**Table IV.** $^{195}Pt$ NMR Parameters from Figure 2

| peak | $\delta$ | $^1J_{PtP}$/Hz | peak | $\delta$ | $^1J_{PtP}$/Hz |
|---|---|---|---|---|---|
| A ($[PtL_4]$) | –5741 | 5393 | D triplet | –5222 | 5456 |
| B ($[PtL_3]$) | –4984 | 6398 | E triplet | –5217 | 5413 |
| C triplet | –5177 | 5471 | | | |

A solution of $[Pt(cod)_2]$ and 2 equiv of $P(O\text{-}n\text{-}Bu)_3$ was treated with pentafluorobenzene. Three major products were observed in the proton-decoupled $^{31}P$ NMR spectrum, two of which were identified as $[PtL_3]$ and $[PtL_4]$. The third component exhibited a $^{31}P$ NMR chemical shift at 123.7 ppm with $^{195}Pt$ satellites; $^1J_{PtP} = 4536$ Hz. The infrared spectrum of the crude materials (recorded in the supplementary material) showed a strong band at 2040 $cm^{-1}$, attributable to $\nu(M—H)$, together with other peaks assignable to a coordinated $C_6F_5$ group. We therefore propose that the compound *trans*-$[PtH(C_6F_5)(P(O\text{-}n\text{-}Bu)_3)_2]$ is present. It has not been possible to obtain a satisfactory $^{195}Pt$ NMR spectrum of this compound owing to the weakness of the signals produced. This is not surprising since the $^{195}Pt$ center will be coupled to $^1H$, $^{19}F$, and $^{31}P$ nuclei. Similarly, we were not able to detect the hydride signal in the $^1H$ NMR spectrum. However, when the $^{31}P$ NMR spectrum is selectively decoupled by irradiating the phosphorus signal at the resonance frequency of the $-OCH_2-$ protons, the signal at $\delta = 123.7$ is split into a doublet with a $^2J_{PH}$ value of 6 Hz.

It has not been possible to isolate a pure sample of the hydride for analysis. Recrystallization from methanol will precipitate most of the $[PtL_4]$ formed in the reaction according to eq 2 and 3. The

$$[PtL_3] + C_6HF_5 \rightleftharpoons [PtH(C_6F_5)L_2] + L \qquad (2)$$

$$[PtL_3] + L \rightarrow [PtL_4] \qquad (3)$$

hydride however appears to be too unstable for isolation. Indeed, heating a crude sample at 80 °C under vacuum at $10^{-2}$ mmHg for 4 h causes the loss of $C_6HF_5$ (indicated by the IR spectrum). The hydride may be regenerated from the resulting platinum-containing compound by treatment with $C_6HF_5$.

If the $^{31}P$ NMR spectrum is run in the presence of excess $C_6HF_5$, no signal due to $[PtL_3]$ is detected, due to eq 2 being shifted to the right.

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**Registry No.** $[Pt(cod)_2]$, 12130-66-4; $[Pt(P(O\text{-}n\text{-}Bu)_3)_4]$, 63372-11-2; $[Pt(PPh_3)_4]$, 14221-02-4; $[Pt(As(n\text{-}Bu)_3)_4]$, 97277-51-5; $[Pt(Sb(n\text{-}Bu)_3)_4]$, 97277-52-6; *cis*-$[PtI_2(P(O\text{-}n\text{-}Bu)_3)_2]$, 97277-53-7; $[PtI_2(cod)]$, 12266-72-7; $[Pt(CO_3)(P(O\text{-}n\text{-}Bu)_3)_2]$, 97277-54-8; $[Pt(C_2O_4)(P(O\text{-}n\text{-}Bu)_3)_2]$, 97277-55-9; $[Pt(P(O\text{-}n\text{-}Bu)_3)_3]$, 97277-56-0; *trans*-$[PtH(C_6F_5)(P(O\text{-}n\text{-}Bu)_3)_2]$, 97277-57-1; $C_6HF_5$, 363-72-4.

**Supplementary Material Available:** $^{195}Pt$ NMR spectrum of $[Pt(P(O\text{-}n\text{-}Bu)_3)_4]$ (Figure 1), $^{31}P$ NMR spectrum of a freshly prepared mixture of $[Pt(P(O\text{-}n\text{-}Bu)_3)_n]$, $n = 3$ and 4 (Figure 2), $^{31}P$ NMR spectrum of the mixture of $[Pt(P(O\text{-}n\text{-}Bu)_3)_3]$ and $[Pt(P(O\text{-}n\text{-}Bu)_3)_4]$ after 5 months (Figure 3), $^{195}Pt$ NMR spectrum of the mixture of $[Pt(P(O\text{-}n\text{-}Bu)_3)_3]$ and $[Pt(P(O\text{-}n\text{-}Bu)_3)_4]$ after 5 months (Figure 4), infrared spectrum of $[Pt(CO_3)(P(O\text{-}n\text{-}Bu)_3)_2]$ (Figure 5), infrared spectrum of $[Pt(C_2O_4)(P(O\text{-}n\text{-}Bu)_3)_2]$ (Figure 6), and infrared spectrum of *trans*-$[PtH(C_6H_5)(P(O\text{-}n\text{-}Bu)_3)_2]$ (Figure 7) (7 pages). Ordering information is given on any current masthead page.

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(34) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIa become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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## Catalytic Effect of Nitrate Ions on Cobalt(III) Substitution Reactions. Solvent-Exchange Data from Oxygen-17 NMR Measurements

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A rather remarkable nitrate ion catalysis of various substitution and isomerization reactions involving Co(III) and Cr(III) complexes in aqueous solution has been reported by several groups in recent years.[2-8] This is a rather discouraging observation since nitrate media are often selected and preferred for ionic strength adjustments mainly because many metal complexes are significantly more soluble in nitrate than for instance in perchlorate medium. Plane and Taube[9] reported that the rate of water exchange for $Cr(H_2O)_6^{3+}$ varied directly with the anion concentration at high salt concentrations, and nitrate ion was found to be the most effective catalyst in this sense. Later work[10] showed that the rate constant for solvent exchange at infinite dilution was similar for both nitrate and perchlorate media. Similar catalytic effects of nitrate ions were reported for the trans to cis isomerization of $Cr(C_3H_2O_4)_2(H_2O)_2^-$,[2] the anation of *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ by oxalate,[3,4] and the substitution of $Cr(C_2O_4)_2(NH_2CH_2COO)^{2-}$ by oxalate.[5] However, this is not a general tendency since no specific catalytic effect was observed for the anation of *cis*-$Cr(C_2O_4)(en)(H_2O)_2^+$ by oxalate.[11]

Very similar effects were recently reported for the anation of *cis*-$Co(en)_2(H_2O)_2^{3+}$, $\alpha$-*cis*-$Co(edda)(H_2O)_2^+$ (edda = ethylenediaminediacetate), and $Co(NH_3)_4(H_2O)_2^{3+}$ by oxalic acid.[6-8] The nitrate medium resulted in abnormally high ion-pair formation constants[12,13] when compared to those found in perchlorate medium. It was suggested[6,7] that nitrate ions catalyze solvent exchange on the metal center via a pull-off interaction to produce a five-coordinate intermediate. The dissociative nature of this process was underlined by volume of activation data.[14-16] Other authors prefer to interpret such catalytic effects of nitrate ions as an enhancement of the ion-pair formation process.[8,17,18]

The present study was undertaken to determine the medium sensitivity of solvent exchange for *cis*-$Co(en)_2(H_2O)_2^{3+}$ in acidic medium. Earlier studies[19,20] determined the solvent-exchange rate constant in perchlorate medium with use of an $^{18}O$-labeling technique, which involved precipitation of the exchanged complex, heating to remove the coordinated water, and conversion of the latter to $CO_2$ for a mass spectrometric analysis. Today a neater and less time-consuming method is available with which such solvent-exchange processes can be followed in situ, viz. $^{17}O$ NMR.

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## Experimental Section

*cis*-[Co(en)$_2$CO$_3$]ClO$_4$ was prepared according to standard procedures[21,22] and converted to *cis*-[Co(en)$_2$(H$_2$O)$_2$](ClO$_4$)$_3$ by acidifying with perchloric acid. Chemical analyses[23] and UV-visible absorption spectra recorded on a Perkin-Elmer 555 spectrophotometer were in excellent agreement with the theoretically expected values and those reported elsewhere,[12,14] respectively. The $^{17}$O-enriched aquo complex was prepared by heating a saturated solution of the complex in 20% H$_2$$^{17}$O (Ventron) for 4 days at 40 °C and pH ~2.[20] The labeled complex was isolated through freeze-drying and exhibited UV-visible absorption spectra identical with that of the unlabeled complex. All other chemicals used were of analytical reagent grade.

Preliminary $^{17}$O NMR measurements were recorded at 13.56 MHz on a Varian XL 100 spectrometer. Kinetic measurements were performed at 67.80 MHz on a Bruker AM 500 spectrometer equipped with a 10-mm broad-band insert. Data acquisition, exponential multiplication, Fourier transformation, and intensity measurements were carried out with an Aspect 3000 computer. The spectrometer was operated with a deuterium lock system to improve its field stability, and acetone-$d_6$ was placed in a coaxial capillary inside the NMR tube to ensure that no deuterium isotope exchange could interfere with the measurements. Temperature control was accomplished with the aid of a Bruker B-VT 1000 variable-temperature unit. A series of carefully planned temperature callibration experiments was performed to determine the sample temperature and its stability during the kinetic measurements. An overall temperature constancy and reproducibility of ±0.5 K was found. In order to be able to distinguish between possible medium effects, great care was taken to perform the solvent-exchange measurements in the different media under identical conditions, i.e. identical sample tubes, timing parameters, temperature adjustments, and spectrometer settings.

A 160-mg amount of the labeled complex was dissolved in 2.6 mL of 99.99% H$_2$$^{16}$O (Ventron) that contained the appropriate quantity of concentrated HNO$_3$ or HClO$_4$. The data accumulation is fast as a result of the short quadrupolar relaxation time of the $^{17}$O nucleus (acquisition time is 0.045 s). For example, the exchange rate at 50 °C was such that an accumulation time of 7.5 min (10 000 scans) was selected, and between 20 and 25 spectra were used for the kinetic analysis. The exchange process is considerably slower at 40 °C[20] such that an accumulation time of 19 min (20 000 scans) and a delay of 20 min were adopted. Appropriate conditions were selected for the measurements at the remaining temperatures.

The determination of the exchange rate constant was carried out either manually, i.e. by measuring the signal height ($h$) as a function of reaction time ($t$) and plotting ln $h$ vs. $t$, or automatically with use of a Bruker software package (peak-picking and exponential-fitting routine). The results of these procedures were in excellent agreement within the statistical error limits involved.

## Results and Discussion

The solvent-exchange rate constant for *cis*-Co(en)$_2$(H$_2$O)$_2$$^{3+}$ was determined according to the described procedure in 2 M HClO$_4$ and 2 M HNO$_3$ media. These conditions were adopted since the earlier reported catalytic effect of nitrate ion was observed under such conditions.[6] It is furthermore known that no cis to trans isomerization or the participation of aquohydroxo complexes will interfere with the solvent-exchange process under such conditions.[20,24]

A typical set of $^{17}$O NMR spectra for an exchange experiment is given in Figure 1. Some time was allowed for temperature equilibration after dissolution of the labeled complex in the preheated solvent before the first spectrum was recorded. The intensity of the signal for coordinated water at 126 ppm decreases whereas the signal for free (uncoordinated) water at 0 ppm increases as a function of reaction time. Under the employed conditions, i.e. dissolution of the labeled complex in 99.99% H$_2$$^{16}$O (containing HNO$_3$ or HClO$_4$), the exchange reaction goes almost to completion and the signal for coordinated water disappears at longer reaction times. A semilogarithmic plot of peak height vs. time is linear for more than 3 half-lives of the reaction as seen from the examples given in Figure 2. Some preliminary measurements in pure water (natural-abundance $^{17}$O) demonstrated that a correction for the peak intensity at infinity must be made under such conditions. A summary of the obtained solvent-exchange data and those reported in the literature is given in Table I.

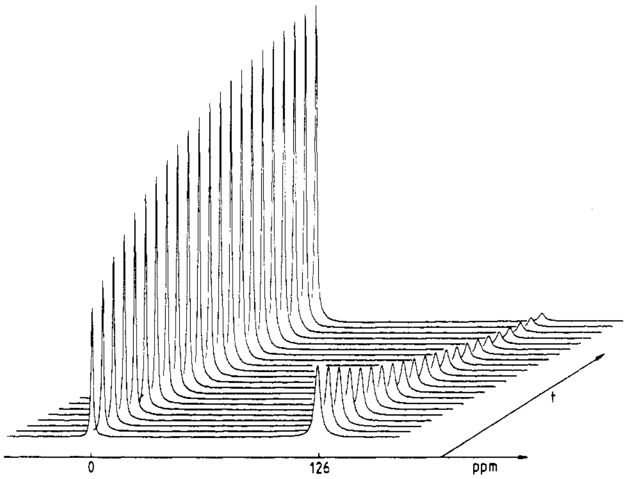

**Figure 1.** $^{17}$O NMR spectra recorded during the reaction *cis*-Co(en)$_2$(H$_2$$^{17}$O)$_2$$^{3+}$ + H$_2$O → *cis*-Co(en)$_2$(H$_2$O)$_2$$^{3+}$ + H$_2$$^{17}$O. Conditions: [Co(III)] = 0.12 M; [HClO$_4$] = 2 M; temp = 40 °C; data accumulation time 20 min; delay 20 min.

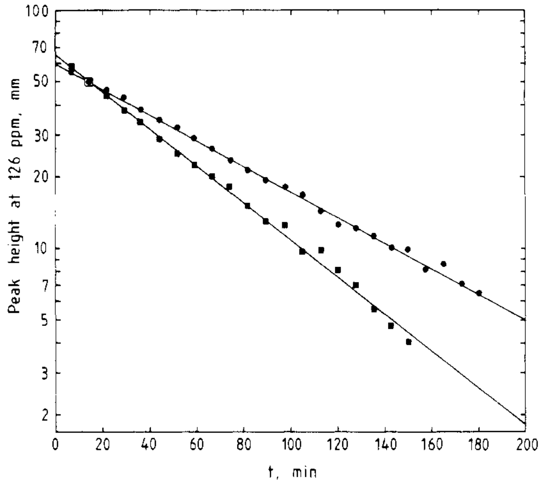

**Figure 2.** Plot of log (peak height) vs. reaction time: (●) [HClO$_4$] = 2 M; (■) [HNO$_3$] = 2 M. Conditions: [Co(III)] = 0.12 M; temp = 50.0 °C; data accumulation time 7.5 min; delay 0.

Before discussing these data, it is important to note that the NMR spectra also showed that a slight $^{17}$O enrichment occurred for perchlorate, but not for nitrate ion, during the exchange process. This is a remarkable observation since the spontaneous exchange of oxygen for HClO$_4$ is much slower ($t_{1/2} >$ 100 years[25]) than that for HNO$_3$ in the absence of the complex. This observation indicates that perchlorate may be coordinated to the Co(III) center at some stage during the exchange process. However, no evidence for the formation of any stable perchlorato or nitrato complexes during the solvent-exchange process could be obtained from the NMR spectra. This observation depends on the detection limit of the NMR method, which can safely be assumed to be of the order of a few percent of the total complex concentration in the present case. In addition, this is in agreement with the general instability of such species[26-28] and kinetic findings reported elsewhere.[6] From this we conclude that perchlorato and

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**Table I.** Solvent-Exchange Data for *cis*-$Co(en)_2(H_2O)_2^{3+}$ in Acidic Aqueous Solution

| reacn medium | temp, °C | $k$, $s^{-1}$ | $\Delta H^*$, kcal $mol^{-1}$ | $\Delta S^*$, cal $K^{-1}$ $mol^{-1}$ | ref |
|---|---|---|---|---|---|
| 2 M $HNO_3$ | 25.5 | $(7.91 \pm 0.19) \times 10^{-6}$ | 27.4 ± 0.5 | +9.8 ± 1.6 | *a* |
| | 40.0 | $(6.50 \pm 0.10) \times 10^{-5}$ | | | |
| | 50.0 | $(2.98 \pm 0.05) \times 10^{-4}$ | | | |
| | 60.0 | $(1.01 \pm 0.04) \times 10^{-3}$ | | | |
| 2 M $HClO_4$ | 25.5 | $(4.98 \pm 0.08) \times 10^{-6}$ | 27.8 ± 0.5 | +10.4 ± 1.4 | *a* |
| | 40.0 | $(4.62 \pm 0.01) \times 10^{-5}$ | | | |
| | 50.0 | $(2.05 \pm 0.02) \times 10^{-4}$ | | | |
| | 60.0 | $(6.93 \pm 0.24) \times 10^{-4}$ | | | |
| 0.8 M $HClO_4$ | 25.0 | $7.5 \times 10^{-6}$ | 29.2 ± 0.4 | +15.8 ± 1.4 | 20 |
| | 39.9 | $7.7 \times 10^{-5}$ | | | |

[a] This work.

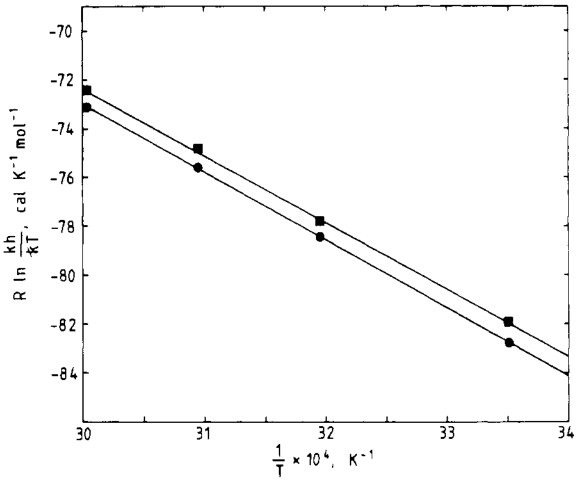

**Figure 3.** Plot of $R \ln (kh/\kappa T)$ vs. $1/T$: (■) $[HNO_3]$ = 2 M; (●) $[HClO_4]$ = 2 M. Conditions: [Co(III)] = 0.12 M.

nitrato complexes could represent at most only a few percent of the cobalt(III) species in solution and can therefore not rule out their possible participation as unstable intermediates.

On the average the exchange rate constant is approximately 50% higher in nitric acid than in perchloric acid medium. The activation parameters are identical within the low experimental error limits and are in close agreement with those reported by Kruse and Taube.[20] However, the enhancement in nitric acid medium is observed at each temperature and must be due to slightly smaller values for $\Delta H^*$ and $\Delta S^*$ (see Figure 3). The catalytic effect of the nitrate medium is rather disappointing in the light of the very strong effects observed for the substitution reaction with oxalic acid.[6-8] From this we conclude that direct chemical effects cannot account for the observed data but that these are most probably due to secondary medium effects. We can offer a few possible explanations, of which one has been mentioned above.

Earlier similar observations[2,3] led to the suggestion that some interaction occurs between water in the first solvation sphere of the nitrate ion and coordinated water. If these water molecules exchange, i.e. coordinated water replaces the water of solvation around the nitrate ion, it is expected to show up in $\Delta S^*$ as a solvational effect. In such a case nitrate ions influence the magnitude of the rate constant but not the mechanism of the process. Such an interaction of nitrate ion with the coordinated water molecule could be due to its higher basicity than perchlorate ion and could result in the partial formation of an aquohydroxo complex ion. This process could also be visualized in terms of specific ion-pair formation accompanied by the partial deprotonation effect. Such an interaction would then result in a more labile coordinated water molecule since it is known that *cis*-$Co(en)_2(H_2O)OH^{2+}$ is ca. 100 times more labile than the diaquo complex species.[20] It follows that only a weak interaction could account for the observed 50% enhancement in the exchange rate constant. Deprotonation of coordinated water accompanied by an increase in the solvent-exchange lability has also been reported for the $Fe(H_2O)_6^{3+}$ species, where $Fe(H_2O)_5OH^{2+}$ is suggested to exchange its coordinated solvent according to a dissociative reaction mode compared to a much slower associative reaction mode for the $Fe(H_2O)_6^{3+}$ species.[29,30]

In respect to the above, our original suggestion[6] of nitrate-catalyzed formation of a five-coordinate intermediate is not that unrealistic, even if it occurs only to a minor extent. However, the present results do force us to modify our earlier view from a direct catalytic effect (which should show up in $\Delta H^*$) to an indirect medium effect with very similar activation parameters. The more dissociative nature of the solvent exchange on *cis*-$Co(en)_2(H_2O)_2^{3+}$ in the presence of nitrate ion is furthermore in agreement with the slightly more positive $\Delta V^*$ value found for the substitution reaction with oxalic acid in nitrate as compared to that in perchlorate medium.[16]

In conclusion, the effect of nitrate on the solvent exchange of *cis*-$Co(en)_2(H_2O)_2^{3+}$ is small and is of the same order as found for the exchange of $Cr(H_2O)_6^{3+}$ at 2-4 M ionic strength and 27 °C.[9] Whether this effect can really account for the large effect observed during the reaction with oxalic acid remains unanswered, and the possible involvement of oxalic acid itself with the solvent-exchange process cannot be excluded. It is further obvious that a diaquo arrangement is required,[6-8] since such catalytic effects do not show up for monoaquo species.[31] This in turn is also in line with our suggestion of the partial formation of an aquohydroxo intermediate to account for the nitrate effect.

The results of this investigation demonstrate the sensitivity and accuracy of the method employed to determine the solvent-exchange rate constants. Further studies on the medium and pH dependencies of such exchange reactions involving Co(III) and Cr(III) complexes are presently under way.

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**Registry No.** *cis*-$[Co(en)_2(H_2O)_2]^{3+}$, 21247-59-6; $NO_3^-$, 14797-55-8; $H_2O$, 7732-18-5.

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## Mononuclear, Low-Valent Osmium Nitrosyl Complexes

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Recently we have reported novel $\{RuNO\}^5$ and $\{RuNO\}^7$ complexes.[1] Only one monomeric osmium(I) complex, [Os(N-

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