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## Crystal and Molecular Structure of Pyridine and 3-Methylpyridine Adducts of [N,N-Bis[(5-chloro-2-hydroxyphenyl)phenylmethylene]-4-thiaheptane-1,7-diaminato]cobalt(II) and -nickel(II)

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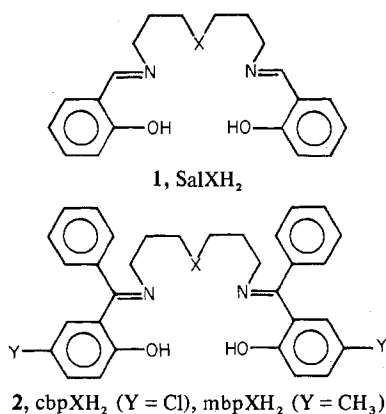
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Complexes of *N,N*-bis[(5-chloro-2-hydroxyphenyl)phenylmethylene]-4-thiaheptane-1,7-diamine (cbpSH<sub>2</sub>) and 3-methylpyridine (mpy) or pyridine (py) with cobalt(II) and nickel(II), [Co(cbps)mpy], [Ni(cbps)mpy], and [Ni(cbps)py], have been synthesized and studied by single-crystal x-ray diffraction. In each case the metal complexes were found to consist of distorted octahedra, with the pentadentate ligand forming a square pyramid about the metal atom, having approximately linear N–M–N' and O–M–O' arrangements. The Lewis base mpy or py occupies the sixth octahedral position, opposite the sulfur atom. The metal–thioether bond is of special interest, and in each case this is found to be a normal metal–sulfur bond (Ni, 2.484 (1) Å; Co, 2.537 (1) Å). Although the formation of this bond, especially in the cobalt(II) complex, is unexpected from earlier literature data, it is proposed that such bonds are not the exception but the rule. Each of the three complexes contains a small amount of solvent included in the crystal lattice and the solvent molecules could not be fully located due to extreme positional disorder. No unsolvated complexes were obtained in crystalline form. Crystal data for [Co(cbps)mpy]: space group *P2*<sub>1</sub>/*c*, *Z* = 4, *a* = 16.456 (7) Å, *b* = 14.74 (1) Å, *c* = 16.56 (1) Å,  $\beta$  = 112.79 (5)°, *V* = 3704 Å<sup>3</sup>, *R* = 3.7%, 2825 reflections. Crystal data for [Ni(cbps)mpy]: space group *P2*<sub>1</sub>/*c*, *Z* = 4, *a* = 16.450 (6) Å, *b* = 14.674 (1) Å, *c* = 16.59 (1) Å,  $\beta$  = 112.56 (3)°, *V* = 3698 Å<sup>3</sup>, *R* = 3.7%, 2103 reflections. Crystal data for [Ni(cbps)py]: space group *P2*<sub>1</sub>/*c*, *Z* = 4, *a* = 18.002 (9) Å, *b* = 15.691 (4) Å, *c* = 16.401 (9) Å,  $\beta$  = 116.07 (4)°, *V* = 4164 Å<sup>3</sup>, *R* = 4.6%, 4466 reflections.

### Introduction

Complexes of the potentially pentadentate ligands salX (1), cbpX (2), and mbpX (X = N, O, S, P) with the metals Cu,



Ni, Zn, and Mn have been investigated by a variety of physical techniques.<sup>2–7</sup> Single-crystal x-ray diffraction data have shown that an M–X bond is formed, and hence the ligands act as pentadentates, when X = N,<sup>2,3,6,7</sup> the M–N bond being a normal single bond for M = Zn<sup>7</sup> and Ni<sup>2,3,6</sup> and a dramatically elongated bond for M = Cu.<sup>6</sup> Other physical methods had failed to demonstrate the existence of such a Cu–N bond. Moreover, the results of earlier physical measurements suggest that the M–X bonds are nonexistent or very weak when M–X represents such combinations as Co<sup>II</sup>–S and Cu<sup>II</sup>–S. We will not only demonstrate the formation of M–S bonds for M = Ni(II) and Co(II) with cbpS but also show that the bonds are normal rather than very weak. We further propose that this is not an abnormal but a usual occurrence for such ligands.

We present here the crystal and molecular structures of three complexes with the thioether ligand *N,N*-bis[(5-chloro-2-hydroxyphenyl)phenylmethylene]-4-thiaheptane-1,7-diamine, cbpSH<sub>2</sub> (2, X = S), and 3-methylpyridine (mpy) or pyridine (py): [Co(cbps)mpy], [Ni(cbps)mpy], and [Ni(cbps)py].

### Experimental Section

The thioether ligand cbpSH<sub>2</sub> was prepared as described elsewhere.<sup>8</sup>

**Preparation of the Complexes.** [Co(cbps)] and [Ni(cbps)]. A solution of the Schiff base ligand cbpSH<sub>2</sub> (2 mmol) in 1,1-dimethoxypropane was added to a hot methanol solution of the metal acetate. Piperidine (5 ml) was then added to the solution and the volume reduced until the complex precipitated. Anal. Calcd (Co) for CoCl<sub>2</sub>SO<sub>2</sub>N<sub>2</sub>C<sub>32</sub>H<sub>28</sub>: C, 60.58; H, 4.45; N, 4.42. Found: C, 60.48; H, 4.42; N, 4.43. Anal. Calcd (Ni) for NiCl<sub>2</sub>SO<sub>2</sub>N<sub>2</sub>C<sub>32</sub>H<sub>28</sub>: C, 60.60; H, 4.45; N, 4.42. Found: C, 60.55; H, 4.64; N, 4.34.

[Co(cbps)mpy](mpy)<sub>1/2</sub> was prepared by recrystallization of [Co(cbps)] from hot 3-methylpyridine. Anal. Calcd for CoCl<sub>2</sub>SO<sub>2</sub>N<sub>3.5</sub>C<sub>41</sub>H<sub>38.5</sub>: C, 63.62; H, 5.01; N, 6.33. Found: C, 63.60; H, 5.02; N, 6.28.

[Ni(cbps)mpy](mpy)<sub>1/2</sub> was prepared as above. Anal. Calcd for NiCl<sub>2</sub>SO<sub>2</sub>N<sub>3.5</sub>C<sub>41</sub>H<sub>38.5</sub>: C, 63.62; H, 5.01; N, 6.33. Found: C, 63.96; H, 5.06; N, 6.33.

[Ni(cbps)py]*m*-xylene was prepared as above, from pyridine solution. The complex was then recrystallized from *m*-xylene. Anal. Calcd for NiCl<sub>2</sub>SO<sub>2</sub>N<sub>3</sub>C<sub>45</sub>H<sub>43</sub>: C, 65.95; H, 5.28; N, 5.13. Found: C, 66.34; H, 5.38; N, 5.19. For brevity, the included (uncoordinated) solvent molecules will hereafter be omitted from the compound names.

Crystal densities were measured by flotation in aqueous potassium iodide containing detergent as wetting agent.

**Crystal Data for [Co(cbps)mpy].** CoCl<sub>2</sub>SO<sub>2</sub>N<sub>3.5</sub>C<sub>41</sub>H<sub>38.5</sub>: mol wt 727, space group *P2*<sub>1</sub>/*n*, *Z* = 4, *a* = 16.456 (7) Å, *b* = 14.74 (1) Å, *c* = 16.56 (1) Å,  $\beta$  = 112.79 (5)°, *V* = 3704 Å<sup>3</sup>, *d*<sub>calcd</sub> = 1.32 g cm<sup>-3</sup>, *d*<sub>obsd</sub> = 1.30 g cm<sup>-3</sup>,  $\mu(\text{Mo } K\alpha)$  = 7.3 cm<sup>-1</sup>; crystal dimensions (distances in mm of faces from centroid) (111) 0.07, (11 $\bar{1}$ ) 0.07, (110) 0.08, (1 $\bar{1}$ 0) 0.08, (1 $\bar{1}$ 0) 0.08; red crystal; maximum and

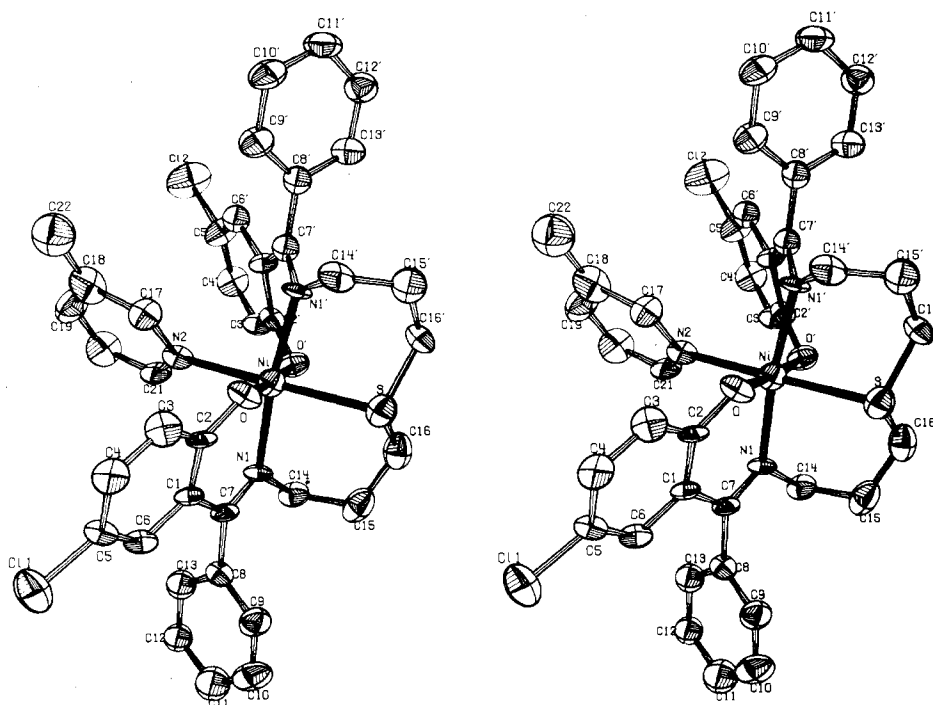


Figure 1. Stereoview of [Ni(cbpS)mpy].

minimum transmission coefficients 0.946 and 0.919.

**Crystal Data for [Ni(cbpS)mpy].**  $\text{NiCl}_2\text{SO}_2\text{N}_3\text{C}_{41}\text{H}_{38.5}$ ; mol wt 727, space group  $P2_1/m$ ,  $Z = 4$ ,  $a = 16.450$  (6) Å,  $b = 14.674$  (5) Å,  $c = 16.59$  (1) Å,  $\beta = 112.56$  (3)°,  $V = 3698$  Å<sup>3</sup>,  $d_{\text{calcd}} = 1.32$  g cm<sup>-3</sup>,  $d_{\text{obsd}} = 1.34$  g cm<sup>-3</sup>,  $\mu(\text{Mo K}\alpha) = 7.7$  cm<sup>-1</sup>; crystal dimensions (mm from centroid) (110) 0.09, ( $\bar{1}10$ ) 0.09, (1 $\bar{1}0$ ) 0.11, ( $\bar{1}10$ ) 0.11, (001) 0.10, (00 $\bar{1}$ ) 0.10; reddish yellow crystal; maximum and minimum transmission coefficients 0.905 and 0.903.

**Crystal Data for [Ni(cbpS)py].**  $\text{NiCl}_2\text{SO}_2\text{N}_3\text{C}_{45}\text{H}_{43}$ ; mol wt 820, space group  $P2_1/c$ ,  $Z = 4$ ,  $a = 18.002$  (9) Å,  $b = 15.691$  (4) Å,  $c = 16.401$  (9) Å,  $\beta = 116.07$  (4)°,  $V = 4164$  Å<sup>3</sup>,  $d_{\text{calcd}} = 1.31$  g cm<sup>-3</sup>,  $d_{\text{obsd}} = 1.35$  g cm<sup>-3</sup>,  $\mu(\text{Mo K}\alpha) = 6.9$  cm<sup>-1</sup>; crystal dimensions (mm from centroid) (100) 0.085, ( $\bar{1}00$ ) 0.085, (011) 0.315, (0 $\bar{1}1$ ) 0.315, (01 $\bar{1}$ ) 0.315, (0 $\bar{1}1$ ) 0.315; yellow crystal; maximum and minimum transmission coefficients 0.926 and 0.937.

For each crystal, the Enraf-Nonius program SEARCH was used to obtain 15 accurately centered reflections which were then used in the program INDEX to obtain approximate cell dimensions and an orientation matrix for data collection. Refined cell dimensions and their estimated standard deviations were obtained from least-squares refinement of 28 accurately centered reflections. The mosaicity of each crystal was examined by the  $\omega$ -scan technique and judged to be satisfactory.

**Collection and Reduction of Data.** Diffraction data were collected at 292 K on an Enraf-Nonius four-circle CAD-4 diffractometer controlled by a PDP8/M computer, using Mo K $\alpha$  radiation from a highly oriented graphite crystal monochromator. The  $\theta$ - $2\theta$  scan technique was used to record the intensities for all nonequivalent reflections for which  $0^\circ < 2\theta < 48^\circ$ ,  $0^\circ < 2\theta < 46^\circ$ , and  $0^\circ < 2\theta < 50^\circ$  for [Co(cbpS)mpy], [Ni(cbpS)mpy], and [Ni(cbpS)py], respectively. Scan widths (SW) were calculated from the formula  $\text{SW} = A + B \tan \theta$  where  $A$  is estimated from the mosaicity of the crystal and  $B$  allows for the increase in width of peak due to  $K\alpha_1$  and  $K\alpha_2$  splitting. The values of  $A$  and  $B$  were 0.50 and 0.30°, respectively, for [Co(cbpS)mpy], 0.60 and 0.30 for [Ni(cbpS)mpy], and 0.70 and 0.30 for [Ni(cbpS)py]. The calculated scan angle is extended at each side by 25% for background determination (BG1 and BG2). The net count is then calculated as  $\text{NC} = \text{TOT} - 2(\text{BG1} + \text{BG2})$  where TOT is the integrated peak intensity. Reflection data were considered insignificant if intensities registered less than 10 counts above background on a rapid prescan, such reflections being rejected automatically by the computer.

The intensities of four standard reflections, monitored for each crystal at 100 reflection intervals, showed no greater fluctuations during the data collection than those expected from Poisson statistics. The

raw intensity data were corrected for Lorentz-polarization effects (including the polarization effect of the crystal monochromator) and then for absorption. After averaging the intensities of equivalent reflections, the data were reduced to 3977 independent intensities for [Co(cbpS)mpy], 2851 for [Ni(cbpS)mpy], and 5095 for [Ni(cbpS)py], of which 2825 for [Co(cbpS)mpy], 2103 for [Ni(cbpS)mpy], and 4466 for [Ni(cbpS)py] had  $F_o^2 > 3\sigma(F_o^2)$ , where  $\sigma(F_o^2)$  was estimated from counting statistics.<sup>9</sup> These data were used in the final refinement of the structural parameters.

**Determination and Refinement of the Structures.** The positions of the metal, the sulfur, and the ligand atoms, in the plane perpendicular to the M-S bond, were determined for all three complexes from three-dimensional Patterson functions calculated from all intensity data. For each crystal the intensity data were phased sufficiently well by these positional coordinates to permit location of the remaining nonhydrogen and some hydrogen atoms. The compounds [Co(cbpS)mpy] and [Ni(cbpS)mpy] are isostructural.

Full-matrix least-squares refinement was based on  $F_c$  and the function minimized was  $\sum w(|F_o| - |F_c|)^2$ . The weights  $w$  were then taken as  $[2F_o/\sigma(F_o^2)]^2$ , where  $|F_o|$  and  $|F_c|$  are the observed and calculated structure factor amplitudes. The atomic scattering factors for nonhydrogen atoms were taken from Cromer and Waber,<sup>10</sup> and those for hydrogen, from Stewart et al.<sup>11</sup> The effects of anomalous dispersion for all nonhydrogen atoms were included in  $F_c$  using the values of Cromer and Ibers<sup>12</sup> for  $\Delta f'$  and  $\Delta f''$ . Agreement factors are defined as  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  and  $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$ . To minimize computer time, the initial calculations were carried out on the first 1000 reflections collected.

Anisotropic temperature factors were introduced for all nonhydrogen atoms. Further Fourier difference functions permitted location of the remaining nonmethyl hydrogen atoms, which were included in the refinement, with fixed temperature factors (5.0 Å<sup>2</sup>). Peaks due to atoms of the disordered solvent molecules were observed in the Fourier difference functions calculated for all three complexes. In the case of the [Ni(cbpS)py] complex, most of a (partially occupied) xylene molecule was located, but it was not possible to locate contiguous solvent molecules in any of the compounds, due to partial occupancy and the positional disorder. Therefore a final Fourier difference map was calculated with all atoms including hydrogen, and the most intense peaks observed included in the least-squares refinement calculations (occupancy also being refined). The included solvent molecules are of no chemical interest. A number of weaker peaks, having intensities lower than that of the hydrogen atoms, were ignored. The models converged with  $R = 3.7$ ,  $R_w = 4.0\%$ ;  $R = 3.6$ ,  $R_w = 4.1\%$ ; and  $R = 4.6$ ,  $R_w = 6.6\%$  for [Co(cbpS)mpy], [Ni(cbpS)mpy], and [Ni-

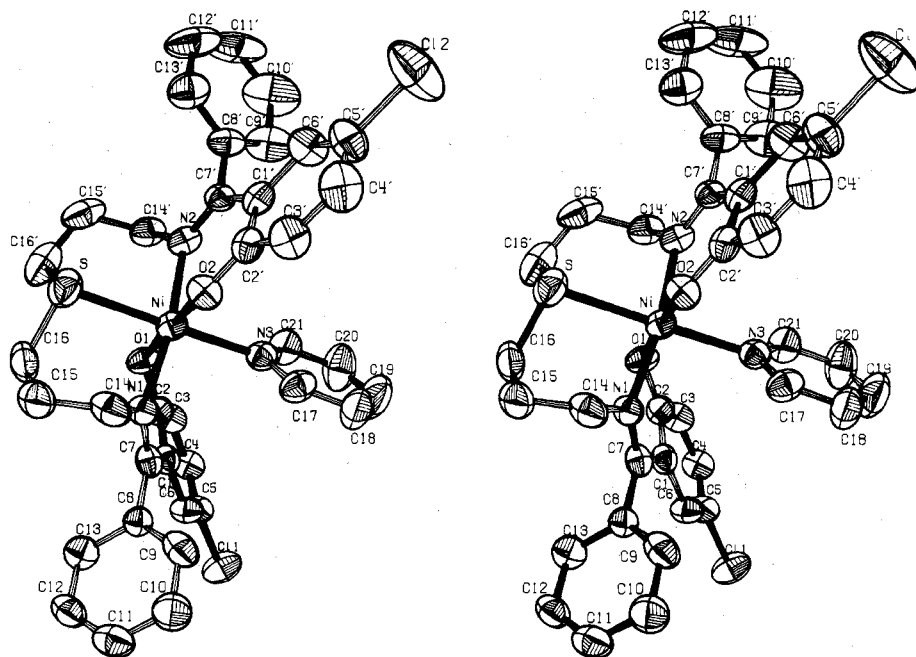


Figure 2. Stereoview of  $[\text{Ni}(\text{cbpS})\text{py}]$ .

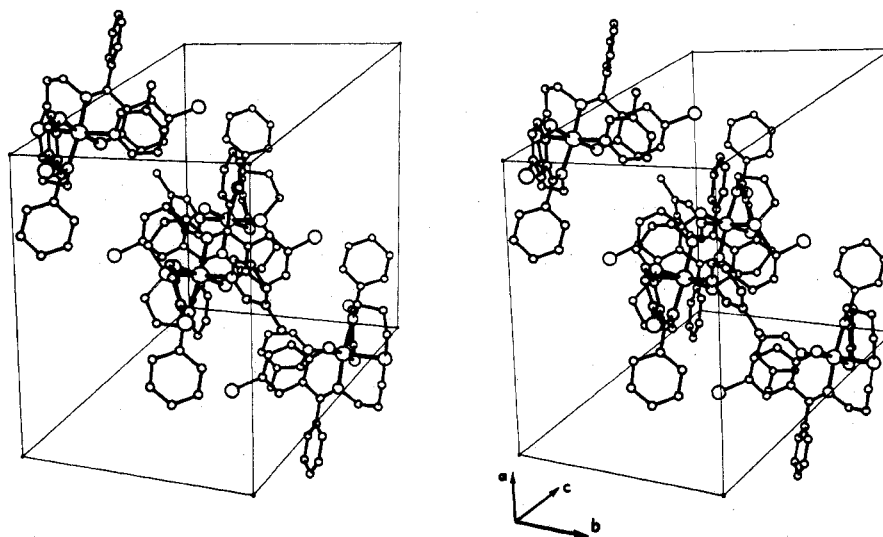


Figure 3. Molecular packing in  $[\text{Ni}(\text{cbpS})\text{mpy}]$ .

(cbpS)py], respectively. A structure factor calculation with all observed and unobserved reflections included (no refinement) gave  $R = 4.4, 4.5, 5.1\%$  for  $[\text{Co}(\text{cbpS})\text{mpy}]$ ,  $[\text{Ni}(\text{cbpS})\text{mpy}]$ , and  $[\text{Ni}(\text{cbpS})\text{py}]$ , respectively; on this basis it was decided that careful measurement of reflections rejected automatically during data collection would not significantly improve the results. A final Fourier difference function was featureless. Tables of the observed structure factors are available.<sup>13</sup> The principal programs used are as previously described.<sup>7</sup>

### Results and Discussion

Final positional and thermal parameters for  $[\text{Co}(\text{cbpS})\text{mpy}]$ ,  $[\text{Ni}(\text{cbpS})\text{mpy}]$ , and  $[\text{Ni}(\text{cbpS})\text{py}]$  are given in Table I. Tables II and III contain the bond lengths and angles. The digits in parentheses in the tables are the estimated standard deviations in the least significant figures quoted and were derived from the inverse matrix in the course of least-squares refinement calculations. Figures 1 and 2 are stereoscopic pair views of  $[\text{Ni}(\text{cbpS})\text{mpy}]$  and  $[\text{Ni}(\text{cbpS})\text{py}]$ , respectively, while Figures 3 and 4 show the molecular packing in the unit cells of the same compounds. Single molecule and packing diagrams of  $[\text{Co}(\text{cbpS})\text{mpy}]$  do not show well the small but significant differences between this molecule and  $[\text{Ni}(\text{cbpS})\text{mpy}]$  with which it is nearly isomorphous, and no diagrams are included for the cobalt complex for that reason.

Variable analyses obtained for a wider range of complexes related to the present series<sup>14</sup> show that there is a proportion of included solvent which varies from compound to compound, from solvent to solvent, and in some cases from preparation to preparation. This suggests that "crystallographic holes" exist in the lattices of the compounds which can accommodate whatever solvent molecules are present during the crystallization. The observation of partial occupancy by solvent molecules in the present series of complexes agrees with the microanalyses which indicate the presence of fractional solvent molecules. The high degree of disorder prevented the location of complete solvent molecules and suggests that the lattice holes are significantly larger than the solvent molecules they accommodate and do not constrain them in any way. We were unable to obtain the unsolvated complexes in crystalline form, which may be fortuitous or may indicate a requirement that the lattice holes be filled for crystals to form.

The molecular structures of the three complexes consist of distorted octahedra with the cbpS ligands wrapped around the

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations<sup>a</sup> (a) [Co(cbps)mpy]

Atom	x	y	z	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$	Atom	Occupancy	$B, \text{\AA}^2$	x	y	z	$B, \text{\AA}^2$
Co	0.022 51 (4)	0.106 78 (4)	0.236 23 (4)	0.003 08 (2)	0.003 54 (3)	0.002 93 (2)	0.000 17 (6)	0.002 55 (3)	-0.000 26 (6)							
Cl(1)	-0.032 67 (9)	0.325 1 (1)	-0.174 78 (9)	0.005 70 (7)	0.005 63 (9)	0.003 97 (6)	0.000 0 (1)	0.002 9 (1)	0.002 8 (1)							
Cl(2)	0.089 28 (11)	0.337 8 (1)	0.632 63 (10)	0.006 70 (8)	0.009 10 (11)	0.006 17 (8)	-0.002 2 (2)	0.003 7 (1)	-0.009 1 (2)							
S	0.004 44 (9)	-0.063 0 (1)	0.210 25 (8)	0.004 68 (6)	0.003 92 (7)	0.003 74 (6)	0.000 4 (1)	0.002 94 (9)	-0.000 6 (1)							
O	-0.068 6 (2)	0.125 9 (2)	0.115 8 (2)	0.003 0 (1)	0.004 7 (2)	0.003 5 (1)	-0.000 6 (3)	0.002 5 (2)	0.000 7 (3)							
O'	0.109 0 (2)	0.092 0 (2)	0.362 8 (2)	0.003 1 (1)	0.004 5 (2)	0.003 1 (1)	0.001 3 (3)	0.002 1 (2)	0.000 7 (3)							
N(1)	0.115 7 (2)	0.098 9 (3)	0.180 2 (2)	0.002 7 (2)	0.003 8 (2)	0.003 0 (2)	0.000 9 (4)	0.001 7 (2)	-0.000 1 (4)							
N(1')	-0.072 4 (2)	0.094 2 (3)	0.291 6 (2)	0.003 0 (2)	0.004 1 (2)	0.003 2 (2)	-0.001 5 (4)	0.002 7 (2)	0.001 7 (4)							
N(2)	0.030 8 (2)	0.254 9 (3)	0.254 9 (2)	0.003 1 (2)	0.004 2 (2)	0.003 4 (2)	0.000 1 (4)	0.002 7 (3)	-0.000 2 (4)							
C(1)	0.027 5 (3)	0.174 8 (3)	0.044 8 (3)	0.002 5 (2)	0.003 7 (3)	0.002 5 (2)	0.000 3 (4)	0.001 5 (3)	-0.000 2 (4)							
C(2)	-0.055 5 (3)	0.168 4 (3)	0.053 2 (3)	0.003 3 (2)	0.002 8 (3)	0.003 0 (2)	-0.000 3 (4)	0.001 9 (3)	-0.001 3 (4)							
C(3)	-0.129 4 (3)	0.208 6 (3)	-0.013 8 (3)	0.002 8 (2)	0.004 0 (3)	0.003 6 (2)	0.001 2 (4)	0.001 3 (3)	-0.000 0 (5)							
C(4)	-0.122 5 (3)	0.255 9 (3)	-0.082 6 (3)	0.003 4 (2)	0.003 9 (3)	0.003 6 (2)	0.000 9 (5)	0.000 8 (4)	0.000 5 (5)							
C(5)	-0.041 6 (3)	0.263 3 (4)	-0.088 8 (3)	0.003 9 (2)	0.004 2 (3)	0.002 9 (2)	0.000 1 (5)	0.002 4 (3)	0.000 5 (4)							
C(6)	0.030 9 (3)	0.222 6 (3)	-0.027 7 (3)	0.003 4 (2)	0.004 0 (3)	0.003 1 (2)	0.000 2 (5)	0.002 3 (3)	-0.000 4 (5)							
C(7)	0.108 5 (3)	0.130 2 (3)	0.105 1 (3)	0.002 8 (2)	0.002 8 (3)	0.003 0 (2)	-0.000 1 (4)	0.002 4 (3)	0.000 5 (4)							
C(8)	0.183 2 (3)	0.122 2 (3)	0.074 6 (3)	0.002 9 (2)	0.003 6 (3)	0.002 5 (2)	0.000 7 (4)	0.001 9 (3)	-0.000 4 (5)							
C(9)	0.184 9 (3)	0.053 5 (4)	0.018 0 (3)	0.003 5 (2)	0.004 3 (3)	0.003 6 (2)	0.000 9 (5)	0.002 5 (3)	0.000 1 (5)							
C(10)	0.256 9 (3)	0.044 6 (4)	-0.005 0 (3)	0.005 0 (3)	0.006 6 (4)	0.003 3 (2)	0.000 6 (5)	0.003 2 (4)	-0.001 1 (5)							
C(11)	0.326 5 (3)	0.105 7 (4)	0.025 8 (3)	0.004 3 (2)	0.008 3 (4)	0.004 4 (2)	0.003 1 (6)	0.004 9 (3)	0.000 9 (6)							
C(12)	0.324 2 (3)	0.173 0 (4)	0.079 9 (3)	0.003 2 (2)	0.008 4 (4)	0.005 4 (3)	-0.003 3 (6)	0.003 9 (4)	-0.000 8 (6)							
C(13)	0.253 9 (3)	0.182 7 (4)	0.104 3 (3)	0.004 2 (2)	0.004 6 (3)	0.004 5 (2)	-0.001 3 (5)	0.003 7 (4)	-0.001 5 (5)							
C(14)	0.194 6 (3)	0.044 2 (4)	0.232 1 (3)	0.003 8 (2)	0.004 9 (3)	0.003 9 (2)	0.002 5 (5)	0.003 1 (3)	0.001 0 (5)							
C(15)	0.174 6 (3)	-0.057 2 (4)	0.217 9 (3)	0.004 6 (2)	0.004 7 (3)	0.003 9 (2)	0.003 8 (5)	0.002 8 (4)	0.000 8 (5)							
C(16)	0.118 5 (3)	-0.097 0 (4)	0.263 8 (3)	0.005 1 (3)	0.003 9 (3)	0.004 4 (2)	0.001 6 (5)	0.002 6 (4)	0.000 6 (5)							
C(1')	0.017 5 (3)	0.167 9 (3)	0.426 2 (3)	0.003 1 (2)	0.002 9 (3)	0.002 8 (2)	0.000 3 (4)	0.001 8 (3)	-0.000 1 (4)							
C(2')	0.100 7 (3)	0.142 4 (3)	0.424 0 (3)	0.003 2 (2)	0.003 3 (3)	0.003 4 (2)	0.000 2 (4)	0.002 1 (3)	0.001 6 (4)							
C(3')	0.177 5 (3)	0.174 3 (4)	0.492 9 (3)	0.003 2 (2)	0.004 8 (3)	0.003 4 (2)	-0.000 3 (5)	0.001 9 (3)	-0.000 7 (5)							
C(4')	0.174 0 (3)	0.233 0 (4)	0.555 7 (3)	0.003 6 (2)	0.005 5 (3)	0.003 7 (2)	-0.001 9 (5)	0.000 7 (4)	-0.000 8 (5)							
C(5')	0.093 1 (3)	0.260 6 (4)	0.553 3 (3)	0.004 2 (2)	0.005 3 (3)	0.003 5 (2)	-0.000 8 (5)	0.002 4 (4)	-0.002 0 (5)							
C(6')	0.016 5 (3)	0.228 2 (4)	0.492 3 (3)	0.003 2 (2)	0.004 8 (3)	0.003 6 (2)	0.000 1 (4)	0.002 1 (3)	0.000 0 (4)							
C(7')	-0.066 2 (3)	0.130 0 (3)	0.365 0 (3)	0.003 0 (2)	0.002 7 (3)	0.003 1 (2)	-0.000 1 (5)	0.002 4 (4)	0.000 1 (5)							
C(8')	-0.142 8 (3)	0.130 1 (3)	0.393 1 (3)	0.002 8 (2)	0.004 7 (3)	0.002 7 (2)	-0.000 4 (4)	0.002 3 (3)	-0.001 2 (4)							
C(9')	-0.212 3 (3)	0.189 8 (4)	0.354 5 (3)	0.004 1 (2)	0.004 8 (3)	0.004 4 (2)	0.000 8 (5)	0.003 9 (3)	0.001 7 (5)							
C(10')	-0.284 6 (3)	0.189 0 (4)	0.377 2 (3)	0.003 8 (2)	0.005 1 (3)	0.005 1 (3)	0.002 9 (5)	0.003 9 (4)	0.002 0 (5)							
C(11')	0.128 8 (4)	0.128 8 (4)	0.438 6 (3)	0.004 1 (2)	0.005 2 (3)	0.004 7 (2)	-0.000 4 (5)	0.005 2 (3)	-0.000 8 (5)							
C(12')	-0.218 9 (3)	0.069 4 (4)	0.479 0 (3)	0.004 6 (2)	0.005 0 (3)	0.003 8 (2)	0.000 2 (5)	0.004 5 (3)	0.001 0 (5)							
C(13')	-0.145 3 (3)	0.070 4 (4)	0.456 4 (3)	0.003 7 (2)	0.004 6 (3)	0.003 2 (2)	0.000 9 (5)	0.002 2 (3)	0.000 8 (5)							
C(14')	-0.148 3 (3)	0.037 4 (4)	0.240 4 (3)	0.003 3 (2)	0.004 9 (3)	0.003 6 (2)	-0.002 4 (5)	0.002 4 (3)	-0.002 4 (5)							
C(15')	-0.131 3 (3)	-0.060 0 (4)	0.269 3 (3)	0.005 2 (3)	0.004 8 (3)	0.005 0 (3)	-0.003 7 (5)	0.004 4 (4)	-0.001 6 (5)							
C(16')	-0.036 1 (3)	-0.093 2 (4)	0.293 4 (3)	0.006 1 (3)	0.003 4 (3)	0.005 6 (3)	-0.001 7 (5)	0.005 4 (4)	-0.000 1 (5)							
C(17)	-0.044 0 (3)	0.302 5 (4)	0.235 2 (3)	0.003 7 (2)	0.003 8 (3)	0.004 5 (2)	-0.000 0 (5)	0.002 3 (4)	-0.001 5 (5)							
C(18)	-0.048 5 (4)	0.392 9 (4)	0.258 4 (3)	0.006 7 (3)	0.004 6 (3)	0.004 8 (3)	-0.000 6 (6)	0.003 4 (5)	-0.002 5 (6)							
C(19)	0.031 8 (4)	0.433 7 (4)	0.306 9 (4)	0.007 7 (3)	0.004 2 (3)	0.007 2 (3)	0.000 4 (6)	0.005 2 (5)	-0.003 6 (6)							
C(20)	0.109 5 (3)	0.386 1 (4)	0.327 5 (4)	0.005 0 (3)	0.005 5 (3)	0.005 7 (3)	-0.003 5 (6)	0.003 0 (4)	-0.002 7 (6)							
C(21)	0.106 8 (3)	0.297 4 (4)	0.300 3 (3)	0.003 6 (2)	0.004 8 (3)	0.004 8 (3)	-0.000 5 (5)	0.003 3 (4)	0.000 4 (5)							
C(22)	-0.137 9 (4)	0.442 5 (5)	0.232 3 (5)	0.005 8 (3)	0.006 8 (4)	0.012 4 (5)	0.006 7 (6)	0.003 6 (7)	-0.002 8 (8)							
C(100)	-0.0514 (4)	0.4577 (4)	0.0184 (4)	5.3 (1)	0.87	0.123 (2)	-0.159 (3)	0.264 (2)	5.0	H(162)						
C(101)	0.0352 (6)	0.4704 (7)	0.0388 (6)	5.3 (2)	0.63	0.235 (2)	0.156 (3)	0.496 (2)	5.0	H(3')						
C(102)	0.8805 (7)	0.4774 (8)	-0.0323 (7)	5.6 (3)	0.49	0.227 (2)	0.255 (3)	0.605 (2)	5.0	H(4')						
C(103)	0.1105 (7)	0.4281 (8)	0.1085 (7)	5.2 (3)	0.43	-0.042 (2)	0.248 (3)	0.492 (2)	5.0	H(6')						

Atom	x	y	z	B <sub>11</sub>	B <sub>22</sub>	B <sub>33</sub>	B <sub>12</sub>	B <sub>13</sub>	B <sub>23</sub>	
C(104)	0.1201 (7)	0.4703 (9)	0.0796 (7)	5.5 (3)	0.43	H(9')	-0.210 (2)	0.233 (3)	0.311 (2)	5.0
C(105)	0.0642 (9)	0.4217 (10)	0.1005 (9)	5.3 (4)	0.42	H(10')	-0.330 (2)	0.234 (3)	0.352 (2)	5.0
C(106)	-0.0008 (9)	0.4205 (10)	0.0743 (9)	5.5 (4)	0.42	H(11')	-0.336 (2)	0.125 (3)	0.458 (2)	5.0
H(3)	-0.184 (2)	0.201 (3)	-0.010 (2)	5.0		H(12')	-0.222 (2)	0.027 (3)	0.518 (2)	5.0
H(4)	-0.173 (2)	0.286 (3)	-0.126 (2)	5.0		H(13')	-0.095 (2)	0.025 (3)	0.486 (2)	5.0
H(6)	0.084 (2)	0.225 (3)	-0.033 (2)	5.0		H(141')	-0.203 (2)	0.059 (3)	0.244 (2)	5.0
H(9)	0.137 (2)	0.012 (3)	-0.004 (2)	5.0		H(142')	-0.157 (2)	0.046 (3)	0.181 (2)	5.0
H(10)	0.258 (2)	-0.005 (3)	-0.042 (2)	5.0		H(151')	-0.164 (2)	-0.098 (3)	0.226 (2)	5.0
H(11)	0.375 (2)	0.095 (3)	0.009 (2)	5.0		H(152')	-0.146 (2)	-0.075 (3)	0.319 (2)	5.0
H(12)	0.371 (2)	0.212 (3)	0.098 (2)	5.0		H(161')	-0.034 (2)	-0.154 (3)	0.301 (2)	5.0
H(13)	0.253 (2)	0.229 (3)	0.142 (2)	5.0		H(162')	0.001 (2)	-0.060 (3)	0.350 (2)	5.0
H(141)	0.240 (2)	0.056 (3)	0.217 (2)	5.0		H(17)	-0.099 (2)	0.269 (3)	0.203 (2)	5.0
H(142)	0.210 (2)	0.056 (3)	0.291 (2)	5.0		H(19)	0.037 (2)	0.499 (3)	0.325 (2)	5.0
H(151)	0.231 (2)	-0.085 (3)	0.241 (2)	5.0		H(20)	0.166 (2)	0.415 (3)	0.361 (2)	5.0
H(152)	0.145 (2)	-0.070 (3)	0.156 (2)	5.0		H(21)	0.161 (2)	0.260 (3)	0.310 (2)	5.0
H(161)	0.143 (2)	-0.074 (3)	0.324 (2)	5.0						

(b) [Ni(cbpS)mpy]

Atom	x	y	z	B <sub>11</sub>	B <sub>22</sub>	B <sub>33</sub>	B <sub>12</sub>	B <sub>13</sub>	B <sub>23</sub>
Ni	0.021 61 (6)	0.107 18 (5)	0.236 35 (4)	0.003 20 (7)	0.003 31 (3)	0.002 65 (3)	0.000 12 (8)	0.001 84 (7)	-0.000 36 (6)
Cl(1)	-0.032 4 (1)	0.323 9 (1)	-0.175 7 (1)	0.005 8 (2)	0.005 76 (8)	0.003 74 (7)	-0.000 5 (2)	0.002 8 (2)	0.002 7 (1)
Cl(2)	0.088 1 (1)	0.339 1 (1)	0.633 0 (1)	0.006 6 (2)	0.009 26 (11)	0.006 07 (8)	-0.002 1 (2)	0.003 4 (2)	-0.009 1 (2)
S	0.004 2 (1)	-0.059 8 (1)	0.210 97 (9)	0.004 4 (2)	0.003 80 (7)	0.003 61 (7)	0.000 2 (2)	0.002 5 (2)	-0.000 6 (1)
O	-0.071 1 (3)	0.126 9 (2)	0.116 4 (2)	0.002 8 (3)	0.004 6 (2)	0.002 8 (2)	-0.001 7 (4)	0.002 9 (4)	0.000 2 (3)
O	0.108 6 (3)	0.091 3 (2)	0.363 1 (2)	0.002 7 (3)	0.004 7 (2)	0.002 9 (2)	0.001 3 (4)	0.001 7 (4)	-0.000 5 (3)
N(1)	0.114 3 (3)	0.099 8 (3)	0.182 2 (2)	0.001 7 (4)	0.003 7 (2)	0.003 1 (2)	0.000 3 (5)	0.003 2 (4)	0.000 0 (4)
N(1')	-0.072 8 (3)	0.096 0 (3)	0.290 4 (3)	0.002 0 (4)	0.003 6 (2)	0.002 8 (2)	-0.001 6 (5)	0.003 6 (4)	0.000 1 (3)
N(2)	0.029 2 (3)	0.252 5 (3)	0.254 3 (2)	0.000 4 (4)	0.004 4 (2)	0.002 9 (2)	-0.000 9 (5)	0.000 6 (4)	-0.000 0 (4)
Cl(1)	0.025 9 (4)	0.174 6 (3)	0.045 2 (3)	0.001 0 (5)	0.003 4 (2)	0.002 7 (2)	0.000 7 (6)	0.002 4 (5)	-0.000 6 (4)
Cl(2)	-0.056 4 (4)	0.168 3 (3)	0.053 5 (3)	0.000 7 (5)	0.003 3 (2)	0.002 7 (2)	0.000 7 (5)	0.002 4 (5)	-0.000 2 (4)
C(3)	-0.130 8 (4)	0.207 7 (4)	-0.013 8 (3)	0.001 6 (5)	0.004 6 (3)	0.003 6 (3)	-0.000 2 (6)	0.001 3 (6)	-0.000 4 (5)
C(4)	-0.122 2 (4)	0.255 5 (4)	-0.083 1 (3)	0.000 3 (5)	0.004 5 (3)	0.004 0 (3)	0.001 2 (6)	-0.000 2 (6)	0.000 6 (5)
C(5)	-0.041 1 (4)	0.262 0 (3)	-0.088 9 (3)	0.000 0 (5)	0.004 1 (3)	0.003 0 (2)	-0.000 4 (6)	0.001 3 (5)	0.000 0 (4)
C(6)	0.031 9 (4)	0.221 7 (3)	-0.027 8 (3)	0.002 0 (5)	0.004 1 (3)	0.002 9 (2)	-0.000 4 (6)	0.001 9 (5)	-0.000 4 (5)
C(7)	0.107 8 (4)	0.130 7 (3)	0.105 9 (3)	0.001 3 (5)	0.003 1 (3)	0.003 4 (2)	0.000 4 (6)	0.003 4 (5)	-0.000 8 (4)
C(8)	0.181 3 (4)	0.122 2 (3)	0.076 3 (3)	0.001 6 (5)	0.003 3 (3)	0.002 7 (2)	-0.000 2 (5)	0.001 5 (5)	0.000 5 (4)
C(9)	0.184 4 (4)	0.053 3 (4)	0.019 8 (3)	0.003 6 (5)	0.004 5 (3)	0.003 2 (3)	-0.000 1 (7)	0.001 5 (5)	0.000 1 (5)
C(10)	0.255 4 (5)	0.042 9 (4)	-0.003 8 (3)	0.005 9 (6)	0.006 6 (4)	0.002 9 (3)	0.002 3 (7)	0.002 8 (6)	-0.001 3 (5)
C(11)	0.325 8 (5)	0.104 0 (4)	0.026 6 (4)	0.002 6 (5)	0.009 2 (4)	0.004 4 (3)	0.004 9 (8)	0.006 2 (6)	0.001 6 (6)
C(12)	0.322 3 (4)	0.174 0 (4)	0.080 9 (4)	0.001 5 (5)	0.007 1 (4)	0.004 7 (3)	-0.002 8 (7)	0.002 9 (6)	-0.000 7 (6)
C(13)	0.251 6 (4)	0.182 7 (4)	0.105 3 (3)	0.001 8 (5)	0.005 1 (3)	0.004 4 (3)	-0.000 3 (6)	0.002 9 (6)	-0.000 5 (5)
C(14)	0.1950 (4)	0.046 4 (4)	0.234 3 (3)	0.002 1 (5)	0.004 5 (3)	0.003 2 (2)	0.002 1 (6)	0.002 1 (6)	0.000 6 (5)
C(15)	0.175 4 (5)	-0.055 8 (4)	0.221 0 (4)	0.005 5 (6)	0.004 3 (3)	0.004 0 (3)	0.003 8 (7)	0.002 4 (6)	0.000 1 (5)
C(16)	0.116 2 (5)	-0.095 9 (3)	0.264 8 (3)	0.006 2 (6)	0.003 7 (3)	0.003 7 (3)	-0.000 7 (7)	0.002 4 (6)	0.000 6 (5)
C(1)	0.017 4 (4)	0.168 3 (3)	0.426 0 (3)	0.001 1 (5)	0.003 7 (3)	0.002 7 (2)	0.001 6 (6)	0.001 1 (5)	-0.000 3 (4)
C(2)	0.099 8 (4)	0.142 2 (3)	0.424 3 (3)	0.001 4 (5)	0.003 5 (3)	0.003 5 (3)	0.000 3 (6)	0.001 6 (5)	0.001 5 (4)
C(3')	0.177 7 (4)	0.173 6 (4)	0.493 6 (3)	0.002 0 (5)	0.004 9 (3)	0.003 5 (3)	0.000 1 (6)	0.001 6 (6)	0.000 2 (5)
C(4')	0.172 4 (4)	0.232 5 (4)	0.556 5 (3)	0.002 8 (5)	0.005 6 (3)	0.003 5 (3)	-0.000 6 (7)	0.000 7 (6)	-0.001 2 (5)
C(5')	0.093 2 (4)	0.261 3 (4)	0.553 7 (3)	0.003 5 (5)	0.004 9 (3)	0.003 6 (3)	0.000 9 (7)	0.000 9 (7)	-0.003 1 (5)
C(6')	0.015 0 (4)	0.229 0 (4)	0.492 2 (3)	0.002 0 (5)	0.004 6 (3)	0.003 4 (3)	0.000 6 (6)	0.003 1 (6)	-0.000 8 (5)
C(7')	-0.065 5 (4)	0.130 5 (3)	0.365 0 (3)	0.000 5 (5)	0.003 4 (3)	0.003 0 (2)	-0.000 5 (5)	0.002 8 (5)	0.000 1 (4)
C(8')	-0.141 7 (4)	0.131 2 (3)	0.392 0 (3)	0.000 2 (5)	0.004 3 (3)	0.002 7 (2)	-0.000 7 (5)	0.003 1 (5)	-0.000 9 (4)
C(9')	-0.212 0 (4)	0.191 3 (4)	0.354 4 (4)	0.001 4 (5)	0.004 7 (3)	0.004 9 (3)	0.002 0 (6)	0.002 2 (6)	0.001 6 (5)
C(10')	-0.285 3 (4)	0.191 6 (4)	0.375 4 (4)	0.001 8 (5)	0.005 3 (3)	0.005 3 (3)	0.002 9 (6)	0.002 7 (6)	0.000 7 (6)
C(11')	-0.289 6 (5)	0.129 7 (4)	0.438 9 (4)	0.003 9 (6)	0.005 6 (3)	0.004 8 (3)	0.001 2 (7)	0.005 4 (6)	-0.001 3 (5)
C(12')	-0.216 8 (4)	0.070 9 (4)	0.477 7 (3)	0.004 4 (6)	0.004 8 (3)	0.003 3 (2)	0.000 7 (7)	0.004 0 (6)	0.000 1 (5)

Atom	x	y	z	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$	
C(13)	-0.145 3 (4)	0.071 1 (4)	0.455 5 (3)	0.003 6 (5)	0.005 0 (3)	0.003 2 (2)	0.001 2 (7)	0.003 1 (6)	0.000 2 (5)	
C(14)	-0.149 6 (4)	0.039 4 (4)	0.238 8 (3)	0.002 2 (5)	0.005 1 (3)	0.003 4 (3)	-0.003 0 (6)	0.001 5 (6)	-0.002 2 (5)	
C(15)	-0.132 6 (4)	-0.059 7 (4)	0.268 3 (4)	0.000 8 (5)	0.005 3 (3)	0.005 7 (3)	-0.003 7 (6)	0.005 4 (6)	-0.002 8 (5)	
C(16)	-0.039 4 (4)	-0.091 9 (4)	0.291 1 (4)	0.003 7 (5)	0.004 0 (3)	0.005 2 (3)	-0.001 9 (6)	0.006 0 (6)	-0.000 1 (5)	
C(17)	-0.044 5 (4)	0.301 2 (4)	0.234 1 (3)	0.002 4 (5)	0.004 4 (3)	0.003 3 (3)	0.000 4 (6)	0.000 3 (6)	-0.000 2 (5)	
C(18)	-0.049 3 (5)	0.393 2 (4)	0.255 2 (4)	0.004 4 (6)	0.004 8 (3)	0.004 6 (3)	-0.004 5 (7)	0.002 8 (6)	-0.003 3 (5)	
C(19)	0.032 3 (5)	0.430 7 (4)	0.304 0 (4)	0.007 3 (6)	0.003 7 (3)	0.006 9 (3)	0.000 2 (7)	0.006 0 (7)	-0.003 0 (6)	
C(20)	0.111 3 (5)	0.383 8 (4)	0.325 5 (4)	0.004 2 (6)	0.005 2 (3)	0.005 2 (3)	-0.002 7 (7)	0.001 4 (7)	-0.002 6 (6)	
C(21)	0.106 8 (4)	0.293 1 (4)	0.299 2 (3)	0.001 3 (5)	0.004 6 (3)	0.004 3 (3)	0.001 4 (6)	0.002 5 (6)	0.000 4 (5)	
C(22)	-0.137 5 (4)	0.442 2 (4)	0.230 1 (5)	-0.001 2 (5)	0.007 2 (4)	0.013 1 (5)	0.009 0 (7)	0.002 1 (8)	-0.001 7 (8)	
Atom	x	y	z	$B_{11}$	Occupancy	Atom	x	y	z	$B_{11}$
C(100)	0.5539 (5)	-0.0462 (5)	0.4802 (4)	5.6 (2)	0.87	H(162)	0.1214 (34)	-0.1604 (32)	0.2615 (30)	5.0
C(101)	0.4690 (7)	-0.0282 (6)	0.4628 (6)	5.7 (3)	0.63	H(3')	0.2375 (33)	0.1589 (32)	0.4985 (29)	5.0
C(102)	0.3825 (9)	0.0245 (8)	0.4693 (8)	5.4 (3)	0.49	H(4')	0.2281 (34)	0.2521 (32)	0.6013 (30)	5.0
C(103)	0.4910 (10)	-0.0789 (9)	0.4230 (8)	5.3 (3)	0.46	H(6')	-0.0430 (32)	0.2498 (31)	0.4945 (29)	5.0
C(104)	0.3928 (10)	-0.0579 (9)	0.4009 (8)	5.2 (3)	0.41	H(9')	-0.2109 (33)	0.2366 (32)	0.3121 (29)	5.0
C(105)	0.5928 (12)	0.0813 (11)	0.6096 (11)	5.8 (5)	0.40	H(10')	-0.3332 (34)	0.2341 (32)	0.3512 (30)	5.0
C(106)	0.3758 (11)	-0.0239 (10)	0.4231 (9)	5.6 (4)	0.39	H(11')	-0.3378 (34)	0.1328 (31)	0.4566 (29)	5.0
H(3)	-0.1917 (4)	0.2003 (3)	-0.0113 (3)	5.0		H(12)	-0.2258 (33)	0.0254 (32)	0.5166 (30)	5.0
H(4)	-0.1688 (32)	0.2869 (31)	-0.1227 (29)	5.0		H(13')	-0.0924 (34)	0.0258 (31)	0.4839 (30)	5.0
H(6)	0.0843 (33)	0.2300 (31)	-0.0368 (30)	5.0		H(14')	-0.2021 (32)	0.0598 (33)	0.2415 (29)	5.0
H(9)	0.1353 (33)	0.0086 (31)	0.0015 (31)	5.0		H(142)	-0.1578 (33)	0.0454 (32)	0.1763 (29)	5.0
H(10)	0.2580 (34)	-0.0051 (31)	-0.0404 (30)	5.0		H(151')	-0.1678 (34)	-0.0997 (31)	0.2242 (30)	5.0
H(11)	0.3779 (34)	0.0941 (30)	0.0083 (30)	5.0		H(152')	-0.1515 (34)	-0.0731 (32)	0.3179 (30)	5.0
H(12)	0.3681 (32)	0.2142 (31)	0.1012 (29)	5.0		H(161')	-0.0360 (33)	-0.1583 (33)	0.2977 (30)	5.0
H(13)	0.2513 (33)	0.2303 (32)	0.1427 (30)	5.0		H(162')	-0.0055 (34)	0.0651 (33)	0.3444 (30)	5.0
H(14)	0.2475 (33)	0.0655 (33)	0.2160 (29)	5.0		H(17)	-0.0975 (33)	0.2680 (32)	0.2043 (29)	5.0
H(142)	0.2099 (33)	0.0607 (32)	0.2909 (30)	5.0		H(19)	0.0355 (32)	0.4879 (31)	0.3250 (30)	5.0
H(151)	0.2314 (34)	-0.0876 (31)	0.2388 (30)	5.0		H(20)	0.1674 (34)	0.4099 (30)	0.3610 (30)	5.0
H(152)	0.1472 (34)	-0.0681 (32)	0.1590 (30)	5.0		H(21)	0.1618 (33)	0.2600 (32)	0.3081 (29)	5.0
H(161)	0.1380 (34)	-0.0769 (32)	0.3233 (30)	5.0						
Atom	x	y	z	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$	
Ni	0.194 39 (3)	0.222 74 (3)	0.058 52 (3)	0.003 29 (2)	0.003 49 (2)	0.003 28 (2)	0.000 16 (4)	0.002 32 (3)	-0.000 31 (4)	
Cl(1)	0.992 99 (9)	0.866 07 (9)	0.759 38 (8)	0.007 05 (6)	0.005 78 (6)	0.005 37 (5)	0.001 2 (1)	0.004 47 (9)	-0.004 1 (1)	
Cl(2)	0.547 18 (9)	0.510 97 (12)	0.216 32 (12)	0.004 52 (6)	0.009 71 (10)	0.011 07 (11)	-0.005 0 (1)	0.000 13 (13)	0.005 6 (2)	
S	0.111 40 (7)	0.271 78 (9)	0.137 01 (8)	0.004 31 (4)	0.005 70 (6)	0.005 62 (5)	-0.000 78 (9)	0.004 87 (7)	-0.003 3 (1)	
O	0.093 2 (2)	0.185 3 (2)	0.054 7 (2)	0.003 5 (1)	0.003 6 (1)	0.004 0 (1)	0.000 6 (2)	0.001 6 (2)	-0.001 1 (2)	
O	0.296 6 (2)	0.252 8 (2)	0.170 7 (2)	0.003 7 (1)	0.004 6 (2)	0.003 4 (1)	-0.000 3 (2)	0.002 0 (2)	0.000 5 (2)	
N(1)	0.187 1 (2)	0.101 6 (2)	0.105 3 (2)	0.004 0 (1)	0.004 1 (2)	0.003 1 (1)	-0.000 9 (3)	0.003 3 (2)	-0.000 7 (3)	
N(2)	0.182 4 (2)	0.348 0 (2)	0.017 8 (2)	0.003 1 (1)	0.003 6 (2)	0.003 5 (2)	0.001 0 (3)	0.001 9 (2)	-0.000 2 (3)	
C(1)	0.130 2 (2)	0.036 9 (3)	-0.000 3 (2)	0.003 0 (1)	0.003 8 (2)	0.003 4 (2)	-0.000 5 (3)	0.002 2 (3)	-0.000 8 (3)	
C(2)	0.093 4 (2)	0.112 2 (3)	-0.092 0 (3)	0.002 8 (2)	0.004 0 (2)	0.003 5 (2)	-0.000 1 (3)	0.002 2 (3)	-0.000 2 (3)	
C(3)	0.054 3 (3)	0.105 2 (3)	-0.188 2 (3)	0.004 6 (2)	0.004 1 (2)	0.003 5 (2)	0.000 2 (4)	0.002 4 (3)	0.000 5 (4)	
C(4)	0.053 8 (3)	0.032 2 (3)	-0.232 6 (3)	0.004 9 (2)	0.005 8 (3)	0.002 9 (2)	-0.000 4 (4)	0.002 4 (3)	-0.000 5 (4)	
C(5)	0.092 1 (3)	-0.039 7 (3)	0.183 9 (3)	0.004 4 (2)	0.004 3 (2)	0.003 5 (2)	-0.000 3 (4)	0.003 4 (3)	-0.001 5 (4)	
C(6)	0.128 1 (3)	-0.038 0 (3)	-0.091 1 (3)	0.003 7 (2)	0.003 7 (2)	0.004 3 (2)	-0.000 3 (3)	0.002 8 (3)	-0.000 0 (4)	
C(7)	0.165 7 (2)	0.032 9 (3)	0.057 6 (3)	0.002 8 (1)	0.003 8 (2)	0.003 4 (2)	-0.000 3 (3)	0.002 4 (2)	-0.000 3 (3)	
C(8)	0.175 6 (3)	-0.052 6 (3)	0.100 1 (3)	0.003 3 (2)	0.003 8 (2)	0.003 1 (2)	-0.000 3 (3)	0.002 2 (3)	-0.000 3 (3)	
C(9)	0.253 4 (3)	-0.089 6 (3)	0.140 2 (3)	0.003 6 (2)	0.005 1 (3)	0.005 6 (2)	-0.000 9 (4)	0.003 8 (3)	0.000 8 (4)	
C(10)	0.265 9 (3)	-0.169 0 (4)	0.183 8 (4)	0.004 3 (2)	0.005 2 (3)	0.006 7 (3)	0.002 2 (4)	0.003 8 (4)	0.003 1 (5)	
C(11)	0.200 0 (3)	-0.211 4 (3)	0.186 5 (3)	0.005 8 (2)	0.004 1 (2)	0.005 4 (2)	-0.000 3 (4)	0.004 9 (3)	0.000 9 (4)	

(c) |Ni(cbpS)py|

Atom	x	y	z	$B_1 A^2$	Atom	x	y	z	$B_2 A^2$	Atom	x	y	z	$B_3 A^2$
C(12)	0.122 5 (3)	-0.174 8 (3)	0.146 7 (3)	0.004 5 (2)	0.004 7 (2)	0.005 2 (2)	-0.002 2 (4)	0.004 6 (3)	-0.000 5 (4)	H(6')	0.381 (2)	0.496 (3)	0.093 (3)	5.0 (0)
C(13)	0.109 7 (3)	-0.096 0 (3)	0.103 0 (3)	0.003 3 (2)	0.004 6 (2)	0.004 3 (2)	-0.000 9 (4)	0.002 3 (3)	0.000 3 (4)	H(9')	0.264 (2)	0.457 (3)	-0.097 (3)	5.0 (0)
C(14)	0.205 5 (3)	0.0990 (3)	0.202 0 (3)	0.005 6 (2)	0.004 6 (2)	0.003 2 (2)	-0.001 4 (4)	0.003 9 (3)	-0.000 1 (4)	H(10')	0.235 (2)	0.590 (3)	-0.168 (3)	5.0 (0)
C(15)	0.126 9 (3)	0.111 4 (4)	0.213 4 (3)	0.007 3 (2)	0.006 7 (3)	0.005 2 (2)	-0.003 8 (5)	0.008 0 (3)	0.000 2 (4)	H(11')	0.199 (2)	0.700 (3)	-0.099 (3)	5.0 (0)
C(16)	0.064 2 (3)	0.172 3 (4)	0.145 1 (3)	0.005 4 (2)	0.007 5 (3)	0.007 5 (2)	-0.003 1 (4)	0.008 8 (3)	-0.004 2 (5)	H(12)	0.175 (2)	0.685 (3)	0.027 (3)	5.0 (0)
C(1)	0.330 4 (3)	0.383 7 (3)	0.117 1 (3)	0.003 1 (2)	0.004 1 (2)	0.003 1 (2)	0.000 5 (3)	0.002 0 (3)	-0.000 3 (3)	H(13)	0.199 (2)	0.552 (3)	0.092 (3)	5.0 (0)
C(2)	0.348 8 (2)	0.311 7 (3)	0.175 9 (3)	0.003 4 (2)	0.004 3 (2)	0.003 0 (2)	0.000 5 (3)	0.002 8 (2)	-0.000 3 (3)	H(14)	0.106 (2)	0.432 (3)	-0.079 (3)	5.0 (0)
C(3)	0.430 5 (3)	0.306 9 (3)	0.247 4 (3)	0.003 4 (2)	0.005 7 (3)	0.003 9 (2)	0.000 2 (4)	0.001 7 (3)	0.001 4 (4)	H(15)	0.075 (2)	0.331 (3)	-0.096 (3)	5.0 (0)
C(4)	0.489 1 (3)	0.365 6 (4)	0.258 8 (3)	0.002 9 (2)	0.007 4 (3)	0.004 6 (2)	0.000 8 (4)	0.001 1 (3)	0.002 0 (3)	H(16)	0.080 (2)	0.438 (3)	0.050 (3)	5.0 (0)
C(5)	0.470 6 (3)	0.433 8 (4)	0.201 2 (3)	0.003 2 (2)	0.006 2 (3)	0.005 6 (3)	-0.001 6 (4)	0.001 8 (3)	0.000 8 (5)	H(17)	0.352 (2)	0.125 (3)	0.111 (3)	5.0 (0)
C(6)	0.393 9 (3)	0.443 4 (3)	0.132 2 (3)	0.003 9 (2)	0.004 5 (2)	0.004 9 (2)	-0.000 4 (4)	0.002 0 (3)	0.000 6 (4)	H(18)	0.434 (2)	0.070 (3)	0.040 (3)	5.0 (0)
C(7)	0.247 2 (3)	0.402 8 (3)	0.045 4 (3)	0.003 3 (2)	0.003 4 (2)	0.003 4 (2)	-0.000 1 (4)	0.002 1 (3)	-0.001 1 (3)	H(19)	0.403 (2)	0.109 (3)	-0.097 (3)	5.0 (0)
C(8)	0.233 9 (3)	0.490 5 (3)	0.004 4 (3)	0.003 7 (2)	0.003 5 (2)	0.003 5 (2)	0.000 1 (4)	0.000 7 (3)	-0.000 7 (4)	H(20)	0.292 (2)	0.190 (3)	-0.183 (3)	5.0 (0)
C(9)	0.244 5 (4)	0.504 3 (4)	-0.073 1 (4)	0.008 1 (3)	0.004 6 (3)	0.004 6 (3)	-0.000 5 (5)	0.002 9 (4)	0.000 5 (5)	H(21)	0.208 (2)	0.236 (3)	-0.120 (3)	5.0 (0)
C(10)	0.230 0 (5)	0.582 1 (4)	-0.114 0 (4)	0.011 9 (5)	0.006 6 (3)	0.006 6 (3)	-0.000 9 (7)	0.003 6 (6)	0.005 3 (5)	H(x)	0.661 (2)	0.401 (3)	0.644 (3)	5.0 (9)
C(11)	0.203 8 (5)	0.647 5 (4)	-0.077 1 (5)	0.008 7 (4)	0.003 9 (3)	0.012 0 (5)	-0.000 1 (6)	0.003 1 (7)	0.003 7 (7)					
C(12)	0.193 9 (4)	0.637 3 (4)	-0.000 0 (5)	0.006 2 (3)	0.004 2 (3)	0.010 7 (4)	0.001 1 (5)	0.002 3 (6)	-0.002 5 (6)					
C(13)	0.209 5 (3)	0.558 1 (3)	0.040 7 (4)	0.004 9 (2)	0.004 3 (3)	0.007 1 (4)	0.000 2 (4)	0.002 9 (4)	0.000 1 (4)					
C(14)	0.102 4 (3)	0.375 5 (3)	-0.047 4 (3)	0.003 5 (2)	0.003 6 (2)	0.005 1 (2)	0.001 4 (4)	0.000 5 (3)	-0.000 1 (4)					
C(15)	0.050 1 (3)	0.395 9 (3)	0.002 9 (4)	0.003 7 (2)	0.004 8 (3)	0.007 8 (3)	0.001 8 (4)	0.001 6 (4)	-0.003 1 (5)					
C(16)	0.024 7 (3)	0.320 5 (4)	0.042 9 (4)	0.003 6 (2)	0.007 2 (3)	0.008 4 (3)	-0.000 4 (4)	0.004 5 (3)	-0.005 8 (5)					
C(17)	0.337 7 (3)	0.133 2 (3)	0.047 1 (3)	0.003 7 (2)	0.005 0 (3)	0.004 8 (2)	0.000 7 (4)	0.003 1 (3)	0.000 6 (4)					
C(18)	0.388 5 (3)	0.101 7 (4)	0.012 1 (4)	0.004 3 (2)	0.006 8 (3)	0.007 6 (3)	0.003 7 (4)	0.005 3 (4)	0.001 7 (5)					
C(19)	0.371 6 (3)	0.123 9 (5)	-0.074 8 (4)	0.007 2 (2)	0.009 6 (4)	0.009 0 (3)	0.002 7 (5)	0.008 0 (3)	0.003 1 (6)					
C(20)	0.305 4 (3)	0.173 5 (5)	-0.124 0 (3)	0.006 9 (2)	0.008 8 (4)	0.005 7 (2)	0.003 0 (5)	0.008 0 (3)	0.002 2 (4)					
C(21)	0.257 2 (3)	0.200 4 (3)	-0.085 6 (3)	0.004 8 (2)	0.005 4 (3)	0.004 4 (2)	0.001 8 (4)	0.004 7 (3)	0.002 2 (4)					
C(1x) [0.80] <sup>b</sup>	0.558 0 (5)	0.227 1 (5)	0.528 7 (4)	0.010 8 (4)	0.010 9 (5)	0.006 4 (3)	0.012 7 (7)	0.008 6 (5)	0.009 1 (7)					
C(2x) [0.75]	0.614 7 (6)	0.270 3 (7)	0.494 5 (5)	0.015 8 (4)	0.025 2 (8)	0.006 1 (4)	0.031 0 (8)	0.011 4 (6)	0.012 9 (9)					
C(3x) [0.75]	0.659 3 (5)	0.347 9 (7)	0.548 3 (7)	0.004 8 (4)	0.017 8 (6)	0.027 0 (7)	0.006 9 (8)	0.011 8 (7)	0.032 3 (9)					
C(4x) [0.70]	0.633 9 (7)	0.354 5 (6)	0.621 1 (7)	0.016 0 (7)	0.009 9 (5)	0.014 9 (7)	0.017 7 (8)	-0.020 2 (11)	-0.014 4 (9)					
C(5x) [0.65]	0.616 0 (10)	0.369 4 (11)	0.690 7 (17)	0.008 5 (8)	0.011 7 (10)	0.033 5 (24)	0.009 1 (15)	-0.004 7 (25)	0.017 9 (24)					
C(6x) [0.85]	0.572 2 (4)	0.278 8 (6)	0.607 1 (4)	0.009 3 (8)	0.013 9 (5)	0.009 6 (3)	0.013 9 (7)	0.014 0 (4)	0.014 6 (7)					
C(7x) [0.50]	0.498 4 (9)	0.149 5 (8)	0.494 0 (9)	0.010 7 (8)	0.004 5 (6)	0.007 3 (7)	-0.006 6 (12)	0.005 2 (12)	-0.005 0 (11)					
C(8x) [0.33]	0.618 2 (20)	0.388 4 (15)	0.728 8 (13)	0.021 2 (21)	0.013 3 (11)	0.005 6 (9)	0.020 1 (21)	-0.004 1 (21)	-0.016 3 (13)					

<sup>a</sup> The form of the anisotropic thermal parameter is  $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$ . <sup>b</sup> Partial occupancies are given in brackets.

Table II. Bond Lengths (Å) for [Co(cbpS)mpy], [Ni(cbpS)mpy], and [Ni(cbpS)py], Respectively<sup>a</sup>

M-S	2.537 (1)	2.484 (1)	2.484 (1)	C(9)-C(10)	1.383 (6)	1.36 (1)	1.404 (4)
M-O	1.997 (3)	2.008 (3)	2.034 (2)	C(10)-C(11)	1.389 (7)	1.40 (1)	1.378 (4)
M-O'	2.039 (3)	2.053 (3)	2.004 (2)	C(11)-C(12)	1.348 (7)	1.393 (9)	1.379 (4)
M-N(1)	2.080 (3)	2.044 (5)	2.076 (2)	C(12)-C(13)	1.374 (6)	1.37 (1)	1.397 (4)
M-N(1')	2.104 (3)	2.076 (5)	2.062 (2)	C(14)-C(15)	1.529 (6)	1.536 (7)	1.517 (4)
M-N(2)	2.202 (4)	2.149 (4)	2.117 (2)	C(15)-C(16)	1.523 (6)	1.534 (8)	1.526 (5)
Cl(1)-C(5)	1.745 (4)	1.755 (6)	1.751 (3)	C(1')-C(2')	1.433 (6)	1.420 (8)	1.426 (4)
Cl(2)-C(5')	1.758 (5)	1.768 (6)	1.769 (3)	C(1')-C(6')	1.416 (6)	1.428 (7)	1.413 (4)
S-C(16)	1.809 (5)	1.790 (7)	1.811 (4)	C(1')-C(7')	1.468 (5)	1.460 (8)	1.473 (3)
S-C(16')	1.803 (5)	1.799 (7)	1.812 (4)	C(2')-C(3')	1.415 (6)	1.434 (7)	1.424 (4)
O-C(2)	1.299 (5)	1.305 (6)	1.302 (3)	C(3')-C(4')	1.375 (6)	1.381 (7)	1.351 (4)
O'-C(2')	1.306 (5)	1.316 (6)	1.294 (3)	C(4')-C(5')	1.371 (6)	1.347 (9)	1.368 (4)
N(1)-C(7)	1.288 (5)	1.318 (6)	1.287 (3)	C(5')-C(6')	1.361 (6)	1.388 (8)	1.355 (4)
N(1)-C(14)	1.487 (5)	1.501 (6)	1.472 (3)	C(7')-C(8')	1.504 (6)	1.486 (8)	1.504 (4)
N(1')-C(7')	1.293 (5)	1.301 (6)	1.292 (3)	C(8')-C(9')	1.388 (6)	1.383 (9)	1.382 (4)
N(1')-C(14')	1.369 (5)	1.488 (6)	1.497 (3)	C(8')-C(13')	1.381 (6)	1.378 (8)	1.379 (4)
N(2)-C(17)	1.342 (5)	1.333 (7)	1.336 (3)	C(9')-C(10')	1.378 (6)	1.369 (9)	1.361 (5)
N(2)-C(21)	1.340 (5)	1.349 (6)	1.334 (3)	C(10')-C(11')	1.369 (6)	1.419 (8)	1.376 (7)
C(1)-C(2)	1.429 (5)	1.413 (7)	1.420 (4)	C(11')-C(12')	1.387 (6)	1.420 (9)	1.361 (7)
C(1)-C(6)	1.412 (6)	1.428 (7)	1.407 (3)	C(12')-C(13')	1.401 (6)	1.358 (9)	1.380 (5)
C(1)-C(7)	1.475 (5)	1.490 (8)	1.483 (3)	C(14')-C(15')	1.517 (6)	1.530 (7)	1.534 (5)
C(2)-C(3)	1.419 (6)	1.425 (8)	1.422 (4)	C(15')-C(16')	1.535 (6)	1.522 (8)	1.518 (5)
C(3)-C(4)	1.376 (6)	1.404 (7)	1.354 (4)	C(17)-C(18)	1.398 (6)	1.403 (7)	1.368 (4)
C(4)-C(5)	1.379 (6)	1.379 (7)	1.379 (4)	C(18)-C(19)	1.390 (7)	1.374 (9)	1.365 (5)
C(5)-C(6)	1.367 (6)	1.370 (8)	1.368 (4)	C(18)-C(22)	1.547 (7)	1.538 (8)	
C(7)-C(8)	1.505 (5)	1.474 (9)	1.486 (4)	C(19)-C(20)	1.380 (7)	1.391 (8)	1.354 (5)
C(8)-C(9)	1.388 (6)	1.391 (8)	1.386 (4)	C(20)-C(21)	1.379 (6)	1.389 (7)	1.345 (4)
C(8)-C(13)	1.396 (6)	1.385 (9)	1.386 (4)				

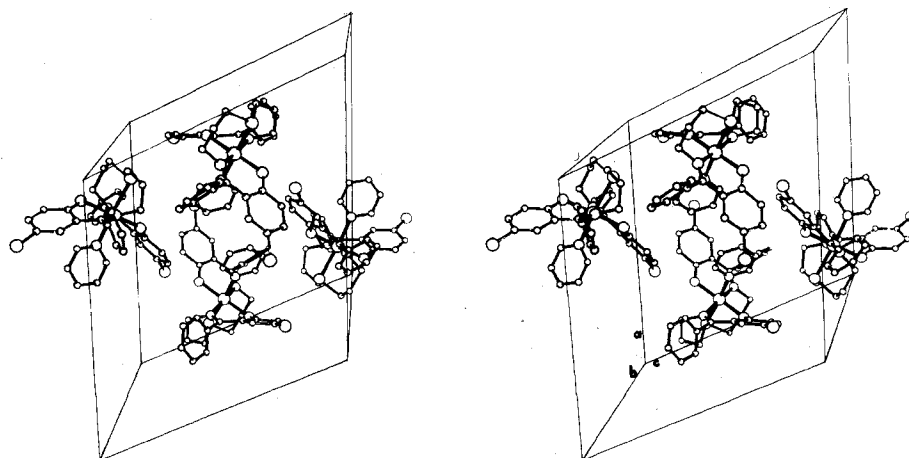
<sup>a</sup> For [Ni(cbpS)py] the second half (') of the cbpS ligand bears closer resemblance to and is therefore listed with the first half for the other two molecules.

Table III. Bond Angles (deg) for [Co(cbpS)mpy], [Ni(cbpS)mpy], and [Ni(cbpS)py], Respectively<sup>a</sup>

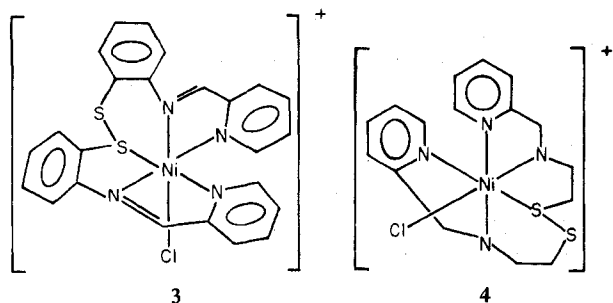
S-M-O	88.7 (1)	88.9 (1)	93.5 (1)	C(7)-C(8)-C(13)	121.2 (4)	119.9 (6)	119.2 (2)
S-M-O'	93.3 (1)	92.9 (1)	88.3 (1)	C(9)-C(8)-C(13)	118.2 (4)	117.8 (9)	118.6 (3)
S-M-N(1)	85.9 (1)	86.0 (1)	86.7 (1)	C(8)-C(9)-C(10)	120.0 (4)	122.2 (9)	121.1 (3)
S-M-N(1')	85.9 (1)	86.5 (1)	84.8 (1)	C(9)-C(10)-C(11)	120.6 (4)	119.9 (7)	119.8 (3)
S-M-N(2)	177.0 (1)	177.1 (2)	176.2 (1)	C(10)-C(11)-C(12)	119.4 (5)	118.2 (8)	119.3 (3)
O-M-O'	175.5 (1)	175.2 (2)	176.7 (1)	C(11)-C(12)-C(13)	121.1 (5)	121.1 (9)	121.0 (3)
O-M-N(1)	87.7 (1)	88.9 (1)	84.1 (1)	C(8)-C(13)-C(12)	120.8 (5)	120.7 (8)	120.1 (3)
O-M-N(1')	92.9 (1)	92.0 (2)	94.5 (1)	N(1)-C(14)-C(15)	110.7 (4)	109.3 (4)	110.4 (2)
O-M-N(2)	89.0 (1)	88.7 (1)	90.2 (1)	C(14)-C(15)-C(16)	115.8 (4)	116.5 (5)	114.8 (3)
O'-M-N(1)	96.4 (1)	95.7 (2)	93.3 (1)	S-C(16)-C(15)	111.3 (3)	111.3 (4)	111.9 (2)
O'-M-N(1')	83.2 (1)	83.7 (2)	88.5 (1)	C(2')-C(1')-C(6')	118.8 (4)	119.2 (7)	118.5 (2)
O'-M-N(2)	88.9 (1)	89.4 (1)	88.0 (1)	C(2')-C(1')-C(7')	122.2 (4)	122.0 (6)	123.7 (2)
N(1)-M-N(1')	171.7 (1)	172.4 (1)	171.2 (1)	C(6')-C(1')-C(7')	119.0 (4)	118.7 (7)	117.7 (2)
N(1)-M-N(2)	95.8 (1)	95.6 (2)	93.2 (1)	O'-C(2')-C(1')	123.8 (4)	124.1 (6)	125.1 (2)
N(1')-M-N(2)	92.4 (1)	92.0 (2)	95.4 (1)	O'-C(2')-C(3')	119.0 (4)	118.0 (8)	118.3 (2)
M-S-C(16)	99.1 (2)	100.4 (3)	100.3 (1)	C(1')-C(2')-C(3')	117.2 (4)	117.9 (6)	116.6 (3)
M-S-C(16')	99.7 (2)	100.8 (3)	100.3 (1)	C(2')-C(3')-C(4')	122.3 (4)	120.7 (6)	122.6 (3)
C(16)-S-C(16')	100.2 (2)	100.2 (3)	99.8 (1)	C(3')-C(4')-C(5')	119.3 (4)	120.5 (7)	120.0 (3)
M-O-C(2)	124.9 (5)	124.1 (4)	119.8 (2)	C(4')-C(5')-C(6')	121.7 (5)	122.2 (6)	120.9 (3)
M-O'-C(2')	119.8 (5)	118.9 (4)	125.1 (2)	Cl(2)-C(5')-C(4')	119.0 (4)	120.1 (6)	120.0 (2)
M-N(1)-C(7)	127.0 (3)	127.8 (5)	126.3 (2)	Cl(2)-C(5')-C(6')	119.4 (4)	117.7 (6)	119.1 (2)
M-N(1)-C(14)	113.7 (3)	114.9 (3)	113.8 (2)	C(1')-C(6')-C(5')	120.6 (4)	119.2 (7)	121.5 (3)
M-N(1')-C(7')	124.9 (3)	125.2 (5)	126.8 (2)	N(1')-C(7')-C(1')	121.1 (4)	121.4 (8)	122.7 (2)
M-N(1')-C(14')	114.1 (3)	114.3 (3)	113.7 (2)	N(1')-C(7')-C(8')	121.4 (4)	121.1 (7)	120.6 (2)
M-N(2)-C(17)	118.9 (3)	119.8 (4)	119.4 (2)	C(1')-C(7')-C(8')	117.4 (4)	117.5 (6)	116.7 (2)
M-N(2)-C(21)	122.5 (3)	120.9 (4)	123.0 (2)	C(7')-C(8')-C(9')	119.9 (4)	120.5 (6)	119.6 (3)
C(17)-N(2)-C(21)	117.5 (4)	118.3 (5)	117.0 (2)	C(7')-C(8')-C(13')	120.6 (4)	119.7 (7)	122.0 (3)
C(2)-C(1)-C(7)	123.4 (4)	124.3 (6)	122.1 (2)	C(9')-C(8')-C(13')	119.5 (4)	119.7 (8)	118.4 (3)
C(2)-C(1)-C(6)	118.1 (4)	119.7 (6)	119.0 (2)	C(8')-C(9')-C(10')	120.9 (4)	122.0 (8)	121.3 (4)
C(6)-C(1)-C(7)	118.4 (4)	115.9 (7)	118.8 (2)	C(9')-C(10')-C(11')	119.9 (4)	119.7 (8)	118.7 (4)
O-C(2)-C(1)	124.8 (4)	125.5 (7)	124.3 (2)	C(10')-C(11')-C(12')	120.2 (4)	116.1 (8)	122.1 (4)
O-C(2)-C(3)	118.0 (4)	116.7 (8)	119.2 (2)	C(11')-C(12')-C(13')	119.9 (4)	123.3 (7)	118.2 (4)
C(1)-C(2)-C(3)	117.2 (4)	117.8 (6)	116.5 (2)	C(12')-C(13')-C(8')	119.5 (4)	119.1 (8)	121.3 (4)
C(2)-C(3)-C(4)	122.7 (4)	120.8 (7)	123.0 (3)	N(1')-C(14')-C(15')	110.5 (4)	109.8 (4)	110.7 (2)
C(3)-C(4)-C(5)	119.5 (4)	120.2 (7)	119.8 (3)	C(14')-C(15')-C(16')	115.1 (4)	114.9 (6)	116.3 (3)
C(4)-C(5)-C(6)	120.1 (4)	120.8 (6)	120.0 (3)	S-C(16')-C(15')	111.6 (4)	112.6 (5)	112.7 (2)
Cl(1)-C(5)-C(4)	119.4 (4)	118.5 (6)	120.1 (2)	N(2)-C(17)-C(18)	125.0 (4)	125.7 (6)	123.1 (3)
Cl(1)-C(5)-C(6)	120.5 (4)	120.7 (6)	119.8 (2)	C(17)-C(18)-C(19)	115.6 (5)	113.6 (7)	117.6 (3)
C(1)-C(6)-C(5)	122.5 (4)	120.7 (7)	121.7 (2)	C(17)-C(18)-C(22)	121.4 (5)	121.2 (6)	
N(1)-C(7)-C(1)	122.4 (4)	120.7 (8)	120.5 (2)	C(19)-C(18)-C(22)	123.1 (5)	125.1 (6)	
N(1)-C(7)-C(8)	121.0 (4)	121.6 (7)	121.8 (2)	C(18)-C(19)-C(20)	120.4 (5)	123.3 (6)	120.2 (3)
C(1)-C(7)-C(8)	116.7 (4)	117.6 (6)	117.6 (2)	C(19)-C(20)-C(21)	119.5 (5)	117.6 (6)	118.8 (3)
C(7)-C(8)-C(9)	122.0 (4)	122.4 (8)	119.2 (2)	N(2)-C(21)-C(20)	122.2 (4)	121.4 (6)	123.4 (3)

<sup>a</sup> See footnote *a* of Table II.

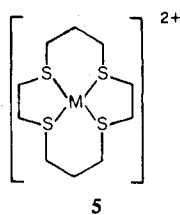


Figure 4. Molecular packing in  $[\text{Ni}(\text{cbpS})\text{py}]$ .

metal atom in a square-pyramidal configuration with the sulfur atom at the apex. In each case the Lewis base mpy or py is coordinated via the nitrogen atom approximately opposite the sulfur atom so as to complete the octahedron. The metal-sulfur distances ( $\text{Co-S} = 2.537$  (1) Å,  $\text{Ni-S} = 2.484$  (1) Å) compare with Ni-S distances of 2.470 (5) and 2.472 (5) Å for high-spin octahedral nickel(II) complexes 3<sup>15</sup> and 4,<sup>16</sup>



respectively. A much stronger metal-sulfur bond is expected in low-spin planar nickel(II) complexes and observed<sup>22</sup> ( $\text{Ni-S} = 2.177, 2.175$  Å, Table IV) in the tetrafluoroborate nickel(II) complexes, 5. Some typical metal-sulfur distances are given



in Table IV for complexes of nickel and other transition metals.

The fact that the thioether sulfur atom is coordinated to the cobalt atom in the cbpS complex is of particular interest in relation to observations on the analogous cobalt(II) complexes with SaS ligands.<sup>4</sup> Spectral data suggest that the sulfur atom does not bond to the cobalt atom in the SaS complexes,<sup>4</sup> while cobalt-sulfur coordination was postulated in the cbpS complexes on the basis of similar studies. Such failure of a potential cobalt-sulfur bond to form is not uncommon. Kadooka et al.<sup>35</sup> have drawn attention to the fact that in dichloro-[bis(2-pyridyl) disulfide]cobalt(II) neither of the two sulfur atoms acts as a donor, whereas copper-sulfur bonding is observed with the same ligand. However there is no intrinsic reason that cobalt-sulfur bonding is forbidden with ligands of types 1 and 2. The cobalt-sulfur bond observed in the  $\text{Co}(\text{cbpS})\text{mpy}$  molecule is not markedly weaker, at 2.537 Å, than the Ni-S bonds (2.484 Å) in the related nickel complexes. The Co-S bond may therefore be regarded as a normal

Table IV. Some Metal-Sulfur Bond Distances (Å)

Complex	Bond(s) <sup>o</sup>	Length, Å	Ref
3	Ni-S	2.470 (5)	15
4	Ni-S	2.472 (5)	16
<i>trans</i> -Ni(etu) <sub>4</sub> Cl <sub>2</sub> <sup>a,b</sup>	Ni-S	2.490 (6), 2.451 (5)	17
<i>trans</i> -Ni(etu) <sub>4</sub> Cl <sub>2</sub> <sup>c</sup>	Ni-S	2.44 (8), 2.482 (7)	17
Ni(tu) <sub>2</sub> NCS <sub>2</sub> <sup>d</sup>	Ni-S	2.53 (1), 2.56 (1)	18
Ni(dtp) <sub>2</sub> (py) <sub>2</sub> <sup>e</sup>	Ni-S	2.482 (4), 2.523 (3)	19
Ni(tu) <sub>4</sub> Cl <sub>2</sub>	Ni-S	2.462 (4)	20
Ni(tmtu) <sub>4</sub> Cl <sub>2</sub> <sup>f</sup>	Ni-S	2.465 (5), 2.491 (5)	21
5, M = Ni	(Ni-S)	2.176 (2)	22
Ni(dtp) <sub>2</sub>	Ni-S	2.230 (4), 2.236 (4)	23
Ni(dtc) <sup>g</sup>	Ni-S	2.201 (2), 2.217 (2)	24
5, M = Cu	(Cu-S)	2.303 (1)	22
Cu(tam) <sub>4</sub> Cl <sup>h</sup>	Cu-S	2.343 (5)	26
Zn(tu) <sub>2</sub> Cl <sub>2</sub>	Zn-S	2.35 (1)	27
Zn(tu) <sub>2</sub> (OAc) <sub>2</sub>	Zn-S	2.326 (2), 2.261 (4)	28
Zn(dtc) <sub>2</sub> py	Zn-S	2.598 (4), 2.612 (4) <sup>i</sup> , 2.330 (4), 2.325 (4) <sup>j</sup>	29
Zn(mtb) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> <sup>k</sup>	Zn-S	2.278 (2)	30
Co(dtc) <sub>3</sub>	(Co-S)	2.266 (7)	31
Cr(pcd) <sup>l</sup>	(Cr-S)	2.404 (8)	32
Fe(pcd)	(Fe-S)	2.422 (1), 2.449 (1) <sup>m</sup>	32
Cr(enS) <sub>2</sub> en <sup>n</sup>	Cr-S	2.389 (2)	33
[Cr(en) <sub>2</sub> (SCH <sub>2</sub> CO <sub>2</sub> )]ClO <sub>4</sub>	Cr-S	2.337 (2)	34

<sup>a</sup> etu = ethylenethiourea. <sup>b</sup> Triclinic form. <sup>c</sup> Monoclinic form.  
<sup>d</sup> tu = thiourea. <sup>e</sup> dtp = *O,O'*-diethyldithiophosphate. <sup>f</sup> tmtu = trimethylthiourea. <sup>g</sup> dtc = *N,N*-diethyldithiocarbamate. <sup>h</sup> tam = thioacetamide. <sup>i</sup> Axial in trigonal bipyramid. <sup>j</sup> Equatorial.  
<sup>k</sup> mtp = monothiobenzoate. <sup>l</sup> pcd = 1-pyrrolidinecarbodithioato.  
<sup>m</sup> Minimum and maximum lengths. <sup>n</sup> enS = mercaptoethylamine.  
<sup>o</sup> Indicates values averaged over very similar bond lengths.

metal-ligand bond, although it is clearly not at the strong end of the range of metal-sulfur bonds listed in Table IV. The observation of the normal Co-S bond has further ramifications: the proposed different structures for the SaX analogues of these complexes are not reflected in the spectral properties.<sup>8</sup> Instead, similar electromagnetic spectra are observed for the two classes of complexes, and the electron impact mass spectra indicate closely analogous fragmentation patterns. It therefore appears that the most significant distortions from octahedral geometry are represented by two features: the deviation of one oxygen-metal-oxygen bond angle by 6° (Ni) or 7° (Co) from a right angle in each complex and the 8–9° deviation from linearity of the angle subtended at the metal by the two cbpS nitrogen atoms. The other ligand-metal-ligand angles are within 5° of being parallel or at right angles, as are the angles between the three squares of ligand atoms which form the octahedral metal environment (planes I-III in Table V). In each case the metal atoms lie close to these planes, and no marked differences are observed between the cobalt and nickel complexes in any of these features.

Table V

Coefficients of Least-Squares Planes for  $AX + BY + CZ = D$  for [Co(cbpS)mpy], [Ni(cbpS)mpy], and [Ni(cbpS)py], Respectively

Plane	Atoms <sup>a</sup>	A	B	C	D	Distances from plane, Å
I	O, O', S, N(2)	-0.942	0.019	-0.335	-2.301	O, -0.01; O', -0.01; S, 0.01; N(2), 0.01; Co, 0.05
		0.940	0.022	-0.339	-2.342	O, -0.02; O', -0.02; S, 0.02; N(2), 0.02; Ni, 0.06
		0.136	0.917	-0.376	3.269	O, -0.02; O', -0.02; S, 0.01; N(2), 0.02; Ni, 0.03
II	O, O', N(1), N(1')	-0.040	-0.993	-0.115	-1.860	O, -0.09; O', -0.09; N(1), 0.09; N(1'), 0.10; Co, -0.07
		-0.041	-0.992	-0.123	-1.911	O, -0.08; O', -0.08; N(1), 0.08; N(1'), 0.09; Ni, -0.05
		0.855	-0.286	-0.434	1.196	O, 0.09; O', 0.09; N(1), -0.09; N(1'), -0.09; Ni, 0.06
III	S, N(1), N(1'), N(2)	-0.405	0.144	-0.903	-2.560	S, 0.03; N(1), -0.03; N(1'), -0.03; N(2), 0.03; Co, -0.02
		-0.399	0.142	-0.906	-2.564	S, 0.03; N(1), -0.03; N(1'), -0.03; N(2), 0.03; Ni, -0.02
		-0.508	-0.196	-0.839	-2.992	S, -0.05; N(1), 0.05; N(1'), 0.05; N(2), -0.05; Ni, 0.02
IV	C(1)-C(6)	0.025	-0.846	-0.533	-2.528	C(1), 0; C(2), -0.02; C(3), 0.02; C(4), 0; C(5), -0.02; C(6), 0.01
		0.020	-0.848	-0.530	-2.546	C(1), 0; C(2), -0.02; C(3), 0.02; C(4), -0.01; C(5), -0.01; C(6), 0.01
		0.605	-0.522	-0.601	-1.090	C(1), -0.01; C(2), 0.01; C(3), -0.01; C(4), 0; C(5), 0; C(6), 0
V	C(8)-C(13)	-0.162	0.597	-0.786	-0.239	C(8), 0; C(9), 0.01; C(10), 0; C(11), 0; C(12), 0; C(13), 0
		-0.163	0.585	-0.795	-0.268	C(8), -0.01; C(9), 0.01; C(10), -0.01; C(11), 0; C(12), 0.01; C(13), 0
		-0.789	-0.258	-0.558	-5.325	C(8), 0.01; C(9), 0; C(10), -0.01; C(11), 0.01; C(12), 0; C(13), -0.01
VI	C(1')-C(6')	0.228	0.780	-0.583	-2.421	C(1'), -0.02; C(2'), 0.03; C(3'), -0.02; C(4'), -0.01; C(5'), 0.03; C(6'), -0.01
		0.242	0.780	-0.577	-2.399	C(1'), -0.02; C(2'), 0.03; C(3'), -0.02; C(4'), -0.01; C(5'), 0.03; C(6'), -0.01
		0.965	0.263	0.008	2.721	C(1'), 0; C(2'), 0.01; C(3'), -0.01; C(4'), -0.01; C(5'), 0.01; C(6'), -0.01
VII	C(8')-C(13')	-0.184	-0.675	-0.715	-4.712	C(8'), 0.01; C(9'), 0; C(10'), -0.01; C(11'), 0.01; C(12'), 0.01; C(13'), -0.01
		-0.181	-0.674	-0.717	-4.728	C(8'), 0.01; C(9'), -0.01; C(10'), 0; C(11'), 0.01; C(12'), -0.01; C(13'), 0
		0.221	-0.457	-0.861	-0.351	C(8'), 0; C(9'), 0; C(10'), 0; C(11'), 0; C(12'), 0; C(13'), 0
VIII	N(2), C(17)-C(21)	0.426	0.307	-0.851	-2.648	N(2), 0; C(17), 0; C(18), 0.01; C(19), 0; C(20), 0; C(21), 0
		0.432	0.287	-0.855	-2.745	N(2), -0.01; C(17), -0.01; C(18), 0.02; C(19), -0.02; C(20), 0.01; C(21), 0.01
		-0.477	-0.816	-0.328	-4.664	N(2), -0.01; C(17), 0; C(18), 0.01; C(19), -0.01; C(20), 0; C(21), 0.01

## Interplanar Angles, Deg

	I,II	I,III	II,III	IV,V	IV,VI	IV,VII	V,VI	V,VII
[Co(cbpS)mpy]	89.0	85.6	88.7	84.8	69.9	18.7	27.5	79.2
[Ni(cbpS)mpy]	88.9	86.3	89.3	86.5	69.5	18.7	28.9	78.2
[Ni(cbpS)py]	89.0	86.2	89.2	89.6	63.2	27.1	55.5	64.9
	VI,VII	VIII,I	VIII,III	VIII,IV	VIII,V	VIII,VI	VIII,VII	
[Co(cbpS)mpy]	81.3	46.2	50.2	78.2	38.5	33.7	71.1	
[Ni(cbpS)mpy]	81.1	45.3	50.0	77.4	39.1	34.7	70.0	
[Ni(cbpS)py]	84.3	43.5	47.4	70.4	39.7	42.2	56.6	

<sup>a</sup> See footnote a of Table II.

The main metal-dependent differences between the complexes appear to be the metal-ligand bond lengths, though again these differences are relatively small. The cobalt complex exhibits a slight bond elongation along two axes relative to the nickel complexes: the S-Co-N and the N-Co-N axes. This would lift the degeneracy of the  $t_{2g}$  orbitals, splitting the octahedral  $d^7$   ${}^4T_1$  state into a lower  ${}^4A$  and a higher  ${}^4E$  state, in keeping with a Jahn-Teller distortion and could therefore be attributed to the latter. This assumes that the  $t_{2g}$  orbitals are still close to being degenerate and that the nickel(II) geometry in an undistorted  ${}^3A_2$  state represents the

geometry of an idealized T state in the absence of distortion. Certainly there is no other obvious cause for the difference between the metal environments of the cobalt and nickel complexes.

The other interplanar angles, involving ligand phenyl or heterocyclic rings, are quite similar for the various complexes. In each case, the phenyl rings in the same half of the cbpS ligand are in approximately orthogonal positions. Each of the heterocyclic base rings is tilted with respect to both chlorophenyl rings near them. The tilted aromatic rings in this molecule leave regions of unoccupied space which probably

enhances the observed tendency for crystals of the complexes to occlude solvent molecules. The symmetrical coordination of the cbpS ligand to the metals (oxygen atoms on opposite sides of the metal and imine nitrogens also opposite) is the most common bonding arrangement for ligands of the cbpX type in both five- and six-coordinated complexes<sup>6,7,36</sup> though an exception is known.<sup>36</sup> Comparison with the known cbpN complexes<sup>6,7</sup> suggests strongly that the five-coordinated complexes [Co(cbpS)] and [Ni(cbpS)], formed by removal of the adducted mpy or py, would have a square-pyramidal structure, distorted markedly in the direction of a trigonal bipyramid. The axis of this hypothetical trigonal bipyramid would pass through the imine nitrogens. Moreover, it now seems likely from the discussion above that the salS analogues of the cbpS complexes generally have similar structures, including a metal-sulfur bond.

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**Registry No.** Co(cbpS), 61218-50-6; Ni(cbpS), 61218-51-7; Co(cbpS)mpy, 61218-52-8; Ni(cbpS)mpy, 61218-53-9; Ni(cbpS)py, 61218-54-0.

**Supplementary Material Available:** Listings of structure factor amplitudes (42 pages). Ordering information is given on any current masthead page.

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# Notes

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## Kinetics and Mechanism of the Reduction of Thiocyanatopentaamminecobalt(III) by Titanium(III)

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There has been considerable upsurge in the literature on kinetic and mechanistic studies involving aquotitanium(III) as the reducing ion.<sup>1-7</sup> The most recent reports have been on the reduction of cobalt(III)-ammine complexes by this ion. Mechanistic classification into the inner- or the outer-sphere type for these latter reactions<sup>4-7</sup> has been predominantly based on the complexity of the rate dependence on hydrogen ion concentration. The rate expressions obtained can only be rationalized by invoking a series of reaction steps involving the formation of binuclear precursor complexes as preceding the electron-transfer step. The reduction of azidopentaamminecobalt(III) by Birk,<sup>6</sup> the reduction of fluoropentaamminecobalt(III) by Thompson and Sykes,<sup>7</sup> and the reduction of a series of carboxylatopentaamminecobalt(III) complexes by Martin and Gould<sup>4</sup> provide such examples. Moreover, Sykes and Thompson suggested the relative "hardness" or "softness" of a potential bridging ligand as an important consideration in the choice of mechanism by the

"hard acid" titanous ion and, hence, explains why the sulfato, acetato, fluoro, and  $\mu$ -superoxo complexes are reduced by the inner-sphere mechanism while the chloro, bromo, and iodo complexes react by the outer-sphere mechanism.<sup>7</sup> In this work, our rate studies are on the reduction of  $\text{Co}(\text{NH}_3)_5\text{SCN}^{2+}$  by  $\text{Ti}^{3+}$ . The potential bridging ligand is very close to  $\text{Cl}^-$  in terms of the hard acid-hard base concept. Our results also provide additional data to Birk's work<sup>6</sup> on the reactivity pattern of the thiocyanato-, azido-, and isothiocyanatopentaamminecobalt(III) complexes with a common reducing ion.

## Experimental Section

$[\text{Co}(\text{NH}_3)_5\text{SCN}]\text{Cl}_2 \cdot 1.5\text{H}_2\text{O}$  was prepared and characterized by means of the UV-visible spectra as reported in the literature.<sup>8</sup> Titanium(III) solutions were prepared by dissolving anhydrous  $\text{TiCl}_3$  in 0.1 M HCl.  $\text{LiClO}_4$  was prepared by neutralizing  $\text{Li}_2\text{CO}_3$  (AR grade) with  $\text{HClO}_4$  (AR grade).  $\text{LiCl}$  and  $\text{HCl}$  (AR grade) were used without further purification. Concentrations of titanium(III) solution were determined by indirect iodometry; viz., a known excess of deaerated  $\text{Ce}(\text{IV})$  solution was added to an aliquot of the titanium(III) solution, and the excess  $\text{Ce}(\text{IV})$  was determined by adding  $\text{KI}$  and titrating the liberated iodine against standardized  $\text{Na}_2\text{S}_2\text{O}_3$  solution.

The course of the reaction was followed by monitoring the decrease in the absorbance of the cobalt(III) complex at  $\lambda$  288 nm, a wavelength, where, for the concentrations of reactants and products, the cobalt complex is the dominant absorbing species. The reaction was followed using a Durrum-Gibson stopped-flow spectrophotometer. In all runs, titanium(III) concentrations were in large excess over cobalt(III), rate profiles were analyzed with a pseudo-first-order rate