$(CH_3)_3\cdot OC_4H_8$, 8.5 ± 1 for $Al(CH_3)_3\cdot(CH_3)_3COCH(CH_3)_2$, 6.9 ± 2 for $Al(CH_3)_3\cdot S(CH_3)_2$, and 5.8 ± 2 for $Al(CH_3)_3\cdot S[CH_2CH(CH_3)_2]_2$. These values are consistent with the bimolecular pathway proposed; the calculated entropies of activation in all cases are on the order of −12 eu.

It is likely that the intermediate in a base-assisted exchange process of the type described is important in determining the rates of reaction of certain substrates with $Al(CH_3)_3$. For example, Ashby and coworkers have shown that the reaction of trimethylaluminum with benzophenone is very strongly influenced by the presence of excess trimethylaluminum.[17] Whereas the reaction of the adduct by itself to form the alkoxide, eq 28, requires 24 hr at reflux for completion, in the presence of excess $Al_2(CH_3)_6$ the reaction proceeds very much more rapidly. Formation of the alkoxide requires the transfer of a methyl group from the metal to the carbonyl carbon. It is reasonable to suppose that this might occur much more readily in an intermediate analogous to I than in the simple adduct by itself. The kinetic data reported for the benzophenone system[17] have been interpreted in terms of an interaction between the $(CH_3)_3AlOC(C_6H_5)_2$ and monomeric $Al(CH_3)_3$, rather than with the dimer as depicted in I. This is quite consistent with our suggestion, since the methyl group transfer is more likely to occur upon interaction of the adduct with the more strongly acidic monomer. Complex formation with $Al_2(CH_3)_6$ has, however, been suggeted in another system.[18]

$$(CH_3)_3AlOC(C_6H_5)_2 \longrightarrow (CH_3)_2AlOC(CH_3)(C_6H_5)_2 \qquad (28)$$

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[17] E. C. Ashby, J. Laemmle, and H. M. Neumann, *J. Amer. Chem. Soc.*, **90**, 5179 (1968).

[18] P. E. M. Allen, B. O. Bateup, and B. A. Casey, *J. Organometal. Chem.*, **29**, 185 (1971).

Nuclear Magnetic Resonance Studies of Methylatobis(dimethylglyoximato)cobalt(III) Adducts[1]

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Contribution from the Materials Research Laboratory and the School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801. *Received May 5, 1971*

Abstract: Reaction of bases with dimeric methylatobis(dimethylglyoximato)cobalt(III) in CH_2Cl_2 or C_6H_5Br solution leads to adducts: $[CH_3Co(DH)_2]_2 + 2L \rightleftarrows 2CH_3Co(DH)_2L$. Adduct formation is essentially complete, as evidenced by the proton nmr spectra at temperatures in the slow-exchange region, for L = $N(CH_3)_3$, CH_3CN, C_5H_5N, $P(OCH_3)_3$, $P(C_6H_5)_3$, $(CH_3)_2SO$, and $S(CH_3)_2$. The equilibrium was observed to be incomplete for diphenyl sulfoxide. Coordination isomerism is observed for dimethyl sulfoxide; the ratio of oxygen to sulfur coordination at −25° is 3.7. Addition of aquomethylatobis(dimethylglyoximato)cobalt(III) to d_6-DMSO containing some CH_2Cl_2 results in displacement of H_2O. The reciprocal mean-exchange time of protons between the water and the OHO bridges is estimated from the line shapes to be on the order of 10 and 50 sec^{-1} at 5 and 25°, respectively. Detailed line-shape studies at various temperatures yield Arrhenius activation energies for dissociation of the $P(OCH_3)_3$ and $P(C_6H_5)_3$ complexes of 23 and 21 kcal/mol, respectively, with an estimated uncertainty of about 3 kcal/mol.

In an earlier communication[2] we reported some observations on the ligand-exchange behavior of complexes of methylatobis(dimethylglyoximato)cobalt(III), $CH_3Co(DH)_2$ (also referred to as methylcobaloxime[3]). We report here some further details of the observations regarding ligand exchanges. In the contribution which follows[4] we describe detailed studies of the ligand-free forms of $RCo(DH)_2$ compounds, which are dimeric.

The $[CH_3Co(DH)_2]_2$ dimer is readily disrupted in solution by a variety of bases to form adducts $CH_3Co(DH)_2L$, where L may be an amine, sulfide, phosphite, phosphine, isonitrile, or other base.[5] The adducts vary considerably in the strength of the cobalt–ligand bond, as evidenced by the rates of dissociation of the ligand L, measured using nmr techniques.[2]

Attention has been drawn to the similarity of the cobalt–carbon bond in the alkylcobaloximes to that in methylcobalamin and coenzyme B_{12}.[3,6,7] The behavior of the metal center in the methylcobaloxime with respect to ligation in the position trans to the methyl group is of interest because of its possible relevance to binding of the vitamin to substrates. There is, of course, a great difference in the degree of steric hindrance toward coordination in the two systems. The electronic environments of the cobalt in the two systems may, however, be quite similar,[7] and thus they might be expected to exhibit the same preferential binding of certain ligand types. Comparison of the results reported in this work with the relatively slight evidence regarding coordination to methyl-

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[1] This research was supported in part by Grant No. GP6396X from The National Science Foundation, and in part by The Advanced Research Projects Agency under Contract No. HC 15-67-C-0221.

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

[3] G. N. Schrauzer, *Accounts Chem. Res.*, **1**, 97 (1968).

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

[5] G. N. Schrauzer and R. J. Windgassen, *ibid.*, **88**, 3738 (1966).

[6] (a) G. N. Schrauzer and J. Kohnle, *Chem. Ber.*, **97**, 3056 (1964); (b) G. N. Schrauzer, R. J. Windgassen, and J. Konnle, *ibid.*, **98**, 3324 (1965); (c) G. N. Schrauzer and R. J. Windgassen, *ibid.*, **99**, 602 (1966).

[7] G. N. Schrauzer, L. P. Lee, and J. W. Sibert, *J. Amer. Chem. Soc.*, **92**, 2997 (1970).

cobalamin or methylcobinamide[8] suggests, however, that there may be significant differences between the model and naturally occurring systems.

Experimental Section

Materials. Ligand-free methylcobaloxime was prepared from the aquo complex by azeotropic distillation of a benzene suspension of methylaquocobaloxime.[5,9] When water no longer appeared in the distillate, the suspension was cooled, filtered quickly, and dried under vacuum for several hours. Adducts of the methylcobaloxime were prepared by adding the appropriate basic ligand to a suspension of the ligand-free material in benzene or toluene. In some instances, the adducts were isolated and then dissolved in the solvent of interest, whereas in other instances the complexes were prepared *in situ*. Satisfactory elemental analyses were obtained on all complexes isolated including those of the more weakly bound ligands such as dimethyl sulfoxide (DMSO), diphenyl sulfoxide (DPSO), and tetramethylene sulfoxide (TMSO). Nmr samples were degassed on a vacuum line and sealed. Solvents were dried by treatment with freshly activated Linde 4A Molecular Sieves.

Nmr Spectra. ^{1}H nmr spectra were recorded on a Varian A-60A, A-56/60, or HA-100 spectrometer. Variable temperatures were obtained using the Varian temperature controller. Temperature measurements were made using an iron–constantan thermocouple. An external oscillator was used to calibrate the spectra and determine chemical shift values. A 980-Hz side band of TMS was used to mark the location of the low-field resonances observed (about 18 ppm downfield from TMS). All spectra were referenced to TMS as internal standard.

The nmr exchange spectra were analyzed using a computer program for a two-site system.[10] For selected spectra, a Calcomp routine was used to provide a visual display of calculated and experimental spectra.

Results and Discussion

The chemical shifts of the proton resonances in several $CH_3Co(DH)_2L$ adducts in CH_2Cl_2 solution are listed in Table I. With the exception of diphenyl sulfoxide, DPSO, discussed below, the equilibrium favoring formation of the adduct is essentially complete.

$$[CH_3Co(DH)_2]_2 + 2L \rightleftarrows 2CH_3Co(DH)_2L \qquad (1)$$

Table I. Chemical Shifts of Cobaloxime Protons in $CH_3Co(DH)_2$ Adducts[a]

Ligand	Temp, °C	τ_{CH_3} (axial)	τ_{OHO}	τ_{DH}
		CH_2Cl_2 Solutions		
C_5H_5N	−30	9.35	−8.75	7.91
$N(CH_3)_3$	5	9.43	−8.40	7.81
CH_3CN	−52	9.33	−8.59	7.80
$P(OCH_3)_3$	−40	9.08	−8.53	7.81
$P(OC_2H_5)_3$	−40	9.18	−8.40	7.97
$P(C_6H_5)_3$	−44	8.97	−8.57	8.18
$S(CH_3)_2$	−30	9.09	−8.39	7.79
$SO(C_6H_5)_2$	−55	9.55	−8.84	7.98
$SO(CH_2)_4$	−40	9.60		7.78
$SO(CH_3)_2$	−44	9.59, 8.84	−8.68, −8.35	7.78
		C_6H_5Br Solutions		
$N(CH_3)_3$	40	9.16	−8.73	7.96
$P(OCH_3)_3$	40	8.68	−7.78	7.95
$P(C_6H_5)_3$	36	8.57	−8.76	8.27
$S(CH_3)_2$	−30	8.73	−9.02	7.97
$O(CH_2CH_2)_2S$	36	8.74		7.94

[a] Based upon TMS as an internal standard at τ 10.00.

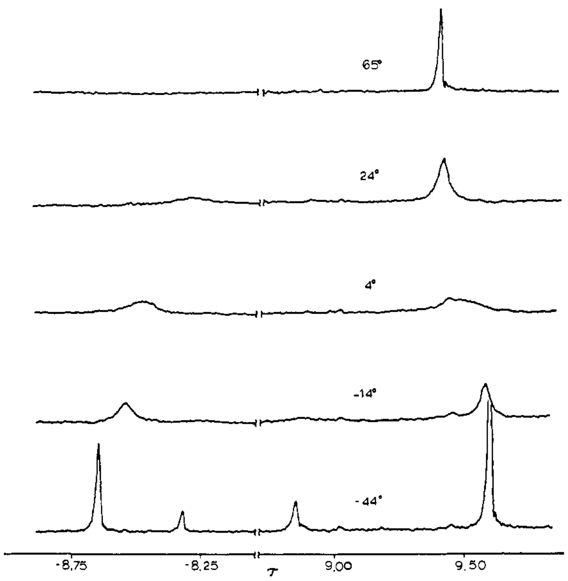

Figure 1. Proton magnetic resonance spectra of $CH_3Co(DH)_2 \cdot$ DMSO in CH_2Cl_2 solution.

The DMSO complex exhibits coordination isomerism in the low-temperature nmr spectrum, Figure 1. Both the axial methyl and OHO resonances appear as pairs of lines of unequal intensity. On the basis of comparisons with the chemical shifts observed in other adducts, Table I, the resonance at τ 9.60 is assigned to the O-bonded form, and that at τ 8.84 to the S-bonded form. The OHO resonances at τ −8.68 and −8.35 are similarly assigned to the O- and S-bonded forms, respectively. These assignments are supported by the observation that the DMSO methyl resonances also appear as a doublet at τ 7.42 and τ 7.32, assigned on the basis of their relative intensities to the O- and S-bonded ligand forms, respectively. Exchange between the two forms is evidenced in the nmr spectra by collapse of the doublets just referred to, as depicted in Figure 1.

The relative areas of the doublets and the temperature dependence of the spectra were found to be independent of the concentration of excess DMSO. The ratio of areas of the methyl and OHO resonances due to the O- and S-bonded forms of the DMSO complex in $CHCl_2$ are O/S = 4.6 at −72° and 3.7 at −25°. Observation of the ratio at a number of intermediate temperatures led to an estimate of ΔH = 0.5 kcal/mol for the O-bonded $\rightleftarrows$ S-bonded equilibrium.

The chemical shifts observed in the low-temperature nmr spectra for the DPSO and tetramethylene sulfoxide complexes are characteristic of oxygen coordination. On the other hand, 1,4-thioxane appears to coordinate exclusively through sulfur, as expected from the observation that $(CH_3)_2S$ forms a stable complex, whereas there is no evidence of complex formation in solutions containing the dimer and ethers.

Addition of aquomethylcobaloxime, $CH_3Co(DH)_2$-H_2O, to d_6-DMSO containing some CH_2Cl_2 (to permit observation of the nmr spectra at lower temperatures) results in formation of the DMSO complex. The displaced water appears as free water in the nmr spectrum in the temperature range −50 (τ 6.43) to above 5° (τ 6.77). At 25° there is considerable broadening of the resonances due to free water and OHO protons. At 50° the lines are too broad to be observed. From the line

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(8) R. A. Firth, H. A. O. Hill, J. M. Pratt, R. G. Thorp, and R. J. P. Williams, *J. Chem. Soc. A*, 381 (1969).

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

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

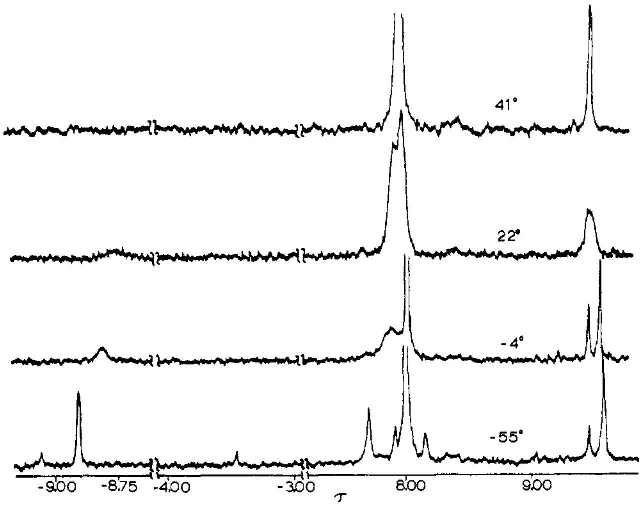

Figure 2. Proton magnetic resonance spectra of $CH_3Co(DH)_2$-DPSO in CH_2Cl_2.

broadening at 5 and 25°, respectively, $1/\tau_e$ values are estimated to be about 10 and 50 sec^{-1}, respectively. Exchange of OHO bridging protons with H_2O in DMSO is considerably slower that the exchange of bridging OHO protons of $Co(DH)_2XY$ complexes with OH^- in aqueous medium at 15°.[11]

Solution of the $CH_3Co(DH)_2H_2O$ complex in a solvent composed of equal parts of volume of CD_3CN and d_6-DMSO results in formation of both the acetonitrile and DMSO complexes in approximately 1:2 molar ratio. At $-30°$ axial CH_3 group resonances due to the DMSO complex occur at τ 9.04 and 9.76; the resonance due to the CD_3CN complex occurs at τ 9.48. As the temperature is raised, the exchange between O- and S-bonded forms of DMSO is evidenced at about $-20°$ by a broadening of the two resonances due to the DMSO complex. Broadening of the line due to the CD_3CN complex first occurs at about $-10°$, suggesting that the exchange involving coordination isomerism in DMSO and the intermolecular exchange process occur at nearly the same rate.

The temperature dependence of the proton resonance spectra of CH_2Cl_2 solutions of $CH_3Co(DH)_2NCCH_3$ + $CH_3Co(DH)_2DMSO$ is very similar to that observed in the CD_3CN-d_6-DMSO mixed solvent system. The fact that exchange seems to occur at about the same rates in the two solvent systems supports the hypothesis that the rate-determining step is dissociative.

For the diphenylsulfoxide (DPSO) complex the equi-

$$2CH_3Co(DH)_2DPSO \rightleftharpoons [CH_3Co(DH)_2]_2 + 2DPSO \qquad (2)$$

librium is shifted extensively to the right, as evidenced by the low-temperature proton resonance spectra, Figure 2. At $-55°$ the spectrum shows the presence of both the dimer and the DPSO complex. The multiplet due to the four distinct methyl group sites of the dimer (major frequency separation between adjacent peaks about 13 Hz) collapses well below 0°, whereas the separate resonances due to the axial methyl groups of the dimer and DPSO adduct ($\delta\omega$ = 7 Hz) reach coalescence only at about 20°. A closely similar exchange situation is obtained by mixing the dimer and a comparable amount of the DMSO adduct, although the low-temperature spectra are complicated by the presence of sulfur–oxygen coordination isomerism.

The dimer–adduct exchange system is of the form

$$[CH_3Co(DH)_2]_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2CH_3Co(DH)_2 \qquad (3)$$

$$CH_3Co(DH)_2 + L \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CH_3Co(DH)_2L \qquad (4)$$

The exchange of methyl resonances between the magnetic sites which represent the two prevalent species is rate determined by either k_1 or k_{-2}. As already indicated, the intermolecular exchange between adduct and dimer is considerably slower than the exchange process giving rise to the collapse of the dimer multiplet. But as shown in the following paper,[4] the collapse of the dimer multiplet is due essentially to dissociation of the dimer.

While it is not possible to obtain information directly on the rate of dissociation of the DPSO complex, there is strong indication from other results that dissociation of the complex is also rapid relative to the rate of intermolecular exchange with dimer. The intermolecular exchange between the CH_3CN and DMSO adducts ($\delta\omega$ = 11 Hz) is rapid on the nmr time scale at 0° and above. But intermolecular exchange in this system, in which there is no detectable dimer concentration, can occur only through dissociation of *both* adducts. Thus the rate is determined by the slower rate of adduct dissociation. It is to be expected, however, that both the ligands should form stronger complexes than DPSO. The fact that the equilibrium expressed in eq 1 is far to the right in CH_2Cl_2 for L = CH_3CN and DMSO supports this assumption. But if the slower of these two adduct dissociations gives rise to rapid exchange at 0°, it is clear that the DPSO adduct dissociation should be rapid on the same time scale at 0° and above. It thus appears that both k_1 and k_{-2} are large compared with the rate constant for intermolecular exchange of adduct and dimer.

The cobaloxime dimer–adduct exchange system is formally analogous to $Al_2(CH_3)_6$–$Al(CH_3)_3L$ exchange systems. The exchanges in the aluminum systems are found for many adducts to be rate determined by dissociation of the adduct.[12] No doubt the same situation would apply in the cobalt systems for the more strongly bound ligands such as phosphines. The one instance in which the dimer association was found to be clearly rate determining is the $Al_2(CH_3)_6$–$Ga(CH_3)_3$ exchange. The most recent results on this exchange system[12] establish that there is no observable cage effect in the dimer dissociation. That is, the exchange of methyl groups between the bridge and terminal positions was found to occur with about the same rate constant as the intermolecular exchange of methyl groups with $Ga(CH_3)_3$. By contrast, it is evident from the spectra that the exchange among the four distinct sites in the $[CH_3Co(DH)_2]_2$ dimer is more rapid than the intermolecular exchange with the DPSO adduct. (We are prevented from drawing a similar conclusion about the DMSO system because the coalesced dimer dimethylglyoxime methyl resonance falls under the analogous resonance for the DMSO adduct.) The reciprocal exchange time for the exchange among the dimer resonances is essentially k_1 on the basis of the presumed mechanism for the exchange.[4] It seems likely that the rate constant for

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(11) J. P. Birk, P. B. Chock, and J. Halpern, *J. Amer. Chem. Soc.*, **90**, 6959 (1968).

(12) T. L. Brown and L. L. Murrell, *ibid.*, in press.

dimer–adduct exchange is less than this as a result of a cage effect. Although a substantial cage effect has been ruled out for the $Al_2(CH_3)_6$ dissociation, the much larger cobaloxime monomers might be retained in a solvent cage, thus giving rise to preferential recombination.

The proton resonance spectral results for the DMSO, DPSO, and CH_3CN complexes permit setting a lower limit of about 30 sec^{-1} for the dissociation rates at 0° in CH_2Cl_2. For $(CH_3)_2S$, $S(CH_2CH_2)_2O$, and $(CH_3)_3N$, direct information regarding ligand exchange is derived from solutions of the complex with free ligand. In these instances it is possible to observe a collapse of the proton resonances due to free and complexed ligand. Overlap of the free $(CH_3)_3N$ resonances with the dimethylglyoxime methyl group resonance precludes accurate line-shape analysis of the $(CH_3)_3N$ complex system over a wide temperature range. The complexity of the spectrum of the $S(CH_2CH_2)O$ system similarly permits only rough estimates of the exchange rates. In the $(CH_3)_2S$ system, addition of excess ligand in the ratio ligand/complex = 0.5 or higher resulted in the expected broadening and eventual collapse of the free and coordinated ligand resonances in the temperature interval above about 65°. In this instance, as well as for the $(CH_3)_3N$, $P(OCH_3)_3$, and $P(C_6H_5)_3$ systems, the temperature dependence of the line shape for the coordinated species was found to be independent of excess ligand concentration. This indicates that the rate-determining process involves dissociation of the ligand.

The phosphorus ligands cause a splitting of the axial methyl and dimethylglyoxime methyl resonances through spin interaction with ^{31}P. Dissociation of the ligand causes collapse of the doublet, thus providing a convenient means of estimating the exchange rate. In the $P(OCH_3)_3$ complex, the scalar coupling to the planar ligand methyl groups is only 4 Hz, whereas it is 7 Hz to the axial methyl. By utilizing data for the line shapes of both of these multiplets and data for the half-height widths in the exchange region above coalescence, it is possible to estimate exchange rates over a reasonably wide temperature range. Figure 3 shows a graph of log $1/\tau$ *vs.* $1/T$ for the $CH_3Co(DH)_2P(OCH_3)_3$ complex in C_6H_5Br, with 1:1 molar excess of $P(OCH_3)_3$. This solvent was chosen because it provides adequate solubility and permits measurements at temperatures above 100°, as required in related exchange systems which will be reported upon later. A few comparative measurements have shown that the exchange behavior in C_6H_5Br and $C_6H_5CH_3$ are essentially identical. The temperature-dependence data in Figure 3 correspond to an Arrhenius energy for the exchange of 23 kcal/mol with an estimated uncertainty of 2.8 kcal/mol at the 90% confidence limit.

The $P(C_6H_5)_3$ system does not permit measurements over quite as large a temperature range as the phosphite system, because the scalar coupling of ^{31}P to the axial methyl, 4 Hz, is only slightly larger than the 3-Hz coupling to the planar ligand methyl groups. The Arrhenius plot for the $P(C_5H_5)_3$ system is shown in Figure 3. The Arrhenius energy for the exchange is estimated to be 20.6 kcal/mol with an estimated uncertainty of 1.2 kcal/mol at the 90% confidence limit.

The rate constant for adduct dissociation is actually twice the value of $1/\tau_e$ as determined from the nmr results. When a phosphorus ligand containing a phosphorus atom in a particular spin state dissociates, there is a 50% probability that it will be replaced with a ligand containing phosphorus in the same spin state. After accounting for this statistical factor, the quasithermodynamic parameters of the exchanges and 90% confidence limits are $\Delta H^{\ddagger} = 22.4 \pm 2.7$ kcal/mol, $\Delta S^{\ddagger} = 8.0 \pm 1$ eu for the $CH_3Co(DH)_2P(OCH_3)_3$ exchange and $\Delta H^{\ddagger} = 20.0 \pm 1.5$ kcal/mol, $\Delta S^{\ddagger} = 5.5 \pm 0.3$ eu for the $CH_3Co(DH)_2P(C_6H_5)_3$ exchange.

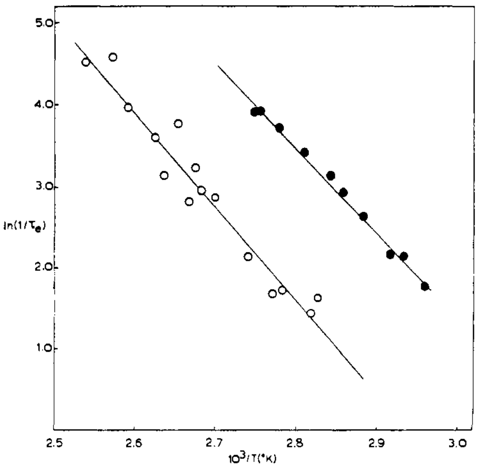

Figure 3. Temperature dependence of the reciprocal mean exchange time, $1/\tau_e$, for the $CH_3Co(DH)_2P(OCH_3)_3$ complex (○) and $CH_3Co(DH)_2P(C_6H_5)_3$ complex (●) in C_6H_5Br. In both cases the solutions contained 1:1 molar concentrations of complex and excess ligand.

From all of the estimates of exchange rates, some of which are based on estimates from line shapes at only one or two temperatures, the relative order of ligand-exchange rates is as reported previously,[2] except that $P(n\text{-}C_4H_9)_3$ is considerably slower than $P(OCH_3)_3$ and $P(C_6H_5)_3$ is faster than $P(OCH_3)_3$. These results, and the observation that $[CH_3Co(DH)_2]_2$ reacts with CO in CH_2Cl_2 solution to form a CO complex,[13] suggest that the cobalt center is a rather highly polarizable acid center, capable of at least some degree of π-bond interaction with ligands which function as π acceptors. By contrast, the formation constants or absence of observable complex formation reported by Hill, Williams, and coworkers for methylcobinamide with various bases[6] are indicative of a rather highly charged, nonpolarizable center which interacts preferentially with σ-donor bases of the first-row elements. These apparent differences may arise in the different solvent media, inasmuch as the work with methylcobinamide was carried out in water, or aqueous methanol. On the other hand, Schrauzer, Lee, and Sibert have presented evidence[7] that although alkylcobaloximes bind axial bases more strongly than alkylcobinamides, the two systems exhibit qualitatively similar behavior. The detailed properties of the planar ligand system may be very important in determining the tendency of the cobalt to form six-coordinate complexes. There is evidence[14,15] that the cobalts

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(13) A. W. Herlinger and T. L. Brown, *J. Amer. Chem. Soc.*, **93**, 1790 (1971).

(14) H. A. O. Hill, J. M. Pratt, and R. J. P. Williams, *Discuss. Faraday Soc.*, No. 47, 165 (1969).

(15) (a) G. Costa, G. Mestroni, G. Tauzher, and L. Stefani, *J. Organometal. Chem.*, **6**, 181 (1966); (b) G. Costa, G. Mestroni, and L. Stefani, *ibid.*, 7, 493 (1967).

in methylato-N,N'-ethylenebis(acetylacetoniminato)cobalt(III) complexes,[16] $CH_3CoBAE \cdot L$, and methylato-N,N'-ethylenebis(salicylaldehydiminato)cobalt(III) complexes, $CH_3Co(salen) \cdot L$, do not bind the sixth ligand as strongly as cobalt in the bis(dimethylglyoximato) complexes. Work in our laboratory[17] has shown that pyridine and $P(OCH_3)_3$ complexes of CH_3CoBAE do not exhibit slow exchange in solutions containing excess ligand and at the lowest temperature studied, −90°. The striking difference between the dimethylglyoximato ligand system and the others must be ascribed to electronic rather than steric effects, but it is not obvious at this point just what qualities of the bonding are most responsible. It seems clear that further work will be required to establish whether any of the simple bisbidentate alkylcobalt(III) complexes can be regarded as suitable model systems for methylcobalamin with respect to the electronic factors which determine relative binding tendencies at the sixth coordination position.

(16) S. Bruckner, M. Calligaris, G. Nardin, and L. Randaccio, *Inorg. Chim. Acta*, 3, 308 (1969).

(17) R. Guschl, unpublished observations.

A Nuclear Magnetic Resonance Investigation of Alkylcobaloxime Dimers[1]

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Abstract: The temperature dependences of the nmr spectra of several alkylcobaloxime dimers $[RCo(DH)_2]_2$, where R is $-CH_3$, $-CH_2Cl$, or $-CHF_2$, have been studied from 40 to −70° in dichloromethane and bromobenzene. Analysis of the temperature dependence of the signals arising from four magnetically distinct methyl groups of coordinated dimethylglyoxime monoanions (DH) indicates that exchange averaging, although primarily a dissociative process, must arise from a combination of two separate pathways. Detailed line-shape calculations for the exchange-broadened spectra lead to exchange parameters $\Delta H^{\ddagger} = 13.1$ kcal/mol, $\Delta S^{\ddagger} = 25.4$ eu and $\Delta H^{\ddagger} = 13.6$ kcal/mol, $\Delta S^{\ddagger} = 25.1$ eu for methyl- and chloromethylcobaloxime, respectively. Attempts to synthesize trihalomethylcobaloxime dimers were unsuccessful.

Several studies of the kinetics of ligand exchange in bis(dimethylglyoximato)cobalt(III) complexes, $Co(DH)_2L$ (cobaloximes), have indicated that ligand substitution proceeds *via* a dissociative interchange or purely dissociative mechanism.[2-5] In these complexes the tendency for cobalt to remain six-coordinate seems much stronger than in the closely related N,N'-ethylenebis(salicylaldehydeiminato)cobalt(III) (Co(Salen)) and N,N'-ethylenebis(acetylacetoneiminato)cobalt(III) (Co(BAE)) systems. These latter complexes and alkylcobinamides are reported to be five-coordinate under some conditions in solution and in the solid.[6-8] By contrast, the tendency of the cobaloxime system to maintain six-coordination is manifested in the dimerization of the ligand-free alkylcobaloxime species (Figure 1).[4,9,10] There is no evidence for a significant concentration of the five-coordinate species in solutions of $[CH_3Co(DH)_2]_2$ at temperatures well above room temperature. The kinetic and thermodynamic parameters of the dimer association, eq 1, are of interest, because a knowledge of

$$[RCo(DH)_2]_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2RCo(DH)_2 \tag{1}$$

these is essential to a complete evaluation of the equilibria between the ligand-free material and a coordinating ligand L, as well as to evaluation of the enthalpy change accompanying reaction of L with the dimer, eq 2.

$$[RCo(DH)_2]_2 + 2L \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} 2RCo(DH)_2L \tag{2}$$

We report here a study of the temperature dependence of the nmr spectra of $[CH_3Co(DH)_2]_2$, $[CH_2ClCo(DH)_2]_2$, and $[CHF_2Co(DH)_2]_2$, conducted with the aim of evaluating the kinetics and mechanism of the exchange process by which dimethylglyoxime methyl groups become magnetically equivalent on the nmr time scale. A distinction between the various mechanistic alternatives which may be envisioned is possible on the basis of the temperature dependence of the ^1H nmr spectra and the

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(1) This research was supported in part by Grant No. GP 6396X from the National Science Foundation, and in part by the Advanced Research Projects Agency under Contract No. HC 15-67-C-0221.

(2) H. G. Tsiang and W. K. Wilmarth, *Inorg. Chem.*, 7, 2535 (1968).

(3) A. L. Crumbliss and W. K. Wilmarth, *J. Amer. Chem. Soc.*, 92, 2593 (1970).

(4) L. M. Ludwick and T. L. Brown, *ibid.*, 91, 5188 (1969).

(5) T. L. Brown, L. M. Ludwick, and R. S. Stewart, *ibid.*, 94, 384 (1972).

(6) (a) H. A. O. Hill, J. M. Pratt, and R. J. P. Williams, *Discuss. Faraday Soc.*, No. 47, 165 (1969); (b) *Chem. Brit.*, 5, 156 (1969).

(7) (a) G. Costa, G. Mestroni, G. Tauzher, and L. Stefani, *J. Organometal Chem.*, 6, 181 (1966); (b) G. Costa, G. Mestroni, and L. Stefani, *ibid.*, 7, 493 (1967).

(8) S. Bruckner, M. Calligaris, G. Nardin, and L. Randaccio, *Inorg. Chim. Acta*, 3, 308 (1969).

(9) G. N. Schrauzer and R. J. Windgassen, *J. Amer. Chem. Soc.*, 88, 3738 (1966).

(10) A complete X-ray structural analysis (G. D. Stucky and J. Swanson, to be published) has confirmed the proposed structure. An analogous structure has recently been reported for $CH_3Co(Salen)$: M. Calligaris, D. Minichelli, G. Nardin, and L. Randaccio, *J. Chem. Soc. A*, 2720 (1971).