ing sodium chloride and shown to have visible, ultraviolet, and infrared spectra identical with those of an authentic sample of $[Co(NH_3)_5CN]Cl_2$. The ion-exchange technique permitted a quantitative evaluation of the amounts of $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5CN^{2+}$ formed in the reaction as indicated in Table III. Small amounts (<2%) of other products were formed as well, including $Co(NH_3)_5H_2O^{3+}$ (eluted with 3 *M* HCl) and a light yellow species which was not eluted from the column with 4.8 *M* HCl and presumably has a charge greater than +3.

TABLE III

PRODUCTS OF REACTION RECOVERED FROM ION-EXCHANGE COLUMN

$[H_2O_2]$, *M*	$[H^+]$, *M*	Initial $[Co(NH_3)_5NCS^{2+}]$, mol × 10^4	λ_{max} of reaction mixture	$[Co(NH_3)_5CN^{2+}]$, mol × 10^4	$[Co(NH_3)_6^{3+}]$, mol × 10^4	% conversion to $Co(NH_3)_6^{3+}$
2.05	0.50	1.22	453	0.77	0.40	32.7
	0.10	1.24	464	0.28	0.69	55.6
1.79	0.50	1.27	456	0.71	0.44	34.6
1.56	0.50	1.27	455	0.77	0.44	34.6
1.03	0.50	1.27	456	...	0.43	35.6
0.77	0.50	1.22	459	0.35	0.51	41.8
	0.20	1.22	469	...	0.96	78.6
	0.10	1.24	469	0.14	1.10	88.9

The data in Table III suggest that at a fixed $[H^+]$ the conversion of starting material to $Co(NH_3)_6^{3+}$ is independent of or only slightly dependent on the hydrogen peroxide concentration over this range while, at a fixed concentration of hydrogen peroxide, the per cent conversion to hexaammine is markedly dependent on the H^+ concentration. The mechanistic implications of these observations and the process by which the cobalt–carbon bond in $Co(NH_3)_5CN^{2+}$ is generated from the original cobalt–nitrogen bond in $Co(NH_3)_5NCS^{2+}$ are under investigation.

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Ligand Redox Studies. II. Formation of Cyano Complexes by Oxidation of Captive Thiocyanate[1a]

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Several examples have been found of the formation of inert cyanide complexes on oxidation of the corresponding thiocyanate species: the oxidation of $(H_3N)_5CoNCS^{2+}$ by either Ce(IV) in H_2SO_4 or $S_2O_8^{2-}$ at low acidity and the oxidation of either $(C_2H_5)_4dienPdNCS^+$ or $(C_2H_5)_4dienPdSCN^+$ by hydrogen peroxide.

Experimental Section

Materials.—Isothiocyanatopentaamminecobalt(III) perchlorate, $[(H_3N)_5CoNCS](ClO_4)_2$, was prepared as described previously.[2] Thiocyanatotetraethyldiethylenetriaminepalladium(II) hexafluorophosphate, $[((C_2H_5)_4dien)PdSCN]PF_6$, was prepared as described by Basolo, Baddley, and Weidenbaum.[3] Isothiocyanatotetraethyldiethylenetriaminepalladium(II) perchlorate, $[((C_2H_5)_4dien)PdNCS]ClO_4$, was prepared[4] by recrystallizing the thiocyanate salt[3] from aqueous sodium perchlorate. Reagent grade chemicals were used elsewhere.

Ce(IV)–$(H_3N)_5$CoNCS^{2+}.—Solutions containing isothiocyanatopentaamminecobalt(III) perchlorate (0.0005–0.0015 *M*), sulfuric acid (0.25 *M*), and cerium(IV) sulfate (8–25 molar excess of cerium) were allowed to react for several weeks at room temperature to ensure complete reaction. The final solutions were treated with hydrogen peroxide to reduce Ce(IV) to Ce^{3+} and passed through anion resin columns (Amberlite IRA-410 in hydroxide form) to remove sulfate and cerium (the cerium(III) hydroxide precipitating on the column). The eluent was slightly acidified with perchloric acid and evaporated to a small volume by warming (60–70°) under reduced pressure. On slow cooling, two solid phases separated out—a powdery amorphous material (A) and a crystalline material (B). These solid phases were separated mechanically and each was recrystallized from perchloric acid. The resultant solids were identified as the cyanopentaammine (A) and the hexaammine (B) cobalt(III) perchlorates on the basis of elemental analyses, infrared spectra, and uv–visible absorption spectra of their aqueous solutions; results for solid A were as follows. *Anal.* Calcd: C, 3.25; H, 4.07; N, 22.77; NH_3, 23.0. Found: C, 3.31; H, 4.08; N, 22.64; NH_3, 22.7. Infrared spectrum: Reported:[5] sharp peak at 2145 cm^{-1} (identified as CN stretch). Found: sharp peak at 2150 cm^{-1}. Uv–visible spectra: absorption maxima and molar absorbancy indices calculated from spectra obtained with a Hitachi recording spectrophotometer are given in Table I.

TABLE I

VISIBLE AND ULTRAVIOLET ABSORPTION MAXIMA

	ν_{max}, cm^{-1}	Log a^d	ν_{max}, cm^{-1}	Log a
$[(H_3N)_5CoCN](ClO_4)_2\cdot 0.5H_2O^a$	22,620	1.69	30,580	1.66
$[CoCN(NH_3)_5]Cl_2^b$	22,725	1.77	30,680	1.82
$Co(NH_3)_5CN^{2+\ c}$	22,700	1.75	30,560	1.72
Reaction products				
Ce(IV) oxidation	22,570	1.74	30,400	1.73
$S_2O_8^{2-}$ oxidation	22,830	(1.75)	30,770	1.72

[a] Sample supplied by J. Espenson, Iowa State University. [b] M. Shibata, M. Mori, and E. Kyuno, *Inorg. Chem.*, **3**, 1573 (1964). [c] H. Siebert, *Z. Anorg. Allgem. Chem.*, **327**, 63 (1964). [d] a is the molar absorbancy index (M^{-1} cm^{-1}).

$S_2O_8^{2-}$–$(H_3N)_5$CoNCS^{2+}.—Oxidation of aqueous isothiocyanatopentaamminecobalt(III) perchlorate (~10^{-4} *M*) with excess sodium peroxodisulfate in acidic solution ($[H^+]$ = 0.1 *M*) produces hexaamminecobalt(III) ion quantitatively. At lower acidities, however, the visible absorption spectrum of the final solution establishes the presence of additional species. Quantitative spectral analyses and cation-exchange studies have been carried out

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(2) K. Schug, M. D. Gilmore, and L. A. Olson, *Inorg. Chem.*, **6**, 2180 (1967).

(3) F. Basolo, W. H. Baddley, amd K. J. Weidenbaum, *J. Am. Chem. Soc.*, **88**, 1576 (1966).

(4) A. J. Sadowski, Doctoral Thesis, Illinois Institute of Technology, 1967.

(5) H. Siebert, *Z. Anorg. Allgem. Chem.*, **327**, 63 (1964).

on the final solutions. A typical experiment is described in detail.

An unbuffered solution (initial pH 4.5) $\sim$0.002 *M* in $(H_3N)_5CoNCS^{2+}$ and $\sim$0.065 *M* in peroxodisulfate was allowed to react at room temperature. Absorption spectra of the yellow solution after 18 and 48 hr were nearly identical and, in the 400–600-mμ region, closely matched that calculated for a mixture containing 50% cyanopentaammine and 50% hexaammine. (Below 400 mμ the observed absorption rises continuously above that calculated.) At 72 hr, one-third of the solution was passed through a cation resin column (Dowex 50 X4, 50–100 mesh, acid form, 1.5 × 20 cm). The yellow band which formed near the top was eluted with 3 *M* $HClO_4$ (which had previously been shown to effect a separation of the cyanopentaammine and hexaammine species). The first 25 ml of eluent (colorless) was discarded; the next 64 ml was collected and the absorption spectrum was obtained. The spectrum coincided with that of cyanopentaamminecobalt(III) ion (except for some increased absorption below 400 mμ) at a concentration about 40% of the total cobalt present. This eluent solution was concentrated by warming to about 60°. After 4 days the reddish black(!) solid (C) which had formed was filtered off and recrystallized from perchloric acid to give a yellow product (D) a portion of which was dissolved in water and scanned (300–600 mμ) on a Beckman DBG spectrophotometer. The similarity of this spectrum to that of an authentic sample of cyanopentaamminecobalt(III) perchlorate is shown by the data in Table I.

Further confirmation of the identity of the product is provided by the infrared spectrum of the yellow solid (D): Reported:[5] sharp peak at 2145 cm^{-1}. Found: sharp peak at 2135 cm^{-1}.

H_2O_2–($(C_2H_5)_4$dien)PdNCS or -SCN.[6]—The product of the oxidation of isothiocyanatotetraethyldiethylenetriaminepalladium(II) ion and its thiocyanate analog with hydrogen peroxide in approximately neutral solution has been identified as the corresponding cyano complex, ($(C_2H_5)_4$dien)$PdCN^+$, on the basis of solution spectra studies. It was also found that the cyano complex formed readily on mixing equimolar quantities of cyanide ion (as the sodium salt) and either of the palladium–thiocyanate linkage isomers described above.

Discussion

The observations reported above leave little doubt that cyano complexes are formed in the oxidation processes studied.

Previous work on the oxidation of free thiocyanate ion has established cyanide ion as a product[7] in several cases. Wilson and Harris, in some careful studies of thiocyanate oxidation by hydrogen peroxide, have shown that HCN is produced nearly quantitatively in acidic solution[8] but that $NH_3 + HCO_3^-$ are formed in neutral solution.[9]

The peroxodisulfate oxidation of captive thiocyanate reported here has the opposite acid dependence, producing $Co(NH_3)_6^{3+}$ in acidic solution and $(H_3N)_5CoCN^{2+}$ in the absence of added acid.

An interesting feature of these reactions is that N-bonded thiocyanate is converted to presumably C-bonded cyanide. For the cobalt cases this is most likely the result of a rapid intramolecular isomerization of the type recently proposed for some similar cyano complexes.[10,11] With the palladium complexes it seems more likely that free cyanide is formed and reenters the coordination sphere in a subsequent substitution step.

Finally it may be suggested that the "oxidative substitution" reaction reported here might be of considerable utility in preparing specific cyano complexes which are presently unknown.

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[6] Previously reported by K. Schug and A. J. Sadowski, Tenth International Conference on Coordination Chemistry, Japan, Sept 1967.

[7] Several examples are given by B. J. Heinrich, M. D. Grimes, and J. E. Puckett, "Treatise on Analytical Chemistry," Vol. 7, I. M. Kolthoff and P. J. Elving, Ed., Interscience Publishers, Inc., New York, N. Y., 1961, Section A, Part II, p 87 ff.

[8] I. R. Wilson and G. M. Harris, *J. Am. Chem. Soc.*, **83**, 286 (1961).

[9] I. R. Wilson and G. M. Harris, *ibid.*, **82**, 4515 (1960).

[10] J. Halpern and S. Nakamura, *ibid.*, **87**, 3002 (1965).

[11] J. Espenson and J. P. Birk, *ibid.*, **87**, 3280 (1965).

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Piperazinobisdiborane and Its Polymeric Consequences[1]

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The chemistry of the aminodiborane type $R_2NB_2H_5$[2] was extended some time ago to include cyclic aminodiboranes of the type $C_nH_{2n}NB_2H_5$.[3] However, attempts to make a double $=NB_2H_5$ from piperazine failed on account of occlusion effects which could not be overcome by using conventional organic solvents. We now confirm that the pyrolysis of $C_4H_8(NH)_2 \cdot BH_3$ (containing some occluded piperazine) leads to polymers which resist strong acids, fail to sublime under high vacuum, and remain solid at 300°. Neither such pyrolysis products nor the original BH_3 adduct could be dissolved in acetone, acetonitrile, triethylamine, methyl chloride, or dichloromethane; and dimethyl sulfoxide or dimethylformamide dissolved them only slightly.

It appeared that the adduct $C_4H_8(NH)_2 \cdot BH_3$ had formed a weakly dipole-bonded polymer in which the second ring-nitrogen atom was protected from attack by more diborane; then heating this adduct in the presence of occluded piperazine would lead to $=N(BH)N=$ patterns serving to connect the $C_4H_8N_2$ rings and so form a strong polymer. Also, the remaining $=NBH_2$ situations would not be chain-terminal because they would dimerize in the manner of $(CH_3)_2NBH_2$.[2]

For a different approach to such polymers, it seemed well to make the new compound $C_4H_8(NB_2H_5)_2$, from which a tertiary base could remove $2BH_3$ to form the $C_4H_8(NBH_2)_2$ unit, just as $(CH_3)_2NBH_2$ is formed from $(CH_3)_2NB_2H_5$.[2] However, this synthesis would re-

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[2] A. B. Burg and C. L. Randolph, Jr., *J. Am. Chem. Soc.*, **73**, 953 (1951), *et ante*.

[3] A. B. Burg and C. D. Good, *J. Inorg. Nucl. Chem.*, **2**, 237 (1956).