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CONTRIBUTION FROM THE CÁTEDRA DE QUÍMICA INORGÁNICA, FACULTAD DE QUÍMICA, MONTEVIDEO, URUGUAY, AND THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF NEW YORK AT STONY BROOK, STONY BROOK, NEW YORK 11790

The Synthesis of μ-Isocyano-pentacyano-pentaamminedicobalt(III)[1a,b]

BY RENATA A. DE CASTELLÓ, CARLOS PÍRIZ MAC-COLL, AND ALBERT HAIM*,[1c]

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Linkage isomerism for terminal and bridging cyanide groups bound to transition metal ions has been reported in recent years. For terminal cyanide groups, the nitrogen-bonded isomers have been detected as metastable intermediates in inner-sphere redox reactions and are known to undergo relatively rapid isomerization to the stable carbon-bonded structures.[2-4] In the case of bridging cyanide groups, linkage isomerism has been reported for the ill-defined, polymeric materials that precipitate on mixing transition metal–aquo ions with transition metal hexacyanides.[5-7] We were interested in the possibility of finding simple binuclear systems with linkage isomers involving a bridging cyanide group. Following our previous report on the preparation of μ-cyano-pentacyanopentaamminedicobalt(III)[8,9] we report herein the preparation and some properties of the linkage isomer μ-isocyano-pentacyanopentaamminedicobalt(III). The synthetic method employed involves the substitution of water in pentacyanoaquocobaltate(III) by the nitrogen end of cyanide in cyanopentaamminecobalt(III)

$$Co(NH_3)_5CN^{2+} + Co(CN)_5OH_2^{2-} \longrightarrow (NH_3)_5CoCNCo(CN)_5 + H_2O \quad (1)$$

Experimental Section

Materials.—Cyanopentaamminecobalt(III) perchlorate was prepared and recrystallized as described by Siebert.[10] Potassium azidopentacyanocobaltate(III) was prepared by the reaction between azidopentaamminecobalt(III) chloride[11] and potassium cyanide.[12] The resins used in the ion-exchange work were Amberlite IRA 124 (hydrogen ion form) and Dowex 2X-8 (chloride ion form). All other chemicals were reagent grade.

Preparation of μ-Isocyano-pentacyanopentaamminedicobalt(III), $(NH_3)_5CoCNCo(CN)_5$.—Preliminary experiments indicated that the desired reaction (eq 1) took place readily when solutions of pentacyanoaquocobaltate(III) and cyanopentaamminecobalt(III) were heated at 50°. For 0.10 *M* $Co(CN)_5OH_2^{2-}$ and 0.10 *M* $Co(NH_3)_5CN^{2+}$, the 380-nm absorption of $Co(CN)_5OH_2^{2-}$ disappeared and a new absorption at 340 nm appeared over a period of 6 hr. Guided by these observations, the following synthetic procedure was adopted. A solution 0.10 *M* in $Co(CN)_5OH_2^{2-}$ (prepared by reaction of $K_3[Co(CN)_5N_3]$ with the stoichiometric amounts of potassium nitrite and perchloric acid[13]) and 0.10 *M* in $[Co(NH_3)_5CN](ClO_4)_2$ was heated at 50° for 6 hr. After cooling in an ice–salt bath and filtering the potassium perchlorate that crystallized, the resulting solution was percolated through a cation- and an anion-exchange resin to remove any unreacted $Co(NH_3)_5CN^{2+}$ and $Co(CN)_5OH_2^{3-}$, respectively.[14] The effluent,[15] yellow in color, was concentrated at 40° in a rotary evaporator, until the solid began to separate. After cooling in an ice bath, the solid was filtered out, washed thoroughly with ice-cold water and acetone, and then air dried; yield 30%. *Anal.* Calcd for $[(NH_3)_5CoCNCo(CN)_5]\cdot H_2O$: Co, 31.3; NH_3, 22.5; C, 19.11; N, 40.85; H, 4.5. Found: Co, 30.15; NH_3, 21.9; C, 19.05; N, 40.32; H, 4.44.

Analytical Methods.—Ammonia and cobalt were analyzed as described previously.[8] Carbon, hydrogen, and nitrogen analyses were performed by Galbraith Laboratories.

Measurements.—Visible and ultraviolet spectra were measured with a Beckman DB or a Cary 14 spectrophotometer. Infrared spectra were recorded with a Perkin-Elmer 521 spectrophotometer. Samples were potassium bromide pellets or Nujol mulls. Conductivity measurements were carried out as described before.[8]

Results and Discussion

The assignment of the structure $(NH_3)_5CoCNCo(CN)_5$ to the complex prepared in the present work is made along lines similar to those used previously for the assignment of the structure $(NH_3)_5CoNCCo(CN)_5$ to the isomeric compound.[8] The nonelectrolytic nature of the complex is established conclusively from the conductivity measurements. The specific conductance at 25° of a solution containing 1.44 g of complex/l. of solution was 1.28×10^{-5} ohm^{-1} cm^{-1}. Expressing the concentration of the complex in terms of gram-atoms of cobalt per liter of solution, the calculated molar conductance is 1.6 ohm^{-1} cm^2 mol^{-1}. The behavior of solutions of the complex toward ion-exchange resins provides additional support for the formulation of the complex as a neutral, binuclear species. The complex passes quantitatively through a cation-exchange resin but, in agreement with previous observations for the

* To whom correspondence should be addressed at the State University of New York at Stony Brook.

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isomeric compound $(NH_3)_5CoNCCo(CN)_5$,[8] is partially retained on an anion-exchange resin by surface adsorption. The infrared measurements in the 2100–2200-cm^{-1} region provide strong evidence for the presence of a cyanide bridge in the binuclear complex. Bands are observed at 2128, 2131, and 2202 cm^{-1}. The terminal cyanide groups give rise to the absorptions at 2128 and 2131 cm^{-1}, whereas the bridging cyanide group is associated with the higher frequency absorption at 2202 cm^{-1}.[16]

The present preparation of $(NH_3)_5CoCNCo(CN)_5$ coupled with the previously[8] reported $(NH_3)_5CoNCCo(CN)_5$ represents an example of linkage isomerism involving a bridging, unsymmetrical, ambidentate ligand bound to two different moieties. The binding mode of the bridging cyanide in the two isomers is assigned on the basis of the electronic spectrum. The pertinent information is summarized in Table I. As pointed out

TABLE I
ELECTRONIC SPECTRA OF SOME CYANOAMMINECOBALT(III) COMPLEXES

Compound	λ, nm	ε	λ, nm	ε	Ref
$Co(NH_3)_6^{3+}$	476	56	339	46	*a*
$Co(NH_3)_5CN^{2+}$	440	56	327	52	*a*
$CoNH_3(CN)_5^{2-}$	346	230	...	...	*b*
$Co(CN)_6^{3-}$	311	196	258	138	*a*
$(NH_3)_5CoNCCo(CN)_5$	474	70	313	250	*c*
$(NH_3)_5CoCNCo(CN)_5$	440	71	343	260	*d*

[a] Reference 10. [b] P. B. Chock, R. B. K. Dewar, J. Halpern, and L. Y. Wong, *J. Amer. Chem. Soc.*, 91, 82 (1969). [c] Reference 8. [d] Present work.

previously, the absorption spectrum of $(NH_3)_5CoNCCo(CN)_5$ is the sum of the spectra of a cobalt(III) in a $(C)_6$ environment (maximum at 313 nm to be compared with 311 nm for $Co(CN)_6^{3-}$) and a cobalt(III) in an $(N)_6$ environment (maximum at 474 nm, to be compared with 476 nm for $Co(NH_3)_6^{3+}$). On the basis of such additivity and by comparison with the spectra of cobalt(III) complexes in known mixed C–N environments, it was predicted earlier that the isomeric compound where the cyanide bridge had flipped would have maxima at 440 and 340 nm. It is seen from Table I that this prediction has been borne out. The observed absorptions at 440 and 343 nm are those expected for the structure $(NH_3)_5CoCNCo(CN)_5$ with a cobalt(III) in a $(C)(N)_5$ environment (compare $Co(NH_3)_5CN^{2+}$ at 440 nm) and a cobalt(III) in a $(C)_5(N)$ environment (compare $CoNH_3(CN)_5^{2-}$ at 346 nm). Moreover, it is noteworthy that adding a $Co(CN)_5$ or $Co(NH_3)_5$ residue to the nitrogen end of cyanide has little or no effect on the ligand field strength of the carbon end and, in agreement with previous conclusions,[17] that the nitrogen end of cyanide in $Co(NH_3)_5CN^{2+}$ and $Co(CN)_6^{3-}$ has a ligand field strength very close to that of ammonia.

A cursory examination of the base hydrolysis of $(NH_3)_5CoCNCo(CN)_5$ was carried out. The reaction is extremely slow and produces a precipitate of cobalt(III) hydroxide and a mixture of cobalt(III) cyanide complexes in solution. The stoichiometry was determined by measuring the cobalt left in solution spectrophotometrically as $Co(NCS)_4^{2-}$ after decomposition with sulfuric acid. The amounts of cobalt left in solution after heating at 80° in 1 *M* sodium hydroxide for 6, 10, and 15 hr were 64, 59, and 50%, respectively, of the total cobalt initially present. At the completion of the hydrolysis, the solution was examined spectrophotometrically and was found to consist of a 1:1 mixture of hexacyanocobaltate(III) and hydroxopentacyanocobaltate(III). The following reaction scheme accounts for the observations.

$$(NH_3)_5CoCNCo(CN)_5 + OH^- \longrightarrow Co(NH_3)_5OH^{2+} + Co(CN)_5NC^{3-} \quad (2)$$

$$Co(NH_3)_5OH^{2+} + 2OH^- \longrightarrow Co(OH)_3 + 5NH_3 \quad (3)$$

$$Co(CN)_5NC^{3-} \longrightarrow Co(CN)_6^{3-} \quad (4)$$

$$Co(CN)_5NC^{3-} + OH^- \longrightarrow Co(CN)_5OH^{3-} \quad (5)$$

Reaction 4 was postulated by Halpern and Nakamura[3] to account for their observations on the reaction between $Co(NH_3)_5CN^{2+}$ and $Co(CN)_5^{3-}$. No mention was made in their work about the possibility of loss of cyanide (eq 5) competing with isomerization (eq 4). However, the conditions used in the present work are very different from those used by Halpern and Nakamura, and, apparently, reaction 5 becomes important compared to reaction 4 under our experimental conditions.

The base hydrolysis of $(NH_3)_5CoCNCo(CN)_5$ is considerably slower than that of the linkage isomer $(NH_3)_5CoNCCo(CN)_5$.[8] Since there is a linear free energy relation between rate constant for hydrolysis and equilibrium constant for aquation,[18] it is concluded that the equilibrium constant for eq 6 is smaller than that for eq 7 and, therefore, that the equilibrium con-

$$(NH_3)_5CoCNCo(CN)_5 + H_2O \rightleftharpoons Co(NH_3)_5OH_2^{3+} + Co(CN)_5NC^{3-} \quad (6)$$

$$(NH_3)_5CoNCCo(CN)_5 + H_2O \rightleftharpoons Co(NH_3)_5OH_2^{3+} + Co(CN)_6^{3-} \quad (7)$$

stant for isocyano to cyano linkage isomerization is smaller for the binuclear complexes than for the monomeric pentacyano species. This conclusion is not unexpected since for the monomeric complexes there is undoubtedly a net gain in energy on isomerization, whereas the isomeric binuclear complexes may show only a small difference in stability, both cobalt(III) centers having a preference for the carbon end over the nitrogen end of cyanide.

Finally, it is noteworthy that the synthetic method used exploits the relative ease of substitution of water in $Co(CN)_5OH_2^{2-}$ [12] and the nucleophilicity of the nitrogen end of cyanide in $Co(NH_3)_5CN^{2+}$. The method is not restricted to the ambidentate ligand cyanide but promises to have some generality since we

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have succeeded in synthesizing $(NH_3)_5CoNCSCo(CN)_5$ by reaction of $Co(NH_3)_5NCS^{2+}$ with $Co(CN)_5OH_2^{2-}$.[19] We are planning to study these reactions kinetically in order to obtain information about the nucleophilicity of ambidentate ions where one of the donor atoms is already bound to a metal center.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO, BOULDER, COLORADO 80302

Synthesis of a 6,9-Deuterium-Labeled Decaborane(14)

BY JANE A. SLATER[1] AND ARLAN D. NORMAN*

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Procedures for the synthesis of decaboranes(14) which are labeled with deuterium atoms in the bridge (μ),[2-4] 1,2,3,4-terminal,[5,6] and the μ,5,6,7,8,9,10-terminal[3,4,6] positions are well known and commonly used. Recently, during the course of our studies of the structure and ^{11}B nmr spectrum of the $B_{10}H_{15}^-$ ion[7] we have found a method for the preparation of a 6,9-deuterium-labeled decaborane(14). Although the labeled molecule contains slightly less than two deuterium atoms, the new compound is designated nominally as 6,9-$B_{10}H_{12}D_2$ in this communication. The new specifically labeled species should prove to be highly useful for further studies of decaborane chemistry.

Experimental Section

Apparatus.—All work which required inert-atmosphere conditions was done in an N_2-flushed glove bag. Vacuum-line manipulations were performed on a standard vacuum line.[8,9]

Boron-11 nmr spectra were obtained using a Varian Associates HA-100 equipped with standard 32.1-MHz probe and radiofrequency unit accessories. Chemical shifts were measured relative to $B(OCH_3)_3$ and are reported relative to $BF_3 \cdot O(C_2H_5)_2$ ($\delta_{B(OCH_3)_3} = \delta_{BF_3 \cdot O(C_2H_5)_2} - 18.1$ ppm). Spectra were calibrated using the audiofrequency integrator side bands and spectral integrals were measured with a planimeter. Infrared spectra were obtained with Perkin-Elmer Model 21 and Beckman IR-5 spectrometers.

Materials.—Decaborane, obtained from a laboratory supply, was sublimed before use. Sodium borodeuteride (Alfa Inorganics) was used without further purification. Deuterium chloride was obtained from the reaction of $SiCl_4$ with D_2O[10] and was shown by mass spectral analysis to contain >95% deuterium. Hydrogen chloride was obtained from Matheson Co. and was purified by routine fractional condensation techniques. Monoglyme and dioxane were distilled from $LiAlH_4$ and stored under an N_2 atmosphere prior to use in an experiment.

The μ-$B_{10}H_{10}D_4$[11] was prepared according to the method of Miller and Hawthorne.[3] The μ-$B_{10}H_{10}D_4$ contained 3.50 D/molecule. Within experimental error, no deuterium migration into terminal positions could be detected in the ^{11}B nmr spectrum.

Deuterium analyses were performed by Mr. Josef Nemeth, Urbana, Ill.

Preparation of 6,9-$B_{10}H_{12}D_2$.—In a typical reaction μ-$B_{10}H_{10}D_4$ (1.0 mmol) in 1 ml of monoglyme was allowed to react under an N_2 atmosphere with $NaBD_4$ (2.0 mmol). Upon completion of the reaction, as evidenced by the discontinuation of slight gas evolution, the solution was decanted from the excess undissolved $NaBD_4$. The monoglyme solution was treated with a 4–5 molar excess of DCl for 1 hr. Hydrogen, unreacted DCl, and monoglyme were removed by passage of the reaction materials through a −30° trap. The intermediate decaborane, nominally described as $B_{10}H_8D_6$, was purified by sublimation. Removal of deuterium from bridging positions was accomplished by a rapid equilibration in H_2O in which the $B_{10}H_8D_6$ was stirred in 5 ml of an equivolume H_2O–dioxane mixture for 3 min. To this mixture several 10-ml portions of ether were added to extract the product. Evaporation of the ether followed by vacuum sublimation of the product yielded 62 mg (0.5 mmol; 50% yield) of 6,9-$B_{10}H_{12}D_2$. A content of 1.90 D/molecule was found.

Results and Discussion

In this study, we have found that 6,9-$B_{10}H_{12}D_2$ can be prepared using the following multistep synthetic procedure. Bridge-deuterium-labeled decaborane (μ-$B_{10}H_{10}D_4$) is converted to the pentadecahydro-*nido*-decaborate(1−) ion, $B_{10}H_{10}D_5^-$, in a reaction with borodeuteride ion in monoglyme (eq 1). The $B_{10}H_{14}$–$NaBH_4$

$$\mu\text{-}B_{10}H_{10}D_4 + BD_4^- \longrightarrow B_{10}H_{10}D_5^- + BH_3 \qquad (1)$$

reaction has been reported previously.[12] In the second step of the synthesis the $B_{10}H_{10}D_5^-$ ion is converted back to decaborane by reaction with DCl (eq 2). Finally,

$$B_{10}H_{10}D_5^- + D^+ \longrightarrow \text{hydrogen} + \mu,6,9\text{-}B_{10}H_8D_6 \qquad (2)$$

exchange of bridge deuterium for hydrogen by reaction with H_2O results in the final 6,9-$B_{10}H_{12}D_2$.

The deuterium content of 6,9-$B_{10}H_{12}D_2$ is established by deuterium analysis and mass spectral data. Deuterium analysis indicated the presence of 1.90 deuterium atoms/molecule. The mass spectrum exhibits peak envelopes characteristic of a decaborane.[13] The most intense peak occurs at m/e 123. Small peaks as high as m/e 130 are evident; however, the main spectral cutoff occurs at m/e 126. The cutoff at m/e 126, compared to m/e 124 for normal $B_{10}H_{14}$, indicates the absence of large quantities of decaboranes containing more than two deuterium atoms. However, the presence of small quantities of more highly deuterated species is recognized.

The infrared spectrum of 6,9-$B_{10}H_{12}D_2$ exhibits strong absorptions at 2560 and 1920 cm^{-1} which can be assigned to terminal B–H and B–D stretching modes,[3,14,15] respectively. The B–D bridge absorption in deca-

* To whom correspondence should be addressed.

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