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Potassium Isocyanatopentacyanocobaltate(III): Synthesis and Spectral Studies

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The first synthesis of $[Co(CN)_5NCO]^{3-}$ *has been accomplished by an ambient temperature substitution reaction, in methanol, between* NCO^- *and* $[Co(CN)_5OP(OC_2H_5)_3]^{2-}$*, the latter being generated by the reaction of* $[Co(CN)_5N_3]^{3-}$ *with* $NOClO_4$ *in triethyl phosphate. The coordinated azide ion is attacked by the nitrosyl ion, yielding* N_2 *and* N_2O*. The substitution reaction yields the N-bonded isomer, isolated as the potassium salt, as the predominant (if not exclusive) product, as determined by infrared and visible-ultraviolet spectral studies.*

Introduction

Our interest in synthesizing the title compound was prompted by the remarkable sensitivity to environmental effects exhibited by the higher homologues of the cyanate ion (the thiocyanate and selenocyanate ions) when they are incorporated in cobalt(III) coordination complexes. Examples of ligand induced linkage isomerism, *e.g.*, $[Co(NH_3)_5NCX]^{2+}$ (aq.)[1-4] *versus* $[Co(CN)_5XCN]^{3-}$ (aq.),[5-7] cation induced linkage isomerism,[6,7] *e.g.*, $[(n{-}C_4H_9)_4N]_3[Co(CN)_5NCX]$ (solid) *versus* $K_3[Co(CN)_5XCN]$ (solid), and solvent induced linkage isomerism,[6-8] *e.g.*, $[Co(CN)_5NCX]^{3-}$ (methylene chloride) *versus* $[Co(CN)_5XCN]^{3-}$ (aq.) have been reported for X = S and Se. To complement the recently reported synthesis[9,10] of the last complex of the pseudohalogenopentaaminecobalt(III) series, $[Co(NH_3)_5NCO]^{2+}$, we now wish to report the synthesis and spectral characterization of the last complex of the pseudohalogenopentacyanocobaltate(III) series, $[Co(CN)_5NCO]^{3-}$.

Experimental Section

Preparation of $K_3[Co(CN)_5NCO]$. All reactions were carried out at room temperature. *Considerable caution* should be exercised if a solvent other than triethyl phosphate is utilized in the first reaction because of the potentially explosive nature[11] of mixtures containing azides, nitrosyl perchlorate and organic solvents. Solid nitrosyl perchlorate[12] was added slowly, in small amounts, with constant stirring to a slurry of 1.0 g (2.88 mmole) of $K_3[Co(CN)_5N_3]$, prepared according to the method of Barca, *et al.*,[13] in 10 ml of triethyl phosphate, until none of the solid azido complex remained. The reaction results in the evolution of N_2 and N_2O. The resulting mixture was filtered to remove any unreacted nitrosyl perchlorate. The addition of anhydrous diethyl ether to the filtrate resulted in the formation of a pale yellow precipitate, presumably $K_2[Co(CN)_5OP(OC_2H_5)_3]$. Filtration yielded a semi-solid oil. The removal of any remaining nitrosyl perchlorate and triethyl phosphate was effected by twice dissolving the oil in methanol and reprecipitating it by the addition of diethyl ether. A crystalline sample was never obtained. The oil was finally dissolved in a minimum amount of methanol, and to this solution was added a solution of 0.6 g (7.4 mmol) of potassium cyanate in 75 ml of methanol. The resulting solution was stirred overnight, whereupon the methanol was removed under reduced pressure. The solid residue was slurried in 100 ml of methanol to remove any excess potassium cyanate. The product was isolated by filtration, washed with two 10 ml portions each of methanol and diethyl ether, and dried *in vacuo;* yield 20%.

Anal. Calcd for $K_3[Co(CN)_5NCO]$: C, 20.7; H, 0.0; N, 24.2. Found: C, 20.66; H, 0.0; N, 24.39.

Physical Measurements. Solid state (Nujol mull) and solution (0.1 mm matched NaCl cells) infrared spectral measurements were carried out using a Perkin-Elmer 180 spectrophotometer. Visible-ultraviolet spectra were measured on a Cary 14 spectrophotometer. Microanalyses were performed by the Meade Microanalytical Laboratory, Amherst, Mass.

The mull and solution (ethylene glycol, $10^{-2}\,M$) infrared spectra of the complex in the $\nu C{\equiv}N$ stretching region are shown in Figure 1. The infrared spec-

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trum, in the same region, of a methylene chloride solution of $[(n\text{–}C_4H_9)_4N]_3[Co(CN)_5NCS]$ is shown in Figure 2 for the sake of comparison. The free cyanate ion, as in KNCO, exhibits a $\nu C{\equiv}N$ band at 2165 cm^{-1} (mull) The visible-ultraviolet spectrum of an ethylene glycol solution of $K_3[Co(CN)_5NCO]$ exhibits absorption maxima at 3670 Å (ε = 184) and 3450 Å (ε = 290).

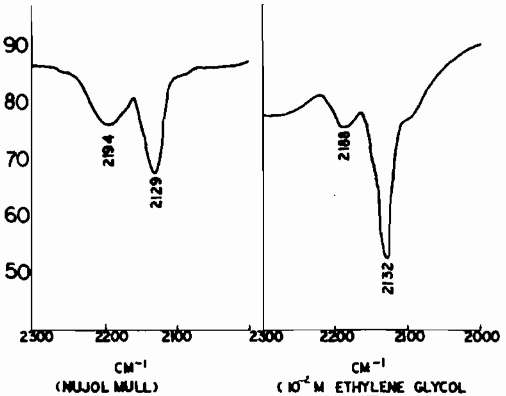

Figure 1. Infrared spectra of $K_3[Co(CN)_5NCO]$ in the $\nu C{\equiv}N$ stretching region.

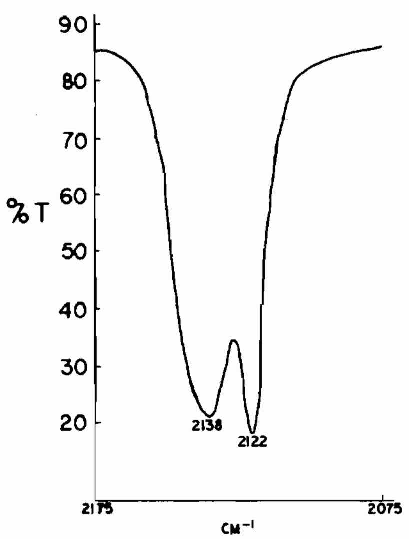

Figure 2. Infrared spectrum (methylene chloride solution) of $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCS]$ in the $\nu C{\equiv}N$ stretching region.

Discussion

Both inner sphere redox reactions and substitution reactions have been used to prepare the other members of the $[Co(CN)_5(pseudohalide)]^{3-}$ series. The reactions, in aqueous solution, of $[Co(NH_3)_5(pseudohalide)]^{2+}$ (pseudohalide = isothiocyanate;[5,14] isoselenocyanate,[7] azide,[14] and cyanide)[15,16] with $[Co(CN)_5]^{3-}$ proceed facilely with essentially quantitative transfer of the pseudohalide groups to yield the corresponding $[Co(CN)_5(pseudohalide)]^{3-}$ complexes. A 70/30 S-/N-bonded mixture of $[Co(CN)_5(thiocyanate)]^{3-}$ can be prepared[6,17] by the reaction of $[Co(CN)_5OH_2]^{2-}$ with NCS^- in aqueous solution.

Severe problems are encountered when either of these approaches are applied to the synthesis of $[Co(CN)_5NCO]^{3-}$. The redox reaction, in aqueous solution, between $[Co(NH_3)_5NCO]^{2+}$ and $[Co(CN)_5]^{3-}$ yields $[Co(CN)_6]^{3-}$ as the product,[9] the possible reasons for this result having already been discussed by Burmeister and DeStefano.[9] The substitution reaction between $[Co(NH_3)_5OH_2]^{3+}$ and NCO^- yields the carbamato complex, $[Co(NH_3)_5O_2CNH_2]^{2+}$, with retention of the original Co–O bond,[18] and it is quite likely that an analogous reaction would take place between $[Co(CN)_5OH_2]^{2-}$ and NCO^-.

Our circumvention of these problems utilized a reaction sequence analogous to one which was first delineated by Jordan, *et al.*,[19] and subsequently used to good advantage in our laboratory[9,20] for the synthesis of pentaamminecobalt(III) and -chromium(III) complexes, including $[Co(NH_3)_5NCO]^{2+}$:

$$[Co(CN)_5N_3]^{3-} + NO^+ + OP(OC_2H_5)_3 \xrightarrow{OP(OC_2H_5)_3} [Co(CN)_5OP(OC_2H_5)_3]^{2-} + N_2 + N_2O \quad (1)$$

$$[Co(CN)_5OP(OC_2H_5)_3]^{2-} + NCO^- \xrightarrow{CH_3OH} [Co(CN)_5NCO]^{3-} + OP(OC_2H_5)_3 \quad (2)$$

In reaction (1), when the coordinated azide is destroyed by the attack of the nitrosyl ion to give N_2 and N_2O, a vacancy is created in the coordination sphere of the cobalt(III) which can only be filled by a triethyl phosphate molecule, since the perchlorate ion is an even weaker coordinating ligand. The coordinated triethyl phosphate molecule can easily be displaced in reaction (2) to give the desired product.

Coordination of the cyanate ion via its nitrogen atom would result in a linear Co–N≡C–O linkage. The symmetry of the complex ion (C_{4v}) would, therefore, be greater than that (C_s) resulting from a non-linear $\text{Co–O}\diagdown_{\text{C}\equiv\text{N}}$ linkage. That N-bonding is, in fact, observed in both the solid state and in ethylene glycol solution, is clearly demonstrated by the infrared spectra shown for $K_3[Co(CN)_5NCO]$ and $[(n\text{–}C_4H_9)_4N]_3[Co(CN)_5NCS]$ (which contains a linear Co–NCS linkage) in, respectively, Figures 1 and 2. The complexes $K_3[Co(CN)_5SCN]$,[5] $K_3[Co(CN)_5SeCN]$,[7] and $K_3[Co(CN)_5N_3]$,[13] all of which involve non-linear M-pseudohalide linkages, exhibit characteristic five band patterns in the $\nu C{\equiv}N$ stretching region (Table I). The higher frequency $\nu C{\equiv}N$ band in each of the spectra shown in Figure 1 is that associated with the isocyanate group.

Strong support for the isocyanate structure is also found in the visible-ultraviolet spectrum of the complex. The frequency of its lowest energy absorption

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Table I. $\nu C\equiv N$ Stretching Bands[a] for $K_3[Co(CN)_5(pseudohalide)]$ Complexes Involving Non-Linear Co-Pseudohalide Linkages.

Complex	$\nu C\equiv N$ Bands (cm^{-1})
$K_3[Co(CN)_5SCN]$[b]	2147m, 2137s, 2129s, 2122s, 2110s
$K_3[Co(CN)_5SeCN]$	2147m, 2139m, 2130s, 2124s, 2107m
$K_3[Co(CN)_5N_3]$	2149m, 2139m, 2130s, 2127s, 2068s[c], br

[a] Nujol mulls. [b] Data taken from ref. 5. [c] $\nu N\equiv N$ band.

Table II. Lowest Eenergy Absorption Bands (kK) in the Visible-Ultraviolet Spectra of Cobalt(III) Complexes[a]

X^-	$[Co(CN)_5X]^{3-}$	$[Co(NH_3)_5X]^{2+}$
$-CN^-$	32.4[b]	22.8[c]
H^-	32.3[b]	—
$-NCSe^-$	27.8	20.3[d]
$-NCS^-$	27.6	20.2[e]
$-NCO^-$	27.3	20.0[e]
Cl^-	27.0[b]	18.7, 21.4 sh[b,f]
$-SCN^-$	26.5	19.5[f,g]
N_3^-	26.1	19.3[h]
Br^-	25.5[b]	18.2, 21.3 sh[b,f]
$-SeCN^-$	23.8	—

[a] Aqueous solutions. [b] Data taken from C. K. Jørgensen, « Absorption Spectra and Chemical Bonding in Complexes », Pergamon Press Ltd., London, 1962, pp. 293-294. [c] H. Siebert, Z. *Anorg. Allgem. Chem.*, *327*, 63 (1964). [d] Ref. 4. [e] Ref. 9. [f] See ref. 2 for discussion of the splitting observed in the first ligand field band for $[Co(NH_3)_5X]^{2+}$ complexes, where X is a ligand whose ligand field strength is quite different from that of NH_3. [g] Ref. 2; lower frequency shoulder observed in spectrum shown in reference, but frequency of shoulder not given. [h] M. Linhard, H. Siebert and M. Weigel, *Z. Anorg. Allgem. Chem.*, *278*, 287 (1955).

band (27.3kK) places it slightly below the corresponding isothiocyanate in the spectrochemical series (Table II). The same ordering has also been observed (Table II) for the corresponding pentaamminecobalt (III) series. The occurrence of an N-bonded cyanate group would be expected on the basis of the known[5] soft character of the $Co(CN)_5^{2-}$ moiety, coupled with the results of calculations by Wagner,[21] which indicate that most of the negative charge in the cyanate ion is localized on the nitrogen atom.

An alternative method[10] of preparation of $[Co(NH_3)_5NCO]^{2+}$ involves the thermal decomposition of $[Co(NH_3)_5NH_2C(O)NH_2]^{3+}$. Our attempts to convert the ureapentaamminecobalt(III) complex to $[Co(CN)_5NH_2C(O)NH_2]^{2-}$ via an inner sphere redox reaction with $[Co(CN)_5]^{3-}$ have been unsuccessful, thereby thwarting any attempt to prepare the $[Co(CN)_5NCO]^{3-}$ complex by the thermal decomposition route.

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