

square-pyramidal five-coordinate structured Co(III) complexes. The crystal structure is in agreement with the chemical studies⁸ and would predict as is observed a difference in thermodynamic and kinetic stability of the two nitro groups in this compound.

Registry No. [Co(PnAO-H)(NO₂)₂], 41444-82-0.

Supplementary Material Available. A listing of structure factor

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Kinetic and Thermodynamic Studies on a Labile *trans*-Dinitrocobalt(III) Complex

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Received February 28, 1973

Cobalt(III) complexes of an α -amine oxime *trans*-[Co(PnAO-H)X₂]⁰ have been prepared where X is one of the following ligands: NO₂⁻, N₃⁻, Cl⁻, or OH₂. The *trans* ligands are relatively labile to substitution even in nearly neutral aqueous media. Replacement of a coordinated NO₂⁻ group by N₃⁻ or the reverse follows the path Co-NO₂ ⇌ Co-OH₂ ⇌ Co-N₃. The forward rate is controlled by the replacement of NO₂⁻ by H₂O which follows the rate law rate = k [Co-NO₂] + k' [Co-NO₂][OH⁻]. The same law and constants are obtained for the ¹⁵NO₂⁻ exchange with the *trans*-dinitro complex. Equilibrium constants are reported for NO₂⁻-N₃⁻ competition for the *trans* coordination positions and for NO₂⁻, Cl⁻, and N₃⁻ competition with H₂O. Using isotopic rates of exchange studies it is shown that in the *trans* complexes (dinitro, diazido, dichloro), the axial ligands are not equivalent and substitute with rates differing by factors of 15–50. Isotopic NO₂⁻ exchange rate studies on other more common *trans*-dinitro complexes are compared in an effort to distinguish between steric and electronic effects as the cause of the nonequivalence of the axial ligands. The solution results are compared with the crystal structure of [Co(PnAO-H)(NO₂)₂]⁰ concurrently presented.¹

Introduction

The presence of a tetradentate ligand occupying equatorial positions around a cobalt(III) ion has been known to give remarkable properties to the ligands in the apical positions.^{2–4} These complexes have been suggested as model systems for the vitamin B₁₂ compounds and considerable effort has been expended (using two hydrogen-bonded dimethylglyoxime ligands) to understand the unusual bonding factors involved.^{5,6} The existence of hydride ion and alkyl complexes⁷ points up the unusual bonding factors, and in a few cases the excessive lability of an axial ligand has been noted. It appeared that quantitative kinetic studies were needed to help decipher the underlying factors involved in these systems. The properties of the dimethylglyoxime complexes do not lend themselves to precise kinetic studies since they are difficult to prepare and maintain pure, have rather nonspecific absorption spectra in the useful visible region, and often have marginal solubility characteristics. Certain substituted ethylenediamines and α -amine oximes tend toward planar coordination⁸ and give cobalt(III) complexes with more suitable properties.⁹ The ligand selected for the majority of this work, PnAO,¹⁰ is tetradentate and forms an intramolecular hydrogen bond of

the highest stability thus becoming a closed multicyclic ligand. The original purpose was to measure, by isotopic ligand exchange, the magnitude of the steric factor which nmr and X-ray studies had shown to exist^{2,11} which would lead to the nonequivalence of structurally identical ligands in the axial positions.

Early in the studies it became apparent that the behavior of the *trans*-[Co(PnAO-H)X₂]⁰ compounds¹² (Figure 1) was abnormal when compared to the analogous NH₃, en, or, to a lesser extent, DMG complexes, the major differences being that "strong ligands" such as NO₂⁻, SCN⁻, and N₃⁻ could be easily and quickly replaced under mild conditions and that the rates of replacement of identical *trans* groups were drastically different. Following these observations, the scope of the investigation was extended to include preparation studies, equilibrium studies, kinetics of aquation, anation, and isotopic ligand-exchange studies, and, reported in a concurrently submitted paper, an X-ray structural study of one compound, *trans*-[Co(PnAO-H)(NO₂)₂]⁰.¹

Experimental Section

The ligand PnAO was prepared as previously described¹⁰ and gave equivalent C, H, and N analyses. The starting complex (Table I) [Co(PnAO-H)Cl₂]⁰ was prepared using several oxidants. The best procedure was with PbO₂.

[Co(PnAO-H)Cl₂]⁰. A 16.3-g (0.06-mol) sample of PnAO and 14.3 g (0.06 mol) of CoCl₂·6H₂O were dissolved in 250 ml of water and NaOH(s) was added until the pH was 6.3. With rapid stirring ten 1-g portions of PbO₂ were added over equally spaced periods, totaling 10 hr. Concentrated HCl was added at intervals to keep the

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Table I. Analysis of Compounds

Compd	% C		% H		% N		% halogen		Equiv wt ^a	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
[Co(PnAO-H)(NO ₂) ₂] ⁰	37.15	37.28	6.42	6.39	20.00	19.81				
[Co(PnAO-H)(N ₃) ₂] ⁰	37.86	37.97	6.55	6.42	33.98	33.75				
[Co(PnAO-H)(NO ₂)N ₃] ⁰	37.59	37.46	6.50	6.74	26.99	27.29				
[Co(PnAO-H)(NO ₂)OH ₂] ⁰ ClO ₄	31.66	31.51	5.88	5.78	14.21	14.22	7.20	7.33	493.8	492.8
[Co(PnAO-H)Cl ₂] ⁰	38.92		7.03		13.97	13.85	17.67	17.69		
[Co(PnAO-H)Br ₂] ⁰	31.85		5.76		11.43	11.36	32.60	32.55		
[Co(PnAO-H)I ₂] ⁰	26.73	26.58	4.83	4.91	9.59	9.70	43.45	43.70		
[Co(tetraMeen) ₂ (NO ₂) ₂] ⁰ ClO ₄	29.85	29.77	6.68	6.53	8.41	8.23	7.34	7.28	482.8	483.5
NH ₄ [Co(DMG-2H)(NO ₂) ₂]	25.21	25.18	3.67	3.44	25.73	25.54				

^a Determined by absorption on an ion-exchange resin in the H⁺ form and titrating the acid released.

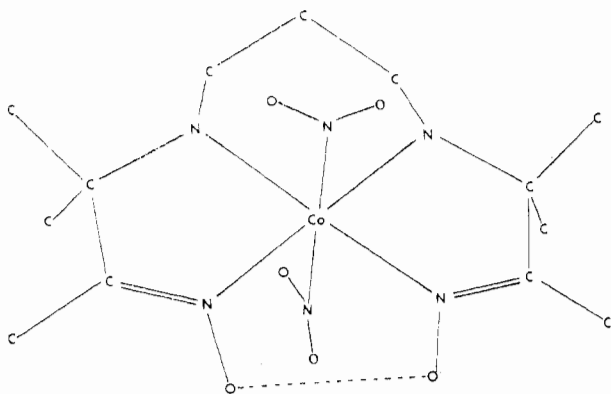


Figure 1. Structure of [Co(PnAO-H)(NO₂)₂]⁰.

pH between 8.0 and 8.3. Evaporation, followed by the addition of 5 ml of concentrated HCl, gave a green crystalline product. It was collected, washed with dilute HCl, and dried under vacuum; yield 15.8 g. Recrystallization was accomplished by dissolving in a small amount of concentrated HCl at 0°, removing suspended particles on a filter, and diluting to 10 times its volume with ice water, whereupon the pure product crystallized.

[Co(PnAO-H)(NO₂)₂]⁰, [Co(PnAO-H)(N₃)₂]⁰, [Co(PnAO-H)(SCN)₂]⁰, and [Co(PnAO-H)(CN)₂]⁰. In each case 1 g of [Co(PnAO-H)Cl₂]⁰ was added to 50 ml of water and dilute KOH solution was added with stirring until complete solution was obtained. About 1 g of KNO₂, KSCN, or KCN was added and immediately thereafter dilute HCl solution was added to a pH of about 5. The solution was warmed to 50° for about 30 min during which time the product crystallized from solution (except with CN⁻); yield 65–85% of theory. The CN⁻ complex was extremely soluble in water and evaporation under vacuum was necessary. The products were recrystallized from either water or methanol and dried under vacuum at room temperature.

[Co(PnAO-H)(OH₂)₂](ClO₄)₂. About 5 g of [Co(PnAO-H)Cl₂]⁰ was added to 100 ml of water and a slight excess of AgClO₄(s) was added with stirring. Dilute HCl was added until the equivalence point for AgCl precipitation. The filtered solution was evaporated to dryness under vacuum at 20 ± 5° and the green solid was dissolved in the minimum amount of acetone. Addition of anhydrous ether precipitated the complex which was redissolved in the minimum amount of water at 35° and recrystallized by the addition of a filtered NaClO₄ solution. The olive green crystals were collected, washed with ether, and dried under vacuum at 50°; yield 70% of theory.

[Co(PnAO-H)(NO₂)Cl]. To 200 ml of a saturated water solution of [Co(PnAO-H)(NO₂)₂]⁰ at 100° was added 1 g of NH₄Cl. After 1 hr at 100° NH₄Cl(s) was gradually added to the hot solution until it was almost saturated. Thereupon a dark red-brown solid was slowly deposited which was collected, washed with water at 0°, and dried under vacuum at room temperature; yield 50–60% of theory. It was recrystallized from water containing NH₄Cl.

[Co(PnAO-H)(NO₂)(OH₂)ClO₄]. To 1.0 g of [Co(PnAO-H)(NO₂)Cl]⁰ dissolved in 100 ml of warm water, a slight excess of AgNO₃ solution was added. After sufficient time had elapsed at 40° for all the AgCl to form, dilute NaCl was added until no large excess of Ag⁺ or Cl⁻ remained. AgCl was removed and the solution was evaporated under vacuum. At 25 ml, a good crop of crystals was collected. The product was recrystallized, once with a large excess of NaClO₄ and once by cooling a concentrated water solution. The yield before final crystallization was 90% and after final purification, 22% of theory. The water of hydration was removed under vacuum at 50°.

[Co(PnAO-H)(NO₂)(N₃)]⁰. Three methods were tried: (a) [Co(PnAO-H)(NO₂)₂]⁰ + N₃⁻, (b) [Co(PnAO-H)Cl₂]⁰ + NO₂⁻ + N₃⁻, (c) [Co(PnAO-H)(NO₂)₂]⁰ + [Co(PnAO-H)(N₃)₂]⁰ (all equimolar amounts). The final product was the same, as judged by ir spectra. In each case the substances were brought together in a large volume of water, allowed to equilibrate for several days, and evaporated to near dryness below 15° under vacuum. The clear red-brown solution deposited crystals over a period of 1 day, which were homogeneous under the microscope; yield about 80%.

It should be pointed out that there are potentially two complexes of the type [Co(PnAO-H)(X)Y]⁰ since, as will be shown, the trans positions are not equivalent. Although various attempts were made to show the presence of an isomer pair, no evidence was found.

NH₄[Co(DMG-2H)(NO₂)₂]¹³ *trans*-[Co(en)₂(NO₂)₂]¹⁴ and [Co(AO)₂(H)(NO₂)₂]¹⁵ were prepared by previously described methods while [Co(tetraMeen)₂(NO₂)₂]¹⁶ClO₄ was prepared by the air oxidation of mixtures of Co²⁺, tetraMeen, and NO₂⁻ in the correct stoichiometric ratios at pH 8–9. After neutralization, the complex was removed from solution by the common ion method and recrystallized three times from water. In all but the latter complex, the trans configuration has been established. No conclusive information about the configuration of [Co(tetraMeen)₂(NO₂)₂]¹⁶ is available. However, it is almost certainly the thermodynamically favored trans isomer, since it shows only one type of -NO₂ ir stretching frequency and has the expected simple proton nmr spectra.

[Co(PnAO-H)Br₂]⁰ and [Co(PnAO-H)I₂]⁰ were prepared from the diaquo complex by the addition of excess KBr or KI followed by extraction into CHCl₃. Evaporation of the CHCl₃ solutions followed by a rapid crystallization from water gave the pure complexes.

All common reagents were of Analytical reagent grade. 2,6-Lutidine and CHCl₃ were redistilled two times. Commercial sodium azide was found to be highly impure and was recrystallized two times from MeOH-water solutions and vacuum dried. ¹⁸O-enriched water was redistilled from alkaline KMnO₄ and then alone and was normalized in deuterium.

All other water was purified with ion-exchange resins and then distilled from acid Cr₂O₇²⁻ and from alkaline MnO₄⁻.

Analytical Work. The C, H, N, and Cl analyses were conducted by Galbraith Laboratories. Equivalent weight determinations were carried out by replacing H_{aq}⁺ from an ion-exchange resin with the complex ion and titrating it with standard base (Table I).

Physical Measurements. Absorption spectra were taken on either a Beckman DU or a Cary 12 spectrometer at constant temperature and standardized with Hg spectral lines. Spectral measurements for rate runs were carried out at constant temperature (±0.05°) with a Beckman DU or B spectrometer: the latter was specially stabilized and attached to a recorder for faster reactions.

A Nuclide RMS-16 mass spectrometer was used for ¹⁸O and ¹⁵N analysis. It has been shown to be linear in the region used and is able to measure to ±0.05% for normal abundances. All values listed have been normalized to 0.00400 for normal CO₂. Radioactivity measurements were made on a Technical Associates DS-5B instrument equipped with a 2-in. flow counter (having a 100-μg/cm² window) working in the proportional region. Infrared spectra were made on a Perkin-Elmer Model 237B spectrometer using Nujol mulls and nmr studies were carried out on a Varian A-60 instrument at 30°.

Equilibrium Measurements. For many of the equilibrium and

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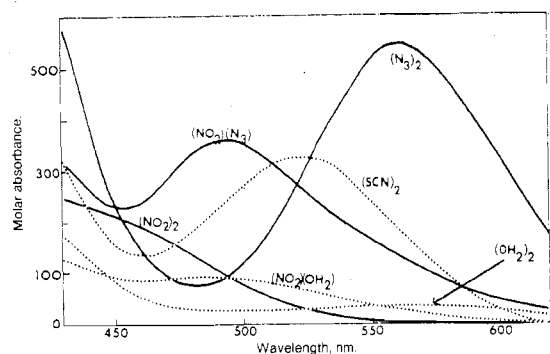
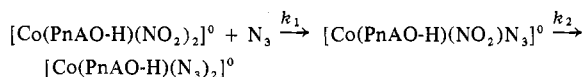


Figure 2. Molar absorbancies for complexes RX_2 , at 25° in H_2O .

kinetic studies, molar absorbancies for the complex ions were needed. These were measured in water solution (25°) and, where needed, contained an excess of the particular negative ion common to that coordinated. With $[Co(PnAO-H)(NO_2)_2N_3]^\circ$ two methods were used. (A) Rapid spectral measurements were made on a solution of the single crystals obtained from an equilibrated solution of 1–2 molar amounts of $[Co(PnAO-H)(NO_2)_2]^\circ$ and NaN_3 or 1–2 molar amounts of $[Co(PnAO-H)(N_3)_2]^\circ$ and $NaNO_2$. Both gave the same spectra. (B) Measurements were taken from the least-squares analysis of the rate of the reaction



using the molar absorbancy of the first product and k_1 as unknowns. For each rate run at a particular wavelength a molar absorbancy at that wavelength was obtained. The results of method B were in qualitative (10%) agreement with those of method A but method B was not as accurate or precise. Thus the values from method A were used. Figure 2 shows the absorbance spectra of several of the $[Co(PnAO-H)X_2]^{n+16}$ complexes.

a. $RX_2^\circ \xrightleftharpoons{K_{eq}} RXOH_2^+ + X^-$. Both the dinitro and the diazido hydrolysis equilibria were measured by three methods: conductivity, spectroscopy, and ion-exchange separation. Aqueous solutions of the complex were equilibrated at 25° and the equilibrium constants were evaluated using measured and estimated ion conductivities or measured absorbancies. Correction was made for the known acid ionization of the aquo complex produced in the conductivity method. In the ion-exchange method the charged aquo complex was adsorbed on a resin and the neutral complex was collected. The adsorbed complex was eluted and converted to the neutral complex and both concentrations were measured spectrally. When K_{eq} was measured in a salt-containing solution, only the spectral or ion-exchange methods could be used.

b. $RXOH_2^+ \rightleftharpoons RXOH^\circ + H_{aq}^+$. The acid dissociation constants were evaluated from the middle 80% of pH titration curves of the aquo complex. In a N_2 atmosphere the titrations were normal for the loss of one H_{aq}^+ , reversibly over the period used (5–10 min), and the constants obtained over the range showed no significant trends. Titration curves constructed from separately prepared solutions, where the time of contact after the addition of base was about 1 min, gave the same K_{eq} values.

c. $R(NO_2)_2^\circ + R(N_3)_2^\circ \xrightleftharpoons{K_{eq}} 2R(NO_2)N_3^\circ$. The equilibrium constant for this reaction was evaluated spectrophotometrically starting with $R(NO_2)_2^\circ + N_3^-$ or $R(N_3)_2^\circ + NO_2^-$. Since there are considerable differences in absorbance spectra, the concentrations of all species could be accurately obtained by measurements at three wavelengths. The same values for K_{eq} were obtained starting with either the diazido or the dinitro complex ion and an excess of coordinating anion.

d. $R(OH_2)_2^{2+} + Cl^- \xrightleftharpoons{K_1} R(OH_2)Cl^+ + H_2O$; $R(OH_2)Cl^+ + Cl^- \xrightleftharpoons{K_2} R(Cl_2)^\circ + H_2O$. Three systems were studied: Cl^- , Br^- , and I^- . Advantage was taken of the fact that $R(Cl_2)^\circ$, $R(Br_2)^\circ$, and $R(I_2)^\circ$ (see exception later) are highly soluble in $CHCl_3$ and distribute themselves between the water and $CHCl_3$ layers. Thus using a measured distribution coefficient and the distribution of complex between the

H_2O and $CHCl_3$ solvents as a function of $[X^-]$ both K_1 and K_2 could be graphically evaluated. The concentration of RX_2 was determined spectrophotometrically in the $CHCl_3$ layer after a 15–20-hr equilibration period. In the Cl^- and Br^- systems these results were checked potentiometrically using an $AgCl$ or $AgBr$ electrode but the precision was not comparable to the distribution method. Within the expected error, however, the two methods agreed. With I^- , abnormal distribution behavior was noted due to two forms of the complex ion being extracted into the organic phase, the most reasonable interpretation being that the ion pair $(R(I)(H_2O))^+I^-$ is extracted in addition to R_1I . The latter molecule was formed only under conditions of low water and high I^- concentration. Spectral evidence was found for the existence of two forms of the complex in the $CHCl_3$ layer.

Assuming the equilibria above (K_1 and K_2) and a constant distribution coefficient defined by $K_d = [RX_2]_{org}/[RX_2]_{aq}$ for equal volumes of the two phases it can be shown that in the aqueous phase

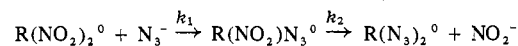
$$[X^-] = \frac{[R(H_2O)X^+] + [R(H_2O)_2^{2+}]}{[RX_2]} K_2 [X^-]^2 - \frac{1}{K_1}$$

$[RX_2]$ can be determined from K_d and the measured $[RX_2]_{org}$, the sum $[R(H_2O)X^+] + [R(H_2O)_2^{2+}]$ can be found from mass balance, and $[X^-]$ is essentially that added with a small correction for the amount of $[RX_2]$ and $[R(OH_2)X^+]$. Thus the data may be graphed in the form of a linear equation and K_1 and K_2 evaluated.

Kinetic Measurements. Rates of substitution at constant temperature of $[Co(PnAO-H)X_2]$ were studied in spectrophotometrically since, in most cases, large spectral differences between reactant and product existed. The reacting anion was in large excess resulting in pseudo-first-order kinetics. The pH was held constant using 2,6-lutidine- $HClO_4$ buffers (a noncomplexing base; useful range pH 5.8–8.0) and constant ionic strength was maintained with recrystallized $NaClO_4$. Graphs of $\ln(1-F)$, F = fraction reacted, vs. time were linear over 3–4 half-times and the rate constant was evaluated by computer using a linear least-squares treatment with each observation weighted according to a constant error estimated to be 0.002 absorbance unit.

The $R(NO_2)_2^\circ + N_3^- \rightarrow R(NO_2)N_3^\circ + NO_2^-$ (k_1) reaction was followed at 518 nm where the ϵ values for $R(NO_2)N_3^\circ$ and $R(N_3)_2^\circ$ are identical. [It should be noted at this point that precise first-order graphs were obtained at 560 nm (maximum for $R(N_3)_2^\circ$) with k_{obsd} about one-tenth as large. This is due to a fortuitous set of values for k_1 , k_2 , and the molar absorbancies.] The buffer-salt solutions were brought to temperature in an absorption cell and small volumes of concentrated, freshly prepared solutions of the complex in either acetone or DMSO were injected to initiate the reaction.

The $R(NO_2)N_3^\circ + N_3^- \rightarrow R(N_3)_2^\circ + NO_2^-$ (k_2) reaction was followed in two ways. (a) This first was the direct measurement of the loss of $R(NO_2)N_3^\circ$ at 496 nm (where $R(NO_2)_2^\circ$ and $R(N_3)_2^\circ$ have equimolar absorbancies). $R(NO_2)N_3^\circ$ was prepared as a crystalline solid and dissolved quickly in DMSO before injection in the reaction media. (b) The second method was an indirect mathematical evaluation of the absorbance changes which occur during the consecutive reactions



For consecutive first-order reactions where k_1 is known it can be shown that

$$Abs = (\epsilon_a - \epsilon_c)A_0 e^{-k_1 t} + (\epsilon_b - \epsilon_c)[A_0 k_1 / (k_2 - k_1)] e^{-k_1 t} - e^{-k_2 t} + \epsilon_c A_0$$

where ϵ is the molar absorbancy of $a = R(NO_2)_2^\circ$, $b = R(NO_2)N_3^\circ$, and $c = R(N_3)_2^\circ$ and A_0 is the initial complex concentration. A nonlinear least-squares program was given absorbance vs. time data, values for k_1 , ϵ_a , and ϵ_c and the best values of ϵ_b and k_2 were calculated. The values of k_2 obtained at several different wavelengths, 475, 500, and 560 nm, agreed within themselves and the molar absorbancies were in fair agreement with that of an independently prepared complex.

The studies on the reactions $R(NO_2)(OH_2)^+ + X^- \rightarrow R(NO_2)X^\circ + H_2O$ (k) where $X^- = NO_2^-$ or N_3^- were carried out by adding a freshly prepared concentrated water solution of $[R(NO_2)(OH_2)]ClO_4$ to a prethermostated absorption cell containing appropriate salts and buffers. The absorption change was measured at 450 nm (NO_2^-) and 518 nm (N_3^-) as a function of time. Linear first-order graphs were obtained from which the observed rate constant was evaluated either from graphs or by least-squares analysis.

(16) The abbreviation RX_2^{n+} will usually be used for this type of complex ion.

Isotopic Exchange and Transfer Experiments. Rates of isotopic exchange of X^- in $[\text{Co}(\text{PnAO-H})\text{X}_2]^0$ were studied for four types of complexes: $X = \text{NO}_2^-, \text{N}_3^-, \text{OH}_2^-$, and Cl^- . With NO_2^- and N_3^- the stable ^{15}N isotope was used. $^{15}\text{NO}_2^-$ and $^{15}\text{N}_3^-$ were prepared from $\text{Na}^{15}\text{NO}_3$ and the enriched complexes were prepared from them by the usual methods. Oxygen-18-enriched $[\text{R}(\text{NO}_2)(\text{OH}_2)]^+$ and $[\text{R}(\text{OH}_2)_2]^{2+}$ was prepared by equilibration with about eight times ^{18}O -enriched water for 48 hr at room temperature. They were crystallized with the aid of NaClO_4 and dried at 50° under vacuum. RCl_2^0 containing ^{36}Cl was prepared by equilibration of RCl_2^0 with H^*Cl followed by crystallization from methanol.

Analysis of NO_2^- and N_3^- and their complexes for ^{14}N was carried out by reaction with normal N_3^- and NO_2^- , respectively, at a pH of about 2.8 giving N_2 and N_2O . The N_2O was purified by vapor-phase chromatography and the 45/(44 + 46) ratio was measured on a Nuclide dual-collector mass spectrometer. The complexes were converted to free NO_2^- and N_3^- by reaction with OH^- .

Analysis of $[\text{Co}(\text{PnAO-H})(\text{NO}_2)(\text{OH}_2)]^+$ and $[\text{Co}(\text{PnAO-H})(\text{OH}_2)_2]^{2+}$ for ^{18}O content in the coordinated water was accomplished by precipitating the complexes with ClO_4^- or BPh_4^- , drying them under vacuum, and allowing them to react completely with $\text{Hg}(\text{CN})_2$ in a sealed tube at 425° to give CO_2 .¹⁹ The CO_2 was purified by vapor-phase chromatography and the 46/(44 + 45) ratio was measured and compared with a standard. All oxygens in the complex salt became equivalent during the conversion to CO_2 and correction was made for the nonexchanging amine oxime oxygens and those of NO_2^- .

Analysis of ^{36}Cl content was made directly on the solid complex by proportional counting of a constant weight ($\approx 10^{-3}$ g) of it spread on a uniform surface area. The usual background corrections were made but absorption corrections were judged to be very small and constant.

A weighted least-squares computer program was used to evaluate the observed exchange rate constants and estimated error. For all isotopic exchange studies reported k_{obsd} represents the observed rate constant, R is the overall rate of reaction, and k is the rate constant of reaction.

For both transfer and exchange studies the separation of the neutral complex from the exchanging or reacting ion was accomplished by absorbing or replacing the ion on an ion-exchange resin and collecting the complex. For example, for the $\text{R}(\text{NO}_2)_2^{0-15}\text{NO}_2^-$ exchange an aliquot of the exchanging solution was cooled and passed through a resin in the Cl^- form, and the yellow complex solution was collected. It was concentrated by rotoevaporation under vacuum at 30° and treated with NaOH to release NO_2^- which was converted to N_2O and isotopically measured. In some cases the absorbed NO_2^- was eluted from the resin and also analyzed.

Isotopic dilution was employed with RCl_2^0 . The cooled reaction mixture was passed through resin in the chloride form. Exchange between Cl^- in solution and the large excess in the resin gave Cl^- in solution free of ^{36}Cl . For exchanging ions of unlike charge, *i.e.*, in $[\text{Co}(\text{en})_2(\text{NO}_2)_2]^+-\text{NO}_2^-$, either the complex ion or the anion was replaced by a single pass through an ion-exchange column. Concentration and analysis of either the effluent or the resin was then easily accomplished. In all cases reported, the zero- and infinite-time samples agreed with that calculated within 5%. Thus induced exchange was less than this value.

When the ^{18}O content of NO_2^- and its complexes was desired, the small exchange which apparently occurs during its conversion to N_2O was a needed correction. Also, since NO_2^- was often obtained from complexes by reaction with 0.1 *M* NaOH , the exchange rate in this media was checked.

Results

The infrared spectra of the dinitro complex *trans*- $[\text{Co}(\text{PnAO-H})(\text{NO}_2)_2]^0$ shows several bands in the 1400-, 1325-, and 825- cm^{-1} regions characteristic of N-bound NO_2^- groups. No indications of absorption in the nitrito regions were seen. The usual absorption at 1780 cm^{-1} , somewhat broad and weak, in all of the complexes of the PnAO ligand listed here is a strong indication that the hydrogen bond exists in agreement with the analytical data. The proton nmr spectrum shows the OHO proton (18.4 ppm) downfield compared to

(17) Prepared by the thermal decomposition of KNO_3 with powdered lead.

(18) R. H. Herber, Ed., "Inorganic Isotopic Synthesis," W. A. Benjamin, New York, N. Y., 1962, pp 99, 117.

(19) M. Anbar and S. Guttman, *Int. J. Appl. Radiat. Isotop.*, **5**, 233 (1959).

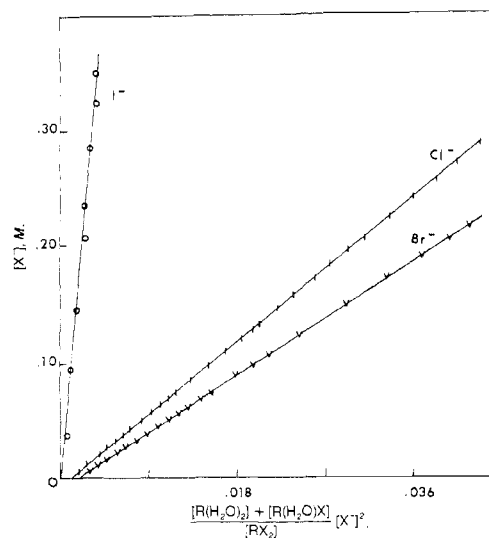


Figure 3. Distribution data for $\text{R}(\text{OH}_2)_2^{2+} + 2\text{X}^- \rightarrow \text{RX}_2^0 + 2\text{H}_2\text{O}$ (25°).

TMS in all the PnAO complexes, as well as the methyl and methylene protons, identical with the spectrum observed for the nickel(II) complex.¹¹ Thus the *gem*-dimethyl groups are not symmetrically placed with respect to the Co-4N plane. The sharp nature of the nmr peaks indicates diamagnetism for the cobalt(III) as was established by Gouy measurements; $\chi_{\text{molar}} = 120 \times 10^{-6}$ cgsu at 30° for solid $[\text{Co}(\text{PnAO-H})(\text{NO}_2)_2]^0$. The X-ray crystal structure¹ confirms the assigned structure. The tetradentate ligand has its four coordinated nitrogens nearly in a plane with the cobalt atom, but the *gem*-dimethyl groups are not symmetrically placed with respect to this plane. The nitro groups are N coordinated, in *trans* positions, and are unsymmetrical with respect to the cobalt. N-Co distances are 1.984 ± 0.003 and 1.937 ± 0.003 Å. The visible spectra of many of the complexes studied are given in Figure 2.

Equilibrium Measurements. The equilibrium constants evaluated in this work are contained in Table II. Each entry is the average of at least three trials with the \pm value being the average deviation. The equations of the dinitro and diazido complexes by the three methods agree sensibly. Due to the uncertainties in the estimated ion conductivities, the values obtained using this method are not highly reliable. Representative distribution data used in this evaluation of the RCl_2^0 , RBr_2^0 , and RI_2^0 systems are given in Figure 3. The appropriate functions are plotted for the evaluation of K_1 and K_2 . Linear behavior is noted over the region of the anion concentrations used justifying the interpretation. Table IIB is a summary of the distribution coefficients and the equilibrium constants obtained together with the molar absorptancies of RX_2^0 in CHCl_3 at the wavelengths used. The wavelengths of maximum absorbance are for RCl_2^0 340 nm, for RBr_2^0 385 nm, and for RI_2^0 505 nm which were not used in the distribution experiments for two reasons: (a) to lessen the effect of trace impurities by working at lower radiation energy; (b) to lower the light absorption at complex concentration of $(5-10) \times 10^{-4}$ *M*, a concentration range most suitable for the equilibrium studies.

With the RI_2^0 complex only, two forms occurred in the CHCl_3 solution. In contact with dilute I^- solutions a pink CHCl_3 layer was present, and with high $[\text{I}^-] > 1$ *M*, it became orange. The molar absorptancy increased by about 15% and the peak shifted from 505 to 491 nm. This was reversible.

Table II

A. Equilibrium Constants (25°)			
Equilibrium	K_{eq}	μ	Method
$R(N_3)_2^0 \rightleftharpoons R(N_3)OH_2^+ + N_3^-$	$(1.16 \pm 0.04) \times 10^{-4} M$	10^{-3}	Spec, ion exch
$R(NO_2)_2^0 \rightleftharpoons R(NO_2)OH_2^+ + NO_2^-$	$(0.92 \pm 0.03) \times 10^{-4} M$	10^{-3}	Spec, ion exch
$R(NO_2)N_3^0 + NO_2^- \rightleftharpoons R(NO_2)_2^0 + N_3^-$	$(8.54 \pm 0.06) \times 10^{-2}$	5×10^{-3}	Spec, ion exch
$R(NO_2)N_3^0 + N_3^- \rightleftharpoons R(N_3)_2^0 + NO_2^-$	$(2.19 \pm 0.07) \times 10^{-1}$	5×10^{-3}	Spec, ion exch
$R(NO_2)_2^0 + R(N_3)_2^0 \rightleftharpoons 2R(NO_2)N_3^0$	58 ± 2	5×10^{-3}	Spec, ion exch
$R(NO_2)OH_2^+ \rightleftharpoons R(NO_2)OH^0 + H^+$	$(1.31 \pm 0.10) \times 10^{-7} M$	0.10	pH
$R(NO_2)OH^0 \rightleftharpoons R(NO_2)OH_2^+ + OH^-$	$(7.7 \pm 0.1) \times 10^{-8} M$	0.10	pH

B. Distribution Coefficients (25°, $\mu = 0.10$) ^a			
X^-	K_d	K_1, M^{-1}	K_2, M^{-1}
Cl ⁻	2.21	140.0 ± 1.1	6.85 ± 0.05
Br ⁻	3.90	124.3 ± 1.2	5.41 ± 0.08
I ⁻	2.75	83.3 ± 1.1	87.3 ± 4.0

^a Conditions: RCl_2 , λ 400 nm, ϵ 990; RBr_2 , λ 450 nm, ϵ 1089; RI_2 , λ 600 nm, ϵ 1705. $K_d = [RX_2^0]CHCl_3/[RX_2^0]H_2O$; $K_1 = [R(OH_2)X^+]/[R(OH_2)_2^{2+}][X^-]$; $K_2 = [RX_2^0]/[R(OH_2)X^+][X^-]$.

Table III. Kinetics of Anion Exchange^a

A. $R(NO_2)_2^0 + N_3^- \rightarrow R(NO_2)N_3^0 + NO_2^-$					
$[N_3^-], M$	$10^3 k, sec^{-1}$		$[N_3^-], M$	$10^3 k, sec^{-1}$	
	<i>b</i>	<i>c</i>		<i>b</i>	<i>c</i>
0.020	5.47	5.58	0.120	5.70	5.80
0.040	5.55	5.37	0.160	5.52	5.65
0.080	5.35	5.27	0.200	5.42	5.63

B. $R(NO_2)N_3^0 + N_3^- \rightarrow R(N_3)_2^0 + NO_2^-$				
$[N_3^-], M$	$10^4 k, sec^{-1}$		$[N_3^-], M$	$10^4 k, sec^{-1}$
	<i>b</i>	<i>c</i>		
0.200	1.692		0.080	1.780
0.160	1.707		0.040	1.737
0.120	1.663, ^d	1.693, ^e		1.677 ^f

^a pH 7.97, $\mu = 0.50$ ($NaClO_4$), 35°. ^b [Complex] = $2 \times 10^{-3} M$. ^c [Complex] = $6 \times 10^{-3} M$. ^d 500 nm. ^e 475 nm. ^f 560 nm.

No I_2 or I_3^- could be detected in the system. Equilibrium constants were evaluated using the dilute I^- data which were not complicated by the subsequent reaction.

Kinetic Measurements for Substitution Reactions.
 $R(NO_2)_2^0 + N_3^- \rightarrow R(NO_2)N_3^0 + NO_2^-$. In the presence of excess N_3^- and at constant pH the reaction showed first-order behavior with respect to the formation of the product over 3–4 half-lives with no consistent deviations. Table III gives some representative results pertaining to the $[N_3^-]$ dependency. Laboratory light had no effect on the observed kinetics. The acidity dependence is shown in Figure 4. The observed rate constant increased linearly with $[OH^-]$ in the more acidic region and reached a constant rate at high pH's. A nonzero intercept was observed. The leveling effect at high pH was due to a change to another reaction as the rate-controlling step. This will be justified later. The pseudo-first-order rate constant is formulated as $k_1 = k_0 + k_{OH}[OH^-]$. Values of k_0 and k_{OH} are found in Table IV. The Arrhenius activation energy was determined from rate constants at four temperatures (22.5–40°). The values of E_a at pH 7.98 and $\mu = 0.245$ were 22.2 ± 0.7 and 22.6 ± 0.4 kcal/mol for $[N_3^-] = 0.08$ and $0.12 M$, respectively.

$R(NO_2)N_3^0 + N_3^- \xrightarrow{k_2} R(N_3)_2^0 + NO_2^-$. Using the solid $R(NO_2)N_3^0$ complex as the reactant and following the formation of $R(N_3)_2^0$ spectrophotometrically at 560 nm, we found that the reaction followed first-order kinetics at constant pH and a large excess of N_3^- . Over the range of 0.05–0.24 $M N_3^-$ the reaction rate was independent of $[N_3^-]$. The observed rate constant increased with increasing $[OH^-]$ and a graph of k_{obsd} vs. $[OH^-]$ was linear in the region $[OH^-] = 10^{-8}$ – 10^{-6}

Table IV. Kinetic Summary

A. Anion Replacement on $R(NO_2)_2^0$ by N_3^- (35°, $\mu = 0.25$)

- $R(NO_2)_2^0 + N_3^- \rightarrow R(NO_2)N_3^0 + NO_2^-$
 $k_0 = (6.83 \pm 0.41) \times 10^{-4} sec^{-1}$
 $k_{OH} = (5.16 \pm 0.06) \times 10^3 M^{-1} sec^{-1}$
 At pH 7.50, $\mu = 0.34$, $\Delta H^\ddagger = 22.7 \pm 0.3$ kcal/mol, $\Delta S^\ddagger = +2.4 \pm 1.0$ eu
- $R(NO_2)N_3^0 + N_3^- \rightarrow R(N_3)_2^0 + NO_2^-$
 $k_0 = (1.0 \pm 0.2) \times 10^{-5} sec^{-1}$
 $k_{OH} = (1.5 \pm 0.09) \times 10^2 M^{-1} sec^{-1}$

B. Anation of $R(NO_2)OH_2^+$ (25°, $\mu = 0.34$)

- $R(NO_2)OH_2^+ + N_3^- \rightarrow R(NO_2)N_3^0 + H_2O$
 $k_0 = (5.0 \pm 0.1) \times 10^{-4} sec^{-1}$
 $k_{OH} = (8.8 \pm 0.1) \times 10^{-3} sec^{-1}$ (0.10 $M N_3^-$)
 Limiting k value at pH 7.50 and large excess of N_3^- is $6.2 \times 10^{-3} sec^{-1}$
 At pH 7.50, $\mu = 0.34$, $\Delta H^\ddagger = 20.9 \pm 0.5$ kcal/mol, $\Delta S^\ddagger = +1.9 \pm 0.9$ eu
- $R(NO_2)OH_2^+ + NO_2^- \rightarrow R(NO_2)_2^0 + H_2O$ (25°, $\mu = 0.34$)
 $k_0 = (5.0 \pm 0.1) \times 10^{-4} sec^{-1}$
 $k_{OH} = (4.7 \pm 0.1) \times 10^{-3} sec^{-1}$ (0.10 $M NO_2^-$)
 Limiting k value at pH 7.50 and large excess of NO_2^- is $6.1 \times 10^{-3} sec^{-1}$
 At pH 7.50, $\mu = 0.34$, $\Delta H^\ddagger = 22.4 \pm 0.8$ kcal/mol, $\Delta S^\ddagger = 5.6 \pm 1.5$ eu

^a Using the exponential equations (see text) $k_0 = (1.2 \pm 0.3) \times 10^{-5} sec^{-1}$ and $k_{OH} = (2.3 \pm 0.3) \times 10^2 M^{-1} sec^{-1}$.

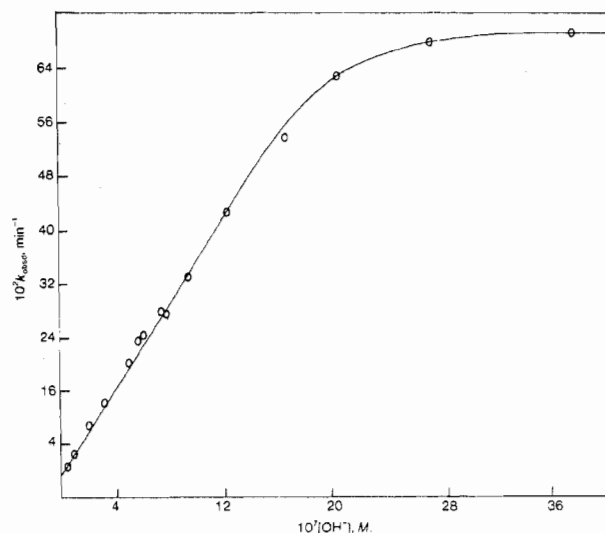


Figure 4. Base dependence of the reaction $R(NO_2)_2^0 + N_3^- \rightarrow R(NO_2)N_3^0 + NO_2^-$ (35°, $\mu = 0.50$).

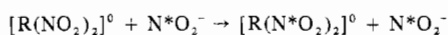
M with a positive intercept at $[\text{OH}^-] = 0$. In the higher pH range the observed rate approached a limiting value. Thus the kinetic behavior for the replacement of the second nitro group has the same characteristics as that for the replacement of the first.

When k_2 was measured using $\text{R}(\text{NO}_2)_2^0$ and N_3^- as the reactants, k_1 as a known, and k_2 and ϵ of $\text{R}(\text{NO}_2)\text{N}_3^0$ as unknowns, the same features were noted. The observed rate constants were independent of wavelength (475, 500, and 560 nm) and of $[\text{N}_3^-]$. The extinction coefficients agreed reasonably well with those obtained with the solid complex and the pH dependence data were consistent with $k_2 = k_0 + k_{\text{OH}}[\text{OH}^-]$ from both sets of data. The values obtained are given in Table IV. The accuracy and precision of the k_2 determination was not judged sufficient to warrant temperature-dependence studies.

The form of the rate equation for the anion exchange on $\text{R}(\text{NO}_2)_2^0$ suggested a reactive intermediate likely to be $[\text{R}(\text{NO}_2)\text{OH}_2]^+$. Thus anation studies (NO_2^- or N_3^-) of the latter compound were initiated. At constant pH and with a large excess of anion, first-order loss of $[\text{R}(\text{NO}_2)\text{OH}_2]^+$ or gain of $\text{R}(\text{NO}_2)_2^0$ or $\text{R}(\text{NO}_2)\text{N}_3^0$ was found. The pH dependence is given in Figure 5 and the anion dependence in Figure 6. Table V gives the temperature-dependence data and the derived activation parameters.

Isotopic Exchange. Table VI contains the studies on the water-exchange kinetics of $[\text{R}(\text{NO}_2)\text{OH}_2]^+$ with solvent at 0° . It is seen that the exchange is essentially independent of acidity in the pH range 4–7 and not affected by the presence of ClO_4^- or 2,6-lutidine. A slight decrease in rate constant in the more basic regions is probably indicated by the data and N_3^- has a small effect. (The concurrent reaction to form the nitro-azido complex is slower than the exchange under the stated conditions.) The activation parameters from measurements at three temperatures (0.0, 4.5 and 8.7°) are $A = (2.5 \pm 5.0) \times 10^{16} \text{ sec}^{-1}$, $E_a = 25.8 \pm 0.6 \text{ kcal/mol}$, $\Delta H^\ddagger = 25.2 \pm 0.6 \text{ kcal/mol}$, and $\Delta S^\ddagger = 19.4 \pm 2.2 \text{ eu}$.

In Figure 7 is a representative graph of $^{15}\text{N}/^{14}\text{N}$ vs. time for the exchange reaction



The data are easily interpreted using two concurrent first-order rate terms which are rather widely separated

$$\frac{-dn}{dt} = k_1 \frac{[c]}{2} + k_2 \frac{[c]}{2}$$

From data of this type, the two rate constants can be obtained as well as the ratio of the two kinds of exchanging nitro groups. This ratio consistently centers around 1 suggesting that the complex contains two kinds of NO_2^- groups and that it is not a mixture of two complexes. Another possibility is that the two oxygens on a nitrogen are not equivalent. It is concluded, however, that two kinds of nitro groups are in the complex ion since the analogous $[\text{RCl}_2]^0$ and $[\text{R}(\text{N}_3)_2]^0$ complexes show the same type of behavior. Also the crystal structure¹ shows structural differences in the nitro-cobalt bonds. Table VII gives the results of isotopic exchange kinetics of NO_2^- , Cl^- , and N_3^- with their corresponding complexes.

Attempts were made to study the water-exchange rates with $[\text{R}(\text{OH}_2)_2]^{2+}$ but difficulty was encountered in obtaining a suitable precipitating agent. Thus the further work in this area is anticipated.

The results of NO_2^- -exchange kinetics of several other dinitro complexes is given in Table VIII. The PnAO com-

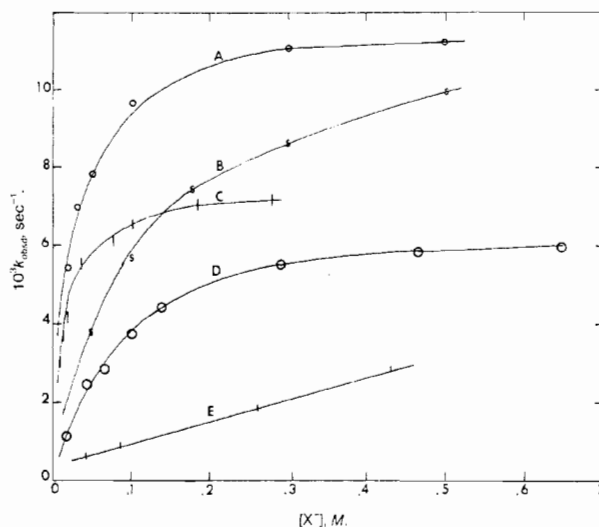


Figure 5. Anion dependence of $\text{R}(\text{NO}_2)\text{OH}_2^+ + \text{X}^- \rightarrow \text{RNO}_2\text{X}^0$ (25°): A = N_3^- , B = NO_2^- at pH 8.50, $\mu = 0.550$; C = N_3^- , D = NO_2^- at pH 7.50, $\mu = 0.335$; E = N_3^- at pH 5.50, $\mu = 0.55$.

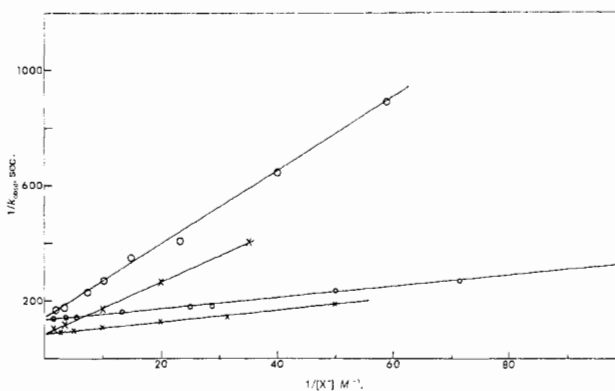


Figure 6. Anation of $\text{R}(\text{NO}_2)\text{OH}_2^+$ at 25° : large points, N_3^- ; small points, NO_2^- ; \times , pH 8.50, $\mu = 0.550$; \circ , pH 7.50, $\mu = 0.335$.

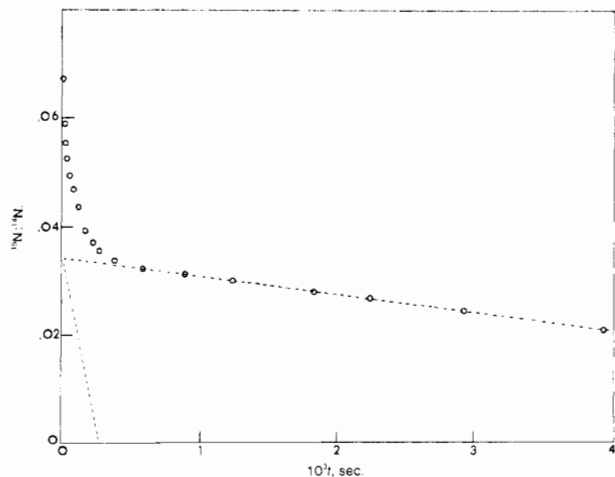


Figure 7. Rate of exchange of $[\text{Co}(\text{PnAO-H})(\text{NO}_2)_2]^0$ with $^{15}\text{NO}_2^-$, at 25° , $\mu = 0.05$, $[\text{NO}_2^-] = 0.05 \text{ M}$, and $[\text{complex}] = 3 \times 10^{-4} \text{ M}$.

plexes are clearly more labile and only with them are two types of nitro group discernible.

Since *trans*- $[\text{Co}(\text{tetraMeen})_2(\text{NO}_2)_2]^+$ and $[\text{Co}((\text{AO})_2\text{-H})(\text{NO}_2)_2]$ had many properties similar to those of the main complex of interest in this paper but did not show two dissimilar NO_2^- groups, some of the rate parameters were examined in detail. The former are presented in Table IX. Figure

Table V. Anation Kinetics of $R(NO_2)_2OH_2^+$, Showing Temperature Dependence^a

Temp, °C (±0.1°)	$10^3 k, \text{sec}^{-1}$		Temp, °C (±0.1°)	$10^3 k, \text{sec}^{-1}$	
	N_3^-	NO_2^-		N_3^-	NO_2^-
17.0	2.59	1.22	27.5	9.57	5.16
20.0	3.61	1.87	30.0	12.3	6.60
25.0	7.35	3.70			

^a $[X^-] = 0.10 M$, pH 7.50, $\mu = 0.335$.

Table VI. Isotopic Water-Exchange Kinetics of $[Co(PnAO-H)(NO_2)_2]^+$ (0°)

$10^3 k, \text{min}^{-1}$	pH	[2,6-Lu-tidine], <i>M</i>	[HClO ₄], <i>M</i>	Total [Na ⁺], <i>M</i>	Other conditions
3.83 ± 0.08	4.05	0	0	0	
3.88 ± 0.12	4.05	0	0	0	
3.16 ± 0.17	5.55	0.0024	0.0024	0	
3.07 ± 0.36	6.05	0.0083	0.0041	0	
2.66 ± 0.04	6.95	0.007	0.0039	0	<i>b</i>
4.02 ± 0.05	5.25	0.015	Unknown	0.010	0.010 <i>M</i> NaN ₃
3.51 ± 0.02	6.80	0.043	0	0.0017	<i>b</i> , NaOH added
2.79 ± 0.09	7.80	0.24	0	0.010	<i>b</i> , NaOH added
3.77 ± 0.20	5.40	0	0.0058	0.101	0.101 <i>M</i> NaN ₃
1.59 ± 0.04	8.10	0.033	0	0.098	<i>b</i> , 0.098 <i>M</i> NaN ₃
3.30 ± 0.03	6.80	0.033	0	0	<i>b</i>
3.11 ± 0.02	6.80	0.033	0	0	<i>b</i>
2.88 ± 0.06	7.85	0.455	0	0	<i>b</i>
14.4 ± 0.4	6.80	0.033	0	0	<i>b</i> , 8.70 ± 0.05°
6.51 ± 0.01	6.80	0.033	0	0	<i>b</i> , 4.50 ± 0.05°

^a Evaluated with weighted least-squares program; ± values represent one standard deviation. ^b Samples were brought to pH 4-5 with HClO₄ before precipitation.

Table VII. Isotopic Anion-Exchange Kinetics

$[Co(PnAO-H)(NO_2)_2]^0 + N^*O_2^- \rightarrow \text{Exchange}$ (25°, $\mu = 0.07$)

Type 1: NO_2^- , $k_0 = 1.15 \times 10^{-4} \text{sec}^{-1}$, $k_{OH} = 4.02 \times 10^3 M^{-1} \text{sec}^{-1}$

Type 2: $N^*O_2^-$, $k_0 = 2.4 \times 10^{-6} \text{sec}^{-1}$, $k_{OH} = 8.96 \times 10^1 M^{-1} \text{sec}^{-1}$

Molar ratio type 1: type 2 = 1.02 ± 0.03 (6 determinations)

Rate constant ratio of k_0 is 48, of k_{OH} is 45

$[Co(PnAO-H)(N_3)_2]^0 + N_3^* \rightarrow \text{Exchange}$ (25°, $\mu = 0.06$, pH 6.84)

Type 1: N_3^- , $t_{1/2} = 14.5 \text{min}$, $k_{obsd} = 7.97 \times 10^{-4} \text{sec}^{-1}$

Type 2: N_3^* , $t_{1/2} = 220 \text{min}$, $k_{obsd} = 5.25 \times 10^{-5} \text{sec}^{-1}$

Molar ratio type 1: type 2 = 1.05 ± 0.03 (3 determinations)

Rate constant ratio at pH 6.84 is 15.2 (3 determinations)

$[Co(PnAO-H)Cl_2]^0 + Cl^* \rightarrow \text{Exchange}$ ($\mu = 0.06$, [HCl] = 0.02 *M*)

Type 1: Cl^- , $k_{obsd} = (1.8 \pm 5) \times 10^{-4} \text{sec}^{-1}$ (0°), $(2.9 \pm 1.0) \times 10^{-3} \text{sec}^{-1}$ (25°)

Type 2: Cl^* , $k_{obsd} = (5.30 \pm 0.20) \times 10^{-6} \text{sec}^{-1}$ (0°), $(8.13 \pm 0.15) \times 10^{-5} \text{sec}^{-1}$ (25°)

Molar ratio type 1: type 2 = 1.03 ± 0.07 (5 determinations)

Rate constant ratio is 34 (4 determinations)

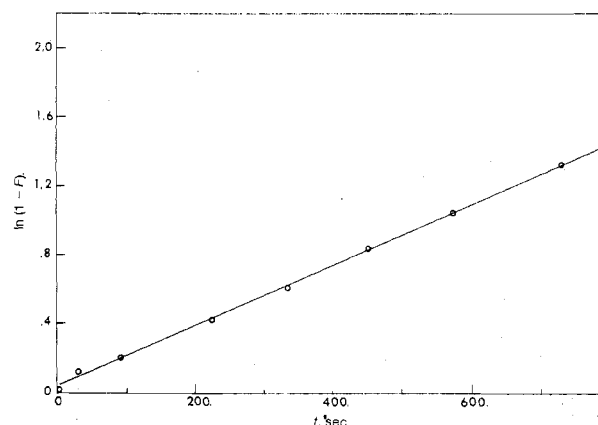
Table VIII. Half-Times of NO_2^- Isotopic Exchange^a

Complex	Half-time, days	$k_{obsd}, \text{sec}^{-1}$
<i>trans</i> -[Co((AO) ₂ -H)(NO ₂) ₂] ⁰	11.0	7.29×10^{-7}
<i>trans</i> -[Co((DMG) ₂ -2H)(NO ₂) ₂] ⁻	499	1.61×10^{-8}
<i>trans</i> -[Co(en) ₂ (NO ₂) ₂] ⁺	150	5.36×10^{-8}
<i>trans</i> -[Co(tetraMeen) ₂ (NO ₂) ₂] ⁺	1.61	5.00×10^{-6}
<i>trans</i> -[Co(PnAO-H)(NO ₂) ₂] ⁰	0.031, 0.94	2.6×10^{-4} , 0.086×10^{-4}

^a At 25°, pH 6.7, [complex] = $5 \times 10^{-3} M$, and $[NO_2^-] = 10^{-1} M$.

8 gives a representative graph for the AO complex. The temperature dependence of the rate constant is described by the equation $k = 6.8 \times 10^{13} e^{25,520/RT} \text{sec}^{-1}$.

Oxygen-Transfer Studies. Since the formation of nitro

**Figure 8.** $[Co((AO)_2-H)(NO_2)_2]^0 + ^{15}NO_2^- \rightarrow \text{exchange}$ (25°).

complexes often proceeds through the nitrito intermediate upon the reaction of $RCo-OH$ with NO_2^- , yielding a retention of the $Co-O$ bond, oxygen-transfer measurements were conducted to ascertain if such a mechanism was important in this system. Also, replacement of nitro groups by OH^- or N_3^- could result in ionic NO_2^- having an oxygen composition partially reflecting that of the solvent. The results of experiments to decide between these possibilities are given in Table X. They offer no suggestion of a nitrito intermediate in the formation or dissociation of these nitro complexes. Table XI proves that no appreciable $NO_2^- \cdot H_2O$ exchange occurs in 0.1 *M* base in the presence or absence of N_3^- which is necessary if the transfer experiments have significance. This is contrary to the results of a previous study.²⁰

Discussion

The equilibrium constants in Table II show that the ionization of N_3^- from the RX_2^0 type complexes is slightly greater than that of NO_2^- . However, entries 3 and 4 show that the diazo complex is thermodynamically more stable than the dinitro complex (compared to the mixed species), which is the usual situation. Thus the first effect is related to the greater thermodynamic trans effect of N_3^- with respect to NO_2^- . The large stability of the mixed-ligand complex attributed to an entropy effect is shown by entry 5. The nitro-aquo complex is a much weaker acid than *trans*-[Co(en)₂-NO₂(OH₂)]²⁺ or similar complexes reflecting the reduced complex ion charge.

The $CHCl_3-H_2O$ distribution constants show an irregularity with I^- which can be understood in terms of the solubility of the I^- ion pair in $CHCl_3$. The distribution coefficient for the ion pair $[RI(OH_2)]^+ I^-$ would be expected to be lower than for RI_2^0 as is apparent. Likewise an abnormality exists with K_2 due to the fact that both forms RI_2^0 and $[RI(H_2O)]^+ I^-$ are being counted as the former which gives an abnormally large value. The K_1 values are regular and show a decrease from Cl^- to I^- . This trend may be rationalized on the basis of size or effective charge and suggests that the cobalt complex prefers a localized-charge ligand and a bonding tending toward ionic. This characteristic is also suggested by the high lability of the apical ligands compared to the usual cobalt(III)-amine complexes.

Anion Exchange on $R(NO_2)_2^0$. The representative data in Table III show that the replacement of either NO_2^- group by N_3^- is first order in complex ion and is independent of N_3^- when carried out in the presence of a large stoichiometric

Table IX. Kinetics of Isotopic Exchange of $[\text{Co}(\text{tetraMeen})_2(\text{NO}_2)_2]^+\text{ClO}_4^-$ with the ^{15}N Nitrite Ion

No.	Temp, °C	$10^3[\text{NO}_2^-]$, M	$10^3[\text{complex}]$, M	pH (25°)	10^3k_{obsd} , min ⁻¹	10^5k , sec ⁻¹
1	40	1.692	7.283	6.48	3.196 ± 0.04	9.81 ± 0.15
2	40	1.354	8.435	6.43	3.281 ± 0.03	9.73 ± 0.09
3	40	1.811	6.927	6.50	3.076 ± 0.019	9.52 ± 0.06
4	40	1.962	5.136	7.48 ^a	3.18 ± 0.02	10.07 ± 0.05
5	40	2.027	5.551	6.22 ^b	2.98 ± 0.03	9.42 ± 0.09
6	30	1.333	5.186	6.52	0.742 ± 0.003	2.89 ± 0.01
7	40	2.694	2.483	6.52	3.06 ± 0.03	10.03 ± 0.10
8	50	1.700	4.991	6.52	12.40 ± 0.05	39.03 ± 0.16
9	40	0.878	5.444	6.52	3.14 ± 0.01	9.32 ± 0.04
10	50	1.583	6.293	c	12.43 ± 0.08	38.35 ± 0.24
11 ^d	50	1.752	6.283	6.52	12.28 ± 0.11	40.63 ± 0.40
12 ^e	50	1.706	6.432	6.52	12.03 ± 0.05	39.80 ± 0.19
13 ^d	50	1.581	5.653	6.52	12.16 ± 0.09	40.25 ± 0.28

^a NaOH added. ^b HClO₄ added; light excluded. ^c 2,6-Lutidine added (pH 8.6). ^d Rate of ¹⁸O depletion from NO₂⁻ in the complex. ^e NaClO₄ (0.10996 M) added; $\mu = 0.3449$.

Table X. Oxygen Atom Transfer Experiments

Reaction ^a	% ¹⁸ O transfer to NO ₂ ⁻
$\text{R}(\text{NO}_2)_2^0 + 2\text{N}_3^- \rightarrow \text{R}(\text{N}_3)_2^0 + 2\text{NO}_2^{*-}$	95.9, 98.2, 98.9
$\text{R}(\text{NO}_2)_2\text{N}_3^0 + \text{N}_3^- \rightarrow \text{R}(\text{N}_3)_2^0 + \text{NO}_2^{*-}$	95.8
$\text{R}(\text{NO}_2)_2\text{OH}_2^+ + \text{N}_3^- \rightarrow \text{R}(\text{N}_3)_2^0 + \text{NO}_2^{*-}$	96.6, 97.1
$\text{R}(\text{NO}_2)_2^0 + 2\text{OH}^- \rightarrow \text{R}(\text{OH})_2^0 + 2\text{NO}_2^{*-}$	97.7
$\text{R}(\text{NO}_2)_2\text{H}_2\text{O}^+ + \text{NO}_2^{*-} \rightarrow \text{R}(\text{NO}_2)\text{NO}_2^+ + \text{H}_2\text{O}$ (pH 6.5–7.5)	109, 105 ^b

^a All carried out at $25 \pm 2^\circ$. ^b High value due to some exchange with other nitro group.

excess of N₃⁻. The reactions are independent of the wavelength of light used in following the reaction and are not affected to any observable extent by laboratory light.

Figure 4 shows the rate dependence on $[\text{OH}^-]$ for the replacement of the first NO₂⁻ group and a similar curve was obtained for the second step. Neglecting, for the time, the leveling effect at high $[\text{OH}^-]$, the pH dependence was evaluated in terms of the rate equation $k_{\text{obsd}} = k_0 + k_{\text{OH}}[\text{OH}^-]$ and values for these terms for both reactions are given in Table IV. The ratio first:second for the k_0 term is 68 and for the k_{OH} term is 34. These are rather high ratios for the replacement of one negative ion for another (usual about 15) and suggest that the nitro groups are kinetically different.

Isotopic exchange studies of $\text{R}(\text{NO}_2)_2^0 + ^{15}\text{NO}_2^- \rightarrow \text{ex-change}$ (25°) show two types of exchanging NO₂⁻ groups, Figure 7. The molar ratio of the two types from the ¹⁸O changes was 1.02 ± 0.03 (Table VII), and the exchange rate for both types followed the equation $k_{\text{obsd}} = k_0 + k_{\text{OH}}[\text{OH}^-]$. For comparison, the rate constant for replacement of NO₂⁻ by N₃⁻ (step 1) was calculated for 25° using the activation parameters at two acidities and compared with the ¹⁵NO₂⁻ exchange rate (step 1); see below.

pH	$10^4k_1(\text{exch})$, sec ⁻¹	$10^4k_1(\text{spec})$, sec ⁻¹
6.25	1.87	1.82
6.65	2.45	2.15

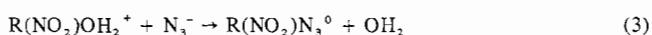
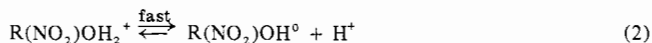
The essential agreement suggested a common mechanism in which, except for $[\text{OH}^-]$, reacting anions play no appreciable role in the reaction kinetics. While no definitive mechanism has been established, the evidence favors for both isotopic and nonisotopic anion exchange an activated complex in which the leaving nitro group is well dissociated without much direct assistance from the entering group. The k_0 term is thus the dissociation rate constant as affected by the solvent while the k_{OH} term probably reflects a S_N1cb type reaction utilizing either an amine or a hydrogen-bond hydrogen.

Table XI. NO₂⁻ Oxygen Exchange in 0.10 M KOH

a. 0.1685 M NaNO ₂		b. 0.1939 M NaNO ₂ , 0.0749 M NaNO ₃	
Time, min	$10^3R_n^a$	Time, min	$10^3R_n^a$
0	4.79	0	4.79
1.25	4.75	1.26	4.78
4.19	4.72	4.25	4.71
8.45	4.77	8.49	4.76
15.87	4.74	15.90	4.78
24.48	4.78	24.50	4.79
1 hr (60°)	4.76 ^b	1 hr (60°)	4.68 ^b

^a R_n is the normalized 46/(44 + 45) ratio in N₂O. Standard N₂O value is 2.00×10^{-3} . ^b Infinite value for complete exchange would be 1.99×10^{-3} , the value for the solvent.

A complete evaluation of the role(s) of OH⁻ in this reaction cannot be made, due in part to the potential involvement of acid-base forms of the OH₂ and OHO groups of the complex ion. However an explanation of the leveling of k_{obsd} at high pH's (Figure 4) lies in the formation of an aquo-hydroxo intermediate whose anation becomes rate determining at about pH 8.5.



At low pH's reaction 1 would be rate determining with reaction 3 being comparatively rapid. At high basicities reaction 3 would be the slow and rate-controlling step. In order to test the correctness of this reaction sequence, reaction 3 was independently studied.

The anation studies on $\text{R}(\text{NO}_2)\text{OH}_2^+$ (Figures 5, 6, and 9) show that the reaction is first order in complex ion, at constant pH and with excess X⁻. The observed rate constant increases with $[\text{X}^-]$ and with $[\text{OH}^-]$. Limiting k_{obsd} values are found at high concentrations of N₃⁻ and NO₂⁻. These characteristics parallel those for systems which are thought to occur²¹ by a dissociative process



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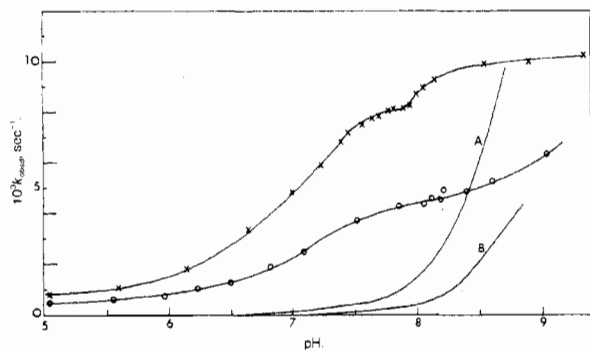


Figure 9. pH dependence of anation rates (25°, $\mu = 0.335$): x, $R(NO_2)OH_2^+ + N_3^-$; o, $R(NO_2)OH_2^+ + NO_2^-$; A, $R(NO_2)_2^0 + N_3^-$; B, $R(NO_2)N_3^0 + N_3^-$.

The steady-state approximation leads to the relationship between the pseudo-first-order rate constant and the other kinetic and concentration parameters²¹

$$\frac{1}{k_{obsd} - k_4} = \frac{1}{k_1 - k_4} + \frac{k_2/k_3}{(k_1 - k_4)[X^-]}$$

Using this form of the equation, a graph of $1/(k_{obsd} - k_4)$ vs. $1/[X^-]$ gives k_1 and k_2/k_3 if k_4 is known. Values for k_4 were obtained for NO_2^- from k_{obsd} of the reaction of $R(NO_2)_2^0$ with N_3^- at the proper pH, while for $R(NO_2)N_3^0$ dissociating a N_3^- group, a value was obtained from the former and K_{eq} for $R(NO_2)_2^0 + N_3^- \rightleftharpoons R(NO_2)N_3^0 + NO_2^-$. A graph of $1/k_{obsd}$ vs. $1/[X^-]$ is given in Figure 6. Estimated values of k_4 at 25° were, for $R(NO_2)_2^0$, 0.46 and $2.5 \times 10^{-3} \text{ sec}^{-1}$ and, for $R(NO_2)N_3^0$, 0.039 and $0.55 \times 10^{-3} \text{ sec}^{-1}$ at pH 7.5 and 8.5, respectively. Graphs of $1/(k_{obsd} - k_4)$ vs. $1/[X^-]$ were linear and gave least-squares values of k_2/k_3 of 0.023 and 0.112 for N_3^- and NO_2^- , respectively. The values of k_1 (which should be equal to the isotopic water-exchange rate constant) should be independent of the anion. At pH 7.50 ($\mu = 0.55$ and 35°) $k_1 = 1.17$ and $1.21 \times 10^{-2} \text{ sec}^{-1}$ for N_3^- and NO_2^- , respectively. At 0° a similar graph gave k_1 values of 3.01 and $3.53 \times 10^{-4} \text{ sec}^{-1}$ (N_3^- and NO_2^- , respectively). The water-exchange rate constant at 0°, pH 7.80, and $\mu = 0.24$ was $4.65 \times 10^{-4} \text{ sec}^{-1}$. This is in the same range as that obtained from the anion-dependence data and probably reflects the same rate constant modified by slightly differing conditions. A comparison of the activation parameters for the anations of $R(NO_2)_2^0$ and $R(NO_2)OH_2^+$ (Results section and Table IV) show no significant differences, suggesting that the metal-nitrogen and metal-oxygen bonds are not energetically very different and that they are "well dissociated in the activated complex."

The overall pH dependence of the anation of $R(NO_2)OH_2^+$ cannot be ascribed to a particular set of kinetic reactions. In the pH range 5-9, at least two factors must be of importance. (a) The complex is changing from $R(NO_2)OH_2^+$ to $R(NO_2)OH^0$. In most other systems this gives a dramatic decrease in k_{obsd} as opposed to the increase found here. (b) OH^- becomes an effective ligand at high pH competing with the substituting anion. If the former factor is important and $R(NO_2)OH_2^+$ reacts slowly compared to $R(NO_2)OH^0$, the curve should and does have its maximum slope near the pK_a , approximately pH 7. The latter factor should tend to lower k_{obsd} due to the competition between OH^- and the anion. This is observed in the higher pH region.

Figure 9 compares the pH dependence of k_{obsd} for the anation of $R(NO_2)OH_2^+$ with the calculated rate constants for anion replacement on $R(NO_2)_2^0$ (based on the equation

$k_{obsd} = k_0 + k_{OH}[OH^-]$). Above a pH of 8.2, the magnitudes of the rate constants become comparable, which would cause deviation from the two-term rate law for anion replacement on $R(NO_2)_2^0$. The leveling at high pH (Figure 4) is explainable in terms of a rapid buildup of $R(NO_2)OH_2^+$ whose anation is base insensitive above pH 8. While kinetic equations can be set up for eq 1-3, they are not of practical use in testing this mechanism since the spectral characteristics are not selective enough in this four-complex system. Thus the data are consistent with eq 1-3. k_{obsd} for the anation of $R(NO_2)_2^0$ has little significance above a pH of about 8.2.

The kinetics of isotopic water exchange seen in Table VI shows three major features: (a) the rate is not highly sensitive to ionic atmosphere, (b) N_3^- lowers the observed rate, and (c) the rate constant decreases slightly in the pH range 4-8. In the runs containing N_3^- , two acidity conditions were used. At low pH the k_0 anation term predominates, and at high pH the $k_{OH}[OH^-]$ anation term predominates. In both cases the aquo complex was analyzed and at high pH considerable $R(NO_2)N_3^0$ was produced. At low pH, the effect of N_3^- is small and positive. At higher pH, N_3^- lowers the observed ^{18}O exchange due apparently to competition for the activated intermediate. The decreasing k_{obsd} with increasing pH may be due to the changeover from the aquo to the hydroxo complex with the resulting stronger M-O bond. Presumably this rate is closely related to the k_0 term in the anation of $R(NO_2)OH_2^+$. The main unexplained feature, however, is the insensitivity of the water-exchange rate and the sensitivity of the anation rates to hydroxide ion.

The large difference between the rates of NO_2^- replacement from $R(NO_2)_2^0$ suggested that the *trans* nitro groups were not chemically identical. The $^{15}NO_2^-$ exchange studies show conclusively on *trans*-[Co(PnAO-H)(NO_2)₂]⁰ that one nitro group is ≈ 45 times more easily exchanged than the other in water solution in either of the two rate terms (Table VII). That this is not a function of the NO_2^- group is established by the same observations with the diazo complex. To be certain a multiatom ligand was not responsible for the difference, the dichloro complex was studied and gave similar behavior. The fast:slow ratio changes with the ligand but does not seem to reflect any major steric factors.

The nitro groups appear to exchange independently since graphical analysis gave, within experimental error, first-order behavior for both exchanges. This would appear to rule out a major contribution from inversion through the Co(III) resulting in NO_2^- interchange. These results are all in agreement with the solid X-ray crystal structure of Co(PnAO-H)(NO_2)₂⁰ concurrently presented. The evidence is strongly in favor of a distortion of the octahedron around Co(III) when a ligand has very strong planar stabilizing tendencies. This distortion takes the form of weakening the *trans* positions (kinetically at least), and with certain ligands, *i.e.*, PnAO, a tendency toward five-coordination is noted which does not appear to be related to steric repulsions between the equatorial and apex ligands.

Two other studies were carried out to amplify this picture. In one (Table VIII) a series of more common *trans*-dinitro complexes were studied with respect to isotopic exchange rates. The planar tendencies of the ligands with respect to Ni(II) are known to be PnAO \approx tetraMeen $<$ AO $<$ DMG $<$ en. Under the given set of conditions the half-times for exchange increase in the order PnAO $<$ tetraMeen $<$ AO $<$ en $<$ DMG. Except for the PnAO complex only one type of nitro group was observed with each complex ion. The order is essentially that predicted on the basis of Ni(II) planar tendencies. The features of the isotopic NO_2^- exchange

with a relatively labile complex having a symmetrical planar ligand $[\text{Co}(\text{tetraMeen})(\text{NO}_2)_2]^+$ were studied in detail (Table IX). The rate constant is essentially pH and NO_2^- independent and unaffected by laboratory light or ionic atmosphere. Using either ^{15}N or ^{18}O as the tracer gives identical results. The major differences between this complex and $[\text{Co}(\text{PnAO-H})(\text{NO}_2)_2]^0$ are the large $[\text{OH}^-]$ dependence and the kinetically different nitro groups in the latter. Since the tetraMeen and AO do not show similar behavior to PnAO complexes, some very novel bonding characteristics appear to be present with the latter. We ascribe this novel character to a tendency toward distortion toward a square-pyramidal geometry which may occur when the equatorial ligand has a great tendency to stabilize the planar configuration. Some similarities in properties seem to be found with vitamin B₁₂, cyano complexes of Co(III), and, to a lesser extent, complexes of DMG.

A feature of the NO_2^- replacement studies is whether the oxygen of complexed NO_2^- is retained in the released NO_2^- and whether the formation of the nitro complex retains the nitrite ion oxygens. Tables X and XI answer these questions. First, free NO_2^- in base does not show any exchange with the solvent in 1 hr at 60°. When NO_2^- is released from any of the three CoPnAO complexes by N_3^- in basic media essentially all the ^{18}O is retained in the NO_2^- . The formation of the nitro complex (neutral conditions) incorporates both NO_2^- oxygens into the complex ion.

Unsuccessful attempts have been made to prepare the

isomer pair of a mixed complex, *i.e.*, $\text{R}(\text{NO}_2)_\text{F}(\text{N}_3)_\text{S}^0$ and $\text{R}(\text{NO}_2)_\text{S}(\text{N}_3)_\text{F}^0$, where F and S refer to the fast and slow positions. Attempts are continuing in search of these unusual isomers.

Summary

It has been shown that *trans*- $[\text{Co}(\text{PnAO-H})\text{X}_2]^0$ has kinetically nonequivalent Co-X bonds ($\text{X}^- = \text{NO}_2^-, \text{N}_3^-, \text{Cl}^-$). Kinetic studies show an abnormal lability for the X^- groups. The mechanism of X^- group replacement resembles other systems presently thought to be primarily dissociative. An unexpected $[\text{OH}^-]$ dependency is observed for anion replacement, anation of the aquo complex, and isotopic anion exchange but not for the water exchange on the aquo complex. *trans*- $[\text{Co}(\text{tetraMeen})_2(\text{NO}_2)_2]^+$, although similar to the PnAO complex with respect to being relatively labile, shows entirely different pH behavior in the exchange reaction and is kinetically symmetrical with respect to the NO_2^- groups.

Acknowledgment. We wish to express our appreciation to the National Science Foundation for the support of this work in the early stages.

Registry No. *trans*- $[\text{Co}(\text{PnAO-H})(\text{NO}_2)_2]$, 41371-79-3; *trans*- $[\text{Co}(\text{PnAO-H})(\text{N}_3)_2]$, 41371-80-6; *trans*- $[\text{Co}(\text{PnAO-H})(\text{NO}_2)(\text{N}_3)]$, 41371-81-7; *trans*- $[\text{Co}(\text{PnAO-H})(\text{NO}_2)(\text{OH}_2)]\text{ClO}_4$, 41371-82-8; *trans*- $[\text{Co}(\text{PnAO-H})(\text{Cl}_2)]$, 41371-83-9; *trans*- $[\text{Co}(\text{PnAO-H})(\text{Br}_2)]$, 41371-84-0; *trans*- $[\text{Co}(\text{PnAO-H})(\text{I}_2)]$, 41371-85-1; *trans*- $[\text{Co}(\text{tetraMeen})_2(\text{NO}_2)_2]\text{ClO}_4$, 41371-86-2; *trans*- $\text{NH}_4[\text{Co}(\text{DMG-2H})(\text{NO}_2)_2]$, 24256-61-9; *trans*- $[\text{Co}((\text{AO})_2\text{-H})(\text{NO}_2)_2]$, 41371-87-3; *trans*- $[\text{Co}(\text{en})_2(\text{NO}_2)_2]\text{NO}_3$, 14240-12-1.

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Crystal Structure of Rhodium Pentafluoride

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Received December 11, 1972

The crystal structure of rhodium pentafluoride has been determined from three-dimensional X-ray data. The compound is monoclinic, $P2_1/a$, with $a = 12.3376$ (13), $b = 9.9173$ (8), $c = 5.5173$ (6) Å; $\beta = 100.42$ (2)°; $V = 663.85$ Å³; $Z = 8$; $d_c = 3.95$ g cm⁻³. A final conventional R factor of 0.029 was obtained using 1207 nonzero reflections. The structural unit is a fluorine-bridged tetramer similar to those reported for $(\text{RuF}_6)_4$ and $(\text{OsF}_6)_4$. Each Rh atom is coordinated by six fluorine atoms in an approximately octahedral arrangement. Each of a cis pair of F atoms in the RhF_6 group is shared with another Rh atom, the Rh-F-Rh angle being $135 \pm 1^\circ$ and the Rh-F interatomic distance $\sim 2.01 \pm 0.01$ Å. For the other F atoms in the RhF_6 group the Rh-F interatomic distances are within the range 1.796 (4)–1.820 (4) with an average distance of 1.808 (8) Å.

Introduction

Of the group VIII transition metals, the following pentafluorides are known: RuF_5 ,¹ OsF_5 ,² RhF_5 ,³ IrF_5 ,⁴ and PtF_5 .⁵ Attempts to prepare PdF_5 have failed so far.⁶ The crystal structures of RuF_5 and OsF_5 have been reported,^{7,8}

and X-ray powder photography has shown^{3,4} all of the platinum-metal pentafluorides to be isomorphous. Evidently these pentafluorides constituted a class which was structurally distinct⁴ from the pentafluorides of Tc⁹ and Re¹⁰ on the one hand and those of Nb,¹¹ Mo¹², Ta,¹¹ and W¹³ on the other hand. Although the close resemblance of the X-ray powder photographs of the pentafluorides of

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