extended Interactions Between Metal Ions in Transition Metal Complexes", ACS Symp. Ser. No. 5, American Chemical Society, Washington, D.C., 1974, Chapter 15, p 205.
- (11) W. M. Reiff, B. Dockum, M. A. Weber, and R. B. Frankel, *Inorg. Chem.*, **14**, 800 (1975).

- (12) W. M. Reiff and S. Foner, *J. Am. Chem. Soc.*, **95**, 260 (1973).
- (13) W. M. Reiff, H. Wong, and C. Cheng, paper presented at the 173rd National Meeting of the American Chemical Society, New Orleans, March 1977, No. 139.
- (14) G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 2213 (1931).

water and twice with diethyl ether. This blue-green product obtained analyzed as Ni(py)<sub>2</sub>(NCS)<sub>2</sub>.

**$\alpha$ - and  $\beta$ -Ni(2,9-dmp)Cl<sub>2</sub> (2,9-dmp = 2,9-Dimethyl-1,10-phenanthroline).**  $\alpha$ -Ni(2,9-dmp)Cl<sub>2</sub> was prepared by the method reported by Preston and Kennard.<sup>15</sup> The following quantities were used: 3.368 g (14.17 mmol) of NiCl<sub>2</sub>·6H<sub>2</sub>O and 0.3016 g (1.388 mmol) of 2,9-dimethyl-1,10-phenanthroline hemihydrate, and they were dissolved in absolute ethanol. A yellow precipitate was formed on mixing.

$\beta$ -Ni(2,9-dmp)Cl<sub>2</sub> was prepared by heating  $\alpha$ -Ni(2,9-dmp)Cl<sub>2</sub> in a tube furnace to 180 °C under vacuum at which temperature a violet material formed. The observed near-infrared-visible spectra agreed with those found previously.<sup>15</sup>

**Physical Measurements.** Magnetic susceptibility measurements were determined with the Faraday method. A description of the Faraday apparatus has been reported elsewhere.<sup>16</sup> The apparatus was calibrated with HgCo(NCS)<sub>4</sub>.<sup>17-19</sup> Diamagnetic corrections to the susceptibility of Ni(bpy)(NCS)<sub>2</sub> were calculated from Pascal's constants:<sup>20</sup> for Ni(bpy)(NCS)<sub>2</sub>,  $\chi_{\text{diam}} = 180 \times 10^{-6}$  cgsu mol<sup>-1</sup>.

Optical spectra were taken on a Cary 14 recording spectrometer. Samples were prepared as mulls with use of Halocarbon 25-5S grease (Halocarbon Products Corp., Hackensack, NH) with finely ground sample which was suspended between two UV-grade quartz plates.

Infrared spectra between 4000 and 200 cm<sup>-1</sup> were obtained on a Perkin-Elmer Model 567 spectrometer. Samples were taken either as mineral oil mulls on a single NaCl plate or as a single polyethylene disk or as KBr pellets.

X-ray powder patterns were determined with a General Electric XRD-6 powder diffractometer. ESR spectra were determined at ambient temperature and 77 K with a Bruker Model ER-10 X-band spectrometer. No ESR signals were detectable at either temperature for Ni(bpy)<sub>2</sub>(NCS)<sub>2</sub> or Ni(bpy)(NCS)<sub>2</sub>.

## Results and Discussion

As was mentioned in the Introduction, the powder patterns of Ni(bpy)(NCS)<sub>2</sub> are not similar to those for the corresponding manganese, iron, cobalt, and copper analogues, implying a different space group for Ni(bpy)(NCS)<sub>2</sub>. Attempts to grow single crystals of Ni(bpy)(NCS)<sub>2</sub> from a variety of solvents resulted in mixtures in which Ni(bpy)(NCS)<sub>2</sub> would not dissolve or dissolves with decomposition to other products. The difference in the powder pattern for Ni(bpy)(NCS)<sub>2</sub> may also indicate different structure types from those observed for other monodiiimine compounds. The reasonable possibilities for a structure for Ni(bpy)(NCS)<sub>2</sub> are as follows: (a) a structure consisting of discrete molecules of Ni(bpy)(NCS)<sub>2</sub>, i.e., a four-coordinate nickel monomer, either square-planar or more likely pseudotetrahedral; (b) a structure consisting of discrete clusters containing pairs of five-coordinate nickel centers resulting from bridging thiocyanate anions, i.e., a dimer with the formula [Ni(bpy)(NCS)<sub>2</sub>]<sub>2</sub> (a dimer containing six-coordinate nickel requires the presence of four thiocyanate bridges which has not, to our knowledge, ever been observed and will not be considered); (c) an infinite zigzag-type polymer structure similar to those proposed for the Mn, Fe, and Co analogues or a Cu(en)(NCS)<sub>2</sub> type<sup>9</sup> structure as proposed for Cu(bpy)(NCS)<sub>2</sub> but with a different packing of atoms within the unit cell; (d) an infinite helical polymer chain containing six-coordinate nickel centers. Since single-crystal X-ray diffraction studies have not as yet proven feasible, a comparative spectral and magnetic study of Ni(bpy)(NCS)<sub>2</sub> and related systems was made to choose between the different structure possibilities presented above. These measurements are presented below.

Table II. Optical Spectral Band Maxima (cm<sup>-1</sup>) of Nickel Imine and Diimine Compounds

compd <sup>a</sup>	band max (rel intens) <sup>b</sup>	ref
Ni(bpy)(NCS) <sub>2</sub>	~6600 (sh), 8800 (m), 11 300 (m), 12 000 (m), 13 800 (m), 17 400 (m)	c
Ni(py) <sub>2</sub> (NCS) <sub>2</sub>	8500 (s), 11 200 (w), 13 460 (w), 16 600 (s), 20 700 (s, sh)	c
Ni(py) <sub>2</sub> Cl <sub>2</sub>	6000, 8400, ~12 200 (sh), 13 900, ~22 200, 24 100	23
Ni(py) <sub>2</sub> Br <sub>2</sub>	5800, 8000, ~11 600 (sh), 13 700, ~19 800 (sh), ~21 400, 23 500	23
Ni(quin) <sub>2</sub> Cl <sub>2</sub>	~6000, 7550, 12 000, 13 150, ~19 200, 22 700	23
Ni(bpy)Cl <sub>2</sub>	7040 (1421 nm), 9259 (1080 nm), ~12 050 (830 nm), 14 025 (713 nm), 23 940 (436 nm)	24
$\alpha$ -Ni(dmp)Cl <sub>2</sub>	6990 (w), 10 600 (w), 13 750 (m), 20 000 (m), 23 300 (vs), 26 300 (sh)	c
$\beta$ -Ni(dmp)Cl <sub>2</sub>	7850 (sh), 10 250 (m), 11 650 (sh), 12 000 (sh), 16 300 (m), ~18 500 (sh), 20 100 (s), 24 200 (sh)	c

<sup>a</sup> bpy = 2,2'-bipyridine, py = pyridine, quin = quinoline, and dmp = 2,9-dimethyl-1,10-phenanthroline. <sup>b</sup> Key: w = weak, m = medium, s = strong, vs = very strong, sh = shoulder, brd = broad. <sup>c</sup> This work.

**Optical Spectra.** The band maxima for the room-temperature optical spectra of Ni(bpy)(NCS)<sub>2</sub> and other nickel compounds containing imine and diimine ligands are presented in Table II. The other nickel systems are examples of nickel diimine systems which are known to have four-, five-, or six-coordinate nickel centers. In this section, the optical spectra of Ni(bpy)(NCS)<sub>2</sub> will be compared with those of these systems.

The violet  $\beta$ -form of Ni(2,9-dmp)Cl<sub>2</sub> is a pseudotetrahedral monomer containing the endobidentate ligand 2,9-dimethyl-1,10-phenanthroline (2,9-dmp), which is isomorphous with Fe(2,9-dmp)Cl<sub>2</sub> and Co(2,9-dmp)Cl<sub>2</sub>.<sup>21</sup> Since the ground state for tetrahedral nickel(II) is <sup>3</sup>T<sub>1</sub>, there should be three spin- and Laporte-allowed transitions of relatively high intensity. These are observed at 10 250 cm<sup>-1</sup> [<sup>3</sup>T<sub>1</sub>(F) → <sup>3</sup>T<sub>2</sub>(F)], 16 300 cm<sup>-1</sup> [<sup>3</sup>T<sub>1</sub>(F) → <sup>3</sup>A<sub>2</sub>(F)], and 20 100 cm<sup>-1</sup> [<sup>3</sup>T<sub>1</sub>(F) → <sup>3</sup>T<sub>1</sub>(P)]. The other bands in the spectrum are probably due to a reduction of symmetry of the electronic states and/or spin-forbidden bands. If the spectrum of Ni(bpy)(NCS)<sub>2</sub> is compared with that for  $\beta$ -Ni(2,9-dmp)Cl<sub>2</sub> (see Table II), there is little, if any, similarity between the positions and relative intensities of the band maxima for each spectrum. The differences between the two spectra effectively eliminate the possibility of a monomeric, four-coordinate nickel chromophore for Ni(bpy)(NCS)<sub>2</sub>.

The structure of  $\alpha$ -Ni(2,9-dmp)Cl<sub>2</sub>, determined from single-crystal X-ray measurements, is a dimer with the formula [Ni(2,9-dmp)Cl<sub>2</sub>]<sub>2</sub> and contains five-coordinate nickel atoms.<sup>15,22</sup> The nickel coordination environment is best described as a distorted trigonal bipyramid<sup>22</sup> generated by the bridging chlorine atoms, the diimine nitrogens, and the non-bridging, terminal chlorine atoms. If the optical spectrum of Ni(bpy)(NCS)<sub>2</sub> and  $\alpha$ -Ni(2,9-dmp)Cl<sub>2</sub> are compared (see Table II), both spectra show a low-energy band at ~7000 cm<sup>-1</sup>. However, at that point the similarity between spectra ends. Ni(bpy)(NCS)<sub>2</sub> shows a strong band near 8800 cm<sup>-1</sup> not found in the spectrum for  $\alpha$ -Ni(2,9-dmp)Cl<sub>2</sub>. The highest energy d-d band occurs at ~17 400 cm<sup>-1</sup> for Ni(bpy)(NCS)<sub>2</sub> while no band is found in  $\alpha$ -Ni(2,9-dmp)Cl<sub>2</sub> in these regions (see Table II). Furthermore, above 18 000 cm<sup>-1</sup> no other higher energy bands, other than a charge-transfer band, occur

(15) H. S. Preston and C. H. L. Kennard, *J. Chem. Soc. A*, 2682 (1969).

(16) W. M. Reiff and C. Cheng, *Inorg. Chem.*, **16**, 2097 (1977).

(17) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 419 (1958).

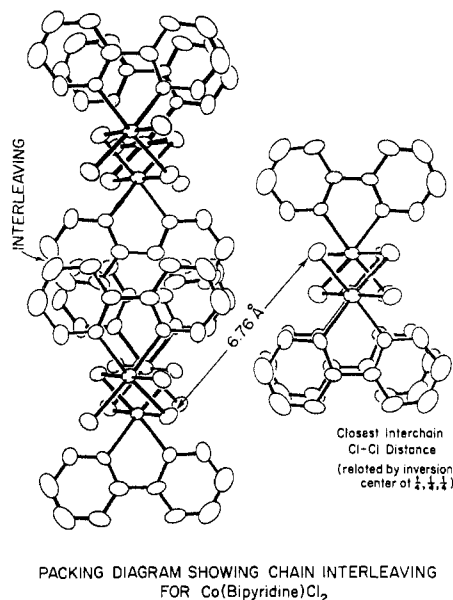
(18) H. St. Rade, *J. Phys. Chem.*, **77**, 424 (1974).

(19) D. B. Brown, V. H. Crawford, J. W. Hall, and W. E. Hatfield, *J. Phys. Chem.*, **81**, 1303 (1977).

(20) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry", J. Lewis and R. G. Wilkins, Eds., Wiley, New York, 1960, p 403.

(21) H. S. Preston, C. H. L. Kennard, and R. A. Plowman, *J. Inorg. Nucl. Chem.*, **30**, 1463 (1968).

(22) R. J. Butcher and E. Sinn, *Inorg. Chem.*, **16**, 2334 (1977).



**Figure 2.** Partial packing diagram for Co(bpy)Cl<sub>2</sub>.

for Ni(bpy)(NCS)<sub>2</sub> while two relatively intense bands at 20 000 and 23 600 cm<sup>-1</sup> are found in the spectrum for α-Ni-(2,9-dmp)Cl<sub>2</sub>. These results effectively eliminate *simple dimerization* and a five-coordinate nickel chromophore for Ni(bpy)(NCS)<sub>2</sub>.

Band maxima for some six-coordinate infinite *linear-chain* nickel polymers such as Ni(py)<sub>2</sub>Cl<sub>2</sub>,<sup>23</sup> Ni(py)<sub>2</sub>Br<sub>2</sub>,<sup>23</sup> Ni(quin)<sub>2</sub>Cl<sub>2</sub> (quin = quinoline,<sup>23</sup> Ni(bpy)(Cl)<sub>2</sub>,<sup>24</sup> and Ni(py)<sub>2</sub>(NCS)<sub>2</sub> (see Table II) clearly show band patterns similar to those of Ni(bpy)(NCS)<sub>2</sub> and suggest a six-coordinate nickel chromophore for the latter system. In each of the halogen polymers, two bands are found at lower energies, one at ~6500 cm<sup>-1</sup> and the other at ~8500 cm<sup>-1</sup>, and a series bands in the range 11 500–14 000 cm<sup>-1</sup> as for Ni(bpy)(NCS)<sub>2</sub>. The optical spectrum, of Ni(py)<sub>2</sub>(NCS)<sub>2</sub> shows bands at 8500 cm<sup>-1</sup>, two shoulders at 11 200 and 13 500 cm<sup>-1</sup>, and a band at 16 650 cm<sup>-1</sup>. These bands are also similar to those found for Ni(bpy)(NCS)<sub>2</sub>. X-ray powder studies for Ni(py)<sub>2</sub>Cl<sub>2</sub><sup>25</sup> and the related complexes Ni(py)<sub>2</sub>(NCS)<sub>2</sub><sup>26</sup> and Ni(bpy)Cl<sub>2</sub><sup>24</sup> show that they are isomorphous and probably isostructural to their cobalt analogues. The structure of Co(py)<sub>2</sub>Cl<sub>2</sub> consists of *linear chains of six-coordinate cobalt atoms* connected by bridging chlorine atoms with trans pyridine groups above and below the chains.<sup>7</sup> The structure of Co(py)<sub>2</sub>(NCS)<sub>2</sub> is similar to that of Co(py)<sub>2</sub>Cl<sub>2</sub>, but with the cobalt atoms bridged by the thiocyanate anions.<sup>27</sup> On the other hand, Co(bpy)Cl<sub>2</sub> consists of *stepwise, zigzag chains of cobalt atoms* bridged by chlorine atoms, a structure imposed on the chain as a consequence of the *cis* ligation of bipyridine nitrogen atoms<sup>6</sup> (Figures 1 and 2). Hence, differences in the spectra of the above compounds are the result of variations in the ligation and geometry of the nickel coordination center. The optical spectra of Ni(bpy)(NCS)<sub>2</sub> indicate the presence of a NiN<sub>2</sub>N<sub>2</sub>S<sub>2</sub> chromophore similar to that found in Ni(py)<sub>2</sub>(NCS)<sub>2</sub>, but it is expected to differ somewhat because of *cis* metal-imine-nitrogen coordination. The preceding optical

**Table III.** Infrared Spectral Results (cm<sup>-1</sup>)<sup>a</sup> for Ni(bpy)(NCS)<sub>2</sub> and Its Precursor Ni(bpy)<sub>2</sub>(NCS)<sub>2</sub>

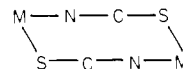
Ni(bpy)(NCS) <sub>2</sub>	Ni(bpy) <sub>2</sub> (NCS) <sub>2</sub>	assignt
2136 (sh)		
2124	2085	N-C, str, ν <sub>1</sub> (NCS)
2106	2059	
2072 (sh)		
810 (w)	815	
772 (sh)	794	C-S str, ν <sub>3</sub> (NCS)
	781	
	496	
465	474	N-C-S bend, δ (NCS)
	420 (sh)	
412	414	bpy band
	305 (sh)	
291 (sh)		
284	285	Ni-N(NCS) str
278		
268		Ni-N(bpy) str
252 (sh)		

<sup>a</sup> Relative intensities: w = weak, m = medium, s = strong, vs = very strong, sh = shoulder.

spectra are included as Figures 1s and 2s of the supplemental material for this publication.

**Infrared Spectra.** The infrared spectra for Ni(bpy)(NCS)<sub>2</sub> and its precursor Ni(bpy)<sub>2</sub>(NCS)<sub>2</sub> are compared in Table III. The table includes spectral data measured near 2000 cm<sup>-1</sup> which represents the C-N stretching mode of the thiocyanate anion. The position of the bands in this region can give information about the metal-thiocyanate bonding in each compound. These bands are located at 2124 and 2106 cm<sup>-1</sup> for Ni(bpy)(NCS)<sub>2</sub> consistent with *metal-nitrogen and metal-sulfur* bonding found for thiocyanate-bridged polymers. This conclusion is confirmed in the infrared spectra of the thiocyanate-bridged nickel polymers NiL<sub>2</sub>(NCS)<sub>2</sub> (L is pyridine, quinoline, β- and γ-picoline, and *p*-toluidine) where the C-N stretch is found between 2100 and 2125 cm<sup>-1</sup>.<sup>28</sup> In contrast, the C-N stretching bands are found at 2085 and 2059 cm<sup>-1</sup> for the monomeric Ni(bpy)<sub>2</sub>(NCS)<sub>2</sub>, as expected for compounds with only nitrogen-bonded, isothiocyanate anions.<sup>28</sup> This information along with the optical spectral data indicates that Ni(bpy)(NCS)<sub>2</sub> is a polymer with bridging thiocyanate anions resulting in six-coordinate metal centers. The infrared spectra of Ni(bpy)(NCS)<sub>2</sub> and Ni(bpy)<sub>2</sub>(NCS)<sub>2</sub> are shown in Figure 3s of the supplemental material.

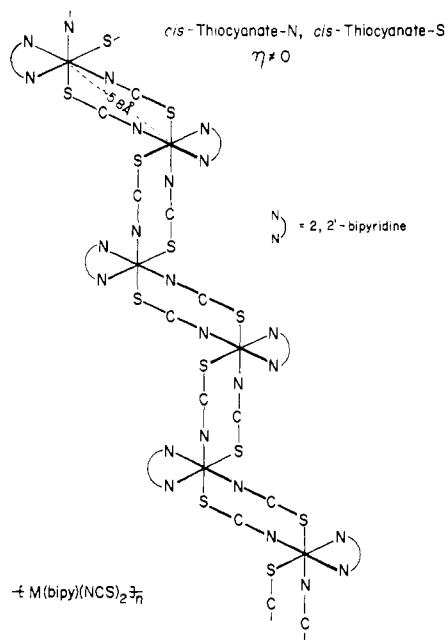
**Structure of Ni(bpy)(NCS)<sub>2</sub>.** The spectral data presented above indicates that Ni(bpy)(NCS)<sub>2</sub> is a polymer whose structure consists of extended chains of six-coordinate nickel atoms. One structure possibility is the *zigzag* chain proposed for Fe(bpy)(NCS)<sub>2</sub>,<sup>2,4</sup> Mn(bpy)(NCS)<sub>2</sub>,<sup>3</sup> and Co(bpy)(NCS)<sub>2</sub>.<sup>3</sup> This chain can be generated from



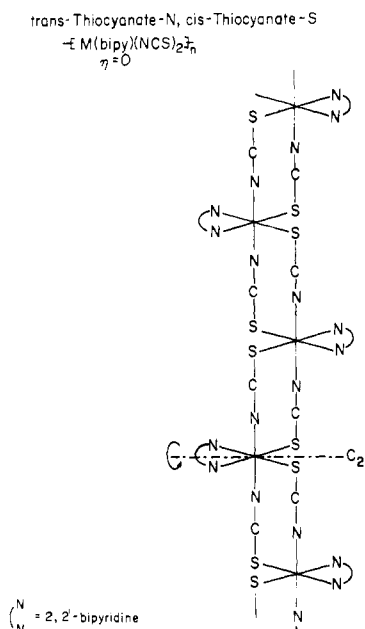
bridging groups as found in the linear-chain polymers Co(py)<sub>2</sub>(NCS)<sub>2</sub>,<sup>27</sup> Cu(py)<sub>2</sub>(NCS)<sub>2</sub>,<sup>27</sup> Co(NCS)<sub>2</sub>·3H<sub>2</sub>O,<sup>29</sup> and Ni(tim)<sub>2</sub>(NCS)<sub>2</sub> (tim = 2-thioimidazolidinone).<sup>30</sup> However, there is a stepwise arrangement of the bridging groups that are near-orthogonal to each other. This arrangement is a consequence of the *cis* coordination of the 2,2'-bipyridine nitrogen atoms. On the basis of magnetically perturbed Mössbauer studies of Fe(bpy)(NCS)<sub>2</sub>, the local coordination environment is nonaxial, and the M N<sub>2</sub>N<sub>2</sub>S<sub>2</sub> core has C<sub>1</sub> local

- (23) D. M. L. Goodgame, M. Goodgame, and M. J. Weeks, *J. Chem. Soc.*, 5194 (1964).  
 (24) R. H. Lee, E. Griswold, and J. Kleinberg, *Inorg. Chem.*, **3**, 1278 (1964).  
 (25) N. S. Gill, R. S. Nyholm, G. A. Barley, T. I. Christie, and P. J. Pauling, *J. Inorg. Nucl. Chem.*, **18**, 88 (1961).  
 (26) V. I. Belova, Ya. K. Syrkin, and A. V. Babaeva, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **6**, 423 (1961).  
 (27) M. A. Porai-Koshits and G. N. Tishchenko, *Sov. Phys.—Crystallogr. (Engl. Transl.)*, **4**, 216 (1960).

- (28) R. J. H. Clark and C. S. Williams, *Spectrochim. Acta*, **22**, 1081 (1966).  
 (29) F. H. Cano, S. Garcia-Blanco, and A. Guerrero-Laverat, *Acta Crystallogr., Sect. B*, **B32**, 1526 (1976).  
 (30) M. Nardelli, G. F. Gasparri, A. Musatti, and A. Manfredotti, *Acta Crystallogr.*, **21**, 910 (1966).



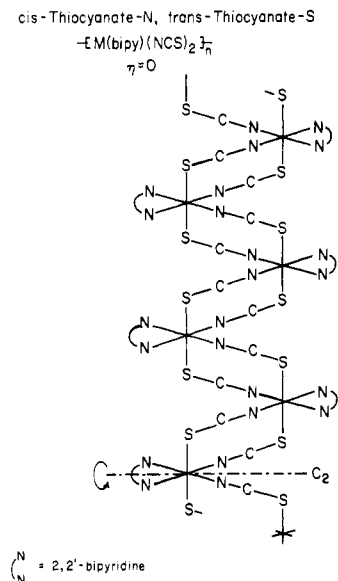
**Figure 3.** Zigzag structure 1 containing cis thiocyanate sulfur and cis thiocyanate nitrogen atoms.



**Figure 4.** Zigzag structure 2 containing cis thiocyanate sulfur and trans thiocyanate nitrogen atoms.

symmetry.<sup>2</sup> The structure proposed for the iron, manganese, and cobalt analogues is represented in Figure 3.

There are two other zigzag-type structures that can be proposed based on the data give above. These structures are presented in Figures 4 and 5. With the assumption that the imine nitrogens from bipyridine lie in the equatorial plane of the metal octahedra with the requirements that the imine nitrogens are cis to each other and the nitrogen and sulfur atoms from different thiocyanate groups that bridge the *same* metal atoms also lie *cis* to each other, the differences between the zigzag chains shown are the result of differences in the coordination position of the sulfur atoms of bridging thiocyanate anions that bond to *different* metal atoms. In the first structure, the sulfur atoms lie in the plane of the octahedra while in the second, they are located in the *trans* positions above and below the equatorial plane of the octahedra. The symmetry of the local coordination environment for each of



**Figure 5.** Zigzag structure 3 containing trans thiocyanate sulfur and cis thiocyanate nitrogen atoms.

these structures is  $C_{2v}$ . For the structure proposed for the manganese, iron, and cobalt systems, the sulfur atoms are cis to each other, but one of the atoms is bonded to the metal atom in the trans position while the second is bonded to the metal atom in the equatorial plane of the metal octahedra.

Another structure possibility is that found for Ni(tam)<sub>2</sub>(NCS)<sub>2</sub> (tam = thioacetamide).<sup>31</sup> Ni(tam)<sub>2</sub>(NCS)<sub>2</sub> (space group  $P_3/2_1$ ) has the same bridging groups as the above linear-chain polymers, but they are arranged in a near-orthogonal orientation forming a *helical chain along the 3<sub>1</sub> screw axis*. The sulfur atoms from the thioacetamide ligand bond with the nickel atom in a cis orientation forming NiN<sub>2</sub>S<sub>2</sub>S'<sub>2</sub> polyhedra with all sulfur atoms in a plane and the nitrogen atoms from the thiocyanate anions in a trans orientation. If Ni(bpy)(NCS)<sub>2</sub> does have a type of helical chain similar to that of Ni(tam)<sub>2</sub>(NCS)<sub>2</sub>, one bipyridine group can be thought of as replacing the two thioacetamide ligands in Ni(tam)<sub>2</sub>(NCS)<sub>2</sub>, giving a local coordination environment similar to that of the second zigzag-type structure. Figure 6 shows the helical-chain-type structure for Ni(bpy)(NCS)<sub>2</sub> based on that for Ni(tam)<sub>2</sub>(NCS)<sub>2</sub>.

The last structure possibility we consider for Ni(bpy)(NCS)<sub>2</sub> is that found for Cu(en)(NCS)<sub>2</sub>.<sup>9</sup> This copper compound has two different, six-coordinate metal centers which are bridged by half the available thiocyanate anions via unusual tricoordinate sulfur centers. This bonding forms a series of four infinite -Cu-S-Cu-S- linear chains connected by the bridging thiocyanate anions. This type of structure cannot be easily distinguished from the zigzag or helical structures if only spectral data are taken into account. Cu(en)(NCS)<sub>2</sub> has been shown to exhibit *weak* antiferromagnetic exchange interactions<sup>1</sup> which are believed to be the result of weak superexchange through the tricoordinate sulfur. If Ni(bpy)(NCS)<sub>2</sub> has the Cu(en)(NCS)<sub>2</sub>-type structure, the magnetic properties would be expected to show the effects of *weak* positive or negative exchange which is not borne out by the magnetic data which is presented in the next section. In summary, the most probable structure for Ni(bpy)(NCS)<sub>2</sub> is one containing zigzag or helical chains as shown in Figures 3-6. The present results do not allow for further refinement of our choice among these. However, it is clear from the foregoing and previous work that the thermal decomposition of monomeric [M(bpy)<sub>3</sub>](NCS)<sub>2</sub>

(31) L. Capacchi, G. F. Gasparri, M. Nardelli, and G. Peliezi, *Acta Crystallogr., Sect. B*, **B24**, 1199 (1968).

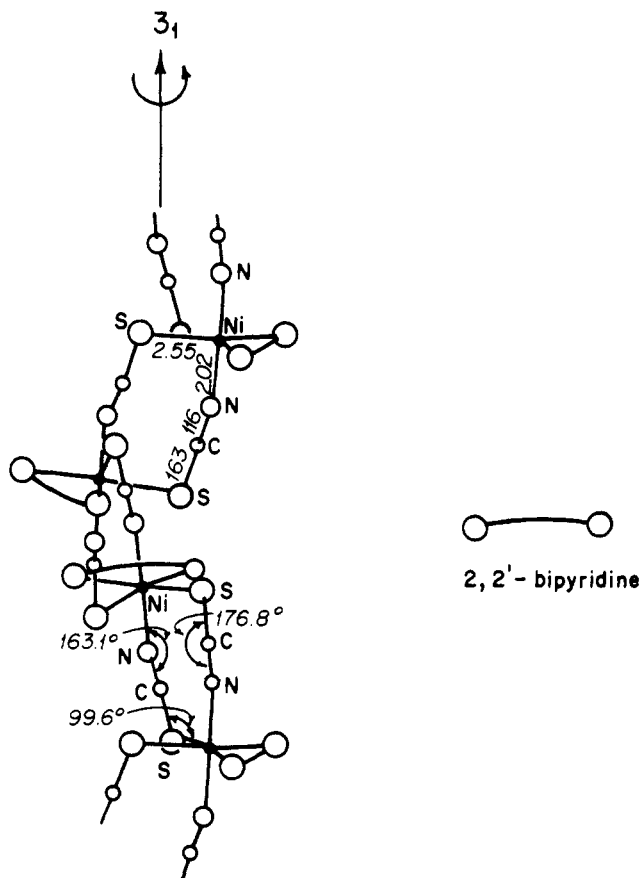


Figure 6. Helical-chain structure based on the  $\text{Ni}(\text{tam})_2(\text{NCS})_2$  structure.

complexes generally results in condensation to polymeric species. This is fully consistent with metal centers avoiding coordinative unsaturation through anion bridging in the absence of steric hindrance from the unsubstituted  $\alpha$ -diimine ligand. Thus for instance, 2,9-dimethylphenanthroline does not form polymeric  $\text{M}(2,9\text{-CH}_3\text{-phen})\text{X}_2$  complexes ( $\text{X}$  = halogen or pseudohalogen) to our knowledge.

**Magnetic Measurements.** Constant field magnetic susceptibility measurements for  $\text{Ni}(\text{bpy})(\text{NCS})_2$  have been made between 302.74 and 1.36 K with magnetic field values between 1.69 and 5.10 kG (see supplementary material). Figure 7 shows the temperature dependence of the magnetic data below 100 K ( $\chi_M$ ,  $\chi_M^{-1}$ , and  $\mu$  vs.  $T$ ).  $\text{Ni}(\text{bpy})(\text{NCS})_2$  obeys the Curie-Weiss law (of the form  $\chi_M = C/(T - \Theta)$ ) above 50 K with the following parameter values:  $\Theta = +10.9$  K,  $C = 1.266$  cgsu mol $^{-1}$ , and  $g = 2.21$  (calculated from  $g = 2.828 [C/(S(S + 1))]^{1/2}$ ). The value of the effective moment ( $3.14 \mu_B$ ) is greater than the spin-only value of  $2.83 \mu_B$  ( $8^{1/2} \mu_B$ ,  $S = 1$ ), which is expected for an orbital singlet ground state ( ${}^3A_{2g}$  in  $O_h$  symmetry) for six-coordinate nickel(II). The higher moment value is probably the result of spin-orbit coupling of orbital angular momentum from the nominal  ${}^3T_{2g}$  first excited state into the ground state. The magnetic moment for  $\text{Ni}(\text{bpy})(\text{NCS})_2$  below 100 K is always above the spin-only moment (Figure 7) and continually increases in value as the temperature decreases until a maximum value of  $\sim 8.4 \mu_B$  at 3.5 K is obtained. Below 3.5 K, the moment decreases in value. This increase in the moment indicates strong ferromagnetic exchange interactions within the polymer chain, which is also implied by the large positive  $\Theta$  value. Sample  $\mu$  vs.  $T$  data are given in the supplemental material.

In the log plot ( $\chi_M$  vs.  $\log T$ ) in Figure 7, the susceptibility increases rapidly below 11 K and appears to level off below 3 K. The susceptibility also shows evidence of being field

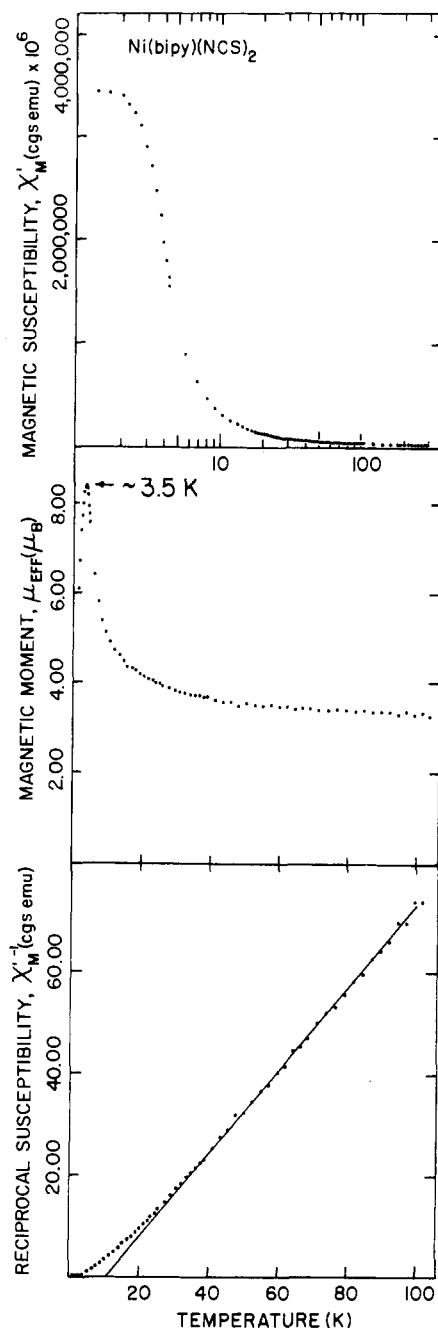


Figure 7. Plot of the magnetic data ( $\chi_M$ ,  $\chi_M^{-1}$ , and  $\mu$ ) for  $\text{Ni}(\text{bpy})(\text{NCS})_2$  between 0 and 100 K with a magnetic field of 1.69 kG.

dependent below 5 K, suggesting that  $\text{Ni}(\text{bpy})(\text{NCS})_2$  is not saturated for fields in the range 1–5 kG. These observations are typical of 3-D ferromagnetism and indicate that  $\text{Ni}(\text{bpy})(\text{NCS})_2$  orders three-dimensionally as a ferromagnet with a Curie temperature ( $T_c$ ) of  $\sim 3.5$  K. The latter is estimated from the inflection point in the  $\chi_M$  vs.  $T$  plot below 5 K. This susceptibility behavior for  $\text{Ni}(\text{bpy})(\text{NCS})_2$  is similar to three other monodiiimine polymers,  $\text{Ni}(\text{bpy})\text{Br}_2$  ( $T_c \approx 4$  K),<sup>13</sup>  $\text{Fe}(\text{phen})\text{Cl}_2$  ( $T_c \approx 4.5$  K),<sup>10,12</sup> and  $\text{Fe}(\text{bpy})\text{Cl}_2$  ( $T_c \approx 3.8$  K),<sup>10,11</sup> which are known to three-dimensionally order as insulating ferromagnets. Isothermal magnetization ( $\sigma$  vs.  $H$ ) measurements were made with a vibrating-sample magnetometer for field sweeps varying from 0 to 14 kG in the range 1.5– $\sim 20$  K. These results are also typical of ferromagnetic order and will be published in detail elsewhere. Suffice it to say now that for the present system, for  $T > T_c$ , we observe gradual rise and  $S = 1$  Brillouin behavior for  $\sigma$  vs.  $H$  and for  $T < T_c$ , a rapid rise and nonBrillouin behavior. The rather significant,

steady increase in moment to values in considerable excess of the spin only at temperatures well above  $T_c$ , e.g.,  $\mu = 3.98 \mu_B$  at 25.1 K, appears to indicate relatively strong 1-D ferromagnetism. To our knowledge, this novel behavior has not been previously observed in systems that also ultimately order three-dimensionally as ferromagnets and is the subject of further study in this laboratory. Finally the present work clearly establishes another member of a rather select group<sup>32</sup> of compounds, namely, three-dimensionally ordered ferromagnetic insulators.

(32) P. Day, *Acc. Chem. Res.*, **12**, 236 (1979).

**Acknowledgment.** The authors wish to acknowledge the support of the National Science Foundation, Division of Materials Research, Solid State Chemistry Program, Grant No. DMR-80-12625. They also express their appreciation to Dr. Arthur Heis of Bruker Instruments, Inc., Billerica, MA, for his assistance in obtaining X-band ESR spectra.

**Registry No.** Ni(bpy)(NCS)<sub>2</sub>, 81340-50-3; Ni(bpy)<sub>2</sub>(NCS)<sub>2</sub>, 15748-25-1; Ni(py)<sub>2</sub>(NCS)<sub>2</sub>, 50388-33-5;  $\alpha$ -Ni(2,9-dmp)Cl<sub>2</sub>, 29115-92-2;  $\beta$ -Ni(2,9-dmp)Cl<sub>2</sub>, 21361-04-6; Ni(bpy)<sub>3</sub>(NCS)<sub>2</sub>, 81340-41-2.

**Supplementary Material Available:** A table of magnetic moments vs. temperature and three figures of visible and infrared spectra (4 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,  
University of Wisconsin—Madison, Madison, Wisconsin 53706

## Single-Crystal Structures of ZrX<sub>3</sub> (X = Cl, Br, I) and ZrI<sub>3.40</sub> Synthesized in Low-Temperature Aluminum Halide Melts

EDWIN M. LARSEN,\* JULIE S. WRAZEL,<sup>1</sup> and LAURENCE G. HOARD

Received March 19, 1981

The single-crystal data for the zirconium trihalides and partially oxidized zirconium iodide, ZrI<sub>3.40</sub>, confirm that all four structures consist of chains of face-shared zirconium halide octahedra with equally spaced metal atoms. The space group is *P6<sub>3</sub>/mcm*. The trihalides were found to contain no crystallographically detectable metal absences or metal atoms disordered to other hexagonal sites in the unit cell. Thus, the trihalides as prepared here are stoichiometric and possess such a very narrow composition range that they may be considered line phases. The elongation of the halogen octahedra along the 3-fold axis, which is greatest for the trichloride, less for the bromide, and negligible for the iodides, may be explained in part by the necessity to reduce repulsive nearest-neighbor metal interactions. The following lattice parameters were found: ZrCl<sub>3</sub>,  $a = b = 6.383$  (1),  $c = 6.139$  (2) Å; ZrBr<sub>3</sub>,  $a = b = 6.728$  (2),  $c = 6.299$  (2) Å; ZrI<sub>3</sub>,  $a = b = 7.298$  (4),  $c = 6.667$  (4) Å; ZrI<sub>3.40</sub>,  $a = b = 7.239$  (2),  $c = 6.673$  (1) Å;  $Z = 2$ . The structures were refined to final *R* values and errors-of-fit as follows: ZrCl<sub>3</sub>,  $R_1 = 2.99\%$ ,  $R_2 = 4.59\%$ , error-of-fit = 1.79; ZrBr<sub>3</sub>,  $R_1 = 7.55\%$ ,  $R_2 = 12.33\%$ , error-of-fit = 1.97; ZrI<sub>3</sub>,  $R_1 = 5.96\%$ ,  $R_2 = 10.41\%$ , error-of-fit = 1.55; ZrI<sub>3.40</sub>,  $R_1 = 5.66\%$ ,  $R_2 = 9.13\%$ , error-of-fit = 1.44. The stoichiometry of the partially oxidized zirconium iodide, ZrI<sub>3.40</sub>, was established by refinement of the zirconium site occupancy.

### Introduction

The initial structure determinations of zirconium trichloride, tribromide and triiodide were derived from powder data.<sup>2</sup> These data yielded a structure consisting of linear chains of face-sharing ZrX<sub>6</sub> octahedra with the metal atoms equally spaced along the *c* axis. The structure determination by Watts,<sup>3</sup> which confirmed this structure, was also based on powder data. Single-crystal diffraction studies<sup>4,5</sup> on zirconium tribromide yielded more precise lattice parameters for the same structure. Recently Daake and Corbett,<sup>6</sup> using the Guinier powder camera technique, reported precise lattice parameters for the trihalides over a range of composition and drew correlations between shifts in the *a* and *c* lattice parameters with composition. Their comparison of parameters with those previously reported<sup>2,4,5</sup> suggests that the earlier data may have been obtained on materials that, in fact, were nonstoichiometric. Whether this correlation is applicable to all products independent of their method of preparation is worthwhile exploring, since the range of nonstoichiometry generally widens

with temperature, and high-temperature structures may be retained upon cooling the preparation to room temperature.

The trihalide samples used for the initial powder pattern studies were prepared by the reduction of the zirconium tetrahalides with zirconium metal at high temperatures (500–700 °C) and high pressures (50–20 atm).<sup>7</sup> The products were contaminated with some residual metal. The reaction times ranged from 70 to 100 h, after which the reaction bomb was rapidly quenched. The Daake–Corbett products were obtained by the reaction of the corresponding tetrahalides with ZrCl, ZrBr, or ZrI<sub>1.8</sub> in a sealed tantalum tube at temperatures ranging from 435 to 775 °C and pressures of 5–20 atm. Both of these syntheses are considered to yield high-temperature preparations.

On the other hand, the powder data by Watts<sup>3</sup> were obtained on a zirconium trihalide sample prepared by the low-temperature (25 °C) reduction<sup>8</sup> of zirconium tetrachloride with atomic hydrogen in an electrodeless discharge. In the work reported here, the single crystals studied were prepared by using the technique of Larsen et al.<sup>4</sup> In this synthesis, the tetrahalides, dissolved in the corresponding liquid aluminum halide at the eutectic composition, are reduced by either metallic zirconium or aluminum at temperatures ranging from 220 (Cl) to 280–300 °C (I) to yield a homogeneous reduced-state solution. The crystals of the trichloride and tribromide grow at the lip of the tilted reaction ampule. In the

(1) Based in part upon a dissertation submitted by Julie Wrazel to the Graduate School of the University of Wisconsin, Madison, WI, in partial fulfillment of the requirement for the Ph.D. degree, 1979.

(2) Dahl, L. F.; Chiang, Tao-I.; Seabaugh, P. W.; Larsen, E. M. *Inorg. Chem.* **1964**, *3*, 1236–1242.

(3) Watts, J. A. *Inorg. Chem.* **1966**, *5*, 281–283.

(4) Larsen, E. M.; Moyer, J. W.; Gil-Arno, F.; Camp, M. J. *Inorg. Chem.* **1974**, *13*, 574–581.

(5) Kleppinger, J.; Calabrese, J. C.; Larsen, E. M. *Inorg. Chem.* **1975**, *14*, 3128–3130.

(6) Daake, R. L.; Corbett, J. D. *Inorg. Chem.* **1978**, *17*, 1192–1195.

(7) Larsen, E. M.; Leddy, J. J. *J. Am. Chem. Soc.* **1956**, *78*, 5983–5986.

(8) Newham, L. E.; Watts, J. A. *J. Am. Chem. Soc.* **1960**, *82*, 2113–2115.