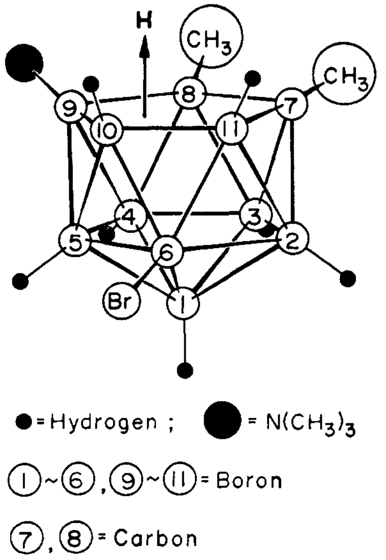


Figure 1.—A possible structure of $[CH_3(B_9C_2H_8Br)CH_3]N(CH_3)_3$.

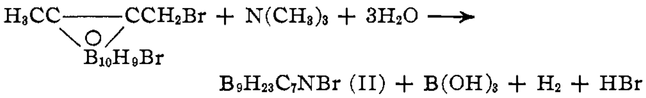
peaks which have characteristic patterns spread over a range of 9–10 mass numbers due to their boron isotopic compositions. The spectra of I and III were almost identical and contained a group of peaks with the highest at *m/e* 205 and with a clear cutoff at *m/e* 207 corresponding to the parent ion $^{11}B_9H_{22}C_6N$. Compound II displayed a similar pattern, with the highest peak at *m/e* 298 and with a clear cutoff at *m/e* 301 corresponding to $^{11}B_9H_{23}C_7N^{81}Br$. All of these products gave peaks due to ions of the parent minus trimethylamine and of trimethylamine.

Discussion

The structure shown in Figure 1 is postulated for II on the basis of its mass and pmr spectra. The pmr signal at τ 6.758 can be assigned to the three methyl groups attached to the nitrogen atom which is inferred from the chemical shift to bear a positive charge. The broad signal at τ 8.425 is doublet-like and has been ascribed to two methyl groups attached to the two nonequivalent skeleton carbons. The presence of two methyl groups implies that the bromine atom attached to the carbon atom in the starting material is replaced by a hydrogen atom, and the trimethylamine molecule must be bonded to a skeletal boron atom or must be present as an ammonium cation. Thus, an alternative conceivable structure is the ammonium salt $NH(CH_3)_3{}^+B_9H_9C_2(CH_3)_2Br^-$. This is, however, incompatible with the above-mentioned solubilities in various organic solvents and lack of an $^+N–H$ stretching band in the ir spectrum. The mass number of the parent peak is also smaller than that of the ionic structure by 2.

The remaining $B_9H_8BrC_2(CH_3)_2$ must be negatively charged. Although the structure has not been unequivocally established, it is quite reasonable to assume an icosahedral geometry with one vertex missing, *i.e.*, a skeleton similar to dodecahydrodicarba-*nido*-undecaborate(1−) ion.[2] The position of trimethylamine is not clear. The bromine atom is probably attached to the 9 or 12 position in the starting material and consequently to the same position in II. A single-crystal X-ray analysis now in progress would afford conclusive evidence for the structure. Preliminary X-ray data yield the cell constants $a = 14.45$ Å, $b = 16.32$ Å, and $c = 25.89$ Å; $Z = 16$, d(calcd) = 1.298 g/cm^3, d(found) = 1.299 g/cm^3, and space group Pbca-$D_{2h}{}^{15}$.

The stoichiometry of the reaction can thus be written



$$H_3C\underset{\underset{B_{10}H_9Br}{\diagdown O \diagup}}{C\text{———}C}CH_2Br + N(CH_3)_3 + 3H_2O \longrightarrow B_9H_{23}C_7NBr\ (II) + B(OH)_3 + H_2 + HBr$$

This scheme also receives further support from the observation of hydrogen evolution and recovery of trimethylammonium bromide.

Only one of the protons in II exchanged in an $CH_3CN–D_2O$ mixed solvent at room temperature within 10 min, as evidenced by the increment in mass number of the parent peak in the mass spectrum. This fact suggests the presence of one bridge hydrogen atom according to Hyatt, *et al.*,[6] consistent with the structure shown in Figure 1, and excludes coordination of the amine molecule to the open face.

Compound I is concluded to have the same skeleton as II on the basis of its mass, ir, and pmr spectra. The ir spectrum is quite different from that of $NH(CH_3)_3{}^+$-$B_9H_{11}C_2(CH_3)^-$ prepared by the method of Hawthorne, *et al.*,[2] from 1-methyl-*o*-carborane. The pmr spectrum of III gives an AB-type quartet as shown in Table I to indicate the presence of a methylene group. This is in contrast to the methyl signal of I and leads to the inner-salt structure $(HCB_9H_{10}C^-)CH_2N(CH_3)_3{}^+$ for III.

Thus, it is concluded that the two isomeric undecaborane derivatives I and III are produced by amine-catalyzed hydrolysis of C-halomethyl-*o*-carborane and that one of the products involves a B–N dative bond binding an amine molecule.

---

[6] D. E. Hyatt, D. A. Owen, and L. J. Todd, *Inorg. Chem.*, **5**, 1749 (1966).

CONTRIBUTION FROM THE CATEDRA DE QUIMICA INORGANICA,
FACULTAD DE QUIMICA, MONTEVIDEO, URUGUAY,
AND THE DEPARTMENT OF CHEMISTRY,
STATE UNIVERSITY OF NEW YORK AT STONY BROOK,
STONY BROOK, NEW YORK 11790

The Synthesis of the Cyano-Bridged Binuclear Complex μ-Cyano-pentacyanopentaammine-dicobaltate(III, III)[1a]

BY RENATA A. DE CASTELLÓ, CARLOS PÍRIZ MAC-COLL,[1b]
NED B. EGEN, AND ALBERT HAIM

Received October 30, 1968

Reference to compounds of formula $[M(NH_3)_5OH_2][M'(CN)_6]$, where M = Co or Cr and M′ = Co,

---

[1] (a) This work was supported in part by Grant GP-6528 from the National Science Foundation. (b) Visiting Professor under the auspices of the Fulbright Commission.

Cr, or Fe, can be found in the early literature.[2] By analogy with the thermal dehydration behavior of simple salts (*e.g.*, halide, nitrate) of the aquopentaamminecobalt(III) ion,[3] it occurred to us that the thermal decomposition of complex cyanide salts of the above formula would lead to the formation of cyano-bridged binuclear complexes. We have explored this possibility and have found that the thermal dehydration of $[Co(NH_3)_5OH_2][Co(CN)_6]$ proceeds, in part, according to eq 1. In addition to the synthetic utility

$$[Co(NH_3)_5OH_2][Co(CN)_6] \longrightarrow [(NH_3)_5CoNCCo(CN)_5] + H_2O \qquad (1)$$

of this type of reaction,[4] studies of cyano-bridged binuclear complexes are of special importance in view of recent interest in structural,[5,6] redox,[7-11] and substitution[12] studies with the ambidentate cyanide ligand. In the present paper we report the synthesis and some of the properties of $(NH_3)_5CoNCCo(CN)_5$.

Experimental Section

Materials.—Aquopentaamminecobalt(III) perchlorate was obtained by treating carbonatopentaamminecobalt(III) nitrate[13] with perchloric acid. The crude product was purified by dissolution in water followed by precipitation upon addition of perchloric acid. *Anal.* Calcd for $[Co(NH_3)_5OH_2](ClO_4)_3$: NH_3, 18.49; Co, 12.80. Found: NH_3, 18.1; Co, 12.6. Potassium hexacyanocobaltate(III) was prepared and recrystallized following standard procedures.[14] *Anal.* Calcd for $K_3[Co(CN)_6]$: N, 25.27; Co, 17.72. Found: N, 25.6; Co, 17.6.

The resins used in the ion-exchange work were Dowex 50W-X8 (hydrogen ion form), Amberlite IRA 410 (chloride ion form), and Dowex 2X-8 (chloride ion form). The water used for the conductivity measurements was triply distilled (the second distillation from alkaline permanganate). All other chemicals were reagent grade.

Preparation of Aquopentaamminecobalt(III) Hexacyanocobaltate(III), $[Co(NH_3)_5OH_2][Co(CN)_6]$.—Equal volumes of 0.05 *M* solutions of $[Co(NH_3)_5OH_2](ClO_4)_3$ and $K_3[Co(CN)_6]$ were mixed, whereby slow precipitation of sparingly soluble, red crystals of $[Co(NH_3)_5OH_2][Co(CN)_6]$ took place. After cooling to 0°, the crystals were filtered out, washed with water, ethanol, and acetone, and then dried in an oven at 80°. The yield was essentially quantitative. *Anal.* Calcd for $[Co(NH_3)_5OH_2]$-$[Co(CN)_6]$: NH_3, 22.56; Co, 31.23. Found: NH_3, 23.3; Co, 30.3.

Preparation of μ-Cyano-pentacyanopentaamminedicobaltate(III,III), $(NH_3)_5CoNCCo(CN)_5$.—Preliminary measurements of the weight loss of $[Co(NH_3)_5OH_2][Co(CN)_6]$ on heating at various temperatures and time intervals were performed in order to arrive at conditions that would yield the desired product. In the temperature range of 80–110°, loss of weight was negligible over a period of 24 hr. Heating at 220° during 2 hr resulted in a 22% weight loss (theoretical value for loss of one water molecule is 4.77%), and visual examination of the product (dark blue) indicated that extensive decomposition takes place under these conditions. Finally, heating at 140° for a period of 18–20 hr resulted in a 4.6 ± 0.1% (average of three measurements) weight loss and a color change from red to light orange. It must be noted, however, that, in spite of the agreement between the experimental weight loss and that expected for reaction 1, it cannot be concluded that reaction 1 proceeds quantitatively under these conditions, since some ammonia is also evolved during heating. Exploratory thermogravimetric studies indicated that a clean separation between loss of water and loss of ammonia could not be achieved, and, therefore, the conditions outlined above, namely, heating at 140° for 20 hr, were arbitrarily chosen for synthetic purposes. Following the thermal decomposition at 140°, the crude product was taken up with water (20 ml of water/g of product). The resulting slurry was filtered out and the solid residue (presumably containing unreacted $[Co(NH_3)_5$-$OH_2][Co(CN)_6]$ as judged from the color) was discarded. The solution was percolated through two ion-exchange columns in series, first the cationic (Dowex 50X-8) and then the anionic (Amberlite 410A), each 10 cm long and 1 cm in diameter for 200 ml of solution. The resins were washed with water until the washings were essentially colorless, and these were collected with the orange solution that had passed directly through the resins. A threefold excess of ethanol was slowly added, whereby a light orange solid precipitated out. The solid was filtered out, washed with ethanol and acetone, and then dried at 60°. Recrystallization was carried out by dissolving the powder in the minimum amount of water, followed by addition of an excess of ethanol; yield, 25%. *Anal.* Calcd for $(NH_3)_5CoNCCo(CN)_5$: NH_3, 23.69; N, 42.86; Co, 32.79. Found: NH_3, 24.3; N, 42.5; Co, 31.6.

Measurements.—Visible and ultraviolet spectra were measured with a Bausch and Lomb Spectronic 505 recording spectrophotometer.[15a] Infrared spectra were measured with a Beckman IR-5A spectrophotometer.[15b] Samples were potassium bromide pellets. Conductivity measurements were carried out at 25° with a Philips GM 4249/01 conductivity bridge. Molecular weight measurements were performed with an Osmette precision osmometer.[15c]

Analytical Methods.—Ammonia was analyzed by treating the complexes with arsenic(III) oxide and sodium hydroxide and then by titrating the ammonia that distilled off. Total nitrogen was analyzed by Dumas' method. Cobalt in $[Co(NH_3)_5OH_2](ClO_4)_3$, $K_3[Co(CN)_6]$, and $[Co(NH_3)_5OH_2][Co(CN)_6]$ was estimated electrolytically using Siebert's method.[16] Cobalt in $(NH_3)_5$-$CoNCCo(CN)_5$ was determined gravimetrically as cobalt metal after thermally decomposing the samples to Co_3O_4, followed by hydrogen reduction.

Results and Discussion

Although the thermal decomposition of $[Co(NH_3)_5$-$OH_2][Co(CN)_6]$ does not proceed stoichiometrically according to eq 1, it was possible to isolate, as described above, a fairly pure sample of the cyano-bridged binuclear complex $(NH_3)_5CoNCCo(CN)_5$. In addition to the analytical data which correspond to this formulation, the conductivity and ion-exchange behavior

---

[2] For a summary of the early work see Gmelin, "Handbuch der Anorganischen Chemie," Cobalt Part B, System No. 58, Verlag Chemie, Berlin, 1930, p 109.

[3] For a comprehensive review of this subject see W. W. Wendlandt and J. P. Smith, "The Thermal Properties of Transition Metal Ammine Complexes," Elsevier Publishing Co., Amsterdam, 1967, Chapter 4.

[4] We are presently engaged in a general study of the dehydration of aquopentaamminecobalt(III) salts of complex anions.

[5] D. Britton in "Perspectives in Structural Chemistry," Vol. I, J. D. Dunitz and J. A. Ibers, Ed., John Wiley & Sons, Inc., New York, N. Y., 1967, p 109.

[6] D. F. Shriver, "Structure and Bonding," Springer-Verlag, Inc., New York, N. Y., 1966, p 32.

[7] A. Haim and W. K. Wilmarth, *J. Am. Chem. Soc.*, **83**, 509 (1961).

[8] J. Burmeister and D. Sutherland, *Chem. Commun.*, 175 (1965).

[9] J. Halpern and S. Nakamura, *J. Am. Chem. Soc.*, **87**, 3002 (1965).

[10] J. H. Espenson and J. P. Birk, *ibid.*, **87**, 3280 (1965); **90**, 1153, 1967, p 2266 (1968).

[11] J. P. Birk and J. Halpern, *ibid.*, **90**, 305 (1968).

[12] J. P. Birk and J. H. Espenson, *Inorg. Chem.*, **7**, 991 (1968).

[13] F. Basolo and R. K. Murmann, *Inorg. Syn.*, **4**, 171 (1953).

[14] J. H. Bigelow, *ibid.*, **2**, 225 (1946).

[15] (a) The authors are grateful to Professors M. Falco and J. DeVries for the use of this instrument. (b) The authors are grateful to Dr. O. Gonzalez-Correa and Miss C. Staffa for running the KBr samples. (c) The authors are grateful to Dr. E. H. Battley for making this instrument available to them.

[16] H. Siebert, *Z. Anal. Chem.*, **206**, 20 (1964).

of solutions of the complex and the molecular weight measurements support the proposed formulation as a neutral binuclear species.

The specific conductances at 25° of aqueous solutions containing 400–450 mg of complex/l. of solution were in the range $(0.9\text{–}1.2) \times 10^{-5}$ ohm^{-1} cm^{-1}. Expressing the concentration of the complex on the basis of gram-atoms of cobalt per liter of solution, the calculated molar conductances are in the range 4–5 ohm^{-1} cm^2 mol^{-1}. For comparison, the molar conductance (concentration based on gram-atoms of cobalt per liter of solution) of $[Co(NH_3)_5OH_2][Co(CN)_6]$ is 350 ohm^{-1} cm^2 mol^{-1}. These results show that the compound under consideration is either a nonelectrolyte with a small amount of an ionic impurity or a polymeric electrolyte.

Additional support for this conclusion was obtained from the behavior of the complex toward cation- and anion-exchange resins. In a typical experiment, 5 ml of a 4×10^{-3} M solution in binuclear complex was added to a 9×1.5 cm column of Dowex 50X-8, 50–100 mesh in the hydrogen ion form. The solution that passed directly through was collected together with water washings of the resin to a total volume of 100 ml. The resulting solution was examined spectrophotometrically in the 550–250-nm region, and it was found that over 90% of the complex passed through the resin. In contrast with the high recovery of the complex from Dowex 50X-8, less than 10% of the complex was recovered from Dowex 2X-8, 50–100 mesh, chloride ion form. In order to test whether the complex was retained in this resin because of ion exchange or simply by surface adsorption, the following experiment was performed. The anion-exchange resin was transformed into the chromate form, and 5 ml of a 4×10^{-3} M solution in binuclear complex was added. The solution that passed directly through and water washings of the resin to a total volume of 100 ml were collected. The resulting solution was examined spectrophotometrically in the 400–250-nm region, and it was found that 0.012 mol of chromate/mol of binuclear complex had been released from the resin. Again these results show that the complex is a nonelectrolyte containing a small amount of an ionic impurity or a polymeric electrolyte.

The molecular weight measurements give the most conclusive evidence for the formulation of the complex as a neutral binuclear species. Because of the limited solubility of the complex, these measurements had to be carried out in relatively dilute solutions (4×10^{-3} M). Therefore, molecular weight determinations of sucrose were first carried out at a concentration of 5.05×10^{-3} M in order to test the reliability of the measurements in the millimolar concentration range. The measured molecular weight was 340 ± 50 (average and standard deviation of six measurements), in excellent agreement with the calculated value 342.3. For the binuclear complex at 4.55×10^{-3} M, the measured molecular weight was 355 ± 50 (average and standard deviation of six measurements) in excellent agreement with the value 359.12 calculated for the formula $Co_2(CN)_6(NH_3)_5$.

Although the results presented so far are consistent with the formulation of the binuclear neutral species as $(NH_3)_5CoNCCo(CN)_5$, they do not rule out the possibility of scrambling of ammonia and cyanide ligands around the two cobalt(III) centers. Evidence that such scrambling does not occur was obtained from an examination of the products of the base-catalyzed hydrolysis. A solution 2.18×10^{-3} M in the binuclear complex and 0.10 M in sodium hydroxide was heated at 70–80° for 2 hr. The cobalt(III) hydroxide formed was filtered out, and the resulting solution (twofold dilution) was examined spectrophotometrically in the 350–220-nm region. Maxima at 311 and 258 nm (*cf.* wavelengths for $Co(CN)_6^{3-}$ in Table II) with absorbances 1.01 and 0.72, respectively, were observed. The absorbance values calculated for the formation of 1 mol of $Co(CN)_6^{3-}$/mol of binuclear complex are 1.07 and 0.75 at 311 and 258 nm, respectively. These results rule out scrambling of ammonia and cyanide ligands in the coordination sphere of the two cobalt(III) centers. However, they do not serve to distinguish between the two possible isomeric formulations $(NH_3)_5CoNCCo(CN)_5$ and $(NH_3)_5CoCNCo(CN)_5$. Regardless of the binding mode of the cyanide bridge, the observable product of the base-catalyzed aquation would be $Co(CN)_6^{3-}$. For the former isomer, this would also be the primary product. For the latter isomer, the expected primary product $Co(CN)_5NC^{3-}$ would not be observed since its isomerization to the stable form $Co(CN)_6^{3-}$ is known to be very rapid.[9] Spectroscopic evidence regarding the mode of attachment of the cyanide bridge is discussed below.

Infrared measurements in the 2100–2200-cm^{-1} region provide strong evidence for the presence of a cyanide bridge in the binuclear complex. In Table I are listed cyanide stretching frequencies for a series of related cyanoaminecobalt(III) complexes. It is seen that the frequency range 2130 ± 10 cm^{-1} is characteristic of terminal cyanide groups bound to cobalt(III), whereas the frequency range 2190 ± 10 cm^{-1} is char-

TABLE I

CYANIDE STRETCHING FREQUENCIES OF SOME CYANOAMINECOBALT(III) COMPLEXES

Compound	Freq, cm^{-1}	Bonding	Ref
$[Co(NH_3)_5CN](NO_3)_2$	2135	Co–CN	*a*
$[Co(NH_3)_5CN]_3Hg(NO_3)_3$	2185	Co–CN–Hg	*a*
cis-$[Co(en)_2(CN)_2]Cl$	2137, 2128	Co–CN	*b*
mer-$Co(NH_3)_3(CN)_3$	2118	Co–CN	*c*
$K[Co(en)(CN)_4]$	2139, 2127, 2121	Co–CN	*d*
$K_3[Co(CN)_6]$	2130	Co–CN	*e*
$[Na_2Co(CN)_5 \cdot H_2O]_x$	2130	Co–CN	*e*
	2202	Co–CN–Co	
$[Co(NH_3)_5OH_2][Co(CN)_6]$	2120	Co–CN	*c*
$(NH_3)_5CoNCCo(CN)_5$	2120	Co–CN	
	2180	Co–CN–Co	*c*

[a] H. Siebert, *Z. Anorg. Allgem. Chem.*, **327,** 63 (1964). [b] S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 966 (1963). [c] Present work. [d] K. Ohkawa, J. Fujita, and Y. Shimura, *Bull. Chem. Soc. Japan*, **38,** 66 (1965). [e] Reference 17.

acteristic of a cyanide ligand that is bridging a cobalt(III) center to another metal atom.[17] The compound formulated as $(NH_3)_5CoNCCo(CN)_5$ exhibits maxima at 2120 (terminal) and 2180 cm^{-1} (bridging). These results, although consistent with the formulation of the binuclear species as $(NH_3)_5CoNCCo(CN)_5$, do not rule out the isomeric complex where the cyanide bridge has flipped. Regardless of the mode of attachment of the cyanide bridge, its absorption maxima would be expected to occur in the vicinity of 2190 cm^{-1}.

TABLE II

ELECTRONIC SPECTRA OF SOME CYANOAMINECOBALT(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*
cis-$Co(en)_2(CN)_2^+$	404	81	309	85	*b*
mer-$Co(NH_3)_3(CN)_3$	361	93	294	89	*c*
$Co(en)(CN)_4^-$	352	182	277	191	*b*
$Co(CN)_5NH_3^{2-}$	346	230	. . .	. . .	*f*
$Co(CN)_6^{3-}$	311	196	258	138	*a*
$(NH_3)_5CoNCCo(CN)_5$	474	70	313	250	*d*
$Co(NH_3)_5NCCH_3^{3+}$	465	57	330	53	*e*

[a] See ref *a* of Table I. [b] Reference 18. [c] M. Shibata, M. Mori, and E. Kyuno, *Inorg. Chem.*, **3**, 1573 (1964). [d] Present work. [e] R. B. Jordan, A. M. Sargeson, and H. Taube, *Inorg. Chem.*, **5**, 1091 (1966). [f] P. B. Chock, R. B. K. Dewar, J. Halpern, and L. Y. Wong, *J. Am. Chem. Soc.*, **91**, 82 (1969).

In Table II are listed the wavelengths (and molar absorbances) for the two ligand field bands of a series of related cyanoaminecobalt(III) complexes. For the mononuclear species, it is seen, as expected from the relative positions of NH_3 and CN^- in the spectrochemical series, that the wavelengths for the two maxima decrease with progressive substitution of NH_3 by CN^-. As noted previously,[18] the positions of the bands conform fairly well to "the rule of average environment." In contrast, the electronic spectrum of the binuclear complex $(NH_3)_5CoNCCo(CN)_5$ does *not* correspond to that expected for an *average* environment of CN^- and NH_3 ligands on a single cobalt(III) center but rather to the *sum* of the spectra of the two cobalt(III) moieties. The cobalt(III) center in the $(C)_6$ environment absorbs at 313 nm (*cf.* $Co(CN)_6^{3-}$, 311 nm), and the cobalt(III) center in the $(N)_6$ environment absorbs at 474 nm (*cf.* $Co(NH_3)_6^{3+}$, 475 nm; $Co(NH_3)_5NCCH_3^{3+}$, 465 nm). If the formulation that has been adopted for the binding mode of the cyanide bridge is correct, it is concluded that adding a $Co(NH_3)_5^{3+}$ residue to the nitrogen end of CN^- has little effect on the ligand field strength of the carbon end and that the nitrogen end of cyanide has a ligand field strength very close to that of ammonia. These conclusions are not inconsistent with results obtained previously in polymeric complex cyanides.[19] The alternate formulation $(NH_3)_5CoCNCo(CN)_5$ where the bridging cyanide has flipped seems less likely. The bands for the $Co(NH_3)_5CN$– and $Co(CN)_5NC$– moieties would have been expected to occur at *ca.* 440 and 340 nm, respectively, by analogy with the known values for $(N)_5(C)$ and $(C)_5(N)$ environments.

---

[17] D. A. Dows, A. Haim, and W. K. Wilmarth, *J. Inorg. Nucl. Chem.*, **21**, 33 (1961).

[18] K. Konya, H. Nishikawa, and M. Shibata, *Inorg. Chem.*, **7**, 1165 (1968).

[19] D. F. Shriver, S. A. Shriver, and S. E. Anderson, *ibid.*, **4**, 725 (1965).