CONTRIBUTION FROM THE
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Synthesis of the Potassium Salt of Thiocyanatopentacyanocobaltate(III)

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Recently work has been reported in the literature concerning, in part, the kinetics of reaction 1 in aqueous

$$[Co(NH_3)_5NCS]^{2+} + 5CN^- \xrightarrow{Co^{2+}} [Co(CN)_5SCN]^{3-} + 5NH_3 \quad (1)^1$$

solution. The product of the reaction was not isolated, and the nature of the thiocyanate bonding in the resultant complex was stated as being unknown. We wish to report the isolation of the product of reaction 1 as the potassium salt, and the determination of the thiocyanate bonding involved, based on the infrared spectrum of the complex.

Experimental

Preparation of $K_3[Co(CN)_5SCN]$.—To a solution, at room temperature, of 1.95 g. (30 mmoles) of KCN in 10 ml. of H_2O was added 2.01 g. (6 mmoles) of solid $[Co(NH_3)_5NCS]SO_4 \cdot 2H_2O$ (prepared according to the method of Werner and Müller).[2] The addition of a small crystal of $Co(NO_3)_2 \cdot 6H_2O$ resulted in the rapid dissolution of the solid, with evolution of NH_3. The SO_4^{2-} was precipitated as $BaSO_4$ by the addition of 2.53 g. (6 mmoles) of solid $Ba(C_2H_3O_2)_2$ and removed by filtration through a fritted glass filter. The filtrate was allowed to pass directly into 50 ml. of absolute ethanol, which had been precooled to 0° in an ice bath. A reddish orange oil formed. The supernatant solution, containing $KC_2H_3O_2$, was decanted, and 50 ml. of 0° absolute ethanol was added. The oil crystallized to form a yellow-orange solid after standing for 1 hr. at 0°. It was isolated by filtration, washed with 100 ml. each of absolute ethanol and ethyl ether, and dried for 72 hr. *in vacuo* over $CaCl_2$. The completely dry solid is pale yellow in color, with a faint orange caste; yield 1.69 g. (77.4% of theory).

Anal. Calcd. for $K_3[Co(CN)_5SCN]$: C, 19.8; N, 23.1. Found: C, 19.5; N, 23.0.

Infrared Spectra.—Infrared spectra of Nujol mulls of the product were measured on a Perkin-Elmer 521 recording spectrophotometer.

Results

The mode of thiocyanate bonding in the complex was found to be through the sulfur atom, this conclusion being based on the position of the thiocyanate C–S stretching frequency, which is shown in Table I, along with the C–N stretching frequencies found in the infrared spectrum of the complex.

The use of the position of the thiocyanate C–S stretching frequency as a diagnostic criterion for thiocyanate bonding assignments has been demonstrated by several authors[3] and was used in the first synthesis of inorganic linkage isomers of the thiocyanate ion.[4] Turco and Pecile[3b] give the following ranges: M–SCN, 690–720 cm.$^{-1}$; M–NCS, 780–860 cm.$^{-1}$.

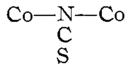
TABLE I

C–N AND C–S STRETCHING FREQUENCIES OF $K_3[Co(CN)_5SCN]$

Band, cm.$^{-1}$	Assignment
2147 (s)	Cyanide C–N stretch
2137 (m)	Cyanide C–N stretch
2129 (s)	Cyanide C–N stretch
2122 (s)	Cyanide C–N stretch
2110 (s)	Thiocyanate C–N stretch (ν_3 SCN)
719 (w)	Thiocyanate C–S stretch (ν_1 SCN)

Discussion

The reaction between $[Co(NH_3)_5NCS)]^{2+}$ and $[Co(CN)_5]^{3-}$ has been shown[1] to proceed predominantly by an inner-sphere electron-transfer mechanism, for which the bridged intermediate, $[(NH_3)_5Co^{III}–NCS–Co^{II}(CN)_5]^-$, was postulated. This would logically lead to the formation of $[Co(CN)_5SCN]^{3-}$ as the initial product. No evidence has been found in the literature in support of a



$$\begin{array}{c} Co—N—Co \\ C \\ S \end{array}$$

bridge which would lead to an isothiocyanate product in this reaction.

The behavior of this system offers an interesting contrast to that found in the reaction between $[Co(NH_3)_5NCS]^{2+}$ and chromium(II). Taube[5] has shown that in this reaction the thiocyanate ion acts as a bridge for the electron transfer and is then itself transferred to the chromium. Assuming, as above, that the bridge is linear, *i.e.*, $[(NH_3)_5Co^{III}–NCS–Cr^{II}(H_2O)_5]^{4+}$, one would anticipate that the initial product of the reaction would be $[Cr(H_2O)_5SCN]^{2+}$. However, Carlin and Edwards[6] found the product to be the stable $[Cr(H_2O)_5NCS]^{2+}$ ion, apparently because of a very rapid rearrangement of the chromium(III) S-bonded kinetic product. Alternatively, the chromium(III) N-bonded product could have resulted from a second activated bridge reaction between the initially formed $[Cr(H_2O)_5SCN]^{2+}$ and excess chromium(II), as shown in reaction 2.

$$[Cr–SCN]^{2+} + Cr^{2+} \longrightarrow [Cr–SCN–Cr]^{4+} \longrightarrow Cr^{2+} + [Cr–NCS]^{2+} \quad (2)$$

Haim and Wilmarth[7] studied the kinetics of the substitution reaction between $[Co(CN)_5OH_2]^{2-}$ and NCS^-, but did not isolate the reaction product and

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[1] J. P. Candlin, J. Halpern, and S. Nakamura, *J. Am. Chem. Soc.*, **85**, 2517 (1963).

[2] A. Werner and H. Müller, *Z. anorg. allgem. Chem.*, **22** ,101 (1900).

[3] (a) M. M. Chamberlain and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 6412 (1959); (b) A. Turco and C. Pecile, *Nature*, **191**, 66 (1961); (c) J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 4590 (1961).

[4] F. Basolo, J. L. Burmeister, and A. J. Poë, *J. Am. Chem. Soc.*, **85**, 1700 (1963).

[5] H. Taube, *ibid.*, **77**, 4481 (1955).

[6] R. L. Carlin and J. O. Edwards, *J. Inorg. Nucl. Chem.*, **6**, 217 (1958).

[7] A. Haim and W. K. Wilmarth, *Inorg. Chem.*, **1**, 573 (1962).

could make no conclusion as to the nature of the thiocyanate bonding involved.

It should be pointed out that N-bonding is the normal bonding mode for cobalt(III) and chromium(III) thiocyanate complexes. Indeed, it is believed that the preparation of $K_3[Co(CN)_5SCN]$ represents the first isolation of a thiocyanate-containing complex of cobalt(III) wherein the thiocyanate is bonded through the sulfur atom. It is evidently the stable form of the complex, for heating the complex at 118° *in vacuo* for several hours did not result in any spectral changes. The stability of the Co–SCN bond in this case is undoubtedly due to the presence of the cyanide ions in the coordination sphere, although a rationale for this effect is, as yet, not available. The opposite effect, *i.e.*, a change from the normal S-bonded mode to one of N-bonding, has been found[3b,4] for platinum(II) and palladium(II) thiocyanate-containing complexes wherein strong π-bonding ligands, *e.g.*, trialkylphosphines, triphenylarsine, and 2,2′-bipyridine, are included in the coordination sphere. Since cyanide ion is believed to be a strong π-bonding ligand, one can obviously not apply the explanation given for the bonding in the platinum(II) and palladium(II) complexes to the cobalt(III) complex discussed above.

The cobalt(III)–cyanide–selenocyanate system is currently being studied.

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CONTRIBUTION FROM THE SHELL DEVELOPMENT CO.,
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Rhenium Heptasulfide-Catalyzed Hydrogenation of Nitric Oxide to Nitrous Oxide or Nitrogen and Sulfur Dioxide to Hydrogen Sulfide

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Rhenium heptasulfide, Re_2S_7, is a stable hydrogenation catalyst for a variety of organic substrates and is not readily poisoned by sulfur- or nitrogen-containing compounds.[1] Furthermore, it is apparently more active for unsaturated organic substrates than other poison-resistant metal sulfides.[1,2] These observations prompted us to test this catalyst for the hydrogenation of nitric oxide, nitrous oxide, and sulfur dioxide. Several interesting qualitative results were obtained.

Experimental

Unsupported rhenium heptasulfide was prepared as described previously[1] by bubbling hydrogen sulfide through a 6 *N* hydrochloric acid solution of ammonium perrhenate (A. D. Mackay, Inc.).

The catalyst (<0.5 g.) and 20 ml. of *n*-dodecane were sealed in an 80-ml., magnetically-stirred autoclave and the gas (50–100 mmoles) to be reduced was injected. The autoclave was heated to the desired temperature and hydrogen introduced (10–30 atm.). After stirring was initiated, the decrease in hydrogen pressure was recorded continuously throughout the length of the experiments (2–100 min.).

The products were analyzed by a combination of mass spectrometry and gas–liquid chromatography. The hydrogen sulfide obtained in the reduction of sulfur dioxide also was determined gravimetrically by the precipitation of lead sulfide from a lead sulfate solution. The ammonia from nitric oxide reductions was determined by acid titration.

The nitric oxide consisted of N_2, 4.9%; N_2O, 6.3%; and NO, 88.8%. The nitrous oxide analyzed: N_2, 2.0%; NO, 0%; N_2O, 98%. A reactant mixture of the two nitrogen oxides employed in one experiment analyzed: N_2, 2.7%; NO, 26.5%; N_2O, 70.8%.

Results and Discussion

While rhenium heptasulfide is capable of catalyzing the hydrogenation of nitric oxide even at room temperature, the product was dependent upon the reaction temperature. At 200° mainly nitrogen and a small amount of ammonia were formed. However, at 100° nitrous oxide was almost the exclusive product. In fact, the hydrogenation of a mixture of nitric oxide and nitrous oxide ceased abruptly when all of the nitric oxide had been converted to nitrous oxide. To our knowledge, this degree of selectivity in the reduction of nitric oxide has not been achieved previously in significant yields. Other catalysts promote the formation of either ammonia, hydroxylamine, or nitrogen[4] at elevated temperatures (usually >200°). Cooke[4a,4h] did find that a small amount of hydrogen occluded on platinum reduced nitric oxide to nitrous oxide, but with more hydrogen, ammonia and hydroxylamine were also produced.

Although nitrous oxide was not hydrogenated at 100°, it was readily reduced at 200° to mainly nitrogen.

In the absence of a catalyst, the hydrogenation of sulfur dioxide to hydrogen sulfide or sulfur does not readily occur below 500°.[5,6] The few catalysts reported for this reaction also require rather high temperatures. For example, nickel metal (probably converted to the sulfide), cobalt sulfide, and iron sulfide are not active below 300°[4g,6] at atmospheric pressure. Iron group metal oxides pretreated with hy-

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(1) H. S. Broadbent, L. H. Slaugh, and N. L. Jarvis, *J. Am. Chem. Soc.*, **76**, 1519 (1954).

(2) In the present study, a comparison of Re_2S_7 with tungsten–nickel sulfide[3] indicated the latter to be considerably less active for the hydrogenation (~34 atm.) of α-methylstyrene at 250° than is Re_2S_7 at 120°.

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