for trialkyltin species may not be unambiguously diagnostic of the cyclic nature of the ligand is illustrated by the Mössbauer data[15] for $(CH_3)_3SnNO_3$ included in Table I. A variety of structural inferences, including a model with a nitrate group bidentate to a single $(CH_3)_3Sn$ fragment, have been drawn earlier from infrared data.[16,17] These data were, however, partially beclouded by the fact that $(CH_3)_3SnNO_3$ picks up water on standing and that consequently some of the infrared bands which are observed are, in fact, characteristic of the hydrated species.

An X-ray diffraction study of the anhydrous material, which can be obtained by vacuum sublimation of the hydrate, has now been carried out[18] and shows that the neat solid compound does *not* contain bidentate NO_3 groups bound to a single $(CH_3)_3Sn$ moiety. The details of this structure will be reported by these authors in a separate communication.

It is clear, then, that Mössbauer data for R_3SnX species must be examined with considerable care, preferably in conjunction with all other available spectroscopic information, before structural inferences are drawn. When this is done, however, a consistent model for the architecture of such molecules can be obtained.

Acknowledgment.—The authors are very grateful to Professor H. C. Clark for making the X-ray diffraction results on $(CH_3)_3SnNO_3$ available to us prior to publication. This work has been supported in part by the U. S. Atomic Energy Commission and constitutes Document No. NYO-2472-63. Support from the Petroleum Research Fund, administered by the American Chemical Society, and the Research Council of Rutgers University is also gratefully acknowledged.

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Isocyanatopentaamminecobalt(III) Bromide: Synthesis and Oxidation–Reduction Reactivity Studies

By John L. Burmeister and Nicholas J. DeStefano

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Although the first pseudohalogenopentaamminecobalt(III) complex, $[Co(NH_3)_5NCS]SO_4 \cdot 2H_2O$, was synthesized by Werner[1] and the corresponding azido complex has also been known[2] for some time, the syntheses of the cyano[3,4] and isoselenocyanato[5] complexes were not accomplished until this decade, due to the special synthetic problems encountered. The synthesis of the remaining member of the series, $[Co(NH_3)_5NCO]^{2+}$, has heretofore been thwarted by the tendency of the cyanate ion to hydrolyze in acidic or basic media, the limited solubility of MNCO salts in all solvents except water, and, most important, the fact that the 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.[6] We now wish to report the synthesis of $[Co(NH_3)_5NCO]Br_2$ and the results of our study of the electron mediating ability of the cyanate group in oxidation–reduction reactions of the complex with $[Co(CN)_5]^{3-}$ and chromium(II).

Experimental Section

Preparation of Reactants.—The chloride[2] and perchlorate[7] salts of azidopentaamminecobalt(III), (triethyl phosphate)pentaamminecobalt(III) perchlorate,[7] nitrosyl perchlorate,[8] and tetraphenylarsonium cyanate dihydrate[9] were prepared by methods given in the literature.

Preparation of $[Co(NH_3)_5NCO]Br_2$.—A solution of 2.0 mmol of tetraphenylarsonium cyanate dihydrate (0.92 g) in 5 ml of dimethyl sulfoxide was added, with stirring, to a solution of 1.0 mmol of $[Co(NH_3)_5OP(OC_2H_5)_3](ClO_4)_3$ (0.62 g) dissolved in 5 ml of DMSO. After the mixture had been stirred for 12 hr at room temperature, the precipitated tetraphenylarsonium perchlorate was removed by filtration. The addition of 10 ml of 8 *M* aqueous sodium bromide to the red filtrate resulted in the immediate formation of a pink precipitate which was isolated by filtration, washed with ethanol and ethyl ether, and air dried after the mixture had been stirred for 15 min in an ice bath. The pink solid was then slurried in 75–100 ml of distilled water for 30 min. Filtration of the mixture yielded a white solid (a mixture of tetraphenylarsonium perchlorate and bromide) and a pink filtrate. The product was precipitated from the latter by the addition of solid sodium bromide, isolated by filtration, washed with ethanol and ethyl ether, and dried over calcium sulfate; yield 26%; mp 256–258° dec (uncorrected from DTA thermogram). *Anal.* Calcd for $CH_{15}N_6Br_2OCo$: C, 3.47; H, 4.37; N, 24.29. Found: C, 3.33; H, 4.49; N, 24.09.

Reaction with $[Co(CN)_5]^{3-}$.—To a solution of 4.1 mmol of potassium cyanide (0.27 g) in 5 ml of distilled water was added 0.82 mmol of $[Co(NH_3)_5NCO]Br_2$ (0.28 g). The addition of a small crystal of cobalt(II) nitrate hexahydrate resulted in partial dissolution of the cyanate complex and the evolution of ammonia. After the slurry had been stirred for 1 min at room temperature, it was filtered directly into 200 ml of 95% ethanol, which had been precooled to 0° in an ice bath. This resulted in the formation of a pale yellow solid. (The solid remaining in the filter proved to be some unreacted $[Co(NH_3)_5NCO]Br_2$.) The product, $K_3[Co(CN)_6] \cdot H_2O$ (*vide infra*), was isolated by filtration, washed with ethanol and ether, and dried over calcium sulfate. A small amount of potassium cyanate impurity ($\nu_{C \equiv N}$ at 2173 cm^{-1}) was removed by dissolving the product in 1 ml of distilled water and reprecipitating the $K_3[Co(CN)_6] \cdot H_2O$ by the addition of 75 ml of cold ethanol. It was isolated, washed, and dried as above; yield, based on available cyanide, 71%. *Anal.* Calcd for $C_6H_2N_6OCoK_3$: C, 20.57; H, 0.57; N, 23.99. Found: C,

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20.03; H, 0.45; N, 23.73. Increasing the time of the reaction to 1 hr did not affect the infrared spectrum of the product.

Reactions with Chromium(II).—(A) Chromium(II) acetate (1.0 mmol, 0.17 g) and $[\mathrm{Co(NH_3)_5NCO}]\mathrm{Br_2}$ (1.0 mmol, 0.35 g) were slurried in 15 ml of deoxygenated water, with nitrogen bubbling through the slurry, for 1 hr at room temperature. No odor of ammonia was noticed. Filtration yielded only unreacted $[\mathrm{Co(NH_3)_5NCO}]\mathrm{Br_2}$. The filtrate was added to 300 ml of ethanol at 0°, but no solid precipitated. Evaporation of the blue tinged solution yielded a solid which did not contain any cyanate groups, as evidenced by the lack of any absorption in the $\mathrm{C{\equiv}N}$ stretching region.

(B) To a slurry of 1.0 mmol of $[\mathrm{Co(NH_3)_5NCO}]\mathrm{Br_2}$ in 10 ml of deoxygenated water was added 10 ml of a 0.1 *N* chromium(II) perchlorate solution[10] (1.0 *N* in perchloric acid). The reaction mixture was stirred for 15 min, under nitrogen, at room temperature, during which time the solution changed in color from pink to purple. The addition of the solution to 300 ml of ethanol at 0° did not yield any solid, and the oily material obtained by evaporating the resulting solution to dryness did not contain any cyanate groups.

Physical Measurements.—Solid state infrared and aqueous solution visible–ultraviolet spectral measurements and microanalyses were carried out as described earlier.[11] The $[\mathrm{Co(NH_3)_5NCO}]\mathrm{Br_2}$ complex exhibited ν_{CN}, ν_{CO}, and δ_{NCO} bands at, respectively, 2254, 1318, and 589 cm^{-1} (Nujol mull). The absorption maxima found in its visible–ultraviolet spectrum (10^{-3} *M* aqueous solution) are shown in Table I, along with those of several related complexes.

TABLE I

VISIBLE–ULTRAVIOLET SPECTRAL DATA FOR $[\mathrm{Co(NH_3)_5X}]^{2+}$ COMPLEXES

X	$\nu_{\max}$, kK	ϵ, M^{-1} cm^{-1}
-NCO	20.0	114
	28.4	87.0
-NCS	20.2	182
	32.8	1570
-NCSe	20.3	163
	30.6	863
$-\mathrm{O}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{NH_2}$	19.8^a	60.0^a

^{a} Ref 6.

Discussion

The synthetic problems mentioned earlier were circumvented by the following reaction sequence

$$[\mathrm{Co(NH_3)_5N_3}]^{2+} \xrightarrow[\mathrm{OP(OC_2H_5)_3}]{\mathrm{NOClO_4}}$$

$$[\mathrm{Co(NH_3)_5OP(OC_2H_5)_3}]^{3+} + \mathrm{N_2} + \mathrm{N_2O} \xrightarrow[\mathrm{DMSO}]{\mathrm{(C_6H_5)_4AsNCO}}$$

$$[\mathrm{Co(NH_3)_5NCO}]^{2+} + \mathrm{OP(OC_2H_5)_3} \xrightarrow[\mathrm{H_2O}]{\mathrm{Br^-}} [\mathrm{Co(NH_3)_5NCO}]\mathrm{Br_2} \quad (1)$$

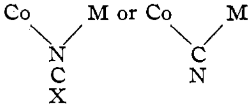
It is of interest to note that, *once formed*, the cyanate complex can be reprecipitated from water without any noticeable conversion to the carbamato complex. The latter exhibits a characteristic $\mathrm{C{=}O}$ stretching frequency at *ca.* 1560 cm^{-1}, but its spectrum does not include any absorption bands in the $\mathrm{C{\equiv}N}$ stretching range.[6] Like its thiocyanate[12] and selenocyanate[5] analogs, the cyanate group is N-bonded in the complex, as evidenced[11] by its increased ν_{CO} frequency (relative to the free ion value) and its reluctance to hydrolyze to form the carbamato complex. This hydrolysis would be expected to occur quite facilely if the cyanate group were O-bonded. Based on the frequencies of the lowest energy absorption maxima in the spectra of the pentaammine cobalt(III) complexes (Table I), the ligand field strengths of the three pseudohalides increase in the order $-\mathrm{NCO} < -\mathrm{NCS} < -\mathrm{NCSe}$, although, as expected, the differences among the three are slight.

Beck and Fehlhammer[13] have reported the transformation of coordinated azide into cyanate by the attack of free carbon monoxide and expulsion of nitrogen.

$$[\mathrm{M(P(C_6H_5)_3)_2(N_3)_2}] + 2\mathrm{CO} \xrightarrow{\mathrm{HCCl_3}} [\mathrm{M(P(C_6H_5)_3)_2(NCO)_2}] + 2\mathrm{N_2}$$
$$[\mathrm{M} = \mathrm{Pd(II)}, \mathrm{Pt(II)}] \quad (2)$$

We attempted to prepare $[\mathrm{Co(NH_3)_5NCO}]^{2+}$ by an analogous reaction between a DMSO solution of $[\mathrm{Co(NH_3)_5N_3}]^{2+}$ and carbon monoxide, but no evidence for cyanate formation was observed, emphasizing the importance of the nature of the metal ion in the reaction.

The failure of the $[\mathrm{Co(NH_3)_5NCO}]^{2+}$ complex to form $[\mathrm{Co(CN)_5NCO}]^{3-}$ and $[\mathrm{Cr(OH_2)_5NCO}]^{2+}$ (or their linkage isomers) in the reactions with the strong reducing agents $[\mathrm{Co(CN)_5}]^{3-}$ and chromium(II) might seem surprising at first glance, since the isothiocyanato-,[14-16] azido-,[14,16] and cyanopentaamminecobalt(III)[17-19] complexes react facilely with these reducing agents *via* activated-bridge inner-sphere electron-transfer reactions, with essentially quantitative transfer of the pseudohalide group to the oxidized form of the reductant. In forming the activated bridge complexes in these reactions, steric considerations strongly favor remote attack by the reductant complex, leading to bridges of the type Co–NCX–M, or Co–CN–M, as opposed to



which would result from adjacent attack. In the case of the thiocyanate, azide, and cyanide ions, this is a happy coincidence, for the former configurations are precisely those which they generally exhibit when they function as bridging ligands in stable complexes. The cyanate group, however, is known[20] to bridge *via* its nitrogen atom in silver cyanate (zigzag Ag–N–Ag chains with a bond angle of 128°) and evidence has recently been presented[21,22] in support of similar bridges in the first series of bridged coordination complexes reported for the cyanate ion. The tendency of the

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cyanate ion to form single atom bridges has been rationalized[21] in terms of the charge distribution in the ion.[9,23] Unlike the thiocyanate, selenocyanate, and azide ions, which have relatively high charge densities on both terminal atoms, the cyanate has, by far, the greater part of its charge localized on the nitrogen atom. Therefore, in the case of the $[Co(NH_3)_5NCO]^{2+}$ complex, remote attack by the reductant would be anticipated to be less favorable than the situations encountered with the other pseudohalide bridging groups.

The question as to what reactions actually take place still remains to be answered, however. In the case of the reaction with $[Co(CN)_5]^{3-}$, the most obvious hypothesis would be that the reaction proceeds *via* an outer-sphere electron transfer between $[Co(NH_3)_5NCO]^{2+}$ and $[Co(CN)_6]^{4-}$, which would yield $[Co(CN)_6]^{3-}$ directly. Another plausible explanation involves the formation of a $[(H_3N)_5Co{-}NCO{-}Co(CN)_5]^-$ bridged activated complex. This would lead to the formation of $[Co(CN)_5OCN]^{3-}$, which would most certainly be unstable, since the $[Co(CN)_5]^{2-}$ moiety is known to be a soft coordination center, *e.g.*, $[Co(CN)_5SCN]^{3-}$ is a stable S-bonded species,[15] whereas the cyanate ion is known to bond through its oxygen atom only to very hard Lewis acids, *e.g.*, Ti(IV),[24] Zr(IV),[24] Hf(IV),[24] Mo(III),[25] Re(IV),[25] and Re(V).[25] Expulsion of the unstable O-bonded cyanate could then lead to cyanide substitution, perhaps *via* an aquo intermediate, to yield $[Co(CN)_6]^{3-}$. Finally, the $[Co(CN)_6]^{3-}$ could result from a disproportion–oxidation reaction between $[Co(CN)_5]^{3-}$ and water with evolution of hydrogen. This is not very likely in the present case, since Poskozim has reported[26] that this reaction does not take place to any noticeable degree until the aqueous $[Co(CN)_5]^{3-}$ solution is heated, even with solutions of much higher concentration than that used in this study. It should be noted that the infrared spectrum of the product is identical with those of authentic samples of $K_3[Co(CN)_6]$, prepared either by Schlessinger's method[27] or by the reaction between $[Co(NH_3)_5CN]^{2+}$ and $[Co(CN)_5]^{3-}$.[17]

In the case of the reaction with chromium(II), the $[Cr(OH_2)_5OCN]^{2+}$ species resulting from a $[(H_3N)_5Co{-}NCO{-}Cr(OH_2)_5]^{4+}$ bridged activated complex would be susceptible to hydrolysis, especially in the strongly acidic solution employed in case (B), perhaps *via* a carbamato intermediate. It is also possible that the color changes observed are due to the oxidation of the chromium(II) by incipient oxygen, and, in case (B), the $[Co(NH_3)_5NCO]^{2+}$ complex simply decomposes in the acidic medium.

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Tris(trifluoromethyl)phosphine Chemistry of Nitrosylcobalt Tricarbonyl[1]

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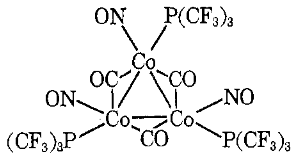
The isoelectronic analogy between nitrosylcobalt tricarbonyl and nickel tetracarbonyl makes it appropriate to compare their chemistry. An obviously expected similarity would be the successive displacement of 2CO by $2(CF_3)_3P$, the steric effect of which would preclude displacement of a third CO.[2,3] In fact, $(CF_3)_3PCoNO(CO)_2$ is formed from $CoNO(CO)_3$ not quite so easily as $(CF_3)_3PNi(CO)_3$ from $Ni(CO)_4$; then it is still harder to produce $[(CF_3)_3P]_2CoNOCO$, and a third-stage displacement of CO seems impossible.

A more subtle analogy concerns the decomposition of $[(CF_3)_3P]_2Ni(CO)_2$ at 25°, to form a deep red soluble material in which CO bridging between nickel atoms could be demonstrated by infrared peaks at 1878 and 1897 cm^{-1}.[4] The search for a somewhat similar polynuclear complex made up of $(CF_3)_3P$, Co, NO, and CO seemed significant because of the question whether NO or CO would be employed for bridge bonding between the cobalt atoms. In fact, the thermal decomposition of $(CF_3)_3PCoNO(CO)_2$ at 40° led to a dark brown, nonvolatile solid, soluble in the usual organic solvents and having the molecular formula $[(CF_3)_3PCoNOCO]_3$. The infrared spectrum of this included peaks at 1860 and 1826 cm^{-1}, assignable to bridging CO and terminal NO; there were no peaks in the terminal CO region (above 2000 cm^{-1} for Ni and Co carbonyls) nor in the 1500-cm^{-1} range characteristic of bridging NO. Reasonably assuming the molecular structure



it seems that, given equal opportunity, CO is better than NO for bridging between cobalt atoms.

Mononuclear Complexes

Formation.—Both of the new $(CF_3)_3P{-}Co$ complexes were made in a single quantitative experiment which determined their empirical formulas. The reactants $(CF_3)_3P$ and $CoNO(CO)_3$ were heated in a sealed glass tube for 10 hr at 120°; then the tube was opened to the Stock-type high-vacuum manifold. The free CO

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