

rise to a more intense dominant CD band than the *SS* (*RR*) isomer. Thus, a mixture of the two isomers should give rise to a more intense dominant CD band than the *SS* (*RR*) isomer alone. That the carbonato complex exhibits a distinctly higher $\Delta\epsilon$ than the corresponding oxalato and malonato complexes is consistent, then, with the distribution of isomers determined by the pmr studies.

Summary. The geometrical isomerism of Co(III)-EDDA complexes permits a study of how changes in the ligand geometry affect rotatory strengths. The changes observed in the CD spectra are consistent with the changes known to occur in two important structural sources of dissymmetry in these complexes, the arrangement of chelate rings and the configurations about the asymmetric nitrogen atoms.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation (Grant GP-34490X), and the National Institutes of Health (GM 18983-01) for support of this research. J. I. L. is grateful for a National Institutes of Health Special Fellowship for study at the Harvard Medical School (1972-1973).

Registry No. *uns-cis*- Λ -[Co(EDDA)CO₃]⁻, 50306-65-5; *uns-cis*- Λ -[Co(EDDA)ox]⁻, 50306-66-6; *uns-cis*- Λ -[Co(EDDA)mal]⁻, 50306-67-7; *uns-cis*-Na[Co(EDDA)CO₃], 50306-68-8; [Co(en)₂ox][Co(EDDA)CO₃], 50306-69-9; *uns-cis*-[Co(EDDA)CO₃]⁻, 26135-69-3; HO₂-CCO₂H, 144-62-7; *uns-cis*-K[Co(EDDA)ox], 50306-71-3; [Co(en)₂-ox][Co(EDDA)mal], 50306-72-4.

Contribution from the School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

Effects of Ligand Modifications on the Kinetics of Base Exchange in Methylatobis(diimine)cobalt(III) Adducts¹

RANDOLPH J. GUSCHL and THEODORE L. BROWN*

Received September 19, 1973

The kinetics of base exchange in CH₃Co(chel)B complexes, where chel = bis(dimethylglyoximate) (I), diacetylmonoxime-iminodiacetylmonoximate-1,3-propane (II), or 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene (III), have been observed in various organic solvents, most notably C₆H₅NO₂. The rates of base exchange with II are in the order CH₃OH > NCCH₃ > N(CH₃)₃ > S(CH₃)₂ > P(OCH₃)₃ > 1-(2-trifluoromethylphenyl)imidazole, which parallels the order previously observed for adducts of I. Adducts with III are of generally lower thermal stability, and extensive kinetics data could not be obtained. For P(OCH₃)₃ as base, ΔG^\ddagger for exchanges with I, II, and III are essentially all the same. For NCCH₃ as base, ΔG^\ddagger varies in the order III > II > I. In all three complexes, exchange of oxygen bases from the axial position was quite rapid, although oxygen bases appear to bind relatively more strongly in the order III > II > I. These results and other base exchange data are consistent with a small variation in positive charge at the central metal in the order III > II > I. Exchange of the proton in the OHO bridge of II with free water in C₆H₅Br is considerably slower than the analogous process for the OHO protons of I. These observations are consistent with the shorter O...O distance in II as compared with I.

Introduction

In previous publications we have reported the rates of base exchange for alkylatobis(dimethylglyoximate)cobalt(III) complexes, RCo(dh)₂B, on the basis of variable temperature nmr studies.^{2,3} These results have served to establish an ordering of a wide range of bases with respect to exchange lability. In addition, variation of the group R has served to point up the existence of a substantial trans effect on base exchange.⁴ More recently we have determined the comparative kinetics of exchange of bases from three methylatocobalt(III) chelate complexes, CH₃Co(chel)B, primarily on the basis of ¹⁹F nmr exchange data for the base 1-(2-trifluoromethylphenyl)imidazole, ImCF₃.⁵ The free energy of activation for exchange of ImCF₃ from CH₃Co(dh)₂, CH₃Co(bae), and methylato(cobyrinic acid heptamethyl ester) was found to be 21.2, 9.4, and 16.7 kcal/mol, respectively. This very large range of ΔG^\ddagger values demonstrates

the importance of the planar ligand system in determining the lability of the cobalt center.

More subtle changes in the nature of the planar ligand system would make it possible to evaluate the effect of changing ligand donor character on the relative labilities of a series of bases. Accordingly, we have observed the nmr spectra of several adducts of the three cobalt systems CH₃-Co(dh)₂, CH₃Co(tmed)⁺, and CH₃Co(tim)²⁺ shown as I, II, and III, respectively.

These complexes differ in the successive replacement of the (-OHO)⁻ groups which bind together the two diimine halves of the ligand by -(CH₂)₃- groups. Since the (-OHO)⁻ group carries a net negative charge, it is expected to be relatively more electron releasing than -(CH₂)₃-. Accordingly, the effective charge on cobalt should increase in the order I < II < III. The overall charge on the cobalt complex also increases, of course, as indicated above. At the same time, the geometry about the metal center changes very little in the series. Variations in base exchange rates may thus be ascribed to predominantly electronic rather than steric effects.

Results and Discussion

In the presence of excess base, the nmr spectra of complexes I, II, and III show resonances assignable to free and coordinated base. Table I lists the chemical shifts of these resonances at a temperature in the stopped-exchange region,

(1) This research was supported in part by The National Science Foundation through Grants GP6396X and GP30256X. Computer calculations were performed on the Sigma-5 Computer in the Materials Research Laboratory, University of Illinois.

(2) L. M. Ludwick and T. L. Brown, *J. Amer. Chem. Soc.*, **91**, 5188 (1969).

(3) T. L. Brown, L. M. Ludwick, and R. S. Stewart, *J. Amer. Chem. Soc.*, **94**, 384 (1972).

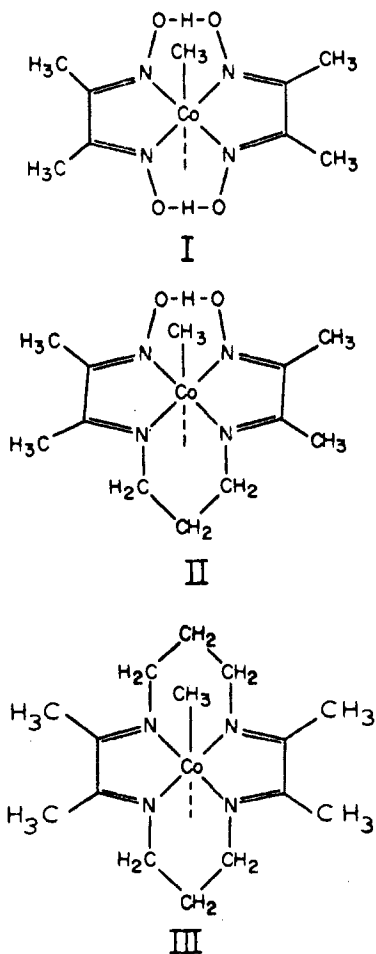
(4) R. J. Guschl, R. S. Stewart, and T. L. Brown, *Inorg. Chem.*, **13**, 417 (1974).

(5) R. J. Guschl and T. L. Brown, *Inorg. Chem.*, **12**, 2815 (1973).

Table I. Nmr Coalescence Data for $\text{CH}_3\text{Co}(\text{chel})\text{B}$ Adducts

Base	Solvent	Temp, °C	Chemical shifts, τ		T_c , °C	k_{T_c} , ^a sec ⁻¹	ΔG^\ddagger ^b
			Coord	Free			
			chel = (dh) ₂				
NCCH ₃	1:1 ^c	-31	8.00	7.95	-9 ^d	3.8	14.7
Thioxane ^e	C ₆ H ₅ Br	36	7.83	7.61	55 ^f	29.2	17.1
S(CH ₃) ₂	C ₆ H ₅ NO ₂	28	8.09	7.98	62 ^d	30.6	17.4
N(CH ₃) ₃	C ₆ H ₅ NO ₂	28	7.95	7.83	78 ^d	32.7	18.3
P(C ₆ H ₅) ₃ ^e	C ₆ H ₅ Br	36		8.63 ^g	75 ^f	17.8	18.5
3-Fluoropyridine	C ₆ H ₅ NO ₂	28	11,547 ^h	11,899 ^h	127 ^h	683 ⁱ	18.5
CNCH ₃ ^j	(Cl ₂ CH) ₂	41	6.70	6.90	110 ^f	26.7	20.1
P(OCH ₃) ₃	C ₆ H ₅ NO ₂	28		8.67 ^g	111 ^d	27.2	20.2
ImCF ₃	C ₆ H ₅ NO ₂	28	5562 ^h	5591 ^h	136 ^h	45.0	21.1
P(<i>n</i> -Bu) ₃	C ₆ H ₅ NO ₂	28		8.82 ^g	150 ^d	6.2	23.5
			chel = tmed				
CH ₃ OH	1:1 ^c	-30	6.94	6.55	-2 ^d	86.5	13.4
NCCH ₃	1:1 ^c	-15	8.21	8.00	19 ^d	20.5	15.3
S(CH ₃) ₂	C ₆ H ₅ NO ₂	28	8.18	7.99	69 ^d	55.7	17.4
N(CH ₃) ₃	C ₆ H ₅ NO ₂	28	7.99	7.83	56 ^d	47.9	16.8
P(OCH ₃) ₃	C ₆ H ₅ NO ₂	28		8.75 ^g	117 ^d	28.2	20.5
ImCF ₃	C ₆ H ₅ NO ₂	28	5557 ^h	5578 ^h	126 ^h	21.6	21.2
			chel = tim				
NCCH ₃	1:1 ^c	-15	7.95	8.11	36 ^d	57.6	15.6
P(OCH ₃) ₃	C ₆ H ₅ NO ₂	28		8.22 ^g	110 ^d	28.0	20.1
ImCF ₃	C ₆ H ₅ NO ₂	28	5573 ^h	5569 ^h	<i>k</i>	<i>k</i>	<i>k</i>

^a Apparent first-order rate constants at the coalescence temperature (T_c) accurate within $\pm 15\%$ unless otherwise stated. ^b Free energy of activation at the coalescence temperature in kcal mol⁻¹, accurate to ± 0.1 kcal mol⁻¹. ^c 1:1 refers to a mixture made from equal volumes of methylene chloride and nitrobenzene. ^d Observed at 100 MHz. ^e L. M. Ludwick, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1969. ^f Observed at 60 MHz. ^g Chemical shift of center of axial methyl doublet. ^h ¹⁹F resonances observed at 94.1 MHz, in Hz upfield from CFCl₃. ⁱ The uncertainties with this base are 683 ± 300 sec⁻¹ for *k* and ± 0.30 kcal mol⁻¹ for ΔG^\ddagger . ^j R. S. Stewart, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1971. ^k Coalescence not observed.



the solvent medium used, the temperature at which free and coordinated resonances coalesce, T_c , and the corresponding

free energies of activation ($\Delta G_{T_c}^\ddagger$) at the coalescence temperature. For ImCF₃ and 3-fluoropyridine (FPy), the ¹⁹F resonances of free and coordinated base were observed, using ¹H-¹⁹F decoupling. In the case of phosphorus donors, ³¹P-¹H coupling to the axial methyl protons was employed to evaluate rates of exchange. When the coordinated base exchanges rapidly with free base, the doublet due to scalar coupling collapses to a singlet.

For dimethyl ether as base, slow exchange was not observed with any system at temperatures as low as -45° in a 1:1 volume mixture of methylene chloride and nitrobenzene. In the presence of I, II, or III the (CH₃)₂O absorption at τ 6.77 is insensitive to the concentration of excess base present. Either free and coordinated base exhibit the same chemical shift or the formation constants for adducts of I, II, and III with (CH₃)₂O are low.

Nmr spectra in the region of intermediate exchange were successfully obtained for I, II, and III with the bases listed in Table II. For these systems, the nmr spectra at various temperatures were subjected to line shape analysis. Arrhenius plots of the calculated first-order rate constants for dissociation were obtained. The resulting kinetics parameters are also listed in Table II. Some of the reported activation energies and ΔH^\ddagger values are subject to considerable uncertainty. The rather high values for the energies lead to a very steep temperature dependence in the nmr spectra, thus aggravating the effect of uncertainties in temperature. Further, the frequency separation between the two lines of the exchanging doublet is small, increasing the difficulty of accurate line shape analysis. The Arrhenius plots generally yield Arrhenius energies accurate to within ± 3 kcal mol⁻¹ at the 99% confidence level. This does not, however, take into account possible systematic errors; thus, an uncertainty of 3 kcal mol⁻¹ must be taken as corresponding to less than a 99% confidence level. The relative ΔG^\ddagger values, on the other hand, are comparatively more reliable. The values

Table II. Comparative Activation Parameters for the Dissociation of Base from Alkyl Cobalt(III) Adducts

Base	Solvent	Temp, °C	k_T , sec ⁻¹	E_a^a	ΔG^\ddagger^a	ΔH^\ddagger^a	ΔS^\ddagger^b	A , sec ⁻¹
chel = (dh) ₂								
NCCH ₃	1:1 ^c	10	51.2	20 ^d	14.3	19	18	1 × 10 ¹⁷
S(CH ₃) ₂	C ₆ H ₅ NO ₂	65	42.9	25	17.4	24	20	4 × 10 ¹⁷
N(CH ₃) ₃	C ₆ H ₅ NO ₂	65	8.3	25	18.5	24	16	6 × 10 ¹⁶
P(C ₆ H ₅) ₃ ^e	C ₆ H ₅ Br	100	136	21	18.4	20	5	3 × 10 ¹⁴
FPy	C ₆ H ₅ NO ₂	130	874	23 ^d	18.4	22	9	3 × 10 ¹⁵
P(OCH ₃) ₃	C ₆ H ₅ NO ₂	100	11.9	24	20.2	23	8	1 × 10 ¹⁵
ImCF ₃	C ₆ H ₅ NO ₂	130	26.1	28	21.2	27	15	4 × 10 ¹⁶
chel = tmed								
NCCH ₃	1:1 ^c	10	6.8	21	15.5	20	16	6 × 10 ¹⁶
S(CH ₃) ₂	C ₆ H ₅ NO ₂	65	38.5	24	17.4	23	16	5 × 10 ¹⁶
N(CH ₃) ₃	C ₆ H ₅ NO ₂	65	129	23	16.6	23	18	2 × 10 ¹⁷
P(OCH ₃) ₃	C ₆ H ₅ NO ₂	100	6.5	24	20.6	24	8	1 × 10 ¹⁵
ImCF ₃	C ₆ H ₅ NO ₂	130	28.7	23	21.2	22	2	6 × 10 ¹³
chel = tim								
NCCH ₃	1:1 ^c	10	2.5	21	16.0	20	16	3 × 10 ¹⁶
P(OCH ₃) ₃	C ₆ H ₅ NO ₂	130	10.9	27	20.2	26	16	7 × 10 ¹⁶

^a kcal mol⁻¹. ^b cal deg⁻¹ mol⁻¹. ^c 1:1 refers to a solvent mixture made of equal volumes of methylene chloride and nitrobenzene. ^d Assumed activation energy (see text). ^e L. M. Ludwick, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1969.

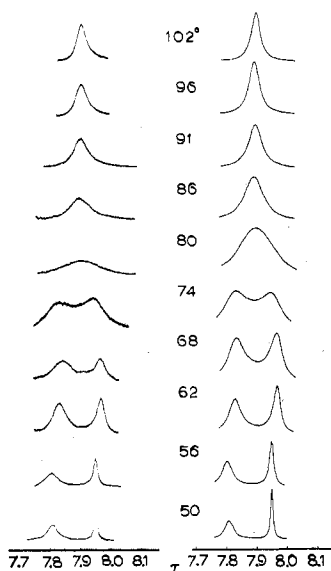


Figure 1. Experimental and calculated 100-MHz ¹H nmr spectra of free and coordinated NH₃ at various temperatures of CH₃Co(dh)₂N(CH₃)₃ in nitrobenzene.

listed in Table II, which correspond to the temperature of coalescence, are accurate to within about 0.1 kcal mol⁻¹.

Typical experimental and calculated spectra are shown for three representative systems: Figure 1, CH₃Co(dh)₂N(CH₃)₃ in nitrobenzene; Figure 2, CH₃Co(tmed)NCCH₃ in a 1:1 mixture of nitrobenzene and methylene chloride; Figure 3, CH₃Co(tmed)ImCF₃ in nitrobenzene. The Arrhenius plots corresponding to P(OCH₃)₃ and NCCH₃ as bases are shown in Figures 4 and 5, respectively.

Unfortunately, comparisons with a common base in all three systems were possible only for P(OCH₃)₃ and NCCH₃ adducts. The nmr spectra for adducts of II and III reveal noticeably broader resonances for free base than those involving I. For example, with S(CH₃)₂, the natural line widths at half-height in the absence of exchange for free base are 1 Hz with I, approximately 10 Hz with II, and so broad in the presence of III that exchange studies are impossible. A similar trend was observed with N(CH₃)₃ and NCCH₃, but with NCCH₃ the free acetonitrile resonance in the presence of III was still narrow enough to be observed and subjected to analysis.

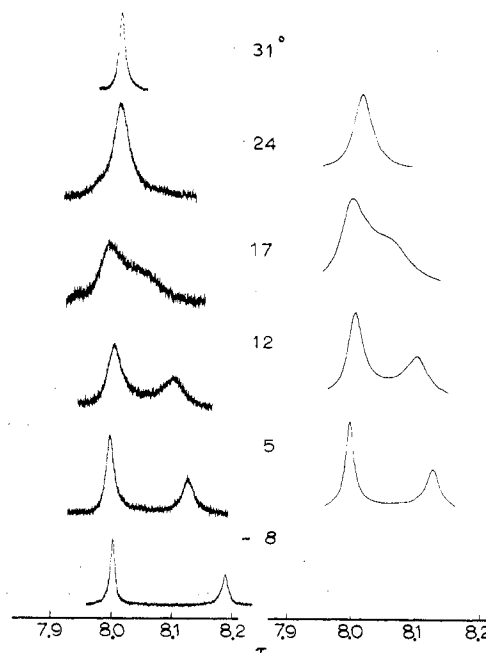


Figure 2. Experimental and calculated acetonitrile resonances in the region of intermediate exchange for CH₃Co(tmed)NCCH₃⁺ in 1:1 CH₂Cl₂-C₆H₅NO₂.

Since free base in solution, in the presence of excess sodium tetraphenylborate, does not show similar broadening, it seems likely that the interactions leading to broadening of the free base signal are with an impurity generated in sample preparation. The presence of a small amount of paramagnetic Co(II) impurity produced by decomposition of the adduct is possibly responsible. Free base would coordinate to this impurity and undergo rapid ligand exchange characteristic of d⁷ complexes.

Decomposition of adducts of II and III was observed for many of the bases employed. Although the P(OCH₃)₃ adduct of I is thermally stable at temperatures in excess of 150°, yellow solutions of the P(OCH₃)₃ adduct of II gradually darken over a period of 1 hr at this temperature. The yellow nitrobenzene solutions of the P(OCH₃)₃ adduct of III turn black in several minutes at temperatures over 110°. To obtain spectra, it was necessary to prepare many samples and use each one only until decomposition became evident. Similar decompositions were noted for other adducts of III,

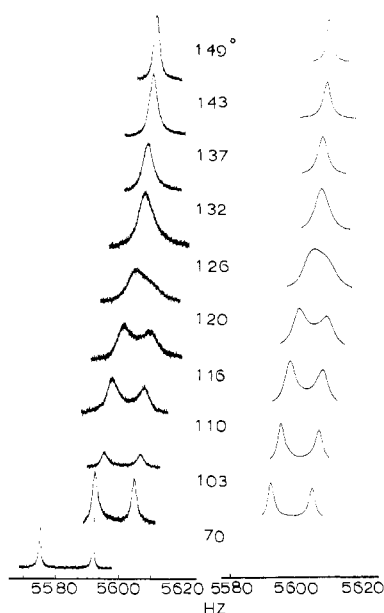


Figure 3. Experimental and calculated ^{19}F nmr spectra at various temperatures for $\text{CH}_3\text{Co}(\text{tmed})\text{ImCF}_3^+$ in nitrobenzene.

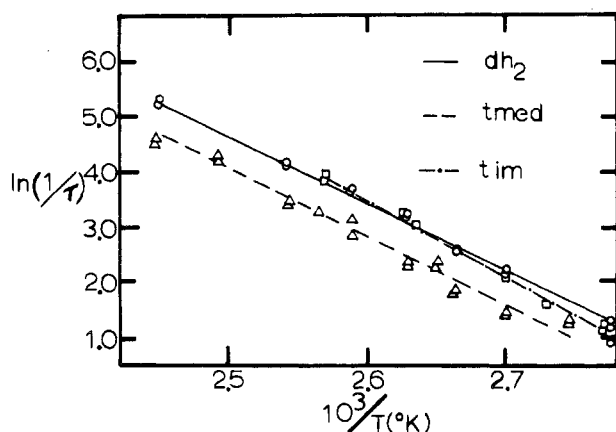


Figure 4. Plot of $\ln(1/\tau)$ vs. $10^3/\text{temp}$ ($^\circ\text{K}$) for the $\text{CH}_3\text{Co}(\text{chel})\text{P}(\text{OCH}_3)_3$ systems in nitrobenzene: (\circ) chel = $(\text{dh})_2$, (Δ) chel = tmed, (\square) chel = tim.

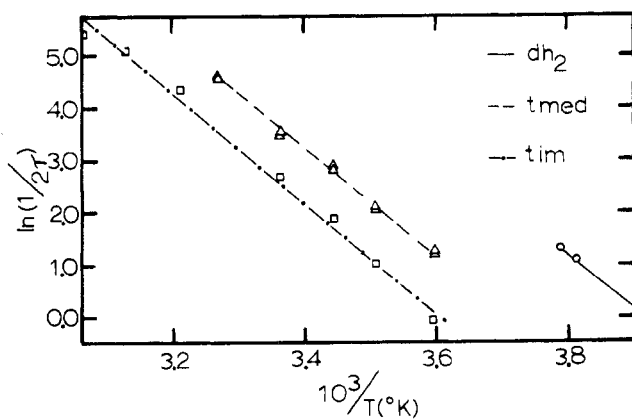


Figure 5. Plot of $\ln(1/2\tau)$ vs. $10^3/\text{temp}$ ($^\circ\text{K}$) for the exchange of NCCH_3 from $\text{CH}_3\text{Co}(\text{chel})$ in 1:1 $\text{CH}_2\text{Cl}_2\text{-C}_6\text{H}_5\text{NO}_2$: (\circ) chel = $(\text{dh})_2$, (Δ) chel = tmed; (\square) chel = tim.

but most noteworthy is the $\text{N}(\text{CH}_3)_3$ adduct of III in nitrobenzene. At room temperature, decomposition is complete within seconds of mixing, even under an inert atmosphere.

To test whether the observed decompositions were a func-

tion of the anions present, trimethyl phosphite adducts of II were isolated and studied as both tetraphenylborate and hexafluorophosphate salts. In nitrobenzene, similar decompositions occur at 150° ; the rates of exchange evaluated from spectra in the region of intermediate exchange are identical within the error limits assigned to these procedures. (Rate constants are accurate within $\pm 15\%$ at near coalescence and to within $\pm 25\%$ in regions of slow or fast exchange.)

Exchange of trimethyl phosphite from $\text{CH}_3\text{Co}(\text{dh})_2\text{-P}(\text{OCH}_3)_3$ has previously been studied and reported^{3,4} to proceed *via* a limiting SN_1 mechanism. The comparable rates in nitrobenzene for adducts of II and III reported in Table II and Figure 4 are also independent of the concentration of base. In each case the collapse of the doublet due to $^{31}\text{P}\text{-}^1\text{H}$ coupling between base to axial methyl protons was followed (6.8 Hz for I, 6.3 Hz for II, and 6.0 Hz for III). Although the differences in the rates of exchange are less than a factor of 2 at 100° , ΔH^\ddagger may be a bit larger for III than for I and II.

The relative rates for interaction with NCCH_3 are in order $\text{I} > \text{II} > \text{III}$. At 10° the estimated rates of exchange are 51.6, 6.8, and 2.5 sec^{-1} , respectively, well outside the ranges of uncertainties associated with these values. The calculated free energies of activation support an order of lability $\text{I} > \text{II} > \text{III}$. To test the reproducibility of these results and determine the effect of solvent, several spectra were run using varying amounts of excess base. Also the interaction of NCCH_3 with II was examined in three different solvent media, Table III.

Although the chemical shift separations between free and coordinated base in these three solvents differ considerably, the observed free energies of activation are essentially the same, within experimental uncertainties, in the solvents studied. The results are consistent with a limiting SN_1 exchange mechanism for acetonitrile exchange. If the transition states were stabilized by solvents such as CH_2Cl_2 as a result of hydrogen bonding interactions, the observed rates would differ noticeably from those in aromatic solvent media. The results in Table III suggest that such interactions are weak or nonexistent.

The Arrhenius plots for rates of acetonitrile exchange with I, II, and III are shown in Figure 5. The $\text{CH}_3\text{Co}(\text{tim})\text{NCC-H}_3^{2+}$ data were obtained over a temperature range of 48° , but for $\text{CH}_3\text{Co}(\text{tmed})\text{NCCCH}_3^+$ the range was only 26° . For $\text{CH}_3\text{Co}(\text{dh})_2\text{NCCCH}_3$, spectra could be analyzed successfully at only two temperatures, -11 and -16° . A value for E_a of 20 kcal mol^{-1} was used to estimate the exchange rate at higher temperatures for the cobaloxime system.

Acetonitrile is normally considered only a σ donor and, like $\text{N}(\text{CH}_3)_3$, is not expected to act as a π acceptor toward the cobalt center. A decrease in electron release from the chelate ligand to the metal center increases the charge on the metal. Such an effect should be reflected in an increase in the strength of the σ interaction with bases. On the other hand, π back-bonding from the metal to the axial base would be expected to become less important, since the d_{xz} and d_{yz} orbitals which mix with the ligand π orbitals in π back-bonding are of lower energy around a more positively charged cobalt center. Accordingly, as the metal center becomes more highly charged, ligands such as NCCH_3 should be bound more tightly. Ligands which also act as π acceptors would be expected to experience a stronger σ interaction, partially offset by the concomitant loss of π bonding stabilization. The observed essentially invariant exchange rate for trimethyl phosphite with I, II, and III might be the net result of such opposing effects.

Table III. Solvent Effects on Chemical Shifts between Free and Coordinated Base, and Kinetics Parameters for $\text{CH}_3\text{Co}(\text{tmed})\text{NCCH}_3^+ + \text{NCCH}_3$ Exchange

Solvent	Temp, °C	Chem shifts, τ		T_c^a	k_{T_c} , sec ⁻¹	E_a^b	ΔH^\ddagger^b	ΔS^\ddagger^c	$\Delta G^\ddagger^{b,d}$
		Coord	Free						
1:1 CH_2Cl_2 - $\text{C}_6\text{H}_5\text{NO}_2$	-15	8.21	8.00	19	20	20.7	20.1	16	15.3
$\text{C}_6\text{H}_5\text{NO}_2$	-4	7.96	7.91	3	3.3	20 ^e	19.4	14	15.5
1:1 $\text{C}_6\text{H}_5\text{Br}$ - $\text{C}_6\text{H}_5\text{NO}_2$	9	8.53	8.39	20	22	20 ^e	19.4	14	15.4

^a T_c = coalescence temperature. ^b kcal mol⁻¹. ^c cal deg⁻¹ mol⁻¹. ^d ΔG^\ddagger at coalescence temperature. ^e Assumed activation energy.

The observed trends for interactions with $\text{S}(\text{CH}_3)_2$, ImCF_3 , and $\text{N}(\text{CH}_3)_3$ are limited to complexes of I and II due to the instability of the adducts with III. The rates of base exchange for ImCF_3 and $\text{S}(\text{CH}_3)_2$ with I and II are essentially identical for a given base similar to the result observed for the corresponding trimethyl phosphite adducts.

The data obtained with trimethylamine as base are satisfactory only with I in nitrobenzene (Figure 1). In similar studies with II and III, rapid decomposition prevented accurate rate determinations.

For many systems in Table I, a complete line shape analysis was not possible, and only at the coalescence temperature were rate assessments possible. Therefore, we base our discussion mainly upon estimates of rates of exchange, *i.e.*, upon comparative free energies of activation.

The data in Tables I and II establish an order of rates of base exchange for II similar to that observed for adducts of I, $\text{CH}_3\text{OH} > \text{NCCH}_3 > \text{N}(\text{CH}_3)_3 > \text{S}(\text{CH}_3)_2 > \text{P}(\text{OCH}_3)_3 > \text{ImCF}_3$. The observed kinetics of CH_3OH exchange with II represents the first semiquantitative evaluation (Table I) of exchange rate for any oxygen base with a complex of the type I, II, or III. In a 1:1 solvent mixture of methylene chloride and nitrobenzene, a resonance at τ 6.94 was observed below 0°, assigned to coordinated methanol. The integrated signal for this absorption is equal to that for the axial methyl. At -2° it coalesces with the free methanol resonance at τ 6.55.

The observed rate of 86.5 sec⁻¹ at -2° is considerably greater than the value of 6.9 sec⁻¹ at 25° reported^{6,7} for the dissociation of H_2O from the aquo complex, followed by substitution with benzimidazole.

In 1 M aqueous NaNO_3 solution⁷ the substitution process appears to follow a more complex rate law, interpreted in terms of a preequilibrium between the aquo cobalt complex and attacking ligand. Although we do not know the rate law for methanol exchange in our experiments, a purely first-order pathway operates in all instances for which we have data. In any event, the methanol exchange rate we observe is unexpectedly fast compared with the water substitution rates observed by Costa and coworkers.^{6,7}

The room temperature nmr spectra of the adducts of all three systems with a given base are remarkably similar, although structural changes are obvious. Figure 6 shows the 100-MHz spectra of the $\text{P}(\text{OCH}_3)_3$ adducts of I, II, and III in nitrobenzene at 28°. The presence of only one (-OHO)⁻ group in II causes a nonequivalence of the planar methyl groups which is not present in either of the other systems. Accordingly, the two chelate resonances at τ 7.49 and 7.54 both show scalar ^{31}P - ^1H coupling to the phosphorus of the coordinated base. The protons of the $-(\text{CH}_2)_3^-$ units appear as broad multiplets for both II and III. For the tim

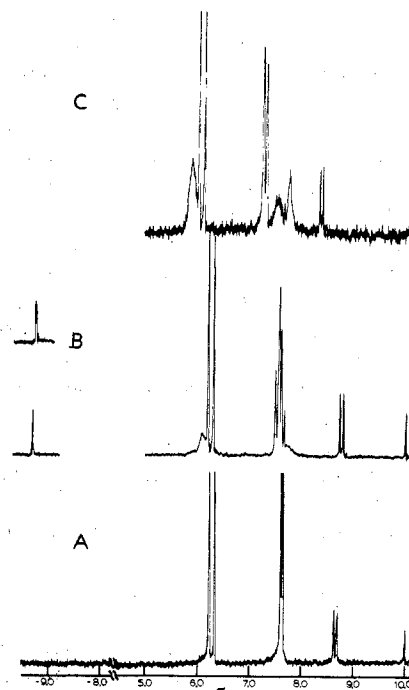


Figure 6. Proton magnetic resonance spectra (100 MHz) of $\text{CH}_3\text{Co}(\text{chel})\text{P}(\text{OCH}_3)_3$ systems in nitrobenzene: (A) chel = $(\text{dh})_2$, (B) chel = tmed, (C) chel = tim.

chelate, Busch, *et al.*, assigned⁸ the downfield multiplets (τ 5.4 to 5.6) to the protons on the carbons α to the imine nitrogens and the upfield patterns (τ 7.1 to 7.3) to the remaining protons. In the analogous tmed system, the α protons appear from τ 6.00 to 6.20 and the β protons from τ 6.70 to 8.00. Neither the triplet pattern of the α protons nor the quintet splitting of the β protons is obvious, but the widths of the observed resonances suggest that such splittings may be present but unresolved because of other couplings to ^{31}P or to the planar methyl groups. Unfortunately, one of the main difficulties associated with obtaining nmr spectra from these systems is the overlap of base resonances with the absorptions due to $-(\text{CH}_2)_3^-$.

The bridging $(-\text{OHO})^-$ protons of I have been shown³ to undergo rapid exchange with free water at room temperature. Even under the conditions in Figure 6, the $(-\text{OHO})^-$ resonance is too broad to observe. In bromobenzene below -10°, this resonance is a sharp singlet at τ -8.98 which broadens significantly when excess water is added. At room temperature, this same resonance is undetectable due to exchange broadening. On the other hand, the bridging $(-\text{OHO})^-$ proton in II appears as a sharp, nonexchanging doublet ($J_{^{31}\text{P}-^1\text{H}} = 1\text{Hz}$) at τ -9.30 in nitrobenzene at room temperature. In the presence of excess water (τ 7.67 in

(6) G. Costa, G. Mestroni, G. Tauzher, D. M. Goodall, M. Green, and H. A. O. Hill, *Chem. Commun.*, 34 (1970).

(7) G. Tauzher, R. Dreos, G. Costa, and M. Green, *J. Chem. Soc., Chem. Commun.*, 413 (1973).

(8) S. C. Jackels, K. Farmery, E. K. Barefield, N. J. Rose, and D. H. Busch, *Inorg. Chem.*, 11, 2893 (1972).

Figure 6), this resonance does not show exchange broadening below 80°.

It is interesting that the bridging proton in II exchanges more slowly than those in I. From a crystal structure determination of the aquo complex of II as a perchlorate salt,⁹ the O-O bond distance is reported to be 2.39 Å. In the P(OCH₃)₃ adduct of I, the O-O bond distance is 2.458 Å.¹⁰ A shortening of the O-O distance is consistent with a tighter (-OHO-) hydrogen bond in compounds of II, thus leading to slower proton exchange.

The chemical shifts of the axial methyl group of adducts of I, II, and III are reported in Table IV. In this listing, the adducts have been ordered relative to the position of the axial resonance of adducts of I. As observed earlier,¹¹ this shift is quite sensitive to the nature of the axial base trans to it, but the observed range varies. For complexes of II, the Co-CH₃ resonance is observed from τ 8.75 to 9.23, almost identical with the range of τ 8.62 to 9.19 observed for adducts of I. Similar resonances for adducts of III are further downfield, in the interval τ 8.08 to 8.61. Dodd and Johnson suggest¹¹ that the chemical shifts of these resonances are influenced by the ring current, if any, of the equatorial chelate. Such effects reportedly shield the methyl group in methylcobalt(aetioporphyrin) to produce an upfield signal of τ 15.15 in CDCl₃. If such an effect is operative in this study, the effect is even less pronounced for tim than tmed or (dh)₂.

No quantitative correlation has been found between the Co-CH₃ shift and some property of the base, but there is a noticeable shift downfield as the coordinating atom has a greater tendency to act as a π acceptor. A similar ordering of adducts arises in connection with the ⁵⁹Co nmr chemical shifts.¹²

To obtain the resonances in Table IV, the appropriate adducts were isolated and dissolved in the solvent, except in the case of oxygen bases. For these systems the dimer (I), ligand-free material (II), or aquo complex (III) was mixed *in situ* with the base and solvent in the nmr tube. Accordingly, there is some doubt as to whether the oxygen adducts were actually formed. Rapid equilibria between adduct, ligand-free material, and the aquo complex could account for the observed room temperature spectra of II and III with the oxygen base in nitrobenzene. Therefore, the same interactions were observed at temperatures of -30° or lower. At this temperature, I exhibits dimeric behavior in the absence of a base which can effectively coordinate to the cobalt.¹³ Since nitrobenzene solidifies at 5.7°, a solvent mixture of equal volumes of methylene chloride and nitrobenzene was employed. In all samples at least a twofold excess of base was present relative to the metal center. The expected dimeric association of I was observed in the presence of dimethyl ether. With THF, dioxane, and methanol, dimerization did not occur, indicating adduct formation. These observations are consistent with the observations of Drago, *et al.*,¹⁴ however, the concentrations of base used in the present study were significantly lower. Contrary to earlier indications,³ I binds to oxygen bases, although the interaction differs significantly from that with sulfur bases.

(9) S. Bruckner, M. Calligaris, G. Nardin, and L. Randaccio, *Inorg. Chim. Acta*, **3**, 278 (1969).

(10) G. D. Stucky and J. Swanson, to be submitted for publication.

(11) D. Dodd and M. D. Johnson, *Organometal. Chem. Rev.*, **52**, 1 (1973).

(12) R. LaRossa and T. L. Brown, *J. Amer. Chem. Soc.*, in press.

(13) A. W. Herlinger and T. L. Brown, *J. Amer. Chem. Soc.*, **94**, 388 (1972).

(14) R. L. Courtright, R. S. Drago, J. A. Nusz, and M. S. Nozari, *Inorg. Chem.*, **12**, 2809 (1973).

Table IV. Chemical Shift^a of Axial Methyl Resonance in Adducts of CH₃Co(chel)B in Nitrobenzene at 28°^b

Base	chel		
	(dh) ₂	tmed	tim
None	9.19	8.98	
N(CH ₃) ₃	9.16	9.13	8.51 (9°)
O(CH ₂ CH ₂) ₂ O	9.14	8.99	8.42
THF	9.14	9.10	8.44
CH ₃ OH	9.11	9.23	8.51
H ₂ O	9.08	9.06	8.40
DMSO	9.06 ^c	9.23	8.60
C ₂ H ₅ N	8.95		8.36
ImCF ₃	8.95 (44°)	8.97 (44°)	8.44
Ppy	8.94 (44°)	8.87 (44°)	8.38
NCCH ₃	8.92	8.99	8.38
P(<i>n</i> -Bu) ₃	8.82		
S(CH ₃) ₂	8.80	8.79	8.14 (2°)
S(CH ₂ CH ₂) ₂ O	8.74	8.74	8.08 (9°)
CNCH ₃	8.70		
P(OCH ₃) ₃	8.67	8.75	8.22
P(C ₆ H ₅) ₃	8.63		
As(C ₆ H ₅) ₃	8.62		

^a Relative to TMS τ 10.00. ^b Except where another temperature is given in parentheses. ^c Resonance broad due to exchange processes.

Results for the interaction of I with H₂O were not observed due to the insolubility of the adduct in most solvents. The interaction of II with H₂O is important; in this case the aquo complex is very soluble. Fortunately, the presence of H₂O does not affect the rates of exchange with stronger bases. A sample containing II, THF, and water shows a single set of exchange-averaged resonances at room temperature. However, at -30° distinct resonances appear for the THF and aquo complexes.

Repeated attempts to remove axially bound water from the aquo complex of III were unsuccessful. The compound was unchanged after two days of drying at 120° *in vacuo*. Nmr samples of the aquo complex with other oxygen bases *in situ* show resonances for only the aquo complex, even at -30°. In contrast, water can be completely removed from the aquo complex of I in less than 6 hr at 80° *in vacuo*. However, 12 hr of vacuum pumping at 110° is necessary to remove H₂O from the aquo complex of II. In the former case, a red dimer is formed,¹³ while in the latter a red ligand-free material of unknown structure results. Regardless of its structure, however, elemental analysis and the nmr spectrum in nitrobenzene are indicative of no axially bound water. The red material readily binds to sulfur, phosphorus, or nitrogen bases to give adducts of good analytical purity.

The observed ease of H₂O removal from the aquo complexes in the order I > II > III is consistent with an increase in σ bonding in the same order. It appears safe, therefore, to speculate that oxygen base adducts of III would be readily accessible if the axially bound base used in preparation of the complex could be removed and replaced in total absence of H₂O.

With dimethyl sulfoxide (DMSO) and I a sulfur bonded \rightleftharpoons oxygen bonded equilibrium has been observed at low temperatures.³ Values for the O/S ratio of 4.6 at -72° and 3.7 at -25° have been reported in a 3:2, *d*⁶-DMSO-CH₂Cl₂ solvent medium. In this same solvent, II and III do not show isomerization even at -70°, the lowest temperature studied. The chemical shifts of the axial methyls for these systems suggest exclusively oxygen binding (Table IV).

Although the cobalt center may have an inherent preference for sulfur bonding, steric interactions with the DMSO methyl groups could force oxygen binding except in the case of I, where the preference for sulfur is strong enough to partially overcome this interference.

The interactions with thioxane ($S(CH_2CH_2)_2O$), a sulfur-oxygen base which shows no steric preferences, were observed and found to involve exclusively sulfur coordination. It appears, therefore, that I, II, and III are all "soft"¹⁵ in the sense of preference for sulfur coordination over oxygen. It also appears that the relative order of this preference in conjunction with the observed stabilities of aquo complexes and measured rates of base exchange is $I > II > III$, consistent with an order of electron donation by the equatorial chelate of $(dh)_2 > tmed > tim$.

Experimental Section

Materials. Complexes were prepared following established procedures or modifications of such procedures. All adducts unless otherwise stated were found to be stable in the solid state and were characterized by nmr and elemental analysis. Analytical results for adducts used in nmr studies are given in the microfilm edition.

Solvents and Bases. All solvents were distilled and stored over freshly activated Linde 4A molecular sieves. The observed boiling range of the nitrobenzene was 207–209° and for methylene chloride 39.5–40.5°. 3-Fluoropyridine was generously donated by the Chemical Division of the Olin Corp., Stanford, Conn. 06904, and was used without further purification. 1-(2-Trifluoromethylphenyl)imidazole was prepared following a published procedure.¹⁶ Trimethyl phosphite was freshly distilled (111–112°). All other bases were reagent grade and stored over molecular sieves.

Syntheses. Adducts of methylatobis(dimethylglyoximate)cobalt(III) were prepared from the ligand-free dimer, which in turn was prepared by removal of water from methylaquocobaloxime by heating *in vacuo* at 80° for several hours. The methylaquocobaloxime was prepared by previously described procedures.¹⁷ To prepare the adducts, base was added either to the dimer itself, and excess base evaporated off, or to a benzene solution of the dimer, followed by removal of the solvent to give crystalline solids. Details regarding syntheses of several *tmed* and (*tim*) complexes are given in the microfilm edition,¹⁸ as are the analytical results for all compounds studied.

(15) R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963).

(16) A. L. Johnson, J. C. Kauer, D. C. Sharma, and R. I. Dorfman, *J. Med. Chem.*, **12**, 1024 (1969).

(17) G. N. Schrauzer, *Inorg. Syn.*, **11**, 61 (1968).

(18) See paragraph at end of paper regarding supplementary material.

Nmr spectra were obtained and line shape analyses performed as described elsewhere.^{4,19,20}

Registry No. $CH_3Co(dh)_2NCCH_3$, 25482-30-8; $CH_3Co(dh)_2S(CH_3)_2$, 25482-40-0; $CH_3Co(dh)_2N(CH_3)_3$, 25482-34-2; $CH_3Co(dh)_2P(C_6H_5)_3$, 15977-37-4; $CH_3Co(dh)_2(FPy)$, 50600-15-2; $CH_3Co(dh)_2P(OCH_3)_3$, 25586-92-9; $CH_3Co(dh)_2ImCF_3$, 42012-06-6; $CH_3Co(dh)_2P(n-Bu)_3$, 51020-41-8; $CH_3Co(tmed)CH_3OH^+$, 50600-16-3; $CH_3Co(tmed)NCCH_3^+$, 50600-17-4; $CH_3Co(tmed)S(CH_3)_2^+$, 50600-18-5; $CH_3Co(tmed)N(CH_3)_3^+$, 50600-19-6; $CH_3Co(tmed)P(OCH_3)_3^+$, 50600-20-9; $CH_3Co(tmed)ImCF_3^+$, 50600-21-0; $CH_3Co(tim)NCCH_3^{2+}$, 47247-19-8; $CH_3Co(tim)P(OCH_3)_3^{2+}$, 50600-22-1; $CH_3Co(tim)ImCF_3^{2+}$, 50790-61-9; $CH_3Co(dh)_2$, 36609-02-6; $CH_3Co(dh)_2O(CH_2CH_2)_2O$, 50600-23-2; $CH_3Co(dh)_2THF$, 50600-24-3; $CH_3Co(dh)_2CH_3OH$, 50600-25-4; $CH_3Co(dh)_2H_2O$, 25360-55-8; $CH_3Co(dh)_2DMSO$, 25482-32-0; $CH_3Co(dh)_2C_6H_5N$, 23642-14-0; $CH_3Co(dh)_2S(CH_2CH_2)_2O$, 25482-33-1; $CH_3Co(dh)_2CNCH_3$, 38141-49-0; $CH_3Co(dh)_2As(C_6H_5)_3$, 29130-83-4; $CH_3Co(tmed)^+$, 50599-98-9; $CH_3Co(tmed)O(CH_2CH_2)_2O^{2+}$, 50599-99-0; $CH_3Co(tmed)THF^+$, 50790-62-0; $CH_3Co(tmed)H_2O^+$, 26334-78-1; $CH_3Co(tmed)DMSO^+$, 50600-00-5; $CH_3Co(tmed)(FPy)^+$, 50600-01-6; $CH_3Co(tmed)S(CH_2CH_2)_2O^+$, 50600-02-7; $CH_3Co(tim)N(CH_3)_3^{2+}$, 50600-03-8; $CH_3Co(tim)O(CH_2CH_2)_2O^{2+}$, 50600-04-9; $CH_3Co(tim)THF^{2+}$, 50600-05-0; $CH_3Co(tim)CH_3OH^{2+}$, 50600-06-1; $CH_3Co(tim)H_2O^{2+}$, 50600-07-2; $CH_3Co(tim)DMSO^{2+}$, 50600-08-3; $CH_3Co(tim)C_6H_5N^{2+}$, 50600-09-4; $CH_3Co(tim)(FPy)^{2+}$, 50600-10-7; $CH_3Co(tim)S(CH_3)_2^{2+}$, 50600-11-8; $CH_3Co(tim)S(CH_2CH_2)_2O^{2+}$, 50600-12-9.

Supplementary Material Available. A table of analytical data and details regarding syntheses will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N. W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-959.

(19) K. C. Williams and T. L. Brown, *J. Amer. Chem. Soc.*, **88**, 4134 (1966).

(20) R. J. Guschl, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1973.

Contribution from the Department of Chemistry,
State University of New York at Buffalo, Buffalo, New York 14214

Kinetics and Mechanism of Aqueation and Formation Reactions of Carbonato Complexes. VI. Rhodium(III) and Iridium(III) Carbonatopentaammine Complex Ions¹

D. A. PALMER and G. M. HARRIS*

Received October 8, 1973

Preparative procedures have been devised for the previously unreported complex salts $[Rh(NH_3)_5CO_3]ClO_4 \cdot H_2O$ and $[Ir(NH_3)_5CO_3]ClO_4$. Kinetic studies have been made of the acid-catalyzed decarboxylation of these compounds in aqueous solution. The kinetics of carbon dioxide uptake by the hydroxo ions $Rh(NH_3)_5OH^{2+}$ and $Ir(NH_3)_5OH^{2+}$ to form carbonato complex ions has also been investigated. At 25° and $I = 0.5 M$, the aqueation rate constants k_1 (see eq 1 below) are 1.13 and 1.45 sec^{-1} for the Rh(III) and Ir(III) carbonato species, respectively, while the rate constants k_2 for CO_2 uptake by the corresponding hydroxo complexes are 470 and $590 M^{-1} \text{ sec}^{-1}$, respectively. Temperature-dependence parameters have been determined and mechanistic conclusions drawn on the basis of comparisons with previously published data concerning the kinetics of various reactions of Co(III), Rh(III), and Ir(III) complex ions.

Introduction

It has frequently been found that comparisons of the ki-

netics of reactions of complex ions which differ only in the identity of the central metal ion provide valuable insights into their properties. Such studies, have been made, for example, of various reactions of complex ions of the type $M(NH_3)_5X^{n+}$, where $M = Co(III), Rh(III),$ or $Ir(III)$, and X is a ligand which differs from NH_3 . A classic comparison

(1) (a) This research was reported in preliminary form at the Northeast Regional Meeting of the American Chemical Society, Buffalo, N. Y., Oct 11–13, 1971. (b) Part V: E. Chaffee, T. P. Dasgupta, and G. M. Harris, *J. Amer. Chem. Soc.*, **95**, 4169 (1973).