the *cis* configuration since vibrations due to coordinated water molecules may appear in the CsBr region.[21] However, in view of the remarkable similarity of the spectra of the copper and *cis*-palladium complexes and the absence of extensive differences in the spectra of the anhydrous platinum chelate and the corresponding monohydrate, it is proposed that the copper complex is *cis*.

(III) The Metal–Nitrogen Bonds.—The N–H stretching frequencies of the coordinated NH_2 groups increase from platinum through copper, which indicates that the covalent character of the metal–nitrogen bonds varies in the order Pt(II) > Pd(II) > Cu(II).[22] This order is supported by a consideration of the relative values for the metal–nitrogen stretching frequencies and masses of the metal ions (and by the approximate bond-stretching force constant values for the platinum and palladium complexes). In addition, the NH_2 rocking frequencies follow the above order, as was the case for glycine and DL-valine chelates.[4,15]

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Synthesis of Nitroammine- and Cyanoamminecobalt(III) Complexes with Potassium Tricarbonatocobaltate(III) as the Starting Material

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Received May 18, 1964

A series of cobalt(III) complexes with the general formula $[Co(NO_2)_n(NH_3)_{6-n}]^{3-n}$ (n = 1–5) was synthesized with a solution of potassium tricarbonatocobaltate(III) as the starting material. The distinctive feature of the method employed in the systematic synthesis is that the amounts of the reagents going into the reactions are stoichiometrically fixed for the products wanted. Of those complexes potassium pentanitroamminecobaltate(III) is to be regarded as a new compound. Two other complexes, cyanopentaamminecobalt(III) chloride and tricyanotriamminecobalt(III), belonging to the cyanoammine series $[Co(CN)_n(NH_3)_{6-n}]^{3-n}$, were also prepared. Very recently the former was prepared by others, but the latter is a new compound. These three complexes were characterized by their absorption spectra in the visible and ultraviolet regions.

Introduction

When cobalt(II) ion is oxidized by hydrogen peroxide in the presence of an alkali bicarbonate, a green coloration occurs. This is known as the "Field–Durant reaction"[2,3] and has been used for cobalt analysis. We attempted to use this reaction for a new synthesis of cobalt(III) complexes; the attempts were first directed to production of the green solution on a preparative scale, and success was attained when potassium bicarbonate was employed instead of the sodium salt which had been used before on an analytical scale. Isolation of the complex as potassium tricarbonatocobaltate trihydrate and synthesis of a carbonatoammine series of cobalt(III) complexes were accomplished.[4] Afterward the method was extended to the synthesis of carbonatoethylenediamine, oxalatoammine, and oxalatoethylenediamine complexes.[5] An important feature of these methods is the successive substitution of carbonate ions by the desired ligands. Furthermore, the green solution of the tricarbonatocobaltate(III) was used for the preparation of some new compounds such as potassium carbonatoammoniatriacetatocobaltate(III),[6] potassium carbonatoethylenediaminediacetatocobaltate(III),[7] and potassium tungstocobaltate(III).[8]

Recently a closely resembling method was reported by Bauer and Drinkard,[9] who used sodium tricarbonatocobaltate(III) trihydrate as the starting material and obtained several new cobalt(III) complexes of easily oxidizable ligands as well as some of the known symmetrical complexes.

In the present paper, systematic preparation of the cobalt(III) complexes containing nitro and ammonia groups as ligands is reported as well as preparation of two other complexes belonging to the cyanoammine series. Most of the former complexes are very familiar substances, but as far as we are aware pentanitromonoamminecobaltate(III), $K_2[Co(NO_2)_5NH_3]$, was never obtained before. The cyanoammine series is much less familiar, and the only known member other than hexacyanocobaltate was pentacyanomonoammine[10] until quite recently. However, the preparation of the complexes $[CoCN(NH_3)_5]X_2$ with X = Cl, Br, NO_3, ClO_4, or $^1/_2SO_4$ has been reported by Siebert.[11]

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(1) Chemistry Department, Ibaraki University, Mito, Japan.

(2) F. Field, *Quart. J. Chem. Soc.*, **14**, 51 (1862).

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(9) H. F. Bauer and W. C. Drinkard, *J. Am. Chem. Soc.*, **82**, 5031 (1960).

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In our preparation, the same complex $[CoCN(NH_3)_5]Cl_2$ and a new complex $[Co(CN)_3(NH_3)_3]$ were obtained.

Experimental

Preparation of the Starting Material.—A cold mixture of an aqueous solution (7 ml.) containing cobalt chloride hexahydrate (7 g., 0.03 mole) and 30% hydrogen peroxide (10 ml.) was added dropwise to an ice-cooled slurry of potassium bicarbonate (23 g., 0.23 mole) in water (20 ml.), and the resulting green solution was quickly filtered. The filtrate was again cooled in an ice bath and used as the starting material. Since the solution is rather unstable, it was prepared anew for each run of the experiments described below and is referred to simply as "the green solution."

Nitropentaamminecobalt(III) Chloride.—Ammonium chloride (15 g., 0.28 mole) and 28% ammonia (20 ml., 0.28 mole) were added to the green solution, and the mixture was heated on a water bath until it assumed the red color of carbonatopentaamminecobalt(III) ion. The insoluble materials were filtered off and sodium nitrite (2.5 g., 0.036 mole) was added to the filtrate, which was then acidified with 6 *N* acetic acid and heated on a water bath until its color became yellow-brown. On standing, the solution gave a crude precipitate of the desired complex, which was purified by recrystallization in the usual way; yield about 9 g.

***cis*-Dinitrotetraamminecobalt(III) Chloride.**—Commercial ammonium carbonate (5 g., 0.03 mole) and 28% ammonia (20 ml., 0.28 mole) were introduced into the green solution, and the mixture was heated on a water bath until it assumed the blood-red color of carbonatotetraamminecobalt(III) ion. Then the solution was filtered and acidified with 6 *N* hydrochloric acid (20 ml.), and sodium nitrite (5 g., 0.07 mole) was gradually added to it. The whole was boiled for a few minutes, filtered, and concentrated. The yellow-brown product was recrystallized from an aqueous solution containing a small amount of acetic acid; yield about 6 g.

The corresponding analog *cis*-dinitrobis(ethylenediamine)cobalt(III) chloride was also synthesized by using 98% ethylenediamine (5 ml.) and sodium nitrite (4.1 g.) in the same procedure as above; yield about 5 g.

***cis-trans*-Trinitrotriamminecobalt(III).**—Ammonium chloride (7 g., 0.13 mole), 28% ammonia (5 ml., 0.07 mole), and sodium nitrite (10 g., 0.15 mole) were added to the green solution, and the mixture was heated on a water bath until its color turned red-brown. After being acidified with 6 *N* acetic acid (15 ml.), the solution was again heated for some time. When the solution was allowed to stand overnight in the cold, massive crystals of the desired complex were obtained with a small amount of the *cis*-dinitro complex as an impurity; yield about 1.5 g.

***trans*-Potassium Tetranitrodiamminecobaltate(III).**—Ammonium chloride (2 g., 0.04 mole) and 28% ammonia (1 ml., 0.014 mole) were added to the green solution, and the mixture was warmed until its color changed to the blue of dicarbonatodiammine cobaltate(III) ion; then it was filtered. Sodium nitrite (8 g., 0.12 mole) was added to the filtrate, which was then acidified with 6 *N* acetic acid. When the resulting solution was allowed to stand, the desired complex was obtained. This is an analog of Erdmann's salt (ammonium salt) and has *trans* configuration about the two ammonia groups; yield about 7 g.

The corresponding analog tetranitro(ethylenediamine)cobaltate(III) was obtained by using 98% ethylenediamine (1.8 ml.) and sodium nitrite (8.1 g.); yield about 6 g.

Potassium Carbonatotrinitroamminecobaltate(III), $K_2[CoCO_3(NO_2)_3NH_3] \cdot H_2O$.—Ammonium chloride (1.6 g., 0.03 mole) and sodium nitrite (10 g., 0.15 mole) were added to the green solution, and the mixture was warmed on a water bath until its color became violet-brown. This was acidified with 6 *N* acetic acid (20 ml.), and the color became orange-brown. It was then filtered and the filtrate was slowly evaporated at temperatures not exceeding 50° until a crust began to appear. On cooling the solution, an orange-brown material separated out, which was dissolved in a minimum amount of water, and the solution was kept in a refrigerator overnight. Massive orange-brown crystals were obtained; yield about 3 g.

Anal. Calcd. for $K_2[CoCO_3(NO_2)_3NH_3] \cdot H_2O$: Co, 15.9; K, 21.1; NH_3, 4.6; NO_2, 37.3. Found: Co, 15.2; K, 21.3; NH_3, 4.8; NO_2, 36.0.

Potassium Pentanitroamminecobaltate(III), $K_2[Co(NO_2)_5NH_3]$.—This was obtained, almost quantitatively, as golden yellow crystals by evaporating an aqueous solution containing equivalent amounts of the carbonatotrinitro complex obtained above and potassium nitrite and a small amount of acetic acid.

Anal. Calcd. for $K_2[Co(NO_2)_5NH_3]$: Co, 15.3; K, 20.3; NO_2, 60.0. Found: Co, 15.1; K, 21.0; NO_2, 60.7.

Cyanopentaamminecobalt(III) Chloride, $[CoCN(NH_3)_5]Cl_2$.—Potassium cyanide (6 g., 0.09 mole) was added to the green solution with constant stirring, whereupon the solution became red-violet in color. Ammonium chloride (10 g., 0.19 mole) and 28% ammonia (20 ml., 0.28 mole) were added to it, and the mixture was kept at 80–90° for about 10 min. Activated charcoal (1 g.) was added to the resulting red solution, and the whole was kept at temperatures close to but not exceeding 60° for about 2 hr. It was then filtered, and the filtrate was concentrated under reduced pressure until a red-yellow precipitate began to appear. The crystals obtained on cooling the solution were recrystallized from water; yield 4 g.

The complex was tolerably stable against alkali hydroxides but was decomposed by concentrated sulfuric acid.

Anal. Calcd. for $[CoCN(NH_3)_5]Cl_2$: Co, 24.5; NH_3, 35.3; N, 34.9. Found: Co, 24.1; NH_3, 35.1; N, 34.2.

The equivalent weight was determined by means of a cation exchanger. From the value the formula weight was estimated as 240.7 against the calculated 240.87.

Tricyanotriamminecobalt(III), $[Co(CN)_3(NH_3)_3]$.—Potassium cyanide (8 g., 0.12 mole) was added to the green solution, and the mixture was stirred for a short time, whereupon its color became red-violet. Then ammonium chloride (6.5 g., 0.12 mole) and 28% ammonia (20 ml., 0.28 mole) were added to it; the mixture was heated on a water bath for a few minutes, and then activated charcoal (1 g.) was introduced into it. The bath was kept boiling for about 2 hr., and then the solution was filtered. The yellow-brown filtrate was evaporated under reduced pressure until yellow crystals began to appear. By recrystallization from water, fine yellow crystals were obtained; yield 1 g.

The solubility of this complex was low, and the aqueous solution was found very stable against alkali hydroxides. Concentrated sulfuric acid decomposed the complex.

Anal. Calcd. for $[Co(CN)_3(NH_3)_3]$: Co, 31.4; NH_3, 27.1; N, 44.7. Found: Co, 29.5; NH_3, 25.9; N, 44.2.

The known complexes in the nitroammine series were identified by the absorption spectra in the visible and ultraviolet regions. For the complexes $K_2[Co(NO_2)_5NH_3]$, $[CoCN(NH_3)_5]Cl_2$, and $[Co(CN)_3(NH_3)_3]$ the absorption spectra were measured in order to characterize the complexes.

Results and Discussion

Absorption Spectra.—The absorption maxima of carbonatotrinitroamminecobaltate(III), pentanitroamminecobaltate(III), and tetranitrodiamminecobaltate(III) are given in Table I, and the absorption curves for the first two of these compounds are shown in Fig. 1.

TABLE I

ABSORPTION MAXIMA ν (CM.$^{-1}$) AND MOLAR EXTINCTION ϵ (L. MOLE^{-1} CM.$^{-1}$)

	ν	log ϵ	ν	log ϵ	ν	log ϵ
$K_2[CoCO_3(NO_2)_3NH_3]\ H_2O$	21,185	2.34	28,820	3.87	38,610	4.41
$K_2[Co(NO_2)_5NH_3]$	...		28,410	3.91	38,910	4.27
trans-$K[Co(NO_2)_4(NH_3)_2]$	...		28,735	4.03	39,370	4.39

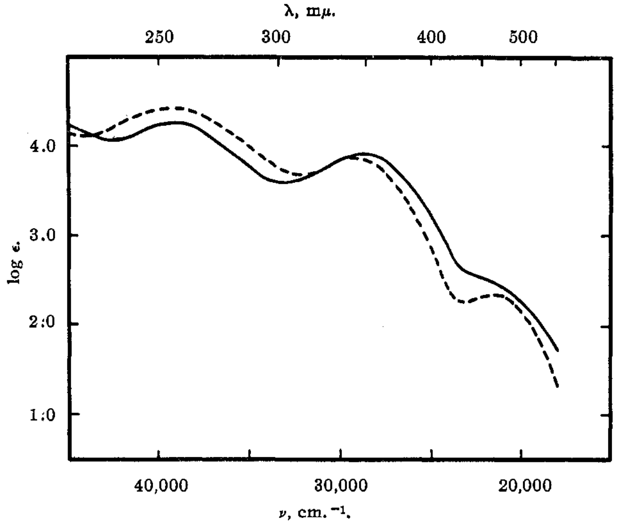

Fig. 1.—Absorption curves of: ———, $K_2[Co(NO_2)_5NH_3]$; - - - - -, $K_2[CoCO_3(NO_2)_3NH_3]\cdot H_2O$.

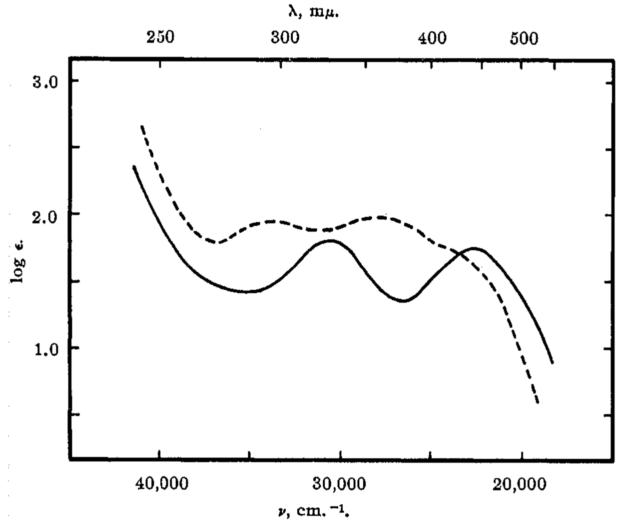

Fig. 2.—Absorption curves of: ———, $[CoCN(NH_3)_5]Cl_2$; - - - - -, $[Co(CN)_3(NH_3)_3]$.

The carbonatotrinitro complex has a well-defined maximum in the visible region, but the pentanitro complex, as well as tetranitrodiamminecobaltate(III), has only a shoulder in the region without showing a maximum. On the other hand, the absorption curves of all three compounds in the ultraviolet region are similar to one another.

When a solution of carbonatotrinitroamminecobaltate(III) in concentrated ammonia was acidified with glacial acetic acid and then kept in a refrigerator, *cis-trans*-trinitrotriammine cobalt(III) crystallized out as a result of substitution of carbonate ion by ammonia groups. This suggests the configuration of the complex is in the *cis-trans* form about the three nitrite ions.

The absorption maxima of cyanopentaammine- and tricyanotriamminecobalt(III), hexacyanocobaltate(III), and hexaamminecobalt(III) are given in Table II and the data for the complex reported by Siebert[11] are also included in the table. The absorption curves for the newly synthesized compounds are shown in Fig. 2. The absorption maxima are displaced to higher frequencies, *i.e.*, shorter wave lengths, with the increase in the number of cyanide ions coordinated. This is easily understandable from the fact that cyanide ion ranks highest in the spectrochemical series, being one of the strongest crystal field ligands. The figure shows that the band in the near-ultraviolet region for tricyanotriamminecobalt(III) is split into two components. From this fact, this complex may be regarded as of the *cis-trans* form. The spectrum for the complex $[CoCN(NH_3)_5]^{2+}$ prepared by us is good agreement with that reported by Siebert.

TABLE II

ABSORPTION MAXIMA ν (CM.$^{-1}$) AND MOLAR EXTINCTION ϵ (L. MOLE.$^{-1}$ CM.$^{-1}$)

	ν	log ϵ	ν	log ϵ
$K_3[Co(CN)_6]$	32,050	2.22	38,760	2.06
$[Co(CN)_3(NH_3)_3]$	*ca.* 23,365	1.70	34,010	1.95
	27,700	1.97		
$[CoCN(NH_3)_5]Cl_2$	22,725	1.77	30,680	1.82
$[CoCN(NH_3)_5](ClO_4)_2$[11]	22,700	1.75	30,560	1.72
$[Co(NH_3)_6]Cl_3$	21,005	1.70	29,410	1.60

The results of chemical analysis and spectroscopic measurement seem to justify the chemical formulas given in the Experimental section for the newly synthesized complexes. The result of analysis of tricyanotriamminecobalt(III), which gave somewhat lower figures than the calculated, may be explained by the difficulty of decomposing the compound.

On the Synthesis.—As described in the Experimental section, a series of cobalt(III) complexes represented by the general formula $[Co(NO_2)_n(NH_3)_{6-n}]$ (n = 1–5) has been synthesized with potassium tricarbonatocobaltate(III) as the starting material. Excepting for the unknown *cis*-tetranitrodiamminecobaltate(III), the only members that could not be prepared in this way were *trans*-dinitrotetraammine- and *cis-cis*-trinitrotriamminecobalt(III). The essential feature of this method is that the amounts of the reagents to be added are prescribed according to the complexes desired. In particular, the amount of sodium nitrite is almost stoichiometric.

The attempt by Block to prepare some of the cyanoammine complexes by the reaction between hexaamminecobalt(III) and a cyanide did not prove successful, but led to the formation of insoluble hexaamminecobalt(III) hexacyanocobaltate(III).[12] In the early stages of our work, partial substitution of the carbonate ions in the complexes $[Co(CO_3)_2(NH_3)_2]^-$ and $[CoCO_3(NH_3)_4]^+$ by the cyanide ion was tried and led to the formation of hexacyanocobaltate(III) alone. Our attempts for partial displacement of the cyanide ion in hexacyanocobaltate(III) with the ammonia group also proved unsuccessful. These facts seemed to indicate that a coordinated ammonia group could be easily replaced with a cyanide ion, but a cyanide ion once complexed could not be replaced with ammonia. Accordingly we adopted the method of first letting a suitable amount of

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[12] B. P. Block, *J. Inorg. Nucl. Chem.*, **14**, 294 (1960).

potassium cyanide react with the tricarbonatocobaltate(III) and then letting ammonium chloride and ammonia react with the product in the presence of activated charcoal. The main difference between the procedure for synthesizing the monocyano complex and that for the tricyano complex is in the amounts of potassium cyanide and ammonium chloride used. These amounts are exactly the factors that decide the end products. The amount of activated charcoal is also important; if it is too small the final product will be a red sirup, and if too large, potassium hexacyanocobaltate(III) will result.

Very recently, potassium pentanitroamminecobaltate(III) was used for the infrared study of the nitroammine series by Nakagawa and Shimanouchi.[13] The tricyanotriamminecobalt(III) was also investigated by Tanaka, Sugi, and Fujita,[14] and they assigned the *cis-trans* form to the complex.

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The Kinetics of Exchange of Thiocyanate between Tetrathiocyanatonickelate(II) and Free Thiocyanate Ion in Aqueous Solution[1]

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Received May 21, 1964

Rate data are reported for the exchange of NCS^- with an assumed $Ni(NCS)_4(H_2O)_2{}^{2-}$ species in aqueous solution. For the rate law $R = 4k_1[Ni(NCS)_4(H_2O)_2{}^{2-}]$, k_1 is $6.9 \pm 0.3 \times 10^5$ sec.$^{-1}$ at 25°, $\Delta H^* = 8.6 \pm 0.7$ kcal./mole, and $\Delta S^* = -5 \pm 3$ e.u. A shift of the N^{14} resonance in NCS^- was observed and gave a scalar coupling constant, A/h, of 2.27×10^7 c.p.s. The effect of thiocyanate concentration, pH, and cation on the rate was studied and the rate of exchange of water was determined through the O^{17} resonance. Possible mechanisms are discussed and it is concluded that a dissociation type mechanism is the most plausible.

Introduction

Measurement of the rates of exchange of ligands in labile complexes is of considerable importance in assessing the role of electronic structure of metal ions in the kinetic behavior of complexes. Several methods are currently being employed in the study of rapid reactions, among them being the use of n.m.r. line-broadening effects.[3,4] We have begun a study of NCS^- complexes and report results on the $Ni(NCS)_4{}^{2-}$–NCS^- exchange reaction in aqueous solution. These results are compared with studies on other Ni(II) complexes using various experimental techniques.

Experimental

The n.m.r. spectrometer used employed a variable, regulated magnetic field of *ca.* 9300 gauss, a Pound–Knight–Watkins marginal oscillator, and a phase-sensitive detector. Square wave field modulation at 30 c./sec. was used rather than the more usual sine wave type. The N^{14} n.m.r. absorption signal was observed on a recorder at *ca.* 2.85 Mc./sec. by sweeping the magnetic field. The observed recorder trace consisted of two identical Lorentzian absorption curves, one inverted with respect to the other and overlapping the first on the field axis. Calibration of the recorder chart in terms of gauss/cm. was effected using the known separations of the N^{14} n.m.r. lines in NH_4NO_3 (347 p.p.m.). The significant information to be obtained from the recorded absorption lines is the line width at half-maximum height (W'). Several factors must be taken into account in order to obtain the correct values for W'. First, the radiofrequency power level must be kept low enough to avoid saturation phenomena. Curves were run as a function of the power level to enable determination of the point at which saturation effects become important. Runs were then made at levels below this point. Second, the modulation frequency and amplitude must be properly chosen to avoid artificial line broadening. The 30 c./sec. frequency used causes no significant error in our results. The modulation amplitude effects were studied, and it was found that large amplitudes caused eddy currents in the magnet pole pieces. Amplitudes used were kept below these levels. Third, because of the overlapping nature of the observed curves (at the modulation amplitudes used) it was necessary to correct the observed heights and widths of such curves. These corrections were obtained graphically by constructing true Lorentzian curves and by measuring the distortion caused by their overlapping. Fourth, field inhomogeneities cause artificial broadening. In our experiments this broadening amounted to *ca.* 0.15 gauss, a value relatively small compared to the line widths of interest. It was assumed that this error would effectively cancel when differences in widths were taken. The over-all precision in the W' measurements was found to be *ca.* ±10%. Samples were run in 12-mm. Pyrex test tubes using a constant volume of solution which just filled the oscillator coil. Sample temperatures were controlled to ±0.5° using a thermostated N_2 gas flow system. Measurements of temperature were made using a glass-protected thermocouple placed directly in the solution.

Solutions were prepared from distilled water. The thiocyanate salts were analytical reagent grade. Thiocyanate concentration was determined by silver titration. Some experiments were done using $K_4Ni(NCS)_6 \cdot 4H_2O$ prepared using the method of

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(1) This work supported in part by U.S.A.E.C. Contract AT(45-1)-1031.

(2) To whom inquiries may be addressed.

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