

(Me)(I)Rh(BPDOBF<sub>2</sub>), 99355-04-1; ((CH<sub>3</sub>)<sub>2</sub>CH)(Br)Rh(BPDOBF<sub>2</sub>), 99355-05-2; (Me)(Br)Rh(PPDOBF<sub>2</sub>), 99355-06-3; (Me)(Cl)Rh(PPDOBF<sub>2</sub>), 99355-07-4; (*t*-C<sub>4</sub>H<sub>9</sub>)(I)Rh(PPDOBF<sub>2</sub>), 99355-08-5; (*t*-C<sub>4</sub>H<sub>9</sub>)(Br)Rh(PPDOBF<sub>2</sub>), 99355-09-6; (*t*-C<sub>4</sub>H<sub>9</sub>)(Cl)Rh(PPDOBF<sub>2</sub>), 99355-10-9; (*t*-C<sub>4</sub>H<sub>9</sub>)(OTs)Rh(PPDOBF<sub>2</sub>), 99355-11-0; ((CH<sub>3</sub>)<sub>2</sub>CH)(I)Rh(PPDOBF<sub>2</sub>), 99355-12-1; ((CH<sub>3</sub>)<sub>2</sub>CH)(Br)Rh(PPDOBF<sub>2</sub>), 99355-13-2; (Bz)(Br)Rh(PPDOBF<sub>2</sub>), 99355-14-3; (Bz)(Cl)Rh(PPDOBF<sub>2</sub>), 99355-15-4; (*c*-C<sub>3</sub>H<sub>5</sub>CH<sub>2</sub>)(I)Rh(PPDOBF<sub>2</sub>), 99355-16-5; ((CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>)(I)Rh(PPDOBF<sub>2</sub>), 99355-17-6; (B)(I)Rh(PPDOBF<sub>2</sub>) (B = 1-adamantyl), 99355-18-7; ((CH<sub>3</sub>)<sub>3</sub>C(CH<sub>2</sub>)<sub>2</sub>)(I)Rh(PPDOBF<sub>2</sub>), 99355-19-8; ((CH<sub>3</sub>)<sub>3</sub>C(CH<sub>2</sub>)<sub>2</sub>)(Br)Rh(PPDOBF<sub>2</sub>), 99355-20-1; (MeCO)(Cl)Rh(PPDOBF<sub>2</sub>), 99355-21-2; (Bz)(SCN)Rh(PPDOBF<sub>2</sub>), 99355-22-3; (*c*-C<sub>6</sub>H<sub>11</sub>)(Br)Rh(PPDOBF<sub>2</sub>), 99355-25-6; (Br<sub>2</sub>)Rh(PPDOBF<sub>2</sub>), 99355-27-8; ((CH<sub>3</sub>)<sub>3</sub>CCHDCHD)(I)Rh(PPDOBF<sub>2</sub>), 99355-28-9; RhCl<sub>3</sub>,

10049-07-7; MeI, 74-88-4; (CH<sub>3</sub>)<sub>2</sub>CHBr, 75-26-3; MeBr, 74-83-9; MeCl, 74-87-3; *t*-C<sub>4</sub>H<sub>9</sub>I, 558-17-8; *t*-C<sub>4</sub>H<sub>9</sub>Br, 507-19-7; *t*-C<sub>4</sub>H<sub>9</sub>Cl, 507-20-0; *t*-C<sub>4</sub>H<sub>9</sub>OTS, 4664-57-7; (CH<sub>3</sub>)<sub>2</sub>CHI, 75-30-9; BzBr, 100-39-0; BzCl, 100-44-7; *c*-C<sub>3</sub>H<sub>5</sub>CH<sub>2</sub>I, 33574-02-6; (CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>I, 15501-33-4; BI (B = 1-adamantyl), 768-93-4; (CH<sub>3</sub>)<sub>3</sub>C(CH<sub>2</sub>)<sub>2</sub>I, 15672-88-5; (CH<sub>3</sub>)<sub>3</sub>C(CH<sub>2</sub>)<sub>2</sub>Br, 1647-23-0; MeCOCl, 75-36-5; BzSCN, 3012-37-1; 1-bromobutane, 109-65-9; bromocyclohexane, 108-85-0; 1-bromoadamantane, 768-90-1; 1-chlorobutane, 109-69-3; 2-methyl-2-phenyl-1-propanol, 100-86-7; 2-methyl-2-phenyl-1-propanol tosylate, 21816-03-5; 1-iodobutane, 542-69-8; *n*-butyl tosylate, 778-28-9.

**Supplementary Material Available:** A table of analytical data (5 pages). Ordering information is given on any current masthead page.

## Arylnickel(III) Species Containing NO<sub>3</sub>, NO<sub>2</sub>, and NCS Ligands. ESR Data and the X-ray Crystal Structure of Hexacoordinate (Pyridine)bis(isothiocyanato)-[*o*,*o'*-bis{(dimethylamino)methyl}phenyl]nickel(III)

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A method for the interconversion of the five-coordinated Ni(III) species [Ni{C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2-*o,o'*</sub>}X<sub>2</sub>] (X = Cl, Br, I) and its application to the synthesis of the new species with X = NO<sub>3</sub> and NO<sub>2</sub> are described. For X = NCS the same route leads to the formation of species in which the Ni(III) center is hexacoordinate and ESR data are reported. For one derivative, [Ni{C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2-*o,o'*</sub>}(NCS)<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>N)] (5b), the molecular geometry has been established by X-ray crystallographic methods. Crystals of 5b, C<sub>19</sub>H<sub>24</sub>NiN<sub>5</sub>S<sub>2</sub>, are orthorhombic with *a* = 13.146 (2), *b* = 16.101 (4) Å, *c* = 10.064 (1) Å, *V* = 2122 (1) Å<sup>3</sup>, and *Z* = 4. Refinement included 1308 reflections leading to a final *R* value of 0.058. The structure of 5b consists of a hexacoordinate Ni(III) center which is directly σ-bonded to the phenyl carbon of the C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2-*o,o'*</sub> ligand (Ni(III)-C = 1.900 (9) Å). The Ni center is further bonded to five nitrogen donor ligands: to two mutually trans N-bonded NCS ligands (1.965 (6) Å), to two trans NMe<sub>2</sub> ligands (2.207 (6) Å), and to the pyridine N atom which is trans to the C donor site (2.057 (8) Å). On the basis of these structural data and in combination with the ESR data with *g*<sub>||</sub> > *g*<sub>⊥</sub>, it is concluded that the unpaired electron resides in the d<sub>x<sup>2</sup>-y<sup>2</sup></sub> orbital.

### Introduction

In the last few years it has become increasingly apparent that nickel plays an important role in certain biological systems, e.g., the hydrogenases,<sup>1</sup> and this has emphasized the relevance of studies concerning the range and stability of the less common Ni(I) and Ni(III) oxidation states.<sup>2</sup> Those inorganic coordination complexes of trivalent (d<sup>7</sup>) nickel are paramagnetic, and in the majority of examples known stabilization of this oxidation state is accomplished by the use of N donor ligands of a polydentate or macrocyclic nature.<sup>3-5</sup>

Recently, with use of the terdentate anionic N,N',C ligand C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2-*o,o'*</sub> we prepared the novel square-pyramidal arylnickel(III) species [Ni{C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2-*o,o'*</sub>}X<sub>2</sub>] (X = Cl, Br, I) (1a-c), which were the first reported true Ni(III) organometallics.<sup>6</sup> The presence of a C-Ni(III) σ-bond makes these compounds also interesting models for the arylnickel(III) intermediates postulated to be key intermediates in the nickel-catalyzed cross-coupling reactions of alkyl Grignards with aryl halides.<sup>7</sup>

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(2) (a) Nag, K.; Chakravorty, A. *Coord. Chem. Rev.* 1980, 33, 87-147.

(b) Haines, R. I.; McAuley, A. *Coord. Chem. Rev.* 1981, 39, 77-119.

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(4) Lati, J.; Koresh, J.; Meijerstein, D. *Chem. Phys. Lett.* 1975, 33, 286-288.

(5) Bencini, A.; Fabrizzi, L.; Poggi, A. *Inorg. Chem.* 1981, 20, 2544-2549.

(6) Grove, D. M.; van Koten, G.; Zoet, R.; Murrall, N. W.; Welch, A. *J. Am. Chem. Soc.* 1983, 105, 1379-1380.

(7) Smith, G.; Kochi, J. K. *J. Organomet. Chem.* 1980, 198, 199-214. Negishi, E. *Acc. Chem. Res.* 1982, 15, 340-348.

In this paper the results of an extension of this study are reported and the synthesis of analogues of 1 with X = NO<sub>3</sub> and NO<sub>2</sub> outlined. More importantly we describe the first examples of a new class of Ni(III) species of general formula [Ni{C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2-o,o</sub>}(NCS)<sub>2</sub>(solvent)] which are shown to contain hexacoordinate nickel(III) in a tetragonally compressed octahedral environment.

### Experimental Section

All reactions were performed with freshly distilled solvents. <sup>1</sup>H NMR spectra were recorded on a Bruker WM-250 spectrometer, and chemical shifts are relative to tetramethylsilane (0 ppm). IR spectra (KBr disks) were recorded on a Perkin-Elmer 283 spectrometer. ESR spectra were obtained from glasses (diglyme, CH<sub>2</sub>Cl<sub>2</sub>) or powdered solids contained in 5-mm i.d. quartz tubes using a Bruker ER 200D-MR X-band spectrometer with g tensors referenced to DPPTH (2.002).

[Ni<sup>III</sup>{C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2-o,o</sub>}(NCS)] (3). To a stirred solution of [Ni{C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2-o,o</sub>}(Br)]<sup>8</sup> (300 mg, 0.91 mmol) in H<sub>2</sub>O (30 mL) was added AgBF<sub>4</sub> (195 mg, 1.00 mmol), and after 15 min AgBr was removed by filtration. To the resulting yellow-brown solution of [Ni{C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2-o,o</sub>}(H<sub>2</sub>O)] [BF<sub>4</sub>]<sup>8</sup> was added excess NH<sub>4</sub>NCS (500 mg, 6.6 mmol), and after 15 min the brown-green solution was evaporated to dryness in vacuo. Extraction with CH<sub>2</sub>Cl<sub>2</sub> and recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/pentane yielded pure olive green 3. Anal. Calcd for C<sub>13</sub>H<sub>19</sub>N<sub>3</sub>SNi: C, 50.68; H, 6.22; N, 13.64; S, 10.41. Found: C, 50.66; H, 6.22; N, 13.70; S, 10.37.

[Ni<sup>III</sup>{C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2-o,o</sub>}(NCS)(H<sub>2</sub>O)] (5a). To a stirred solution of [Ni{C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2-o,o</sub>}(Br)]<sup>8</sup> (145 mg, 0.35 mmol) in acetone (20 mL) was added AgBF<sub>4</sub> (153 mg, 0.79 mmol). After 5 min AgBr was removed by filtration and an excess of NH<sub>4</sub>NCS (1.73 mg, 2.28 mmol) was added to the brownish solution. The solvent was then removed in vacuo from the resulting dark green solution to yield a thick green oil. Attempts to crystallize this oil failed; yield 96 mg (~70%).

[Ni<sup>III</sup>{C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2-o,o</sub>}(X<sub>2</sub>)] (X = NO<sub>3</sub> (1d), NO<sub>2</sub> (1e)). To a stirred solution of [Ni{C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2-o,o</sub>}(Br)]<sup>8</sup> (200 mg, 0.49 mmol) in acetone (20 mL) was added 2.1 equiv of AgBF<sub>4</sub>. After 5 min the precipitated AgBr was removed by filtration and an excess of NaX (5 equiv) was added to the brownish solution. After 15 min the solvent was removed in vacuo and the product was extracted with CH<sub>2</sub>Cl<sub>2</sub>. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/toluene (1:1) afforded pure 1d (yellow-brown) and 1e (dark green) in greater than 70% yield. Anal. Calcd for C<sub>12</sub>H<sub>19</sub>N<sub>4</sub>O<sub>6</sub>Ni (1d): C, 38.53; H, 5.12; N, 14.98. Found: C, 39.04; H, 5.13; N, 14.50. Calcd for C<sub>12</sub>H<sub>19</sub>N<sub>4</sub>O<sub>4</sub>Ni (1e): C, 42.14; H, 5.60; N, 16.38. Found: C, 42.14; H, 5.61; N, 16.25.

The products could also be obtained by either oxidation of the analogous Ni<sup>II</sup> species with an excess of AgX in water or the use of AgNO<sub>3</sub> or AgNO<sub>2</sub> in a 1/>2 molar ratio. After filtration of Ag<sup>0</sup> and AgX precipitates workup of the filtrates was carried out as described above.

[Ni<sup>III</sup>{C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2-o,o</sub>}(NCS)<sub>2</sub>(py)] (5b). On addition of 1 mL of pyridine to the solution of 5a described above small dark green crystals were formed. Recrystallization from pyridine/CH<sub>2</sub>Cl<sub>2</sub>/toluene yielded the title compound. Anal. Calcd for C<sub>18</sub>H<sub>24</sub>N<sub>4</sub>SNi (5b): C, 51.25; H, 5.43; N, 15.73; S, 14.40. Found: C, 51.14; H, 5.44; N, 15.69; S, 14.27.

**Structure Determination and Refinement: X-ray Data Collection.** Dark green, almost black, crystals of 5b were obtained as well-formed plates by slow evaporation of a saturated solution of 5b in pyridine/CH<sub>2</sub>Cl<sub>2</sub>/toluene (1:3:4), and one of suitable dimension was chosen and glued on top of a glass fiber. Unit-cell dimensions were derived from a least-squares fit of the setting angles for 18 reflections (30 < 2θ < 45). The crystal data and details of data collection and structure refinement are summarized in Table I. A total of 3137 reflections were measured on a Nonius CAD4 diffractometer and of these 1829 were below the 2.5σ(I) level and were treated as unobserved. An empirical absorption correction has been applied.

The structure was solved by means of the heavy-atom method using standard Patterson and Fourier techniques and subsequently

Table I. Crystal Data and Details of the Structure Determination

A. Crystal Data	
formula	C <sub>19</sub> H <sub>24</sub> NiN <sub>5</sub> S <sub>2</sub>
mol wt	445.25
space group	<i>Pnab</i> (nonstandard <i>Pbcn</i> , no. 60)
cryst system	orthorhombic
<i>a</i> , Å	13.146 (2)
<i>b</i> , Å	16.101 (4)
<i>c</i> , Å	10.064 (1)
<i>V</i> , Å <sup>3</sup>	2130 (2)
<i>Z</i>	4
<i>D</i> <sub>calcd</sub> , g cm <sup>-3</sup>	1.39
<i>F</i> (000)	932
μ(Mo Kα), cm <sup>-1</sup>	11.2
cryst size, mm	0.23 × 0.18 × 0.13
B. Data Collection	
radiation	Mo Kα λ = 0.71069 Å
<i>T</i> , K	301
θ <sub>min</sub> , θ <sub>max</sub>	1.10, 30.0
max time/refln, min	3
ref refln	402
total refln data	3501
total unique reflns	3501
obsd data	1308 ( <i>I</i> > 2.5σ( <i>I</i> ))
C. Refinement	
no. of refined parameters	350
weighting scheme	<i>A</i> + <i>F</i> + <i>BF</i> <sup>2</sup> + <i>CF</i> <sup>2</sup>
final <i>R</i> values	<i>R</i> ( <i>F</i> ) = 0.058, <i>R</i> <sub>w</sub> ( <i>F</i> ) = 0.101

Table II. Final Values of the Atomic Coordinates (Esd's)

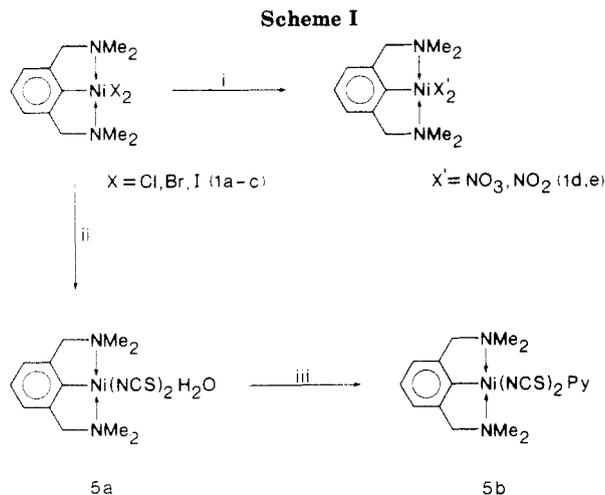
atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Ni	0.2500 (0)	0.1507 (1)	0.0000 (0)
C(1)	0.2500 (0)	0.0327 (6)	0.0000 (0)
C(2)	0.1975 (6)	-0.0067 (4)	0.1014 (7)
C(3)	0.1984 (7)	-0.0937(5)	0.0998 (9)
C(4)	0.2500 (0)	-0.1349 (6)	0.0000 (0)
C(5)	0.1485 (6)	0.0472 (5)	0.2031 (8)
C(6)	0.1190 (7)	0.1931 (6)	0.2464 (9)
C(7)	0.0243 (7)	0.1239 (5)	0.0772 (9)
C(8)	0.3197 (6)	0.3221 (5)	0.0685 (8)
C(9)	0.3219 (7)	0.4087 (5)	0.0701 (9)
C(10)	0.2500 (0)	0.4532 (6)	0.0000 (0)
C(11)	0.3869 (5)	0.1329 (4)	0.2516 (7)
N(1)	0.1243 (4)	0.1295 (4)	0.1414 (6)
N(2)	0.2500 (0)	0.2785 (5)	0.0000 (0)
N(3)	0.3413 (5)	0.1470 (4)	0.1545 (6)
S	0.4518 (2)	0.1153 (2)	0.3831 (2)
H(3)	0.1543	-0.1219	0.1574
H(4)	0.2500	-0.1995	0.0000
H(51)	0.0859	0.0269	0.2445
H(52)	0.2023	0.0470	0.2680
H(61)	0.0772	0.1816	0.2986
H(62)	0.1902	0.2037	0.2942
H(63)	0.0894	0.2473	0.2059
H(71)	-0.0279	0.1060	0.1369
H(72)	0.0031	0.1751	0.0239
H(73)	0.0315	0.0900	0.0044
H(8)	0.3726	0.2809	0.1137
H(9)	0.3807	0.4368	0.1180
H(10)	0.2500	0.5027	0.0000

refined by means of anisotropic block-diagonal least-squares calculations. The molecules were found to be situated on crystallographic binary axes with a 1/2 molecule in the asymmetric unit. The H atoms were introduced at their calculated positions and not refined. The final *R* value for 1308 observed reflections was 0.058 (*R*<sub>w</sub> = 0.101). A weighting scheme *w* = 1/(2.7 + *F*<sub>o</sub> + 0.037*F*<sub>o</sub><sup>2</sup>) was applied, and the anomalous dispersion of Ni taken into account.

Computations were carried out with the X-RAY 76 system<sup>9</sup> using ref 10 for atomic scattering factors and the anomalous

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(9) Steward, J. M. "The X-ray 76 System", Technical Report TR-466, Computer Science Center, University of Maryland, College Park, MD.



<sup>a</sup> i, Ag<sup>+</sup>, acetone, -AgX, MX' (X' = NO<sub>2</sub>, NO<sub>3</sub>, M = Li, Na, K); ii, Ag<sup>+</sup>, acetone, -AgX, NH<sub>4</sub>NCS excess; iii, pyridine, CH<sub>2</sub>Cl<sub>2</sub>/acetone/toluene.

dispersion correction. The final values of the refined parameters are given in Table II.

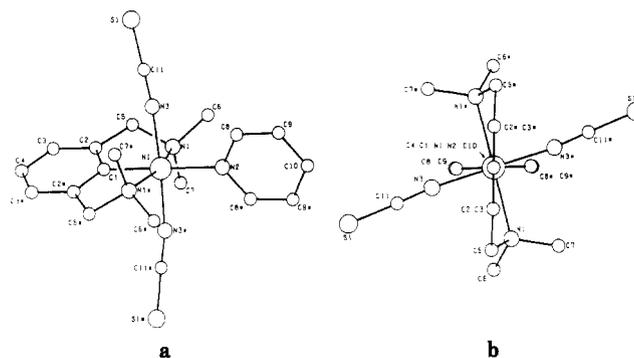
### Results and Discussion

The synthetic results for the various arylnickel(III) species are outlined in Scheme I.

**A. Synthesis of NO<sub>3</sub> and NO<sub>2</sub> Species.** A previous publication described the synthesis of a variety of [Ni<sup>II</sup>{C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2-o,o</sub>}X] species,<sup>8</sup> and for the chloro, bromo, and iodo derivatives the use of oxidizing agents to yield the corresponding Ni(III) species 1a-c has been communicated.<sup>8</sup> In further studies it has now been found that with use of one of these arylnickel(III) species as starting material the overall ligand substitution sequence shown in Scheme I (eq i) is a route of great potential for the ready interconversion of 1a-c and the preparation of further related arylnickel(III) species. In particular with this method the new five-coordinate arylnickel(III) complexes [Ni{C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2-o,o</sub>}{(NO<sub>3</sub>)<sub>2</sub>}] (1d) and [Ni{C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2-o,o</sub>}{(NO<sub>2</sub>)<sub>2</sub>}] (1e) have been synthesized.<sup>11</sup>

In synthetic route i the addition of 2 equiv of Ag(I) (BF<sub>4</sub><sup>-</sup> or CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> anion) leads to quantitative precipitation of 2 equiv of AgX which may be filtered off to leave a clear brown solution of the solvated Ni(III) species [Ni{C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2-o,o</sub>}{(solvent)<sub>n</sub>}]<sup>2+</sup> (2) (solvent = acetone or H<sub>2</sub>O). Treatment of 2 in situ with an excess of a new anion, X<sup>-</sup> (Li<sup>+</sup>, Na<sup>+</sup>, or K<sup>+</sup> cation) generates an unchanged [Ni{C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2-o,o</sub>}X<sub>2</sub>] species that can be isolated by evaporation of the mixture to dryness in vacuo followed by extraction with CH<sub>2</sub>Cl<sub>2</sub> or toluene.

**B. Synthesis of NCS Species.** Our interest in N donor ligands and the successful synthesis of 1d and 1e containing polyatomic anions (as well as of the Ni(II) derivatives [Ni{C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2-o,o</sub>}X] (X = NO<sub>3</sub>, NO<sub>2</sub>)) led us to consider syntheses of the NCS analogues [Ni<sup>II</sup>{C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2-o,o</sub>}{(NCS)}] (3) and [Ni<sup>III</sup>{C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2-o,o</sub>}{(NCS)<sub>2</sub>}] (4). The synthesis of 3,<sup>12</sup> which

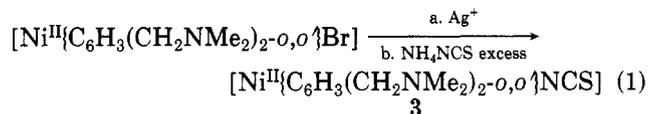


**Figure 1.** (a) Pluto drawing of [Ni{C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2-o,o</sub>}{(NCS)<sub>2</sub>(py)}] (5b). (b) Projection along the C(1)-Ni-N(2) axis showing the relative positions of the aryl and pyridine planes with respect to the N(3)-Ni-N(3\*) axis.

**Table III. Relevant Bond Distances (Å) and Bond Angles (deg) of [Ni{C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2-o,o</sub>}{(NCS)<sub>2</sub>(py)}] (5b)**

Bond Distances			
Ni-C(1)	1.900 (9)	C(5)-N(1)	1.497 (10)
Ni-N(1)	2.207 (6)	C(6)-N(1)	1.474 (11)
Ni-N(2)	2.057 (8)	C(7)-N(1)	1.468 (11)
Ni-N(3)	1.965 (6)	C(8)-N(2)	1.344 (9)
C(1)-C(2)	1.385 (8)	C(8)-C(9)	1.396 (11)
C(2)-C(3)	1.401 (10)	C(9)-C(10)	1.380 (10)
C(2)-C(5)	1.489 (11)	C(11)-N(3)	1.169 (9)
C(3)-C(4)	1.382 (10)	C(11)-S(1)	1.600 (7)
Bond Angles			
C(1)-Ni-N(1)	81.1 (1)	C(2)-C(5)-N(1)	108.8 (6)
C(1)-Ni-N(2)	180.0 (0)	Ni-N(1)-C(5)	104.2 (4)
C(1)-Ni-N(3)	88.2 (2)	Ni-N(1)-C(6)	113.0 (5)
N(1)-Ni-N(2)	98.9 (1)	Ni-N(1)-C(7)	113.4 (5)
N(1)-Ni-N(3)	86.7 (2)	C(5)-N(1)-C(6)	109.1 (6)
N(1)-Ni-N(3*)	92.8 (2)	C(5)-N(1)-C(7)	108.6 (6)
N(2)-Ni-N(3)	91.8 (2)	C(6)-N(1)-C(7)	108.4 (6)
Ni-C(1)-C(2)	117.3 (4)	Ni-N(2)-C(8)	121.5 (4)
C(2)-C(1)-C(2*)	125.5 (8)	C(8)-N(2)-C(8*)	117.0 (7)
C(1)-C(2)-C(3)	116.5 (7)	N(2)-C(8)-C(9)	122.9 (8)
C(1)-C(2)-C(5)	117.1 (6)	C(8)-C(9)-C(10)	119.9 (8)
C(3)-C(2)-C(5)	126.5 (7)	C(9)-C(10)-C(9*)	117.4 (8)
C(2)-C(3)-C(4)	119.5 (8)	Ni-N(3)-C(11)	168.7 (5)
C(3)-C(4)-C(3*)	122.6 (8)	N(3)-C(11)-S(1)	178.3 (6)

is a diamagnetic species, has been achieved according to the reaction of eq 1. However, attempting to prepare 4



by the sequence of route ii in Scheme I (using AgBF<sub>4</sub> and NH<sub>4</sub>NCS) resulted in the isolation of a CH<sub>2</sub>Cl<sub>2</sub> and acetone-soluble thick green oil presumed to be 5a. Treatment of a solution of 5a in CH<sub>2</sub>Cl<sub>2</sub>/toluene with excess pyridine provided dark green poorly soluble crystals of 5b. Elemental microanalytical data for 5b were consistent with a [Ni{C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2-o,o</sub>}{(NCS)<sub>2</sub>(py)}] stoichiometry, and this information taken together with the fundamental differences between ESR spectra of 1a-e and those of 5a and 5b (vide infra) prompted a crystallographic study of the latter complex. Although this study (see below) confirmed that the pyridine was coordinated to the Ni(III) center in the solid state, there is good reason to believe that in CH<sub>2</sub>Cl<sub>2</sub> solution 5b is in equilibrium with [Ni{C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2-o,o</sub>}{(NCS)<sub>2</sub>}] (4)<sup>13</sup> and free pyridine. The comparability of the IR (ν<sub>CN</sub>), UV, and ESR spectra of 5a

(10) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England 1974; Vol. IV.

(11) Compounds 1d and 1e have ESR data similar to those of 1a-c and can also be synthesized directly from the reaction of 1a-c in acetone/H<sub>2</sub>O mixture with excess AgNO<sub>3</sub> and AgNO<sub>2</sub>, respectively. Full synthetic and spectroscopic data for 1a-e will be published.

(12) 3: olive-green solid; air stable; <sup>1</sup>H NMR (30 °C, C<sub>6</sub>D<sub>6</sub>, δ) 7.0 (m, 3, C<sub>6</sub>H<sub>3</sub>), 2.83 (s, 4, CH<sub>2</sub>), 2.05 (s, 12, NMe<sub>2</sub>); IR (KBr) ν<sub>NCS</sub> 2090 cm<sup>-1</sup>; Anal. Found (Calcd) for C<sub>13</sub>H<sub>19</sub>NiN<sub>2</sub>S: C, 50.7 (50.7); H, 6.2 (6.2); N, 13.7 (13.6); S, 10.4 (10.4).

(13) A brown extremely hygroscopic powder (most likely 4) obtained by heating 5b in vacuo at 120 °C is now under investigation.

and **5b** (vide infra) strongly suggests that **5a** is  $[\text{Ni}^{\text{III}}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-o,o'}\}(\text{NCS})_2(\text{H}_2\text{O})]$  though it should be noted that full characterization of this species is not yet complete.

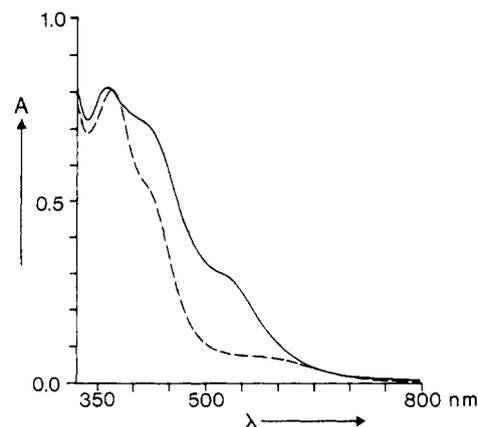
**C. Description of the Structure of  $[\text{Ni}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-o,o'}\}(\text{NCS})_2(\text{py})]$  (**5b**).** The molecular geometry along with the adopted numbering scheme is shown in Figure 1, and relevant bond distances and angles are given in Table III. In **5b**, the Ni(III) center is hexacoordinate, the metal being bonded to two mutually trans N-bonded NCS ligands, the N,N',C-coordinated  $\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-o,o'}$  ligand (with the two hard N donors of the  $\text{CH}_2\text{NMe}_2$  side arms coordinating trans to each other), and a pyridine molecule trans to C(1) of the terdentate system. The only significant distortion from a true octahedral geometry lies in the N(1)–Ni–N(1\*) angle of  $162.2(2)^\circ$  resulting from the constraints of the two five-membered NiNCCC(1) chelate rings. The latter rings show the "twofold axis" type puckering found in complexes of  $\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-o,o'}$  bonded to four- and six-coordinate metal centers.<sup>14</sup>

The bonding of the NCS ligands to the Ni center via the N atoms is to be expected for a "hard" Ni(III) center and both Ni–N distances of 1.965 (6) Å, and the slight bending of these anions (away from the pyridine), Ni–N(3)–C(11) =  $168.7(5)^\circ$ , is not exceptional (cf. data in ref 15). It is difficult to conclude whether these distances are shorter or longer than expected (vide infra) in the absence of data for comparison. The bond distances and angles within the NCS anion are typical those expected for  $\sigma$ -N-bonded isothiocyanate ligands.<sup>16</sup>

The plane of the aryl ring and the pyridine molecule are mutually perpendicular but, as seen in a projection along the C(1)–Ni–N(2) axis (Figure 1b), are rotated about  $70$  and  $20^\circ$ , respectively, out of the coordination plane defined by C(1), N(3), N(3\*), N(2), and Ni. This staggered arrangement would on steric grounds alone appear to be appropriate. The bond distances of the aryl group (Ni–C(1) = 1.900 (9) Å and the pyridine (Ni–N(2) = 2.057 (8) Å) to the nickel are within the range expected for such bonds, and again the present data do not allow conclusions as to the shortening or/and lengthening effects as a result of the electronic features of the bonding (vide infra).

One geometrical feature, which is, however, worthy of comment, is the Ni–N(1) [and Ni–N(1\*)] distances of 2.207 (6) Å for the amine bonding of the terdentate ligand. This Ni–N bond can be considered to be long when compared to the corresponding distance in either the Ni(II) species  $[\text{Ni}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-o,o'}\}(\text{O}_2\text{CH})]$  [1.975 (2) Å (mean)]<sup>8</sup> or the Ni(III) species  $[\text{Ni}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-o,o'}\}[\text{I}_2]]$  [2.044 (4) Å (mean)].<sup>6</sup> The significance of the elongation of these Ni–N(amine) bonds with respect to the location of the unpaired electron in this species is discussed below in combination with the spectroscopic data.

**D. Spectroscopic Data for **5a** and **5b**.** Compounds **5a** and **5b** have a distinctive bright green color, and a solution of **5a** ( $\text{CH}_2\text{Cl}_2$  or acetone) retains this color. The bright green color obviously corresponds to the particular hexacoordinate structural type identified in the crystal



**Figure 2.** UV/vis spectra of **5b** ( $0.27 \times 10^{-3}$  M) in  $\text{CH}_2\text{Cl}_2$  without (full line) and with added pyridine (dotted line).

structure of **5b**. However, a solution of **5b** in  $\text{CH}_2\text{Cl}_2$  at room temperature is, surprisingly, brownish in color, and the expected green color is only obtained either on cooling the solution (ca.  $-30^\circ\text{C}$ ) or on the addition of a small excess of free pyridine. These observations suggest the following solution equilibrium: **5b** (green)  $\rightleftharpoons$  **4** (brown) + pyridine. This dissociation behavior is clearly reflected in the UV/vis spectra of **5b** ( $\text{CH}_2\text{Cl}_2$ ) with and without added pyridine; see Figure 2. IR data for **5a** and **5b** (KBr) show the presence of only one  $\nu_{\text{CN}}$  ( $2083$  and  $2083\text{ cm}^{-1}$ , respectively) consistent with the presence of a trans disposition of two coordinated NCS units. This data is comparable to the  $\nu_{\text{CN}}$  value of  $2089\text{ cm}^{-1}$  observed for **3**.

Probably the most informative data regarding the similarity of **5a** and **5b** is that of their very distinctive ESR spectra. The spectrum of **5a** (diglyme glass, 139 K) is shown in Figure 3, and it may be described to a first approximation as axial with  $g_{\parallel} > g_{\perp}$  ( $g_{zz} > g_{xx} \approx g_{yy}$ ;  $g_{zz} = 2.27$  and  $g_{xx}/g_{yy} \approx 2.08$ ). The latter tensors are clearly broadened, and a second derivative spectrum (Figure 3b) resolves hyperfine splitting (8–9 lines) that can be attributed to coupling of an unpaired electron with four N atoms ( $a_{\text{N}} = 11$  G). The spectrum of **5b** (solid, 143 K) gives tensor values of  $g_{zz} = 2.26$  and  $g_{xx}/g_{yy} \approx 2.10$ , but the lower solubility of this species has precluded good quality second derivative data.

For both **5a** and **5b** ( $g$ )  $> 2.14$ , indicating that these species are low-spin  $d^7$  situations in which the unpaired electron is associated primarily with the nickel ion. For **5b**, and hence by analogy for **5a** also, these ESR spectra arise from a Ni(III) ion in a distorted octahedral environment. For this  $d^7$  ion Figure 4 shows a simplified energy level diagram for an octahedron (Figure 4b) with the most commonly tetragonal distortions arising from extension of two axial bonds (Figure 4a) and the rare situation in which there is extension of four coplanar bonds (Figure 4c), cf. ref 3. For a low-spin  $d^7$  ion these two distortions give rise to a situation in which the unpaired electron is in either the  $d_{z^2}$  or  $d_{x^2-y^2}$  orbital.<sup>17</sup> The former situation is commonly found with Co(II) and Ni(III), and, in theory<sup>18</sup> and practice,<sup>19</sup> this leads to ESR spectra in which  $g_{xx}g_{yy} > g_{zz}$ . Sharp superhyperfine splitting on  $g_{zz}$

(14) (a) Grove, D. M.; van Koten, G.; Louwen, J. N.; Noltes, J. G.; Spek, A. L.; Ubbels, H. J. C. *J. Am. Chem. Soc.* **1982**, *104*, 6609–6616. (b) Grove, D. M.; van Koten, G.; Spek, A. L. *J. Am. Chem. Soc.* **1982**, *104*, 4285–4286. (c) Terheijden, J.; van Koten, G.; de Boijjs, J. L.; Ubbels, H. J. C.; Stam, C. H. *Organometallics* **1983**, *2*, 1882–1883. (d) van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G.; Spek, A. L.; Schoone, J. C.; *J. Organomet. Chem.* **1978**, *148*, 233–245.

(15) MacDougall, J. J.; Nelson, J. H.; Babich, M. W.; Fuller, C. C.; Jacobson, R. A. *Inorg. Chim. Acta* **1978**, *27*, 201–208.

(16) Norbury, A. H. *Adv. Inorg. Chem. Radiochem.* **1975**, *17*, 231–386.

(17) Orgel, L. E. "An Introduction to Transition-Metal Chemistry Ligand Field Theory"; Methuen: London, 1963; pp 53–68; Goodman, A.; Raynor, J. B. *Adv. Inorg. Chem. Radiochem.* **1970**, *13*, 135–162.

(18) Maki, A. H.; Edelstein, N.; Davidson, A.; Holm, R. H. *J. Am. Chem. Soc.* **1964**, *86*, 4580–4587.

(19) Good illustrative examples of ESR spectra for low-spin  $d^7$  Ni(III) complexes in which the unpaired electron is in the  $d_{z^2}$  orbital are given by: Lappin, A. G.; Murray, C. K.; Magerum, D. W. *Inorg. Chem.* **1978**, *17*, 1630–1634.

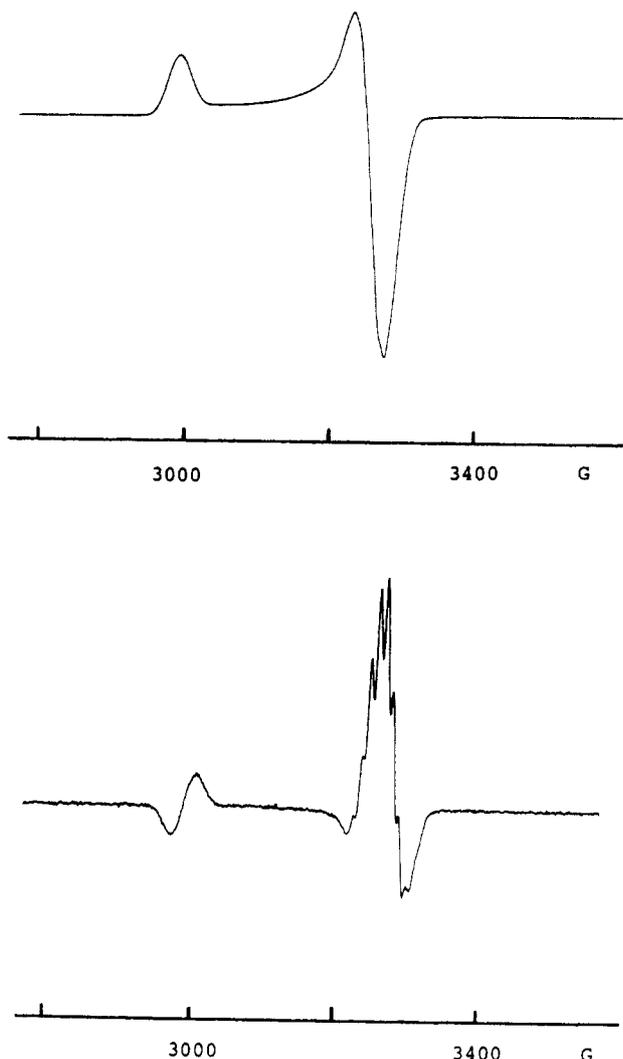


Figure 3. ESR spectrum **5a** in diglyme glass at 139 K (top) and its second derivative (below).

has been found for the  $z$  axis halogen donor X in square-pyramidal  $[\text{Ni}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-o,o'}\text{X}_2\}]^{6,20}$  (X = Cl, Br, or I). Clearly this is not the situation pertaining in **5a** and **5b** and the unexpected  $d_{xy}^2$ ,  $d_{xz}^2$ ,  $d_{yz}^2$ ,  $d_{x^2-y^2}^1$ ,  $d_{z^2}^0$  configuration must be considered as likely. A similar situation has recently been described for a series of bis(dipeptide)nickel(III) complexes which long-lived species in neutral so-

(20) In square-pyramidal  $[\text{Co}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-o,o'}\text{X}(\text{pyridine})\}]$   $g_x, g_y > g_z$  with an eight-line pattern with  $A_z^{\text{Co}} = 70$  G and a superhyperfine splitting of the  $z$  axis N pyridine atom of 9 G: van der Zeijden A. A. H.; van Koten, G., to be submitted for publication.

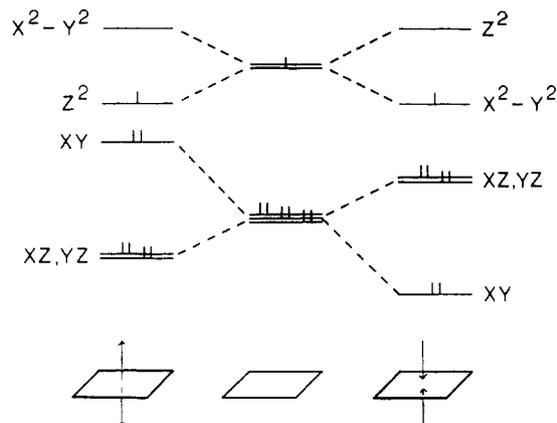


Figure 4. Schematic orbital schemes for various  $d^7$  Ni(III) coordination geometries.

lution are generated by oxidation of the corresponding nickel(II) complexes.<sup>3</sup>

The different ligating groups present in **5b** make positive identification of geometric distortions fairly difficult and hence correlation of  $g$  with the molecular axis system somewhat tentative. Certainly discrimination of the  $x$  and  $y$  axes in the absence of further information is not possible. However, the long Ni-N(1) distance of the amino ligand suggests this bond to be closely associated with either the  $x$  or  $y$  axis. Furthermore, since the multiplicity of  $g_{xx}, g_{yy}$  in the ESR spectrum of **5a** is indicative of superhyperfine splitting from four N atoms ( $a_N \approx 11$  G), we conclude that the Ni-N(3) (isothiocyanate) bonds define the other axis of the  $x, y$  pair. This definition of the axis system has the  $z$  axis then running through the C(1)-Ni-N(pyridine) bonds (see Figure 1a), which assignment is supported by the absence of any coupling of the unpaired electron with the  $z$  axis ligands. It must be noted that since the ESR spectra point to a compressed tetragonal octahedral geometry for **5a** and **5b**, it is the bonds along the  $z$  axis that are shortened in these compounds; i.e., obviously the C(1)-Ni and Ni-N(py) distances are shorter than would be anticipated in the absence of this electronic effect. Further studies are clearly needed to assess this.

**Registry No.** **1b**, 84520-52-5; **1d**, 99532-40-8; **1e**, 99532-41-9; **3**, 99532-38-4; **5a**, 99532-39-5; **5b**, 99532-42-0;  $[\text{Ni}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-o,o'}\text{Br}\}]$ , 84500-93-6.

**Supplementary Material Available:** Tables of positional and thermal parameters for all atoms and their esd's in parentheses and observed and calculated structure factors as well as a stereo ORTEP plot (20% probability ellipsoids) of (pyridine)bis(isothiocyanato)[ $o, o'$ -bis(dimethylamino)methyl]phenyl]nickel(III) (8 pages). Ordering information is given on any current masthead page.