

temperature at which the crystal formed. A change in correlation length might in turn be reflected in the physical properties of the crystal.

While the type of disorder observed in this compound is unusual, packing disorder in tetraphenylporphyrato complexes is relatively common. Several unpublished examples have been observed in this laboratory. In some cases, this disorder occurs because the core of the molecule is insulated from its neighbors by the phenyl substituents, as appears to be true in the present investigation. In other cases, the disorder may arise from inefficient packing due to the perpendicular orientation of the phenyl groups with respect to the porphyrin plane and the relatively rigid geometry of this large ligand. The occurrence of structural equilibria in some ferric tetraphenylporphyrato

complexes appears to be associated with such "loose packing".

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**Supplementary Material Available:** Listings of thermal parameters (Table I-S), hydrogen atom positions (Table II-S), porphyrin phenyl group atom positions (Table III-S), and observed and calculated structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

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## Multidentate Ligands Containing 2,2'-Bipyridine and/or Pyridine Moieties: Structural Aspects of Their Octahedral and Pentagonal-Bipyramidal Complexes

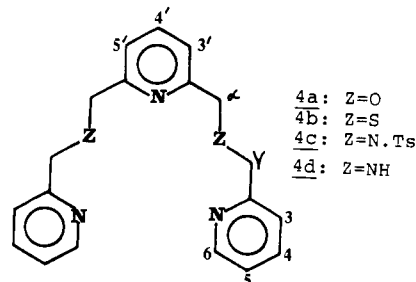
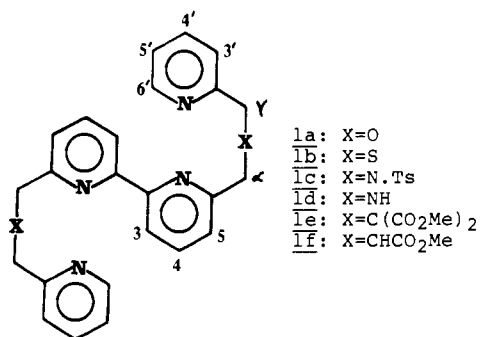
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Multidentate open-chain ligands containing 2,2'-bipyridine and/or pyridine moieties, connected by the CH<sub>2</sub>-X-CH<sub>2</sub> bridges in which X is the heteroatom O, S, or N, have been synthesized and characterized. <sup>1</sup>H NMR spectral data support the ligand structures. Complexation of these ligands with Co(II), Ni(II), and Cu(II) has been demonstrated. Single-crystal X-ray structural investigations showed a pentagonal-bipyramidal geometry for the Co(II) complex of a pyridine diether ligand (X = O); the five equatorial coordination positions are occupied by the ligand heteroatoms, while two water molecules reside at the axial positions. With the ethereal (X = O) bipyridine ligand the pentagonal-bipyramidal arrangement is retained except that one axial water molecule is replaced by the terminal pyridine group. An octahedral environment around Co(II) or Ni(II) was observed for the thioethers (X = S). The complex [Ni(C<sub>24</sub>H<sub>22</sub>N<sub>4</sub>S<sub>2</sub>)]Cl<sub>2</sub>·EtOH·2H<sub>2</sub>O crystallizes in the triclinic space group *P* $\bar{1}$ . The unit cell dimensions are *a* = 11.588 (2) Å, *b* = 11.644 (2) Å, and *c* = 12.421 (1) Å with  $\alpha$  = 114.00 (1)°,  $\beta$  = 99.78 (1)°,  $\gamma$  = 100.98 (1)°, and *Z* = 2. The [Co(C<sub>19</sub>H<sub>19</sub>N<sub>3</sub>O<sub>2</sub>)(H<sub>2</sub>O)<sub>2</sub>]Cl<sub>2</sub> complex forms monoclinic crystals with the space group *P*2<sub>1</sub>/*c* and unit cell dimensions *a* = 13.099 (2) Å, *b* = 8.052 (1) Å, and *c* = 20.952 (5) Å, and  $\beta$  = 106.92 (2)° and *Z* = 4. The complex [Co(C<sub>19</sub>H<sub>19</sub>N<sub>3</sub>S<sub>2</sub>)Cl]<sub>2</sub>[CoCl<sub>4</sub>]·2H<sub>2</sub>O·2MeOH crystallizes in the monoclinic space group *P*2<sub>1</sub>/*c* and has the cell dimensions *a* = 30.780 (4) Å, *b* = 9.278 (2) Å, and *c* = 17.653 (3) Å, and  $\beta$  = 90.80 (1)° and *Z* = 4.

### Introduction

Numerous complexing reagents have been constructed to sequester metal ions, but few have received more attention than those of the pyridine or 2,2'-bipyridine class because of their potential donor abilities.<sup>2</sup> Over the past decade, several ligands, in which an N-heteroaromatic moiety was incorporated within a macrocyclic framework, have been synthesized<sup>3</sup> and their complexation has been demonstrated.<sup>4,5</sup> As a continuation of our work to enhance metal ion selectivity and to better understand the effects of incorporating these binding loci in acyclic vs. cyclic systems, we herein report the synthesis and characterization of the related open-chain polyfunctional ligands **1**. These N-heterocycles were connected by the CH<sub>2</sub>-X-CH<sub>2</sub> linkage, in which X is C, O, S, or N, so that the effect of the  $\beta$  atom in subsequent complexation can be evaluated. The 2,2'-bipyridino moiety in **1** has been substituted



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by a 2,6-pyridino unit to afford the related **4** in order to study the relationship between bi- and monodentate electron-deficient heteroaromatics. To evaluate the chelating tendencies

of these multifunctional ligands, complexes of Co(II), Ni(II), and Cu(II) were prepared. Since the single-crystal X-ray structural investigation for the cobalt(II) complexes of **1a** and **4a** revealed an unusual seven-coordinate pentagonal-bipyramidal (PBP) geometry, this sparked further interest in this class of *non*-Schiff-base ligands. In the literature, such seven-coordinate pentagonal-bipyramidal (PBP) complexes of 3d transition metals are relatively rare;<sup>6</sup> however, Palenik et al.<sup>7,8</sup> have reported PBP complexes of a germane series of Schiff-base ligands: 2,6-diacetylpyridine bis(semicarbazone) (DAPSC) and other hydrazone derivatives.

### Experimental Section

**General Comments.** All melting points were taken in capillary tubes with a Thomas-Hoover Uni-Melt apparatus and are uncorrected. <sup>1</sup>H NMR spectra were determined on an IBM Bruker NR/80 spectrometer using CDCl<sub>3</sub> as solvent, with Me<sub>4</sub>Si as the internal standard. Mass spectral (MS) data (70 eV) were determined by D. Patterson on a Hewlett-Packard HP 5985 GC mass spectrometer and reported (assignment and relative intensity are given in parentheses). X-ray diffraction data were collected with graphite-monochromatized Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) on an Enraf-Nonius CAD-4 diffractometer. For preparative thick-layer chromatography (ThLC), 2-mm silica gel PF-254-366 plates were used. Elemental analyses were performed by either R. Seab in these laboratories or Galbraith Laboratories, Inc. A Du Pont Model 900 thermal analyzer was used to obtain thermal gravimetric analyses (TGA). The magnetic moments of the complexes were determined in MeOH by NMR techniques<sup>9</sup> on a Varian Associates A-60A NMR spectrometer. Electronic spectra were recorded on a Cary 14 spectrophotometer using 10<sup>-2</sup>–10<sup>-3</sup> M MeOH solutions at 25 °C.

**Solvents.** Anhydrous *N,N*-dimethylformamide (DMF) was purified in order to remove the cyanide impurities, which are generated by gradual decomposition upon standing.<sup>10</sup> Anhydrous tetrahydrofuran (THF) was distilled from benzophenone ketyl under an argon atmosphere immediately prior to use. All other solvents and available organic materials were commercial products purified by standard procedures.<sup>11</sup>

**2-Pyridinemethanol (2a)** (bp 63 °C (0.5 mm) (lit.<sup>12</sup> bp 115–118 °C (22 mm)), **2-(mercaptomethyl)pyridine (2b)** (bp 65 °C (1.5 mm) (lit.<sup>13</sup> bp 87–89 °C (10 mm))), **2,6-bis(chloromethyl)pyridine (5a)** (mp 74–75 °C (lit.<sup>14</sup> mp 74–75 °C)), and **2,6-pyridinedimethanethiol (5b)** (bp 117–119 °C (0.9 mm) (lit. bp 94–96 °C (0.35 mm)),<sup>15</sup> 107–108 °C (0.8 mm)<sup>16</sup>) were prepared by known procedures.

**2-(Aminomethyl)pyridine** was purchased from Aldrich Chemical Co. **6,6'-Bis(chloromethyl)-2,2'-bipyridine (3)** was prepared<sup>17</sup> by the free radical chlorination of 6,6'-dimethyl-2,2'-bipyridine; mp 157–158 °C.

**General Nucleophilic Displacement. 6,6'-Bis((2-pyridylmethyl)oxy)methyl]2,2'-bipyridine (1a).** To a stirred solution of 2-pyridinemethanol (436 mg, 4 mmol) in anhydrous THF (20 mL) was added NaH (oil-free, 192 mg). The mixture was refluxed for 15 min under N<sub>2</sub>. A solution of **3** (500 mg, 2 mmol) in anhydrous THF (20 mL) was added dropwise, and the mixture was then refluxed for 3 h. After the mixture was cooled, the solvent was removed in vacuo to give a residue which, after addition of H<sub>2</sub>O, was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3  $\times$  20 mL). The combined extract was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo to give a residue, which was recrystallized (C<sub>7</sub>H<sub>16</sub>) to afford the bis(ether) **1a**, as colorless crystals. The critical data are summarized in Table I.

**6,6'-Bis((2-pyridylmethyl)thio)methyl]-2,2'-bipyridine (1b).** To a hot solution of **3** (500 mg, 2 mmol) in EtOH (40 mL) was added in one portion an EtOH solution of **2b** (500 mg, 4 mmol) containing NaOEt (270 mg, 4 mmol). The workup followed the above general procedure, and the critical data for **1b** are given in Table I.

***N*-Tosyl-2-(aminomethyl)pyridine (2c).** To a stirred mixture of 2-(aminomethyl)pyridine (2.16 g, 20 mmol) and NaOH (1.2 g, 30 mmol) in H<sub>2</sub>O (10 mL) was added rapidly recrystallized tosyl chloride (3.8 g, 20 mmol) in Et<sub>2</sub>O (10 mL). After 1.5 h, the solvent was removed in vacuo to give a residue, which was neutralized with dilute aqueous hydrochloric acid. The precipitate was filtered, washed with H<sub>2</sub>O, and dried. The residue was recrystallized from aqueous EtOH to give **2c**, as white crystals: mp 91–93 °C; yield 4.7 g (98%); <sup>1</sup>H NMR  $\delta$  2.37 (s, Me), 4.23 (d, pyCH<sub>2</sub>,  $J = 5.4 \text{ Hz}$ ), 6.44 (t, NH,  $J = 5.4 \text{ Hz}$ ), 7.12 (m, 5-pyH), 7.19 (bd, 3-pyH), 7.21 (d, 3-phH,  $J = 8 \text{ Hz}$ ), 7.58 (ddd, 4-pyH,  $J = 7.8, 7.4, 1.8 \text{ Hz}$ ), 7.71 (d, 2-phH,  $J = 8 \text{ Hz}$ ), 8.42 (bd, 6-pyH); MS  $m/e$  198 ( $M^+ - \text{SO}_2$ , 100), 120 (C<sub>8</sub>H<sub>10</sub>N, 70), 107 (C<sub>6</sub>H<sub>7</sub>N<sub>2</sub>, 98). Anal. Calcd for C<sub>13</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>S: C, 59.52; H, 5.38; N, 10.68. Found: C, 59.31; H, 5.58; N, 10.61.

***N,N'*-Ditosyl-6,6'-bis((2-pyridylmethyl)amino)methyl]-2,2'-bipyridine (1c).** To a solution of NaOEt (680 mg, 10 mmol) in absolute EtOH (20 mL) was added *N*-tosyl-2-(aminomethyl)pyridine (2.62 g, 10 mmol) in absolute EtOH, and the mixture was then refluxed for 2 h. After concentration by 25%, the salt was filtered, washed with anhydrous Et<sub>2</sub>O, and dried. The salt (2.16 g, 7.6 mmol) was dissolved in hot DMF (15 mL), and then **3** (955 mg, 3.8 mmol) was added in small portions. After 12 h at 100 °C, the general workup afforded the desired tosylate **1c**, as colorless needles. Physical and spectral data are given in Table I.

**6,6'-Bis((2-pyridylmethyl)amino)methyl]-2,2'-bipyridine (1d).** A stirred mixture of **1c** (1.4 g, 2 mmol) and concentrated H<sub>2</sub>SO<sub>4</sub> (5 mL) was gently warmed (80 °C), until the solution turned clear. The temperature was increased to 160–170 °C for 5–10 min. After it was cooled to 50 °C, the mixture was cautiously poured into brine containing excess NaOH. The free amine precipitated as a light yellow oil, which was extracted with CH<sub>2</sub>Cl<sub>2</sub>, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated to dryness (770 mg, 97%). The bis(amine) **1d** was purified further by usual chromatography. Spectral and physical data are given in Table I.

**6,6'-Bis[2,2-bis(methoxycarbonyl)-2-(2-pyridylmethyl)ethyl]-2,2'-bipyridine (1e)** was prepared from **3** (1 g, 1 mmol), 2-[2,2-bis(methoxycarbonyl)ethyl]pyridine<sup>18</sup> (1.78 g, 8 mmol), and anhydrous K<sub>2</sub>CO<sub>3</sub> (3.31 g, 24 mmol) in purified DMF (20 mL) by following the general procedure. Spectral and physical data are given in Table I.

**6,6'-Bis[2-(methoxycarbonyl)-2-(2-pyridylmethyl)ethyl]-2,2'-bipyridine (1f).** A stirred solution of tetraester **1e** (1.88 g, 3 mmol) in concentrated HCl (20 mL) was refluxed for 15 h. After concentration in vacuo, the residue was dissolved in anhydrous MeOH (20 mL), and concentrated H<sub>2</sub>SO<sub>4</sub> (0.5 mL) was added. After the solution was refluxed for 12 h, the solvent was removed and the residue was dissolved in H<sub>2</sub>O, neutralized with saturated aqueous Na<sub>2</sub>CO<sub>3</sub>, extracted with CH<sub>2</sub>Cl<sub>2</sub>, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Concentration in vacuo afforded a yellow oil, which was chromatographed (ThLC) on silica gel, by two elutions with EtOAc/C<sub>6</sub>H<sub>12</sub> (1:1), to give the bis(ester) **1f**, as a colorless oil. Physical and spectral data are given in Table I.

**2,6-Bis((2-pyridylmethyl)oxy)methyl]pyridine (4a).** To a solution of **2a** (1.43 g, 13 mmol) in anhydrous THF (25 mL) was added NaH (340 mg, 14 mmol; 99%). The stirred mixture was gently refluxed for 30 min under N<sub>2</sub>, and then **5a** (1.14 g, 6.5 mmol) was added in

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Table I. Physical and <sup>1</sup>H NMR Spectral Data<sup>a</sup>

| compd  | mp, °C   | % <sup>b</sup> | chem shift (coupling constant(s), Hz) |                    |                      |          |          |                    |                                    |                         |                         |  | others |
|--|--|----------------|---------------------------------------|--------------------|----------------------|----------|----------|--------------------|------------------------------------|-------------------------|-------------------------|--|--------|
|  |  |                | 3-                                    | 4-                 | 5-                   | α-(γ)    | γ-(α)    | 3'-                | 4'-                                | 5'-                     | 6'-                     |  |        |
| 1a (X = O)                                   | 104-105<br>( <i>n</i> -C <sub>7</sub> H <sub>16</sub> ) <sup>c</sup> | 69             | 8.32<br>(7.8, 1)                      | 7.81<br>(7.8, 7.8) | 7.53<br>(7.8, 1)     | 4.83 (s) | 4.87 (s) | 7.53 (m)           | 7.70<br>(-, 7.3, 1.7) <sup>d</sup> | 7.18<br>(7.3, 4.9, 1.2) | 8.57<br>(4.9, 1.7, 1.0) |  |        |
| 1b (X = S)                                   | 106-107<br>(EtOH)  | 70             | 8.30<br>(7.8, 1)                      | 7.75<br>(7.8, 7.8) | 7.38 (m)             | 3.90 (s) | 3.90 (s) | 7.38 (m)           | 7.62<br>(-, 7.3, 1.8)              | 7.14<br>(7.6, 4.9, 1.2) | 8.55<br>(4.9, 1.8, 0.9) |  |        |
| 1c (X = NTs)                                 | 167-168<br>(EtOH)  | 82             | 7.88<br>(7.8, 1)                      | 7.57<br>(7.8, 7.8) | 7.24<br>(7.8, 1)     | 4.63 (s) | 4.69 (s) | 7.42 (m)           | 7.54<br>(-, 7.4, 1.7)              | 7.05<br>(7.4, 4.9, 1.4) | 8.37<br>(4.9, 1.7, 1)   | Me 2.30 (s)<br>C <sub>6</sub> H <sub>4</sub> 7.15, 7.67 (d)<br>NH 4.61 (6 s) |        |
| 1d (X = NH)                                  | oil  | 97             | 8.34 (7.8)                            | 7.71<br>(7.8, 7.8) | 7.32 (7.37)<br>(7.8) | 4.08 (s) | 4.09 (s) | 7.37<br>(7.32) (m) | 7.60<br>(7.7, 1.7)                 | 7.12<br>(7.4, 4.9, 1.1) | 8.54<br>(4.9, 1.7, 0.8) | CO <sub>2</sub> Me 3.75 (s)  |        |
| 1e (X = C(CO <sub>2</sub> Me) <sub>2</sub> ) | 156-157<br>(MeOH)  | 95             | 8.26 (7.8)                            | 7.72<br>(7.8, 7.8) | 7.05 (7.8)           | 3.55 (s) | 3.57 (s) | 6.98 (7.8)         | 7.52<br>(7.8, 1.9)                 | 7.11<br>(7.8, 4.9, 1)   | 8.51<br>(4.9, 1.9, 1)   | CH 3.69 (m)<br>CO <sub>2</sub> Me 3.57                                       |        |
| 1f (X = CHCO <sub>2</sub> Me)                | oil  | 82             | 8.26<br>(7.8, 1)                      | 7.66<br>(7.8, 7.8) | 7.10 (m)             | 3.17 (m) | 3.17 (m) | 7.15 (m)           | 7.56<br>(7.7, 1.8)                 | 7.09<br>(7.6, 4.9, 1.2) | 8.52<br>(4.9, 1.8, 1)   |  |        |

<sup>a</sup> Solvent: CDCl<sub>3</sub> (10%) Me<sub>4</sub>Si standard.<sup>b</sup> Isolated yields.<sup>c</sup> Solvent of recrystallization.<sup>d</sup> The remaining *J* value could not be accurately determined.

one portion, followed by refluxing for 5 h. After the mixture was cooled, EtOH (1 mL) was added and the solvent was removed in vacuo to give a residue that after addition of water, was extracted with CHCl<sub>3</sub>, dried with Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo to give a residue, which was recrystallized from *n*-C<sub>7</sub>H<sub>16</sub> to afford the bis(ether) **4a** as colorless crystals: yield 1.69 g, 81%; mp 90–92 °C; <sup>1</sup>H NMR δ 4.77 (s, pyCH<sub>2</sub>), 7.18 (ddd, 5-pyH, *J* = 7.1, 4.8, 1.7 Hz), 7.37–7.8 (m, 3,4,3',4'-pyH), 8.56 (ddd, 6-pyH, *J* = 4.8, 1.7, 1.0 Hz). Anal. Calcd for C<sub>19</sub>H<sub>19</sub>N<sub>3</sub>O<sub>2</sub>: C, 71.01; H, 5.96; N, 13.07. Found: C, 71.04; H, 6.21; N, 13.03.

**2,6-Bis((2-pyridylmethyl)thio)methylpyridine (4b).** To a solution of 2,6-pyridinedimethanethiol (510 mg, 3 mmol) in 70% EtOH (25 mL) containing NaOH (500 mg, 12.5 mmol) was added **2e** (1 g, 6 mmol). The stirred solution was refluxed for 1.5 h under N<sub>2</sub>. After the mixture was cooled, the solvent was removed in vacuo and the residue was extracted with CHCl<sub>3</sub> (3 × 20 mL). The combined extract was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo, and the residue was chromatographed on neutral alumina, by elution with *n*-C<sub>7</sub>H<sub>16</sub>/EtOAc (1:1), to give the desired bis(sulfide) **4b**, as an oil: yield 920 mg, 87%; *R*<sub>f</sub> 0.13; <sup>1</sup>H NMR δ 3.77, 3.82 (2 s, pyCH<sub>2</sub>, 4 H each), 7.00–7.68 (m, 3,4,5,3',4'-pyH), 8.48 (ddd, 6-pyH, *J* = 4.8, 1.7, 0.9 Hz). Anal. Calcd for C<sub>19</sub>H<sub>19</sub>N<sub>3</sub>S<sub>2</sub>: C, 64.56; H, 5.42; N, 11.89. Found: C, 64.41; H, 5.48; N, 11.69.

***N,N'*-Ditosyl-2,6-bis((2-pyridylmethyl)amino)methylpyridine (4c).** To a solution of NaOEt (1.02 g, 15 mmol) in absolute EtOH (40 mL) was added *N*-tosyl-2-(aminomethyl)pyridine (3.93 g, 15 mmol). The stirred solution was refluxed for 1 h, and then **5a** (1.32 g, 7.5 mmol) was added in one portion. The mixture was refluxed for an additional 5 h. The usual workup gave an oily residue, which was chromatographed on neutral alumina, by elution with a petroleum ether (bp 30–60 °C)/EtOAc (3:1) mixture to afford three fractions:

**Fraction A** (*R*<sub>f</sub> 0.25) gave **2-(ethoxymethyl)-*N*-tosyl-*N'*-(2-pyridylmethyl)-6-(aminomethyl)pyridine**, as an oil: yield 1.42 g, 23%; <sup>1</sup>H NMR δ 1.24 (t, CH<sub>2</sub>CH<sub>3</sub>, *J* = 7.0 Hz), 2.41 (s, TsCH<sub>3</sub>), 3.53 (q, CH<sub>2</sub>CH<sub>3</sub>, *J* = 7.0 Hz), 4.39 (s, CH<sub>2</sub>OEt), 4.56, 4.58 (2 s, pyCH<sub>2</sub>), 6.96–7.75 (m, 3,4,5,3',4',5'-pyH and TosH), 8.36 (ddd, 6-pyH, *J* = 4.8, 1.6, 1.0 Hz); MS *m/e* 256 [(M-Ts)<sup>+</sup>, 100]. Anal. Calcd for C<sub>22</sub>H<sub>25</sub>N<sub>3</sub>O<sub>2</sub>S: C, 64.21; H, 6.12; N, 10.21. Found: C, 64.01; H, 6.16; N, 10.25.

**Fraction B** (*R*<sub>f</sub> 0.20) gave unchanged **2c** (~10%).

**Fraction C** (*R*<sub>f</sub> 0.12) afforded the desired *N,N'*-ditosyl compound **4c**, as a colorless oil: yield 1.65 g, 35%; <sup>1</sup>H NMR δ 2.39 (s, TsCH<sub>3</sub>), 4.37, 4.49 (2 s, pyCH<sub>2</sub>, 4 H ea), 6.96–7.71 (m, 3,4,5,3',4'-pyH and TosH), 8.34 (ddd, 6-pyH, *J* = 4.8, 1.8, 0.9 Hz). Anal. Calcd for C<sub>33</sub>H<sub>33</sub>N<sub>3</sub>O<sub>4</sub>S<sub>2</sub>: C, 63.14, H, 5.30; N, 11.15. Found: C, 62.95; H, 5.41; N, 11.21.

**4c** is also obtained in ca. 80% yield by reacting the isolated sodium salt of **2c** and **5a** in DMF at 100 °C.

**2,6-Bis((2-pyridylmethyl)amino)methylpyridine (4d).**<sup>19</sup> A stirred solution of **4c** (1.25 g, 2 mmol) in concentrated H<sub>2</sub>SO<sub>4</sub> (5 mL) was heated at 110 °C for 2 h. After cooling, the mixture was poured into a brine solution containing NaOH. The precipitated diamine was extracted with CHCl<sub>3</sub>, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo to give an oily residue, which was chromatographed on neutral alumina by elution with a solution of 1% EtOH in CHCl<sub>3</sub> to give diamine **4d**, as an unstable pale yellow oil: yield 520 mg, 81%; *R*<sub>f</sub> 0.24; <sup>1</sup>H NMR δ 2.87 (bs, NH), 3.81 and 3.82 (2 s, pyCH<sub>2</sub>), 6.88–7.24 (m, 3,4,5,3',4'-pyH), 8.38 (ddd, 6-pyH, *J* = 4.8, 1.8, 0.9 Hz).

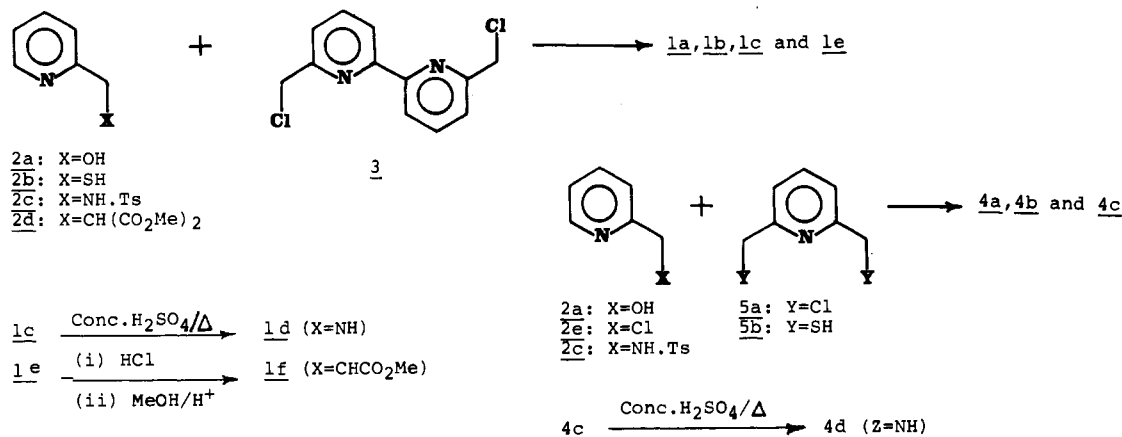
**Preparation of Complexes.** A mixture of CuCl<sub>2</sub>·6H<sub>2</sub>O, or NiCl<sub>2</sub>·7H<sub>2</sub>O and a stoichiometric quantity (1:1) of **1a**, **1b**, **1d**, **1e**, **4a**, **4b**, or **4d** in a solution of MeOH and CHCl<sub>3</sub> (25 mL, 4:1) was refluxed for 4 h. The solution was concentrated to 5 mL, and when it was allowed to stand, crystals were obtained and then recrystallized from MeOH or EtOH and dried in vacuo.

**X-ray Experiments.** Intensity data were collected by ω-2θ scans of variable rate designed to yield measurements of the same precision for all significant data. A maximum was placed on the scan time spent on any reflection. A crystal of [Ni(**1b**)Cl<sub>2</sub>·EtOH·2H<sub>2</sub>O] or [Co(**4b**)Cl<sub>2</sub>][CoCl<sub>4</sub>]·2H<sub>2</sub>O·2MeOH was sealed in a thin-walled glass capillary to prevent solvent loss, while the crystal of [Co(**4a**)(H<sub>2</sub>O)<sub>2</sub>]Cl<sub>2</sub> was mounted on a glass fiber. One hemisphere of data was collected for the triclinic crystal and one quadrant for the monoclinic crystals. Crystal data and specifics of data collection are given in Table II.

Table II. Crystal Data and Data Collection Parameters

|  | Ni(1b)   | Co(4a)   | Co(4b)   |
|--|--|--|--|
| formula                                  | [Ni(C <sub>24</sub> H <sub>22</sub> N <sub>4</sub> S <sub>2</sub> )Cl <sub>2</sub> ·C <sub>2</sub> H <sub>5</sub> OH·2H <sub>2</sub> O | [Co(C <sub>19</sub> H <sub>19</sub> N <sub>3</sub> O <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub> | [Co(C <sub>19</sub> H <sub>19</sub> N <sub>3</sub> S <sub>2</sub> )Cl <sub>2</sub> ·[CoCl <sub>4</sub> ] <sub>2</sub> ·2H <sub>2</sub> O·2CH <sub>3</sub> OH |
| fw                                       | 642.3  | 487.3  | 1196.7   |
| cryst syst                               | triclinic  | monoclinic   | monoclinic   |
| space group:                             | <i>P</i> $\bar{1}$   | <i>P</i> 2 <sub>1</sub> / <i>c</i>   | <i>P</i> 2 <sub>1</sub> / <i>c</i>   |
| <i>a</i> , Å                             | 11.588 (2)   | 13.099 (2)   | 30.780 (4)   |
| <i>b</i> , Å                             | 11.644 (2)   | 8.052 (1)  | 9.278 (2)  |
| <i>c</i> , Å                             | 12.421 (1)   | 20.952 (5)   | 17.653 (3)   |
| $\alpha$ , deg                           | 114.00 (1)   |  |  |
| $\beta$ , deg                            | 99.78 (1)  | 106.92 (2)   | 90.80 (1)  |
| $\gamma$ , deg                           | 100.98 (1)   |  |  |
| <i>V</i> , Å <sup>3</sup>                | 1444.8 (9)   | 2114 (1)   | 5041 (3)   |
| <i>d</i> , g cm <sup>-3</sup>            | 1.474  | 1.531  | 1.577  |
| <i>Z</i> (formulas/cell):                | 2  | 4  | 4  |
| $\mu$ (Mo K $\alpha$ ), cm <sup>-1</sup> | 10.33  | 10.93  | 14.99  |
| min transmission, %                      | 91.26  | 92.69  | 91.00  |
| cryst size, mm                           | 0.25 × 0.35 × 0.48   | 0.20 × 0.36 × 0.60   | 0.12 × 0.18 × 0.22   |
| $\theta$ limits, deg                     | 1 ≤ $\theta$ ≤ 25  | 1 ≤ $\theta$ ≤ 25  | 1 ≤ $\theta$ ≤ 18  |
| scan rates, deg min <sup>-1</sup>        | 0.53-10  | 0.53-20  | 0.45-10  |
| precision                                | <i>I</i> ≈ 50 $\sigma$ ( <i>I</i> )  | <i>I</i> ≈ 50 $\sigma$ ( <i>I</i> )  | <i>I</i> ≈ 20 $\sigma$ ( <i>I</i> )  |
| max scan time, s                         | 120  | 120  | 120  |
| unique data                              | 5072   | 3722   | 3454   |
| obsd data                                | 3719   | 2374   | 1752   |
| variables                                | 343  | 262  | 310  |
| <i>R</i>                                 | 0.038  | 0.035  | 0.049  |
| <i>R</i> <sub>w</sub>                    | 0.057  | 0.054  | 0.056  |
| max residual, e Å <sup>-3</sup>          | 0.67   | 0.44   | 0.64   |
| color                                    | red  | pink   | blue   |
| temp, °C                                 | 25   | 26   | 23   |

Scheme I



Data reduction included corrections for background, Lorentz, polarization, and absorption. The absorption corrections were based on  $\psi$  scans of reflections near  $\chi = 90^\circ$ . Equivalent data were merged, and reflections having  $I > 3\sigma(I)$  were considered "observed" and used in refinements.

**Structure Solutions and Refinements.** All structures were solved by heavy-atom methods and refined by full-matrix least squares based upon *F*, with use of the Enraf-Nonius SDP programs<sup>20</sup> using the scattering factors of Cromer and Waber<sup>21</sup> and the anomalous dispersion coefficients of Cromer.<sup>22</sup> Except in specific cases noted below, non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from difference maps but included as fixed contributions and placed in calculated positions where possible. *R* factors and residuals in final difference maps are noted in Table II.

A. [Co(4a)(H<sub>2</sub>O)<sub>2</sub>]Cl<sub>2</sub>. No unusual steps were required.

B. [Ni(1b)]Cl<sub>2</sub>·EtOH·2H<sub>2</sub>O. A Cl atom and a water molecule are disordered into two regions separated by ca. 3.2 Å. The model used for the disorder involved atoms Cl2 and Cl2' half-populated in the two regions. Half-atom Cl2 shares its region with three sites of 1/6

occupancy by a water molecule (O3SA-O3SC), all within 0.8 Å of it. Half-atom Cl2' shares its region with four sites of 1/8 occupancy by a water molecule (O3SD-O3SG), all within 0.7 Å of it. Due to the low electron densities (1-2 e Å<sup>-3</sup>) of the partial water positions and their high correlations with Cl2 and Cl2', they were not refined. The acidic hydrogen of the EtOH (C2S-C1S-O1S) and the hydrogen atoms on H<sub>2</sub>O were not located.

C. [Co(4b)]Cl<sub>2</sub>·[CoCl<sub>4</sub>]<sub>2</sub>·2H<sub>2</sub>O·2MeOH. Due to the small crystal size and its limited scattering ability, sufficient data were not obtained to allow full anisotropic refinement. Only Co, Cl, and S atoms were refined anisotropically. All other non-hydrogen atoms except those of a disordered MeOH were refined with isotropic thermal parameters. The model used for the disordered MeOH molecule involves one orientation with population 2/3 (O2S-C2S) and one with population 1/3 (O2S'-C2S') sharing the same region. All four atoms were assigned *B* = 10 Å<sup>2</sup>, and their positions were adjusted via difference maps. No solvent H atoms were located.

## Results and Discussion

**A. Ligands. 1. Synthesis.** When 2-(hydroxymethyl)- (2a), 2-(mercaptomethyl)- (2b), *N*-tosyl-2-(aminomethyl)- (2c), or 2-[2,2-bis(methoxycarbonyl)ethyl]pyridine (2d) was reacted with 0.5 equiv of 6,6'-bis(chloromethyl)-2,2'-bipyridine (3) in the presence of a base, 1a-c and 1e are isolated in good yields, respectively. Detosylation of 1c by heating with concentrated H<sub>2</sub>SO<sub>4</sub> liberates (97%) the free amine 1d. The diacid is readily

(20) Frenz, B. A.; Okaya, Y. "Enraf-Nonius Structure Determination Package"; Enraf-Nonius: Delft, Holland, 1980.

(21) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(22) Cromer, D. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

Table III. Analytical, TGA, Magnetic, and Spectral Data for the Complexes

| complex  | color            | yield,<br>% | anal. data found (calcd) |                |                  | TGA  | $\mu, \mu_B$ | $10^3 \tilde{\nu}, \text{cm}^{-1}$ |
|--|------------------|-------------|--------------------------|----------------|------------------|--|--------------|------------------------------------|
|  |                  |             | % C                      | % H            | % N              |  |              |                                    |
| [Co(1a)H <sub>2</sub> O]Cl <sub>2</sub> ·6H <sub>2</sub> O           | pink             | 67          | 43.87<br>(44.05)         | 5.63<br>(5.54) | 8.56<br>(8.56)   | -5H <sub>2</sub> O (50 °C); -2H <sub>2</sub> O<br>(108 °C); 267 °C dec | 5.24         | 18.7                               |
| Ni(1a)Cl <sub>2</sub> ·3H <sub>2</sub> O                             | green            | 84          | 49.70<br>(49.52)         | 5.01<br>(4.85) | 9.48<br>(9.62)   | -3H <sub>2</sub> O (75 °C); 270 °C dec                                 | 2.98         | 8.7, 16.7, 24.4                    |
| Cu(1a)Cl <sub>2</sub> ·2H <sub>2</sub> O                             | brown            | 77          | 50.44<br>(50.67)         | 4.99<br>(4.61) | 9.84<br>(9.85)   | -2H <sub>2</sub> O (40 °C); 145 °C dec                                 | 1.94         | 12.5, 23.0                         |
| Co(1b)Cl <sub>2</sub> ·7H <sub>2</sub> O                             | brown            | 91          | 41.92<br>(41.99)         | 5.18<br>(5.29) | 7.90<br>(8.16)   | -7H <sub>2</sub> O (80 °C); 140 °C dec                                 | 5.11         | 19.1                               |
| [Ni(1b)]Cl <sub>2</sub> ·EtOH·2H <sub>2</sub> O                      | red              | 94          | 48.52<br>(48.62)         | 5.13<br>(5.02) | 8.63<br>(8.72)   | -[EtOH + 2H <sub>2</sub> O] (90 °C);<br>215 °C dec                     | 3.12         | 12.1, 18.9, 30.1                   |
| Cu(1b)Cl <sub>2</sub> ·MeOH·H <sub>2</sub> O                         | brown            | 86          | 48.85<br>(48.82)         | 4.39<br>(4.59) | 8.91<br>(9.11)   | -MeOH (40 °C); -H <sub>2</sub> O<br>(105 °C); dec                      | 1.88         | 32.0                               |
| Co(1d)Cl <sub>2</sub> ·5H <sub>2</sub> O                             | blue             | 87          | 47.86<br>(48.24)         | 5.07<br>(5.24) | 6.76<br>(6.62)   | -5H <sub>2</sub> O (50 °C); 135 °C dec                                 | 4.74         | 18.2                               |
| Cu(1d)Cl <sub>2</sub> ·H <sub>2</sub> O                              | greenish<br>blue | 76          | 52.12<br>(52.41)         | 4.88<br>(4.66) | 7.07<br>(7.19)   | -H <sub>2</sub> O (40 °C); 208 °C dec                                  | 1.98         | 13.7                               |
| Co(1e)Cl <sub>2</sub> ·7H <sub>2</sub> O                             | brown            | 78          | 43.86<br>(44.18)         | 5.77<br>(5.87) | 12.47<br>(12.88) | 140 °C dec   | 5.18         | 18.5                               |
| Ni(1e)Cl <sub>2</sub> ·4H <sub>2</sub> O                             | brown            | 75          | 47.91<br>(48.19)         | 5.01<br>(5.39) | 13.80<br>(14.05) | -4H <sub>2</sub> O (50 °C); 235 °C dec                                 | 3.20         | 8.3, 13.3, 24.7                    |
| Cu(1e)Cl <sub>2</sub> ·3H <sub>2</sub> O                             | green            | 70          | 49.09<br>(49.28)         | 5.07<br>(5.17) | 14.05<br>(14.37) | -3H <sub>2</sub> O (95 °C); 200 °C dec                                 | 2.01         | 13.3, 26.3                         |
| [Co(4a)(H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub>              | purple           | 90          | 47.10<br>(46.84)         | 4.93<br>(4.76) | 8.63<br>(8.62)   | -2H <sub>2</sub> O (80 °C); 165 °C dec                                 | 5.19         | 18.2                               |
| [Co(4b)Cl] <sub>2</sub> [CoCl <sub>4</sub> ]·2H <sub>2</sub> O·2MeOH | blue             | 64          | 38.25<br>(38.11)         | 4.06<br>(4.00) | 6.77<br>(6.67)   | -[2H <sub>2</sub> O + 2MeOH] (65 °C);<br>177 °C dec                    | 4.90         | 14.7, 19.2                         |
| Co(4d)Cl <sub>2</sub> ·3H <sub>2</sub> O <sup>19</sup>               | brown            | 88          | 45.31<br>(45.34)         | 5.28<br>(5.41) | 13.69<br>(13.92) | 170 °C dec   | 5.02         | 18.1                               |

Table IV. Coordinates for [Ni(C<sub>24</sub>H<sub>22</sub>N<sub>4</sub>S<sub>2</sub>)]Cl<sub>2</sub>·C<sub>2</sub>H<sub>5</sub>OH·2H<sub>2</sub>O<sup>d</sup>

| atom              | x           | y           | z           | atom | x          | y          | z          |
|-------------------|-------------|-------------|-------------|------|------------|------------|------------|
| Ni                | 0.80038 (4) | 0.67700 (4) | 0.60128 (3) | C5   | 0.7663 (3) | 0.5509 (3) | 0.7668 (3) |
| Cl1               | 0.6893 (1)  | 0.2601 (1)  | 0.3854 (1)  | C6   | 0.8477 (4) | 0.4763 (3) | 0.7045 (3) |
| Cl2 <sup>b</sup>  | 0.0716 (2)  | 0.6250 (2)  | 0.0073 (1)  | C7   | 1.0565 (3) | 0.6698 (4) | 0.7323 (3) |
| Cl2 <sup>b</sup>  | 0.3364 (2)  | 0.6942 (2)  | 0.0007 (2)  | C8   | 1.0410 (3) | 0.8059 (4) | 0.7887 (3) |
| S1                | 0.92525 (8) | 0.53926 (8) | 0.61729 (7) | C9   | 1.1334 (4) | 0.9118 (5) | 0.8852 (3) |
| S2                | 0.61329 (7) | 0.55161 (7) | 0.44238 (7) | C10  | 1.1167 (4) | 1.0336 (4) | 0.9281 (4) |
| O1S               | 0.5536 (3)  | 0.7433 (3)  | 0.2105 (3)  | C11  | 1.0090 (4) | 1.0523 (4) | 0.8776 (3) |
| O2S               | 0.5793 (5)  | 0.1240 (5)  | 0.0890 (6)  | C12  | 0.9211 (3) | 0.9443 (3) | 0.7829 (3) |
| O3SA <sup>c</sup> | 0.0273      | 0.6660      | 0.0000      | C13  | 0.8038 (3) | 0.9478 (3) | 0.7202 (3) |
| O3SB <sup>c</sup> | 0.0566      | 0.6113      | 0.0293      | C14  | 0.7622 (4) | 1.0583 (4) | 0.7511 (4) |
| O3SC <sup>c</sup> | 0.1113      | 0.6406      | 0.0000      | C15  | 0.6483 (4) | 1.0457 (4) | 0.6854 (4) |
| O3SD <sup>d</sup> | 0.3613      | 0.6680      | 0.0293      | C16  | 0.5775 (4) | 0.9261 (3) | 0.5891 (4) |
| O3SE <sup>d</sup> | 0.3594      | 0.7500      | 0.0000      | C17  | 0.6231 (3) | 0.8196 (3) | 0.5613 (3) |
| O3SF <sup>d</sup> | 0.3047      | 0.6934      | 0.0273      | C18  | 0.5497 (3) | 0.6875 (3) | 0.4591 (3) |
| O3SG <sup>d</sup> | 0.3047      | 0.6660      | -0.0293     | C19  | 0.6773 (3) | 0.5285 (3) | 0.3147 (3) |
| N1                | 0.7283 (2)  | 0.6339 (2)  | 0.7305 (2)  | C20  | 0.7988 (3) | 0.6229 (3) | 0.3429 (3) |
| N2                | 0.9391 (2)  | 0.8250 (3)  | 0.7404 (2)  | C21  | 0.8398 (4) | 0.6310 (3) | 0.2472 (3) |
| N3                | 0.7329 (2)  | 0.8310 (2)  | 0.6264 (2)  | C22  | 0.9523 (4) | 0.7149 (3) | 0.2706 (3) |
| N4                | 0.8674 (2)  | 0.6948 (2)  | 0.4600 (2)  | C23  | 1.0213 (4) | 0.7896 (4) | 0.3906 (3) |
| C1                | 0.6487 (3)  | 0.6923 (3)  | 0.7833 (3)  | C24  | 0.9773 (3) | 0.7762 (3) | 0.4812 (3) |
| C2                | 0.6067 (3)  | 0.6712 (4)  | 0.8734 (3)  | C1S  | 0.6393 (6) | 0.8513 (6) | 0.2182 (5) |
| C3                | 0.6471 (4)  | 0.5875 (4)  | 0.9112 (3)  | C2S  | 0.7269 (5) | 0.9300 (5) | 0.3349 (5) |
| C4                | 0.7286 (4)  | 0.5269 (4)  | 0.8579 (3)  |      |            |            |            |

<sup>a</sup> Estimated standard deviations in the least significant digits are shown in parentheses. <sup>b</sup> Population 1/2. <sup>c</sup> Population 1/6. <sup>d</sup> Population 1/8.

obtained by hydrolysis and decarboxylation of the tetraester **1e** upon boiling in concentrated HCl, and subsequent esterification gives the syn-bis(ester) **1f**. The ligands **4a-d** were also obtained by similar routes (Scheme I).

**2. NMR Spectral Aspects.** The chemical shifts of the  $\alpha$ -methylene protons directly reflect the effect of the neighboring heteroatom influence (Table I) and are reminiscent of the parent  $\text{pyCH}_2\text{-X-CH}_3$  chemical shifts.<sup>23</sup> The carbon analogues **1e** and **1f** are upfield with respect to **1a-d**, and the  $\Delta\delta = 0.4$  difference between **1e** and **1f** reflects the diminished electron withdrawal of the single ester group. The juxtapo-

sition of the methoxycarbonyl groups can be further realized by the upfield ( $\Delta\delta = 0.4$ ) shift experienced in H<sub>3</sub>. Lastly, the bulk of the tosylate moiety in **1c** is demonstrated by upfield shift ( $\Delta\delta = 0.5$ ) in H<sub>3</sub>; such a shift reflects a diminished diamagnetic anisotropy by the 3-pyridyl hydrogens caused by the orthogonal N electrons of the adjacent pyridine ring. Such dramatic shifts have been previously noted<sup>24</sup> in macrocyclic ligands.

**B. Complexes. 1. Complex Formation.** Ligands **1a-f**, **4a**, **4b**, and **4d** were each treated with 1 equiv of CoCl<sub>2</sub>·6H<sub>2</sub>O,

(23) Newkome, G. R.; Nayak, A.; Fronczek, F.; Kawato, T.; Taylor, H. C. R.; Meade, L.; Mattice, W. *J. Am. Chem. Soc.* **1979**, *101*, 4472.

(24) (a) Newkome, G. R.; Pappalardo, S.; Gupta, V. K.; Fronczek, F. R. *J. Org. Chem.* **1983**, *48*, 4848. (b) Newkome, G. R.; Kohli, D. K. *Heterocycles* **1981**, *15*, 739.

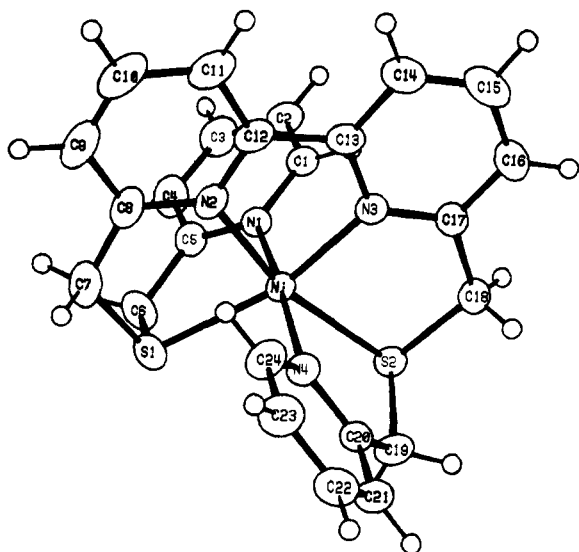


Figure 1. Perspective drawing of the  $[\text{Ni}(\mathbf{1b})]^{2+}$  ion.

Table V. Coordination Geometry of  $[\text{Ni}(\mathbf{1b})]^{2+}$

| Distances (Å) |            |          |            |
|---------------|------------|----------|------------|
| Ni-S1         | 2.398 (1)  | Ni-N2    | 2.030 (2)  |
| Ni-S2         | 2.392 (1)  | Ni-N3    | 2.021 (2)  |
| Ni-N1         | 2.116 (2)  | Ni-N4    | 2.103 (2)  |
| Angles (deg)  |            |          |            |
| S1-Ni-S2      | 111.03 (3) | S2-Ni-N4 | 84.10 (6)  |
| S1-Ni-N1      | 84.12 (6)  | N1-Ni-N2 | 89.63 (8)  |
| S1-Ni-N2      | 84.93 (7)  | N1-Ni-N3 | 95.16 (8)  |
| S1-Ni-N3      | 164.45 (6) | N1-Ni-N4 | 172.98 (8) |
| S1-Ni-N4      | 91.54 (6)  | N2-Ni-N3 | 79.53 (9)  |
| S2-Ni-N1      | 92.30 (6)  | N2-Ni-N4 | 95.49 (8)  |
| S2-Ni-N2      | 164.04 (7) | N3-Ni-N4 | 90.50 (9)  |
| S2-Ni-N3      | 84.51 (6)  |          |            |

$\text{NiCl}_2 \cdot 7\text{H}_2\text{O}$ , or  $\text{CuCl}_2$ , respectively, to give complexes whose physicochemical characteristics are summarized in Table III. Attempts were made to grow single crystals of all these complexes from a variety of solvents; however, only suitable single crystals of cobalt(II) complexes of **1a**, **4a**, and **4b**, respectively, and the nickel(II) complex of **1b** could be obtained. X-ray structural investigations were conducted on these complexes so as to afford precise insight into the geometry and modes of binding sites.

**2. Structure Description. a. The  $[\text{Ni}(\mathbf{1b})]^{2+}$  Ion.** The hexadentate ligand **1b** forms an octahedral complex with Ni(II) having local symmetry  $C_2$  in which the terminal pyridine rings span axial positions approximately normal to the square plane formed by the remainder of the ligand (Figures 1 and 2). Ni-S distances average 2.395 Å, equatorial (bipyridine) Ni-N distances 2.026 Å, and axial Ni-N distances 2.110 Å. Individual distances and angles within the coordination sphere are given in Table V. All pyridine rings are planar within experimental error, and those of the bipyridine are nearly coplanar, forming a dihedral angle of  $3.2^\circ$ . The axial pyridine containing N1 forms a dihedral angle of  $84.9^\circ$  with the bipyridine best plane, that containing N4 forms a similar angle of  $87.1^\circ$ , and the two axial pyridines form a dihedral angle of  $82.9^\circ$ . The Ni atom lies within 0.16 Å of all aromatic planes. The largest deviation from ideal octahedral coordination is found in the large S-Ni-S angle ( $111.03(3)^\circ$ ), which opens by  $21^\circ$  to accommodate the [5.5.5.5] ring system.

Drew et al.<sup>25</sup> reported a similar octahedral nickel(II) complex containing a hexadentate ligand derived from the con-

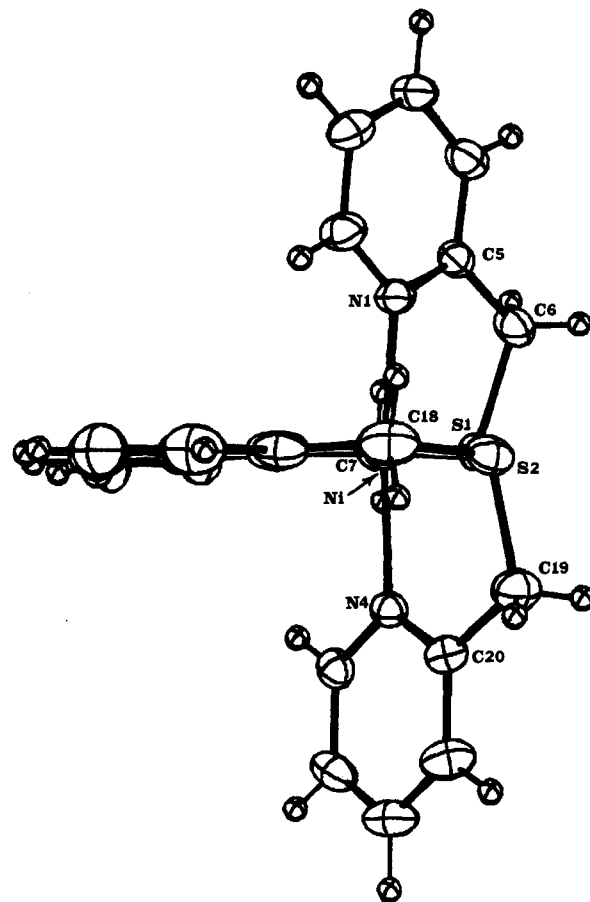


Figure 2. Side view of the  $[\text{Ni}(\mathbf{1b})]^{2+}$  ion.

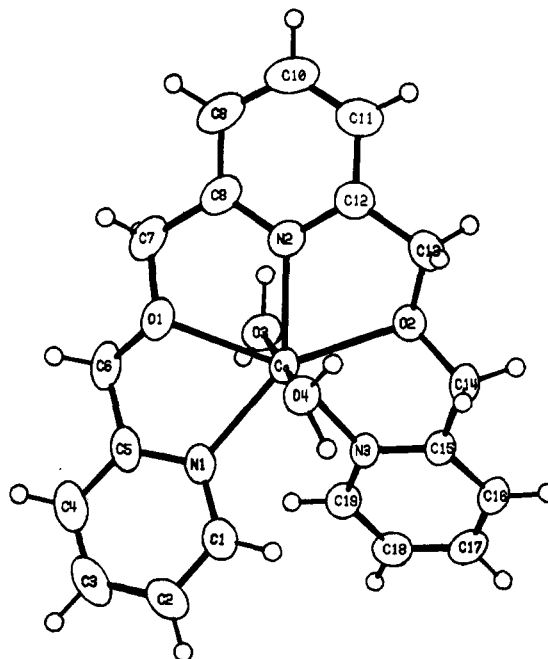


Figure 3. Perspective drawing of the  $[\text{Co}(\mathbf{4a})(\text{H}_2\text{O})_2]^{2+}$  ion.

densation of one molecule of 2,6-diacetylpyridine with two molecules of diethylenetriamine and subsequent isomerization. The pyridine in this molecule occupies one of the equatorial positions, and the Ni-N(py) distance is 2.026 (16) Å, which is significantly different from the axial Ni-N distances and resembles equatorial (bipyridine) Ni-N distances in our molecule.

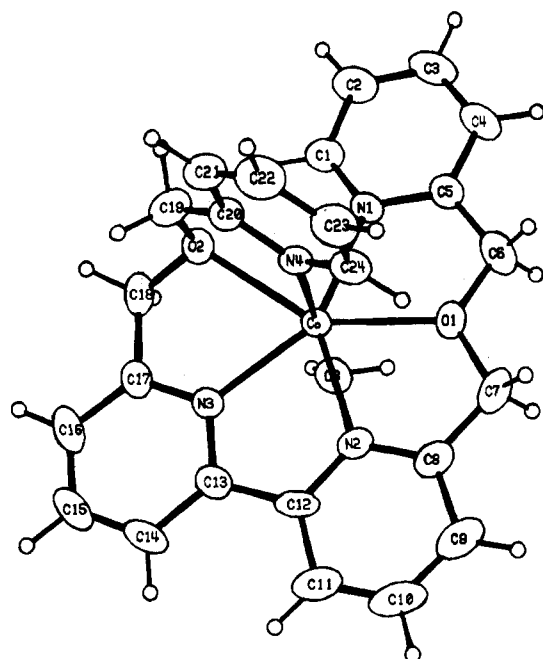
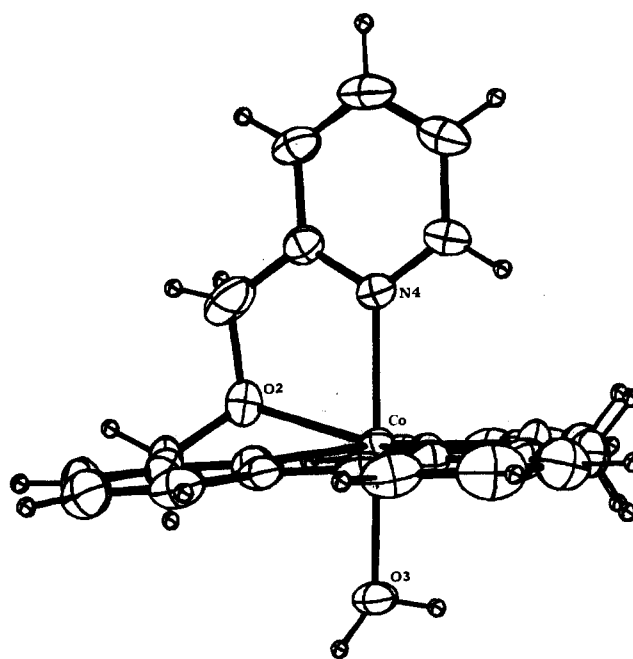
**b. The  $[\text{Co}(\mathbf{4a})(\text{H}_2\text{O})_2]^{2+}$  Ion.** The pentadentate ligand **4a** forms a diaquo complex with Co(II) having local symmetry

(25) Drew, M. G. B.; Nelson, J.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* 1981, 1691.

Table VI. Coordinates for  $[\text{Co}(\text{C}_{19}\text{H}_{19}\text{N}_3\text{O}_2)(\text{H}_2\text{O})_2]\text{Cl}_2^a$ 

| atom | x           | y           | z           | atom | x          | y           | z          |
|------|-------------|-------------|-------------|------|------------|-------------|------------|
| Co   | 0.26647 (3) | 0.14088 (6) | 0.64878 (2) | C6   | 0.4951 (3) | -0.0150 (6) | 0.6996 (2) |
| C11  | 0.18566 (8) | -0.3533 (1) | 0.74031 (5) | C7   | 0.4122 (4) | -0.0093 (6) | 0.7863 (2) |
| C12  | 0.2703 (1)  | -0.3735 (1) | 0.53845 (5) | C8   | 0.3118 (3) | 0.0502 (5)  | 0.7989 (2) |
| O1   | 0.4249 (2)  | 0.0720 (3)  | 0.7292 (1)  | C9   | 0.2938 (4) | 0.0264 (6)  | 0.8603 (2) |
| O2   | 0.0931 (2)  | 0.2030 (3)  | 0.6402 (1)  | C10  | 0.1946 (4) | 0.0653 (6)  | 0.8666 (2) |
| O3   | 0.2524 (2)  | -0.1204 (3) | 0.6442 (1)  | C11  | 0.1187 (4) | 0.1299 (5)  | 0.8141 (2) |
| O4   | 0.2877 (2)  | 0.4017 (3)  | 0.6604 (1)  | C12  | 0.1439 (3) | 0.1609 (4)  | 0.7556 (2) |
| N1   | 0.4037 (2)  | 0.1551 (4)  | 0.6065 (1)  | C13  | 0.0661 (3) | 0.2467 (5)  | 0.6987 (2) |
| N2   | 0.2383 (2)  | 0.1201 (3)  | 0.7474 (1)  | C14  | 0.0431 (3) | 0.2987 (5)  | 0.5829 (2) |
| N3   | 0.1661 (2)  | 0.1376 (3)  | 0.5434 (1)  | C15  | 0.0717 (3) | 0.2163 (4)  | 0.5265 (2) |
| C1   | 0.4020 (3)  | 0.2431 (5)  | 0.5517 (2)  | C16  | 0.0028 (3) | 0.2142 (5)  | 0.4624 (2) |
| C2   | 0.4868 (3)  | 0.2496 (5)  | 0.5264 (2)  | C17  | 0.0310 (3) | 0.1275 (5)  | 0.4137 (2) |
| C3   | 0.5783 (3)  | 0.1629 (6)  | 0.5584 (2)  | C18  | 0.1266 (3) | 0.0426 (5)  | 0.4305 (2) |
| C4   | 0.5824 (3)  | 0.0768 (6)  | 0.6144 (2)  | C19  | 0.1910 (3) | 0.0499 (5)  | 0.4953 (2) |
| C5   | 0.4942 (3)  | 0.0745 (5)  | 0.6373 (2)  |      |            |             |            |

<sup>a</sup> Estimated standard deviations in the least significant digits are shown in parentheses.

Figure 4. Perspective drawing of the  $[\text{Co}(\mathbf{1a})(\text{H}_2\text{O})]^{2+}$  ion.Figure 5. Side view of the  $[\text{Co}(\mathbf{1a})(\text{H}_2\text{O})]^{2+}$  ion.

$\text{C}_2$  and distorted-pentagonal-bipyramidal coordination geometry;  $\mathbf{4a}$  occupies the pentagonal girdle while the water oxygen atoms take the axial positions (Figure 3). A similar environment around the  $\text{Co}(\text{II})$  ion is also observed with  $\mathbf{1a}$  (Figures 4 and 5), where the equatorial positions are taken by two ether oxygens, two bipyridine nitrogens, and one pyridine nitrogen; a water molecule and a pyridine nitrogen occupy the axial sites.<sup>26</sup> In  $[\text{Co}(\mathbf{4a})(\text{H}_2\text{O})_2]^{2+}$ ,  $\text{Co}-\text{N}$  bonds average 2.217 Å,  $\text{Co}-\text{O}(\text{ether})$  bonds 2.304 Å, and  $\text{Co}-\text{O}(\text{aquo})$  bonds 2.118 Å. Individual values are given in Table VII. In the reported PBP cobalt(II) complex  $[\text{Co}(\text{DAPSC})\text{Cl}(\text{H}_2\text{O})]^{+}$ , the average  $\text{Co}-\text{N}$  and  $\text{Co}-\text{O}$  distances are 2.190 and 2.170 Å, respectively,<sup>7</sup> while in a cryptate<sup>6f</sup> these are 2.222 and 2.216 Å, respectively. Similar distances are

Table VII. Coordination Geometry of  $[\text{Co}(\mathbf{4a})(\text{H}_2\text{O})_2]^{2+}$ 

| Distances (Å) |            |          |            |
|---------------|------------|----------|------------|
| Co-O1         | 2.327 (2)  | Co-N1    | 2.226 (2)  |
| Co-O2         | 2.280 (2)  | Co-N2    | 2.208 (2)  |
| Co-O3         | 2.112 (2)  | Co-N3    | 2.217 (2)  |
| Co-O4         | 2.123 (2)  |          |            |
| Angles (deg)  |            |          |            |
| O1-Co-O2      | 140.09 (7) | O3-Co-O4 | 175.97 (8) |
| O1-Co-O3      | 80.97 (8)  | O3-Co-N1 | 95.90 (8)  |
| O1-Co-O4      | 95.36 (7)  | O3-Co-N2 | 86.05 (8)  |
| O1-Co-N1      | 69.32 (8)  | O3-Co-N3 | 85.64 (8)  |
| O1-Co-N2      | 70.22 (8)  | O4-Co-N1 | 84.28 (8)  |
| O1-Co-N3      | 149.67 (8) | O4-Co-N2 | 91.15 (8)  |
| O2-Co-O3      | 98.24 (8)  | O4-Co-N3 | 98.39 (8)  |
| O2-Co-O4      | 83.49 (7)  | N1-Co-N2 | 138.62 (9) |
| O2-Co-N1      | 149.10 (8) | N1-Co-N3 | 85.27 (8)  |
| O2-Co-N2      | 69.93 (8)  | N2-Co-N3 | 135.97 (8) |
| O2-Co-N3      | 68.66 (7)  |          |            |

(26) The crystal structure of  $[\text{Co}(\mathbf{1a})(\text{H}_2\text{O})]\text{Cl}_2 \cdot X(\text{solvent})$  has been partially solved (Figures 4 and 5). Crystals are triclinic,  $P\bar{1}$ , with  $a = 9.155$  (3) Å,  $b = 12.879$  (3) Å,  $c = 15.072$  (4) Å,  $\alpha = 111.22$  (2)°,  $\beta = 93.89$  (3)°,  $\gamma = 102.30$  (2)°,  $Z = 2$ , and  $d_{\text{calc}} \approx 1.28 \text{ g cm}^{-3}$  at 25 °C. Although the complex cation portion of the structure seems well defined, including location of the H atoms of the aquo ligand, one of the chloride ions and solvent of unknown quantity and identity are involved in a complex disorder. At the present state of refinement,  $R = 0.051$  for 2873 observations and 424 variables and a satisfactory model for the disorder has not yet been found. The disordered region is extensive, and its correlations with atoms in the complex cation are appreciable. Thus, little confidence can be placed in the accuracy of the bond lengths and angles of the complex, despite their small formal esd's.

observed for  $\text{Co}-\text{N}(\text{py})$  and  $\text{Co}-\text{O}$  bonds in the diaquo[2,6-diacetylpyridine bis(2-pyridylhydrazone)]cobalt(II) ion, abbreviated as  $[\text{Co}(\text{H}_2\text{dapp})(\text{H}_2\text{O})_2]^{2+}$ , which average 2.244 and 2.149 Å, respectively.<sup>7</sup> The two  $\text{Co}-\text{O}(\text{etheral})$  bond distances are significantly different, and a significant increase is observed as compared to the known PBP cobalt(II) complexes.<sup>6-8</sup> All the other metal-ligand bond distances are in a comparable range. Although the pyridine rings are individually planar to

Table VIII. Coordinates and Thermal Parameters for  $[\text{Co}(\text{C}_{19}\text{H}_{19}\text{N}_3\text{S}_2)\text{Cl}]_2[\text{CoCl}_4] \cdot 2\text{H}_2\text{O} \cdot 2\text{CH}_3\text{OH}^a$ 

| atom | x           | y           | z           | B or $B_{\text{eq}}$ , Å <sup>2</sup> | atom             | x           | y          | z            | B or $B_{\text{eq}}$ , Å <sup>2</sup> |
|------|-------------|-------------|-------------|---------------------------------------|------------------|-------------|------------|--------------|---------------------------------------|
| Co1  | 0.58452 (8) | 0.2896 (3)  | 0.8985 (1)  | 2.67 (6)                              | C15              | 0.5559 (6)  | 0.003 (2)  | 0.8244 (10)  | 3.9 (5)                               |
| Co2  | 0.92143 (7) | 0.2501 (3)  | 0.0887 (1)  | 2.79 (6)                              | C16              | 0.5397 (6)  | -0.135 (2) | 0.8162 (11)  | 5.2 (5)                               |
| Co3  | 0.26555 (8) | 0.2285 (3)  | 0.8395 (1)  | 3.50 (6)                              | C17              | 0.5292 (6)  | -0.208 (2) | 0.8816 (11)  | 5.2 (5)                               |
| C11  | 0.5144 (2)  | 0.3852 (5)  | 0.8847 (3)  | 4.0 (1)                               | C18              | 0.5357 (6)  | -0.148 (2) | 0.9492 (11)  | 5.0 (5)                               |
| C12  | 0.9902 (1)  | 0.2489 (6)  | 0.0328 (3)  | 4.2 (1)                               | C19              | 0.5517 (6)  | -0.008 (2) | 0.9518 (10)  | 3.4 (4)                               |
| C13  | 0.2199 (2)  | 0.2721 (6)  | 0.7395 (3)  | 5.7 (1)                               | C20              | 0.8693 (6)  | 0.256 (2)  | -0.0620 (10) | 4.4 (5)                               |
| C14  | 0.2231 (2)  | 0.1891 (6)  | 0.9420 (3)  | 5.1 (1)                               | C21              | 0.8453 (6)  | 0.211 (2)  | -0.1243 (11) | 5.6 (5)                               |
| C15  | 0.3089 (2)  | 0.0346 (6)  | 0.8204 (3)  | 5.2 (1)                               | C22              | 0.8404 (6)  | 0.066 (2)  | -0.1349 (11) | 4.8 (5)                               |
| C16  | 0.3083 (2)  | 0.4250 (6)  | 0.8528 (3)  | 5.7 (2)                               | C23              | 0.8595 (6)  | -0.028 (2) | -0.0839 (11) | 4.7 (5)                               |
| S1   | 0.5888 (2)  | 0.3016 (5)  | 1.0376 (3)  | 3.5 (1)                               | C24              | 0.8847 (6)  | 0.025 (2)  | -0.0246 (10) | 3.9 (5)                               |
| S2   | 0.5971 (2)  | 0.2504 (6)  | 0.7636 (2)  | 3.7 (1)                               | C25              | 0.9077 (7)  | -0.072 (2) | 0.0287 (11)  | 4.9 (5)                               |
| S3   | 0.9189 (2)  | -0.0064 (5) | 0.1239 (3)  | 3.6 (1)                               | C26              | 0.8662 (6)  | -0.004 (2) | 0.1654 (11)  | 4.8 (5)                               |
| S4   | 0.9064 (2)  | 0.5072 (5)  | 0.0659 (3)  | 4.1 (1)                               | C27              | 0.8401 (6)  | 0.131 (2)  | 0.1625 (10)  | 3.2 (4)                               |
| N1   | 0.6136 (4)  | 0.499 (2)   | 0.9105 (7)  | 2.7 (3)                               | C28              | 0.7981 (6)  | 0.124 (2)  | 0.1840 (11)  | 4.9 (5)                               |
| N2   | 0.6489 (4)  | 0.207 (2)   | 0.9113 (7)  | 3.3 (3)                               | C29              | 0.7743 (6)  | 0.252 (3)  | 0.1823 (11)  | 5.7 (5)                               |
| N3   | 0.5616 (4)  | 0.069 (1)   | 0.8910 (8)  | 3.0 (3)                               | C30              | 0.7932 (6)  | 0.379 (2)  | 0.1599 (11)  | 5.2 (5)                               |
| N4   | 0.8882 (4)  | 0.167 (1)   | -0.0107 (7) | 2.8 (3)                               | C31              | 0.8361 (5)  | 0.376 (2)  | 0.1400 (10)  | 3.1 (4)                               |
| N5   | 0.8596 (4)  | 0.253 (2)   | 0.1379 (7)  | 3.3 (3)                               | C32              | 0.8582 (6)  | 0.516 (2)  | 0.1220 (11)  | 5.2 (5)                               |
| N6   | 0.9457 (4)  | 0.336 (1)   | 0.1962 (8)  | 3.2 (3)                               | C33              | 0.9481 (6)  | 0.564 (2)  | 0.1328 (11)  | 5.2 (5)                               |
| C1   | 0.6326 (6)  | 0.563 (2)   | 0.8521 (10) | 3.3 (4)                               | C34              | 0.9512 (6)  | 0.479 (2)  | 0.2024 (10)  | 4.0 (5)                               |
| C2   | 0.6528 (6)  | 0.695 (2)   | 0.8592 (11) | 4.6 (5)                               | C35              | 0.9609 (7)  | 0.542 (2)  | 0.2718 (11)  | 5.1 (5)                               |
| C3   | 0.6532 (6)  | 0.766 (2)   | 0.9291 (11) | 5.5 (5)                               | C36              | 0.9662 (6)  | 0.452 (2)  | 0.3335 (11)  | 4.8 (5)                               |
| C4   | 0.6331 (6)  | 0.700 (2)   | 0.9880 (10) | 4.2 (5)                               | C37              | 0.9604 (5)  | 0.313 (2)  | 0.3293 (9)   | 3.1 (4)                               |
| C5   | 0.6132 (6)  | 0.568 (2)   | 0.9756 (10) | 3.0 (4)                               | C38              | 0.9502 (5)  | 0.254 (2)  | 0.2596 (9)   | 3.2 (4)                               |
| C6   | 0.5891 (6)  | 0.496 (2)   | 1.0396 (10) | 4.0 (5)                               | O1W              | 0.0592 (5)  | 0.417 (2)  | 0.1560 (9)   | 9.2 (5)                               |
| C7   | 0.6454 (5)  | 0.257 (2)   | 1.0468 (10) | 4.0 (4)                               | O2W              | 0.1506 (6)  | 0.400 (2)  | 0.1416 (11)  | 11.0 (6)                              |
| C8   | 0.6676 (5)  | 0.193 (2)   | 0.9807 (9)  | 2.7 (4)                               | O1S              | 0.7893 (6)  | -0.026 (2) | 0.4630 (11)  | 11.7 (6)                              |
| C9   | 0.7066 (6)  | 0.121 (2)   | 0.9893 (10) | 3.8 (5)                               | C1S              | 0.7500 (10) | 0.024 (4)  | 0.4287 (18)  | 12.0 (10)                             |
| C10  | 0.7265 (6)  | 0.068 (2)   | 0.9285 (11) | 4.4 (5)                               | O2S <sup>b</sup> | 0.4258      | 0.389      | 0.3320       | 10.0                                  |
| C11  | 0.7095 (6)  | 0.082 (2)   | 0.8574 (10) | 3.9 (5)                               | C2S <sup>b</sup> | 0.4062      | 0.277      | 0.3320       | 10.0                                  |
| C12  | 0.6701 (6)  | 0.153 (2)   | 0.8496 (10) | 3.3 (4)                               | O2S <sup>c</sup> | 0.3945      | 0.443      | 0.3828       | 10.0                                  |
| C13  | 0.6501 (7)  | 0.183 (2)   | 0.7734 (12) | 5.7 (6)                               | C2S <sup>c</sup> | 0.4277      | 0.471      | 0.3340       | 10.0                                  |
| C14  | 0.5640 (7)  | 0.094 (2)   | 0.7543 (12) | 5.8 (6)                               |                  |             |            |              |                                       |

<sup>a</sup> Estimated standard deviations in the least significant digits are shown in parentheses. <sup>b</sup> Population 2/3. <sup>c</sup> Population 1/3.

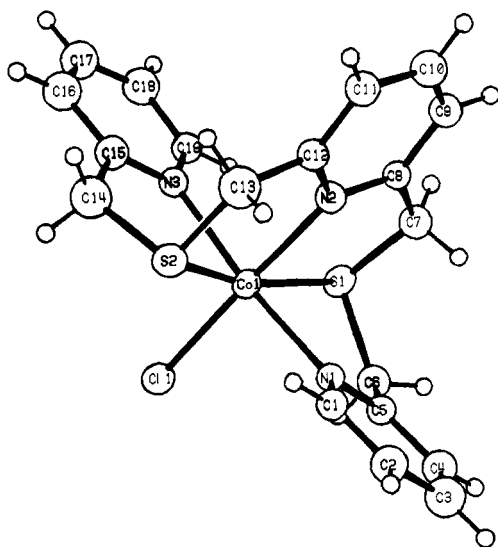


Figure 6. Perspective view of  $[\text{Co}(\mathbf{4b})\text{Cl}]^+$ , cation 1.

within 0.025 Å, the pentadentate ligand is decidedly nonplanar, with intraannular torsion angles in the chelate rings varying up to 46° in magnitude. While the Co atom and the central three donor atoms of **4a** are planar to within 0.024 Å, N1 and N3 lie 0.315 and -0.550 Å from this plane, respectively. The terminal pyridines are tilted such that they form dihedral angles of 24.0° (N1) and 32.5° (N3) with this plane. The central pyridine forms an analogous angle of 9.1°. Two water molecules bonded to the metal ion are approximately normal to the plane of the ligand, and the O(aquo)-Co-O(aquo) angle is not significantly different from that in the  $[\text{Co}(\text{H}_2\text{dapp})(\text{H}_2\text{O})_2]^{2+}$  ion.<sup>7</sup>

**c.**  $[\text{Co}(\mathbf{4b})\text{Cl}]_2[\text{CoCl}_4]$ . The pentadentate ligand **4b** forms an octahedral chloro complex with local symmetry  $C_2$ . It

Table IX. Coordination Geometry of  $[\text{Co}(\mathbf{4b})\text{Cl}]^+$  and  $[\text{CoCl}_4]^{2-}$  Ions

| Distances (Å) |             |             |             |
|---------------|-------------|-------------|-------------|
| Co1-Cl1       | 2.344 (2)   | Co2-Cl2     | 2.349 (2)   |
| Co1-S1        | 2.460 (2)   | Co2-S3      | 2.460 (2)   |
| Co1-S2        | 2.445 (2)   | Co2-S4      | 2.462 (2)   |
| Co1-N1        | 2.151 (6)   | Co2-N4      | 2.163 (6)   |
| Co1-N2        | 2.133 (6)   | Co2-N5      | 2.103 (6)   |
| Co1-N3        | 2.170 (6)   | Co2-N6      | 2.182 (6)   |
| Co3-Cl3       | 2.279 (2)   | Co3-Cl5     | 2.268 (3)   |
| Co3-Cl4       | 2.276 (2)   | Co3-Cl6     | 2.259 (2)   |
| Angles (deg)  |             |             |             |
| Cl1-Co1-S1    | 97.05 (8)   | Cl2-Co2-S3  | 97.64 (9)   |
| Cl1-Co1-S2    | 96.51 (8)   | Cl2-Co2-S4  | 95.97 (9)   |
| Cl1-Co1-N1    | 92.8 (2)    | Cl2-Co2-N4  | 94.4 (2)    |
| Cl1-Co1-N2    | 178.7 (2)   | Cl2-Co2-N5  | 179.3 (2)   |
| Cl1-Co1-N3    | 93.0 (2)    | Cl2-Co2-N6  | 93.9 (2)    |
| S1-Co1-S2     | 166.42 (9)  | S3-Co2-S4   | 166.38 (9)  |
| S1-Co1-N1     | 81.0 (2)    | S3-Co2-N4   | 81.0 (2)    |
| S1-Co1-N2     | 82.8 (2)    | S3-Co2-N5   | 83.0 (2)    |
| S1-Co1-N3     | 96.7 (2)    | S3-Co2-N6   | 98.4 (2)    |
| S2-Co1-N1     | 99.2 (2)    | S4-Co2-N4   | 97.4 (2)    |
| S2-Co1-N2     | 83.7 (2)    | S4-Co2-N5   | 83.4 (2)    |
| S2-Co1-N3     | 81.7 (2)    | S4-Co2-N6   | 81.3 (2)    |
| N1-Co1-N2     | 85.9 (2)    | N4-Co2-N5   | 85.4 (2)    |
| N1-Co1-N3     | 173.9 (2)   | N4-Co2-N6   | 171.8 (2)   |
| N2-Co1-N3     | 88.3 (2)    | N5-Co2-N6   | 86.3 (2)    |
| Cl3-Co3-Cl4   | 106.82 (10) | Cl4-Co3-Cl5 | 109.68 (9)  |
| Cl3-Co3-Cl5   | 112.56 (10) | Cl4-Co3-Cl6 | 112.82 (10) |
| Cl3-Co3-Cl6   | 106.81 (10) | Cl5-Co3-Cl6 | 108.19 (9)  |

crystallizes from wet MeOH solution as the blue solvated salt with  $[\text{CoCl}_4]^{2-}$ . A result of the charge mismatch is that two independent cations exist in the crystal. The geometries of the two are in excellent agreement (Figure 6, Tables VIII and IX). Averaging over chemically equivalent bonds in the two independent cations yields 2.346 Å for Co-Cl, 2.457 Å for Co-S, 2.167 Å for terminal Co-N, and 2.118 Å for central Co-N. The Co, Cl, and three N atoms lie within 0.015 Å of



a plane; the main distortion from ideal octahedral geometry is the bending of the Co-S bonds away from the perpendicular to this plane by an average of 7.3°, due to the meridional spanning by the central portion of the ligand. In the cation containing Co1, the trans pyridine planes form a dihedral angle of 13.8° with each other and dihedral angles of 89.4 and 97.7° with the central pyridine plane. Analogous values in the cation containing Co2 are 23.5, 72.7, and 94.0°, respectively.

A linear pentadentate ligand, 1,9-bis(2-pyridyl)-2,5,8-triazanonane, which is similar to ligand **4b**, also forms an octahedral cobalt(III) complex where the sixth coordination site is taken by a chloro ligand.<sup>27</sup>

The [CoCl<sub>4</sub>]<sup>2-</sup> anion exhibits only small deviations from ideal tetrahedral geometry.<sup>28</sup> The average Co-Cl distance is 2.271 Å, and the average angle is 109.48°. These are significantly different as compared to the orthorhombic form of K<sub>2</sub>[CoCl<sub>4</sub>] and agree very well with the monoclinic form where the mean Co-Cl distance is 2.274 Å and the average angle is 109.45°.<sup>28</sup>

**3. Magnetic and Spectral Properties.** The magnetic and spectral data for various complexes are listed in Table III. The visible spectra of all the cobalt(II) complexes were dominated by a very intense band around 18 200–19 200 cm<sup>-1</sup>, which is typical of the highest energy transition, <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>T<sub>1g</sub>(P), for octahedral cobalt(II) complexes.<sup>29</sup> An additional strong transition, [<sup>4</sup>A<sub>2</sub> → <sup>4</sup>T<sub>1</sub>(P)], at 14 700 cm<sup>-1</sup> was observed in the [Co(**4b**)Cl]<sub>2</sub>[CoCl<sub>4</sub>] complex due to the presence of the tetrahedral species [CoCl<sub>4</sub>]<sup>2-</sup>.

The PBP complexes [Co(**1a**)H<sub>2</sub>O]<sup>2+</sup> and [Co(**4a**)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> showed only one very strong band at 18 700 and 18 200 cm<sup>-1</sup>, respectively, while in the similar PBP complexes of Co(II), e.g., [Co(DAPSC)(Cl)H<sub>2</sub>O]<sup>+</sup> and [Co(DAPSC)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> Gerloch et al.<sup>30</sup> reported a single band at ca. 15 800 cm<sup>-1</sup> and

a split band at ca. 18 000 cm<sup>-1</sup>, all assigned as involving transitions to components of <sup>4</sup>P. However, they recorded the electronic spectra of single crystals. The magnetic moments of the Co(II) complexes range from 4.74 to 5.24 μ<sub>B</sub>. For the two PBP complexes these values lie at the upper end of this range given for six-coordinate Co(II) complexes in a pseudooctahedral field.<sup>29</sup> Similar values have been reported for the [Co(H<sub>2</sub>dapp)(H<sub>2</sub>O)<sub>2</sub>]Cl<sub>2</sub> complex.<sup>31</sup>

In all the nickel(II) complexes three bands were observed, which can be assigned to the three spin-allowed transitions, ν<sub>1</sub> [<sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>2g</sub>], ν<sub>2</sub> [<sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>1g</sub>(F)], and ν<sub>3</sub> [<sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>1g</sub>(P)], which is a characteristic feature of the spectra of octahedral Ni(II) species, and the pattern resembles the spectra of dichlorotetraaza macrocyclic nickel(II) complexes.<sup>32</sup> The magnetic moments of the Ni(II) complexes reported herein range from 2.98 to 3.20 μ<sub>B</sub>, which corresponds to two unpaired electrons along with some orbital contribution.

### Conclusion

The hexa- and the penta-dentate ligands are a potential source of pentagonal-bipyramidal transition-metal complexes when CH<sub>2</sub>-O-CH<sub>2</sub> is the connecting bridge between the 2,2'-bipyridine and/or pyridine units (e.g., **1a** and **4a**, respectively). Octahedral species are formed when a sulfur atom is substituted in the bridge instead of an oxygen atom (e.g., **1b** and **4b**). Attempts to obtain single crystals and thereby know precisely the geometry of the complexes with CH<sub>2</sub>-NH-CH<sub>2</sub> bridged ligands are in progress.

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**Supplementary Material Available:** Tables of bond distances, bond angles, coordinates for H atoms, anisotropic thermal parameters, and structure factor amplitudes for the complexes [Ni(C<sub>24</sub>H<sub>22</sub>N<sub>4</sub>S<sub>2</sub>)]·Cl<sub>2</sub>·EtOH·2H<sub>2</sub>O (Tables S1-S5), [Co(C<sub>19</sub>H<sub>19</sub>N<sub>3</sub>O<sub>2</sub>)(H<sub>2</sub>O)<sub>2</sub>]Cl<sub>2</sub> (Tables S6-S10), and [Co(C<sub>19</sub>H<sub>19</sub>N<sub>3</sub>S<sub>2</sub>)Cl]<sub>2</sub>[CoCl<sub>4</sub>]·2H<sub>2</sub>O·2MeOH (Tables S11-S14), respectively (67 pages). Ordering information is given on any current masthead page.

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## Structure and Bonding in Dirhodium(II) Tetrasalicylate

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The tetrakis(salicylato)dirhodium(II) molecule has been obtained in crystalline form as the ethanol-aquo adduct, [Rh<sub>2</sub>(O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>OH)<sub>4</sub>(C<sub>2</sub>H<sub>5</sub>OH)(H<sub>2</sub>O)], and the structure has been determined by X-ray crystallography. The molecular structure, though interesting, does not contain any unconventional or "unique" features. The Rh-Rh distance is 2.385 (2) Å, and the eight equatorial ligand sites are occupied by the carboxyl oxygen atoms in the usual way, with an average Rh-O distance of 2.040 [4] Å. One axial site has an ethanol molecule, Rh-O = 2.30 (1) Å, and the other a water molecule, Rh-O = 2.30 (1) Å. Within each salicylate moiety the *o*-OH group is hydrogen bonded to a carboxyl oxygen atom, with O...O distances in the range 2.49 (2)-2.60 (2) Å. Each phenyl ring is within an average of 7.7° of being coplanar with its own carboxyl group. The *o*-OH oxygen atoms are not involved in any intermolecular interactions. The infrared spectrum exhibits a broad band at ca. 3250 cm<sup>-1</sup> characteristic of these intramolecularly hydrogen-bonded OH groups. The visible spectrum is quite typical of Rh<sub>2</sub>(O<sub>2</sub>CR)<sub>4</sub>L<sub>2</sub> compounds with L ligands such as alcohols or water. The crystalline compound used for the X-ray work had a total composition [Rh<sub>2</sub>(O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>OH)<sub>4</sub>(C<sub>2</sub>H<sub>5</sub>OH)(H<sub>2</sub>O)]·C<sub>2</sub>H<sub>5</sub>OH·H<sub>2</sub>O and formed monoclinic crystals in space group *P2<sub>1</sub>/n* with unit cell dimensions of *a* = 14.830 (4) Å, *b* = 15.953 (4) Å, *c* = 15.130 (2) Å, β = 90.90 (2)°, and *V* = 3579 (2) Å<sup>3</sup>, with *Z* = 4.

### Introduction

In a recent paper from this laboratory<sup>1</sup> the structures of two compounds containing the dimolybdenum tetrasalicylate,

Mo<sub>2</sub>(O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>OH)<sub>4</sub>, unit (in which the OH group is ortho to the carboxyl group) were reported. The most interesting feature of these structures was the fact that in every carboxylato ligand there is an internal hydrogen bond that constrains the phenyl ring to be approximately coplanar with its carboxyl

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