

Figure 1.—Near-infrared spectra of crystals of  $\text{Pt}(\text{NH}_3)_4\text{PtCl}_4$  and  $\text{Pt}(\text{ND}_3)_4\text{PtCl}_4$ . Corresponding bands are indicated by Greek letters, the primed letters referring to the deuterated case. The band labeled H is assigned to the fundamental N-H stretching vibration due to residual hydrogen.

this assignment has been reported.<sup>5</sup> In our experiments on single crystals of MGS using a double beam instrument, no absorption band was observed at 7.5 kK, although in single beam work on the same crystals an absorption which was attenuated upon purging with dry  $\text{N}_2$  was noted at this position, indicating that its origin is the first overtone of the O-H stretching vibration of atmospheric water vapor.

Representative examples of the spectra obtained using the double beam instrument for both MGS and perdeuterio-MGS crystals are shown in Figure 1. In the case of the MGS crystals, six absorption bands were observed in the region between 12 and 2.8 kK, at 6.40, 4.85, 4.60, 4.12, 4.05, and 3.14 kK. The extinction coefficients of the first five bands ranged from 1 to 6 l./ (mol cm). The much stronger band at 3.14 kK has been previously observed in infrared spectra of  $\text{Pt}(\text{NH}_3)_4^{2+}$  salts<sup>11</sup> and is assigned to the  $\text{NH}_3$  stretching fundamental. A band at this frequency also appears in the spectrum of the perdeuterio-MGS crystal and probably arises from residual hydrogen in the sample. The other five absorption bands all shift to lower energies in the spectrum of the deuterated crystal. The fractional shift ( $\nu_{\text{D}}/\nu_{\text{H}}$ ) in each case was close to  $1/\sqrt{2}$  (1/1.38, 1/1.32, 1/1.34, 1/1.33, and 1/1.37, respectively) indicating that they all arise as overtones and combinations of the  $\text{NH}_3$  vibrations in  $\text{Pt}(\text{NH}_3)_4^{2+}$ . A qualitative survey of the infrared spectra of these same crystals down to 0.8 kK also failed to reveal any bands which could not be accounted for on the basis of vibrational transitions of the  $\text{Pt}(\text{NH}_3)_4^{2+}$  ions.

In light of these observations, it is clear that the spectral properties of MGS in the near-infrared region and the results of the conductivity and photoconductivity measurements reported earlier<sup>4</sup> cannot be reconciled using the intrinsic band description previously presented for MGS.<sup>8</sup> This description presumes that the conductivity ( $\sigma$ ) varies with temperature according

to the relation,  $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ , where  $\sigma_0$  is a preexponential term which varies only slowly with temperature and  $\Delta E$  is the band gap.<sup>12</sup> Consequently, from measurements of  $\sigma$  vs.  $T$  and from photoconductivity studies, it should be possible to derive an estimate of the band-gap energy. These considerations and the appropriate experimental data lead to a value of  $\sim 0.6$  eV for the  $d_{z^2} \rightarrow p_z$  gap.<sup>4</sup> Therefore, we would anticipate that the absorption edge for MGS should occur in the vicinity of 5 kK, resulting in strong absorption over a significant portion of the near-infrared. The absence of any absorption bands of electronic origin with  $\epsilon > \sim 0.2$  l./ (mol cm) in the entire region between 2.8 and 12 kK thus does not argue well for the applicability of the intrinsic model to MGS. On the other hand, the possibility of very weak ( $\epsilon < \sim 0.2$  l./ (mol cm)) absorption bands in this region, such as might arise from transitions involving impurities present in very small concentrations in the solid, cannot be excluded on the basis of the data obtained. As a result, a band description, suitably modified to include a small number of impurity levels within a few tenths of an electron volt of the  $d_{z^2}$  or  $p_z$  band edge and a band gap of  $>1$  eV, remains as a possible alternative. Such an extrinsic band model would also account for the rather large impurity effects noted in a recent reexamination of the electrical conductivity of MGS.<sup>7</sup>

**Acknowledgment.**—This work was supported in part by the Air Force Office of Scientific Research, Air Force Systems Command, U. S. Air Force, under AFOSR Contract F44620-72-C-0006.

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## The Linkage Isomerism of Bridging Thiocyanate in Binuclear Complexes

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Considerable interest has been shown recently in complexes containing the thiocyanate ligand because of its ability to coordinate through either the sulfur or nitrogen atoms. Infrared spectroscopy has been a valuable tool<sup>2-4</sup> in distinguishing between thiocyanato (M-SCN), isothiocyanato (M-NCS), and bridging (M-NCS-M) thiocyanato complexes.

While linkage isomerism of nonbridging thiocyanate complexes is well known,<sup>5</sup> including several instances in which the same molecule contains both metal-NCS

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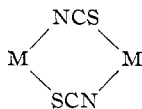
(2) A. Turco and C. Pecile, *Nature (London)*, **191**, 66 (1961).

(3) A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 1665 (1965).

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and metal-SCN bonds,<sup>6-10</sup> linkage isomers of bridging SCN have been limited to molecules containing the group<sup>11-13</sup>



A recent report<sup>14</sup> of the successful preparation of a binuclear cobalt(III) complex,  $\mu$ -cyano-pentaammine-pentacyanodicobalt(III), containing a bridged cyanide by a thermal condensation reaction suggested to us a way of preparing a pair of cobalt(III) complexes containing linkage isomers of thiocyanate in a bridged position. This, coupled with the fact that the necessary precursor complexes have previously been characterized, made these syntheses particularly attractive. We report herein the successful synthesis and characterization of these complexes and also present evidence for a bridging thiocyanate in two chromium-containing binuclear complexes and one complex in which the thiocyanate is bridging between a cobalt(III) and a chromium(III) center. During the course of this study, de Castelló, Mac-Coll, and Haim<sup>15</sup> reported the synthesis of  $(\text{NH}_3)_5\text{CoNCSCo}(\text{CN})_5$  which we have prepared in this work.

#### Experimental Section

The necessary starting materials were prepared by well-known procedures. Thiocyanatopentaamminecobalt(III) perchlorate was obtained by treating a solution of  $[\text{Co}(\text{NH}_3)_5\text{SCN}]\text{Cl}_2^{16}$  with perchloric acid at 0°. Solutions containing the aquopentacyanocobaltate(III) ion were prepared by treating a solution of  $\text{K}_3[\text{Co}(\text{CN})_5\text{N}_3]^{17}$  with equimolar amounts of sodium nitrate and trichloroacetic acid.

$\mu$ -Isothiocyanato-pentaamminecobalt(III)pentacyanocobalt(III) Monohydrate,  $[(\text{NH}_3)_5\text{CoNCSCo}(\text{CN})_5] \cdot \text{H}_2\text{O}$ .—Preliminary experiments were performed in which the change in absorbance of  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$  at 380 nm was measured when equivalent amounts of  $\text{K}_2[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{17}$  and  $[\text{Co}(\text{NH}_3)_5\text{NCS}](\text{ClO}_4)_2^{18}$  were mixed in solution at various temperatures to determine the conditions that would yield the desired product. It was found that the reaction is complete after 3 hr at 50°. On the basis of this a solution containing 2 mmol of  $\text{Co}(\text{CN})_5\text{H}_2\text{O}^{2-}$  in 50 ml of water was added to a solution containing 0.802 g (2 mmol) of  $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$  dissolved in 30 ml of water. The resulting solution was made slightly acidic with perchloric acid, heated to 50° for 3 hr, and passed through ion-exchange columns (Amberlite IR-120 (H) and DEAE-cellulose (OH)). The eluate was concentrated to 30 ml at 40° under reduced pressure, cooled to 0°, and filtered. The orange product was washed with alcohol, followed by ether, and dried under vacuum over  $\text{CaCl}_2$ ; yield 0.37 g (49%). *Anal.* Calcd for  $(\text{NH}_3)_5\text{CoNCSCo}(\text{CN})_5 \cdot \text{H}_2\text{O}$ : C, 17.61; H, 4.20; N, 37.65; S, 7.84. Found: C, 17.42; H, 4.20; N, 37.46; S, 8.01.

$\mu$ -Thiocyanato-pentaamminecobalt(III)pentacyanocobalt(III) Monohydrate,  $[(\text{NH}_3)_5\text{CoSCNC}(\text{CN})_5] \cdot \text{H}_2\text{O}$ .—A solution containing 1 mmol of  $\text{K}_2[\text{Co}(\text{CN})_5\text{H}_2\text{O}]$  in 10 ml of water was added to 0.401 g (1 mmol) of  $[\text{Co}(\text{NH}_3)_5\text{SCN}](\text{ClO}_4)_2$ . The resulting

solution was cooled to 0° in an ice bath and the precipitate of  $\text{KClO}_4$  which formed was removed by filtration. The filtrate was treated with 150 ml of alcohol, and after precipitation was complete (12 hr) the crude product was isolated by filtration; yield 0.33 g. The product was dissolved in a minimum volume of water and purified by passing through ion-exchange columns (Amberlite IR-120 (H) and DEAE-cellulose (OH)). The eluate was concentrated to 10 ml in a vacuum evaporator, and 100 ml of alcohol was added. The pale pink product was isolated by filtration, washed with alcohol and ether, and dried under vacuum over  $\text{CaCl}_2$ ; yield 0.072 g (11%). *Anal.* Calcd for  $[(\text{NH}_3)_5\text{CoSCNC}(\text{CN})_5] \cdot \text{H}_2\text{O}$ : C, 17.61; H, 4.20; N, 37.65; S, 7.84. Found: C, 17.59; H, 4.16; N, 37.47; S, 7.57.

$\mu$ -Thiocyanato-pentaamminecobalt(III)pentaisothiocyanatochromium(III) Trihydrate,  $[(\text{NH}_3)_5\text{CoSCNCr}(\text{NCS})_5] \cdot 3\text{H}_2\text{O}$ .—A solution containing 0.59 g (1.0 mmol) of  $\text{K}_3[\text{Cr}(\text{NCS})_6] \cdot 4\text{H}_2\text{O}^{19}$  in 20 ml of water and 5 drops of 70% perchloric acid was added to a solution containing 0.304 g (0.5 mmol) of  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]_2(\text{SO}_4)_3^{20}$  in 30 ml of water. This resulted in the immediate formation of red platelets. The resulting mixture was digested on a water bath at 40° for 15 min, cooled to room temperature, and filtered; the precipitate was washed with water, ethanol, and ether. The pink platelets were dried in the dark over  $\text{CaCl}_2$  for 12 hr; yield 0.5 g (83%). *Anal.* Calcd for  $[(\text{NH}_3)_5\text{CoSCNCr}(\text{NCS})_5] \cdot 3\text{H}_2\text{O}$ : C, 12.04; H, 3.54; N, 25.74; Co, 9.84;  $\text{H}_2\text{O}$ , 9.03. Found: C, 12.11; H, 3.51; N, 25.56; Co, 9.90;  $\text{H}_2\text{O}$ , 8.45.

$\mu$ -Thiocyanato-pentaamminechromium(III)pentaisothiocyanatochromium(III) Trihydrate,  $[(\text{NH}_3)_5\text{CrSCNCr}(\text{NCS})_5] \cdot 3\text{H}_2\text{O}$ .—Solutions containing equivalent amounts of  $\text{K}_3[\text{Cr}(\text{NCS})_6] \cdot 4\text{H}_2\text{O}$  and  $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_2^{21}$  were treated by the above procedure; yield 0.55 g (93%). *Anal.* Calcd for  $(\text{NH}_3)_5\text{CrSCNCr}(\text{NCS})_5 \cdot 3\text{H}_2\text{O}$ : C, 12.18; H, 3.58; N, 26.04; Cr, 17.58;  $\text{H}_2\text{O}$ , 9.14. Found: C, 12.35; H, 3.64; N, 26.18; Cr, 17.64;  $\text{H}_2\text{O}$ , 8.07.

Hexaamminecobalt(III) Hexaisothiocyanatochromate(III) Dihydrate,  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{NCS})_6] \cdot 2\text{H}_2\text{O}$ .—Solutions containing equivalent amounts of  $\text{K}_3[\text{Cr}(\text{NCS})_6] \cdot 4\text{H}_2\text{O}$  and  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2^{22}$  were treated by the above procedure. *Anal.* Calcd for  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{NCS})_6] \cdot 2\text{H}_2\text{O}$ : C, 12.03; H, 3.68; N, 28.15; Co, 9.84. Found: C, 11.92; H, 3.80; N, 27.54; Co, 10.20.

Hexaamminechromium(III) Hexaisothiocyanatochromate(III) Dihydrate,  $[\text{Cr}(\text{NH}_3)_6][\text{Cr}(\text{NCS})_6] \cdot 2\text{H}_2\text{O}$ .—Solutions containing equivalent amounts of  $\text{K}_3[\text{Cr}(\text{NCS})_6] \cdot 4\text{H}_2\text{O}$  and  $[\text{Cr}(\text{NH}_3)_6](\text{NO}_3)_2^{23}$  were treated as above; yield 0.51 g (83%). *Anal.* Calcd for  $[\text{Cr}(\text{NH}_3)_6][\text{Cr}(\text{NCS})_6] \cdot 2\text{H}_2\text{O}$ : C, 12.18; H, 3.72; N, 28.45. Found: C, 12.07; H, 3.79; N, 27.85.

**Measurements.**—Visible and ultraviolet spectra were measured vs. solvent as a reference with a Perkin-Elmer Coleman 124 double beam spectrophotometer or Cary 14 spectrophotometer. Infrared spectra were recorded with a Perkin-Elmer 521 grating spectrophotometer. Samples were determined as potassium bromide pellets and were checked with Nujol mulls.

Conductance measurements were carried out at 25° with an Industrial Instruments Inc. Model RCIB conductance bridge.

**Analytical Methods.**—Cobalt was analyzed by converting the complex to the tetrachlorocobaltate(II) ion by refluxing with 0.5 M tin(II) chloride in concentrated HCl and measuring the absorbance at 650 nm.<sup>24</sup> Chromium was analyzed by converting the complex to chromium(III) hydroxide with 1 N NaOH and oxidizing with potassium bromate in acid solution to form dichromate ion. Potassium iodide was then added and the liberated iodine was titrated with a standard solution of thiosulfate.<sup>25</sup> Water was determined by thermal gravimetric analysis. Carbon, hydrogen, nitrogen, and sulfur analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

## Results and Discussion

### The binuclear complexes $(\text{NH}_3)_5\text{CoNCSCo}(\text{CN})_5$ and

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$(\text{NH}_3)_5\text{CoSCNCo}(\text{CN})_5$  have been prepared and characterized by their elemental analyses, infrared spectra, electronic spectra, and conductivity measurements of the aqueous solutions. As far as we know, these represent the first reported instance of complexes containing linkage isomers of a single SCN in a bridging position. These complexes are lightly colored materials moderately soluble in water but insoluble in most organic solvents.

Evidence for the nonionic nature of these complexes is found in the low molar conductivities of their aqueous solutions. At 25°  $\Lambda$ 's for freshly prepared solutions of  $(\text{NH}_3)_5\text{CoNCSCo}(\text{CN})_5$  and  $(\text{NH}_3)_5\text{CoSCNCo}(\text{CN})_5$  are in the ranges 6–7 and 25–27  $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ , respectively. Changes in the conductance with time indicate that ionization of these complexes occurs fairly rapidly in neutral aqueous solution. For this reason the absorption spectra of these complexes were determined in acid solution (0.1–0.5  $M$   $\text{HClO}_4$ ). Under these conditions the solutions were optically stable for several hours. The spectra exhibited no dependence on the  $\text{H}^+$  concentration. The complexes were found to dissolve slowly in water at room temperature. Thus, to complete solution rapidly, the mixture was warmed gently (40°) until the sample was completely dissolved (2 min) and then cooled rapidly to 25°. The molar conductance of solutions prepared in this way in water showed that only slight ionization occurred during the dissolution process.

Examination of the infrared spectra of these complexes support their formulation as bridged complexes. The region of greatest interest is 2000–2200  $\text{cm}^{-1}$  where the C–N stretching frequencies of both SCN ( $\nu_3(\text{SCN})$ ) and CN are observed. The C–N stretch for terminal CN or SCN occur between 2065 and 2120  $\text{cm}^{-1}$ , while for a bridging ligand the stretching frequency is increased to 2135–2180  $\text{cm}^{-1}$ .<sup>11,26</sup> The infrared spectra of both compounds (Table I) show that in

TABLE I  
INFRARED SPECTRA OF Co(III)–THIOCYANATE COMPLEXES  
(2000–2200  $\text{cm}^{-1}$ )

Complex	$\nu(\text{CN}), \text{cm}^{-1}$	Assignment
$[\text{Co}(\text{NH}_3)_5\text{NCS}](\text{NO}_3)_2^a$	2120	Co–NCS
$[\text{Co}(\text{NH}_3)_5\text{SCN}]\text{Cl}_2^b$	2100	Co–SCN
$\text{K}_3[\text{Co}(\text{CN})_5\text{SCN}]^c$	2110	Co–SCN
	2147, 2137, 2129, 2122	Co–CN
$\text{K}_3[\text{Co}(\text{CN})_5\text{NCS}]^d$	2065	Co–NCS
	2131, 2124	Co–CN
$\text{K}_3[(\text{NC})_4\text{Co}(\text{NCS})_2\text{Co}(\text{CN})_4]^e$	2180	Co–NCS–Co
	2120	Co–CN
$(\text{NH}_3)_5\text{CoNCSCo}(\text{CN})_5$	2175	Co–NCS–Co
	2141, 2131, 2114	Co–CN
$(\text{NH}_3)_5\text{CoSCNCo}(\text{CN})_5$	2170	Co–SCN–Co
	2120	Co–CN

<sup>a</sup> M. W. Chamberlin and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **81**, 6412 (1959). <sup>b</sup> Reference 16. <sup>c</sup> J. L. Burmeister, *Inorg. Chem.*, **3**, 919 (1964). <sup>d</sup> I. Stotz, W. K. Wilmarth, and A. Haim, *ibid.*, **7**, 1250 (1968). <sup>e</sup> Reference 11.

addition to the bands in the terminal cyanide region, bands are observed in the bridging region at 2170  $\text{cm}^{-1}$  for  $(\text{NH}_3)_5\text{CoSCNCo}(\text{CN})_5$  and 2175  $\text{cm}^{-1}$  for  $(\text{NH}_3)_5\text{CoNCSCo}(\text{CN})_5$ . While the infrared spectra do not distinguish between bridging cyanide or thiocyanate (both 2135–2180  $\text{cm}^{-1}$ ), the methods of preparation and the known kinetic inertness of cobalt(III) complexes argue for a bridging SCN.

(26) P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1912 (1960).

Additional support for this assignment comes from the absorption spectra of these complexes. Haim, *et al.*,<sup>14,15</sup> have observed that the absorption spectra of two analogous binuclear cyano complexes  $(\text{NH}_3)_5\text{CoCNC}(\text{CN})_5$  and  $(\text{NH}_3)_5\text{CoNCCo}(\text{CN})_5$  correspond closely to the sum of the spectra of the two parent cobalt(III) moieties rather than to the average ligand environment of  $\text{NH}_3$  and CN ligands on a single cobalt(III) center. This same additivity is also observed in the present case. Thus examination of Table II

TABLE II  
ELECTRONIC SPECTRA OF Co(III)–THIOCYANATE COMPLEXES

Complex	$\lambda, \text{nm} (\epsilon)$	$\lambda, \text{nm} (\epsilon)$
$\text{Co}(\text{NH}_3)_5\text{NCS}^{2+ a}$	497 (177)	306 (1550)
$\text{Co}(\text{NH}_3)_5\text{SCN}^{2+ b}$	512 (74)	288 (15,600)
$\text{Co}(\text{CN})_5\text{NCS}^{3- c}$	363 (500)	265 (2,360)
$\text{Co}(\text{CN})_5\text{SCN}^{3- c}$	378 (191)	265 (17,100)
$(\text{NH}_3)_5\text{CoNCSCo}(\text{CN})_5$	482 (120)	267 (16,700)
$(\text{NH}_3)_5\text{CoSCNCo}(\text{CN})_5$	508 (74)	282 (9240)
		274 (9400)

<sup>a</sup> Reference 18. <sup>b</sup> Reference 16. <sup>c</sup> D. F. Gutterman and H. B. Gray, *J. Amer. Chem. Soc.*, **91**, 3105 (1969).

shows that the spectrum of  $(\text{NH}_3)_5\text{CoNCSCo}(\text{CN})_5$  closely approximates the sum of the spectra of the parent complexes  $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$  and  $\text{Co}(\text{CN})_5\text{SCN}^{3-}$  with the weaker absorbances being hidden by the stronger bands. Similarly, the spectra of  $\text{Co}(\text{NH}_3)_5\text{SCN}^{2+}$  and  $\text{Co}(\text{CN})_5\text{NCS}^{3-}$  when taken together resemble that of  $(\text{NH}_3)_5\text{CoSCNCo}(\text{CN})_5$ . This similarity of the spectra of bridged complexes to the parent ions indicates the ligand environments of the cobalt(III) centers are not altered during the formation of the binuclear complexes. To further show that no rearrangement has occurred, an experiment was performed in which the reaction between  $(\text{NH}_3)_5\text{CoNCSCo}(\text{CN})_5$  and  $\text{H}_2\text{O}_2$  was followed spectrophotometrically. It is known that oxidation of  $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$  by  $\text{H}_2\text{O}_2$  occurs without breakage of the cobalt–nitrogen bond to yield the hexaamminecobalt(III) ion.<sup>27</sup> Therefore, if no scrambling of ligands has occurred,  $(\text{NH}_3)_5\text{CoNCSCo}(\text{CN})_5$  should react to yield  $\text{Co}(\text{NH}_3)_6^{3+}$ . Schug<sup>18</sup> found that, in 0.5  $M$   $\text{H}^+$  and 0.25  $M$   $\text{H}_2\text{O}_2$ ,  $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$  is quantitatively converted to  $\text{Co}(\text{NH}_3)_6^{3+}$ . A solution  $6.2 \times 10^{-4} M$  in  $(\text{NH}_3)_5\text{CoNCSCo}(\text{CN})_5$ , 0.5  $M$  in  $\text{HClO}_4$ , and 0.25  $M$  in  $\text{H}_2\text{O}_2$  was therefore prepared and the reaction was followed by observing the change in absorbance of the 482-nm band. The absorbance maximum gradually decreased in intensity and shifted to 476 nm ( $\text{Co}(\text{NH}_3)_6^{3+}$ ,  $\lambda$  476 nm,  $\epsilon$  56)<sup>18</sup> over a period of 19 days, thus confirming  $\text{Co}(\text{NH}_3)_6^{3+}$  as the product of the reaction. (Qualitative tests for Co(II) proved negative.) The extreme slowness of this reaction compared to  $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$  is consistent with the postulated mechanism for the oxidation of thiocyanate with  $\text{H}_2\text{O}_2$  which is thought to involve attack on the sulfur atom. If the sulfur is coordinated, this pathway is blocked and the rate will depend on the rate of dissociation of the coordinated sulfur. A similar decrease in rate has been observed in the reaction of  $\text{Co}(\text{NH}_3)_5\text{NCSHg}^{4+}$  with  $\text{H}_2\text{O}_2$ .<sup>28</sup>

An attempt was made to prepare  $(\text{NH}_3)_5\text{CoNCSCo}$

(27) A. Werner, *Z. Anorg. Chem.*, **22**, 91 (1900); *Chem. Ber.*, **44**, 876 (1911).

(28) Reference 18, footnote 20.

TABLE III  
INFRARED SPECTRA OF Cr(III)-THIOCYANATE COMPLEXES  
(2000–2200  $\text{cm}^{-1}$ )

Complex	$\nu(\text{CN})$ , $\text{cm}^{-1}$	Assignment
$\text{K}_2[\text{Cr}(\text{NCS})_6]^a$	2118, 2098, 2058	Cr-NCS
$[\text{Cr}(\text{NH}_3)_5\text{NCS}](\text{ClO}_4)_2$	2090	Cr-NCS
$[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{NCS})_6]$	2088	Cr-NCS
$[\text{Cr}(\text{NH}_3)_6][\text{Cr}(\text{NCS})_6]$	2082	Cr-NCS
$(\text{NH}_3)_5\text{CoSCN}(\text{NCS})_5$	2137	Co-SCN-Cr
	2100, 2083	Cr-NCS
$(\text{NH}_3)_5\text{CrSCN}(\text{NCS})_5$	2135	Cr-SCN-Cr
	2098, 2080	Cr-NCS

<sup>a</sup> M. A. Bennett, R. J. H. Clark, and A. D. J. Goodwin, *Inorg. Chem.*, **6**, 1625 (1967).

$(\text{CN})_5$  by a thermal rearrangement from  $(\text{NH}_3)_5\text{CoSCN}(\text{CN})_5$ . According to the hard-soft acid-base theory,  $(\text{NH}_3)_5\text{CoNCS}(\text{CN})_5$  should contain the thiocyanate in the more favorable bonding mode. Ample precedent for this type of rearrangement is shown by the known conversions:  $\text{Co}(\text{CN})_5\text{NCS}^{3-}$  to  $\text{Co}(\text{CN})_5\text{SCN}^{3-}$ ,<sup>29</sup>  $\text{Co}(\text{NH}_3)_5\text{SCN}^{2+}$  to  $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$ ,<sup>16</sup> and  $\text{Fe}(\text{II})\text{-NC-Cr}(\text{III})$  to  $\text{Fe}(\text{II})\text{-CN-Cr}(\text{III})$ .<sup>30</sup> However,  $(\text{NH}_3)_5\text{CoSCN}(\text{CN})_5$  failed to rearrange upon heating the solid complex to 140° for several hours. Changes in the infrared spectrum in the 2100–2200- $\text{cm}^{-1}$  region showed an overall decrease in intensity, indicating decomposition occurred.

The complexes  $(\text{NH}_3)_5\text{CoSCN}(\text{NCS})_5$  and  $(\text{NH}_3)_5\text{CrSCN}(\text{NCS})_5$  were prepared from the reaction of  $\text{Cr}(\text{NCS})_6^{3-}$  with the appropriate aquopentaammine-

metal cation. Evidence for the assignment of bridging structures to these complexes rests on their infrared spectra. For  $(\text{NH}_3)_5\text{CoSCN}(\text{NCS})_5$  a peak is observed at 2137  $\text{cm}^{-1}$  (Table III) in addition to the terminal stretching frequencies at 2083 and 2100  $\text{cm}^{-1}$ . While this is at a lower frequency than observed for the bridged SCN in the previous cobalt(III) complexes ( $\sim 2170$   $\text{cm}^{-1}$ ), the spectrum of the related ionic complex  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{NCS})_6]$  shows no peaks above 2090  $\text{cm}^{-1}$ , thus strengthening the possibility that the 2137- $\text{cm}^{-1}$  peak is due to a bridged thiocyanate ligand. Similarly  $(\text{NH}_3)_5\text{CrSCN}(\text{NCS})_5$  exhibits at band at 2135  $\text{cm}^{-1}$  which is not observed in the spectrum of the analogous ionic complex  $[\text{Cr}(\text{NH}_3)_6][\text{Cr}(\text{NCS})_6]$ .

The low solubility of these compounds in water prevented determination of the conductance and the absorption spectra of these complexes. Other polar solvents such as acetonitrile and dimethylformamide were found to cause destruction of the thiocyanate bridge as evidenced by loss of the SCN peak near 2135  $\text{cm}^{-1}$  upon recovery of the compounds from these solvents.

No bridged products were obtained in several attempts to prepare the corresponding linkage isomers  $(\text{NH}_3)_5\text{CoNCS}(\text{NCS})_5$  and  $(\text{NH}_3)_5\text{CrNCS}(\text{NCS})_5$  by treating  $\text{Cr}(\text{NCS})_6\text{H}_2\text{O}^{2-}$  with  $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$  and  $\text{Cr}(\text{NH}_3)_5\text{NCS}^{2+}$  in aqueous media.

The binuclear complexes studied here which contain thiocyanate bridged between two identical metal centers appear to be relatively stable to light and to thermal decomposition. In contrast  $(\text{NH}_3)_5\text{CoSCN}(\text{NCS})_5$  is decomposed fairly rapidly by light and is stable only for a few days in the dark at room temperature.

(29) D. F. Gutterman and H. B. Gray, *J. Amer. Chem. Soc.*, **91**, 3105 (1969).

(30) J. E. House, Jr., and J. C. Bailar, Jr., *Inorg. Chem.*, **8**, 672 (1969).