in methylato-*N*,*N*′-ethylenebis(acetylacetoniminato)cobalt(III) complexes,[16] $\mathrm{CH_3CoBAE \cdot L}$, and methylato-*N*,*N*′-ethylenebis(salicylaldehydiminato)cobalt(III) complexes, $\mathrm{CH_3Co(salen) \cdot L}$, 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 $\mathrm{P(OCH_3)_3}$ complexes of $\mathrm{CH_3CoBAE}$ 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[17] R. Guschl, unpublished observations.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 $\mathrm{[RCo(DH)_2]_2}$, where R is $\mathrm{-CH_3}$, $\mathrm{-CH_2Cl}$, or $\mathrm{-CHF_2}$, 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, $\mathrm{Co(DH)_2L}$ (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 $\mathrm{[CH_3Co(DH)_2]_2}$ at temperatures well above room temperature. The kinetic and thermodynamic parameters of the dimer association, eq 1, are of interest, because a knowledge of

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

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.

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

We report here a study of the temperature dependence of the nmr spectra of $\mathrm{[CH_3Co(DH)_2]_2}$, $\mathrm{[CH_2ClCo(DH)_2]_2}$, and $\mathrm{[CHF_2Co(DH)_2]_2}$, 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 ^{1}H 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).

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[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).

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[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 $\mathrm{CH_3Co(Salen)}$: M. Calligaris, D. Minichelli, G. Nardin, and L. Randaccio, *J. Chem. Soc. A*, 2720 (1971).

Table I. Analytical Data for Several Alkylcobaloximes

			Per cent composition							
			Calculated				Found			
Ligand	Formula	Mol wt	C	H	N	Cl	C	H	N	Cl
				$CH_3Co(DH)_2L$						
$S(CH_3)_2$	$C_{11}H_{25}N_4O_4SCo$	366.3	36.07	6.33	15.30		36.35	6.43	15.45	
H_2O	$C_9H_{19}N_4O_5Co$	322.2	33.55	5.95	17.39		33.59	5.85	17.30	
None	$C_9H_{17}N_4O_4Co$	304.2	35.33	5.63	18.42		35.27	5.54	18.40	
				$CH_2ClCo(DH)_2L$						
H_2O	$C_9H_{18}N_4O_5ClCo$	356.6	30.30	5.08	15.71	9.94	30.40	5.14	15.97	9.85
None	$C_9H_{16}N_4O_4ClCo$	338.6	31.92	4.77	16.55	10.47	31.75	4.74	16.50	10.47
				$CHF_2Co(DH)_2L$						
H_2O	$C_9H_{17}N_4O_5F_2Co$	358.2	30.18	4.78	15.64		30.70	4.73	15.91	
None	$C_9H_{15}N_4O_4F_2Co$	340.2	31.78	4.44	16.47		32.17	4.39	16.64	

unsymmetrical collapse of the CH_3 resonances arising from the planar ligand system. The temperature dependence of the estimated preexchange lifetime (τ) has been used to calculate Arrhenius energies. Comparisons in the $-CH_3$, $-CH_2Cl$, $-CHF_2$ series provide the opportunity for observing trends in the cobalt–oxygen interaction as a function of the electron-withdrawing ability of the σ-bonded alkyl.

Experimental Section

A. Synthesis of Compounds. Alkylcobaloximes ($RCo(DH)_2L$) were prepared using established procedures.[11] The results of elemental analyses are recorded in Table I. Ligand-free complexes were obtained by azeotropic distillation of benzene suspensions of the corresponding aquoalkylcobaloximes or by heating *in vacuo* for several hours at 80–100°. The dimers are slightly hygroscopic in the solid state, but generally are quite stable. Solutions are somewhat less stable to heat and light, and they are particularly prone to uptake of water, with precipitation of the aquo complex. Consequently, all solvents were dried by distillation after refluxing with P_2O_5 for several hours and were stored over freshly activated 4A molecular sieves. $[CHF_2Co(DH)_2]_2$, reported here for the first time, decomposes gradually even in the solid state. Solutions of this material must be kept cold and used immediately. Although the pyridine adduct of trifluoromethylcobaloxime has been reported,[9] attempts to synthesize the corresponding dimeric compound were unsuccessful.

B. Nmr Spectra. ^1H nmr spectra were recorded on a Varian A-56/60 spectrometer equipped with a variable-temperature controller. Because of the slight solubility of $CHF_2Co(DH)_2$ dimer in noncoordinating solvents, it was necessary to use a Varian HA-220 to improve resolution and enhance the signal due to the axial alkyl group. Temperature measurements were made using a methanol standard. The values obtained using this method were checked with an iron–constantan thermocouple, and the estimated accuracy is $\pm 2°$.

Samples were prepared in a nitrogen atmosphere, degassed, and sealed in nmr tubes under vacuum. The nmr samples were stored at $-78°$ in the dark until their spectra could be recorded. No decomposition was evident in the time required to obtain spectra for freshly prepared solutions. Although identical spectra were obtained for CH_2Cl_2 and C_6H_5Br solutions, the dimers are more soluble in CH_2Cl_2. Consequently, unless specified otherwise, all reported values are referenced to TMS as an internal standard in CH_2Cl_2. Spectra to be compared directly with computer-plotted spectra were recorded at 100-Hz sweep width.

The nmr exchange spectra were analyzed using the computer program NMRCTL,[12] following the method recently reviewed by Johnson,[13] in which theoretical line shapes are calculated for each of the possible exchange schemes. The input parameters for the calculation are line frequencies and corresponding line widths, relative intensities, values of the mean preexchange lifetime (τ) describing the rate of exchange, and the kinetic exchange matrix which specifies the details of the relative rates of transfer of magnetization between each site. T_2 values were calculated from the line widths at half-intensity taken from spectra under conditions of no exchange. Experimental spectra were compared directly with spectra calculated for various τ values for each exchange matrix. Thus, the line-shape analysis yields a τ value for the "best-fit," related to the first-order rate constant, as well as giving information about the process which averages the chemical shifts of the methyl protons.

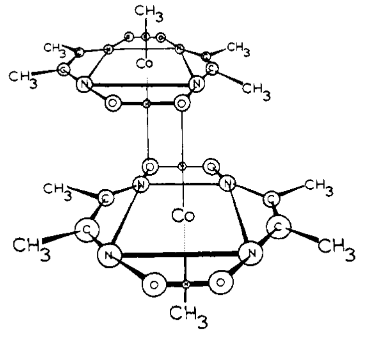

Figure 1. Proposed structure for dimeric $CH_3Co(DH)_2$. $CH_2ClCo(DH)_2$ and $CHF_2Co(DH)_2$ presumably are associated in an analogous manner.

Results

The dimethylglyoxime methyl groups ($DH-CH_3$) of the alkylcobaloxime dimers in dichloromethane solution at 41° give rise to a sharp line in the nmr spectrum at 2.20 ppm downfield from internal tetramethylsilane. The temperature dependence of this signal, qualitatively the same for all three dimers, is illustrated for $[CH_3Co(DH)_2]_2$ in Figure 2. As the sample temperature is lowered, the resonance broadens and splits characteristically into four lines having relative areas of approximately 2:1:1. The low-field peaks are a closely spaced doublet which integrates as a single peak. The chemical shifts of the resonances due to the alkylcobaloxime dimers at two different temperatures are reported in Table II along with the temperature (T_c) at which the $DH-CH_3$ resonances are observed to show some asymmetry at 60 MHz. The T_c values give only a qualitative indication of the relative exchange rates of these compounds, since they also are dependent upon peak separation. The $CH-CH_3$ resonances of $[CHF_2Co(DH)_2]_2$ exhibit a slightly smaller range of chemical shifts as compared to those in $[CH_2ClCo(DH)_2]_2$, and are probably undergoing exchange at about the same rate as for the chloro derivative. Unfortunately, the limited solubility of

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

[12] The computer program was obtained from Professor G. M. Whitesides and has been previously described: G. M. Whitesides and J. S. Fleming, *J. Amer. Chem. Soc.*, **89**, 2855 (1967).

[13] C. S. Johnson, Jr., *Advan. Magn. Resonance*, **1**, 33 (1965).

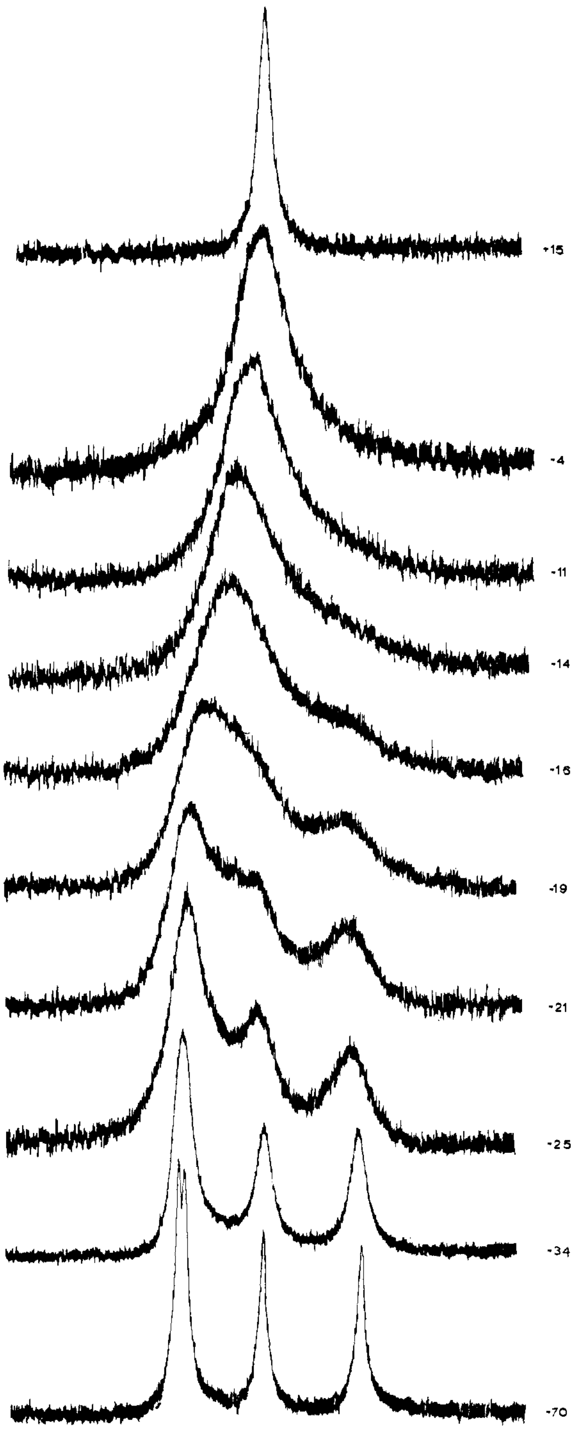

Figure 2. DH–CH_3 region of the ^1H nmr spectra of $[CH_3Co(DH)_2]_2$ in CH_2Cl_2 solution as a function of temperature. The four peaks in the lowest temperature spectrum (−70°) occur at τ 8.13, 7.88, 7.69, and 7.67 relative to internal TMS (sweep width is 100 Hz).

Table II. Chemical Shifts as a Function of Temperature for Alkylcobaloxime Dimers, $[RCo(DH)_2]_2$

			Chemical shift, τ^a		
R	T_c, °C^{b,c}	T, °C^c	Co–R	DH–CH_3	O–H–O
CH_3	−12	41	9.42	7.87	d
		−70	9.43	8.13	−3.46
				7.88	−9.13
				7.69	
				7.67	
CH_2Cl	13	41	6.57	7.82	d
		−70	6.58	8.09	−3.07
				7.79	−8.98
				7.60	
				7.58	
CHF_2	9	41	4.64^e	7.82	d
		−70	4.64^e	8.06	−2.85
				7.80	−8.68
				7.60	
				7.59	

[a] Spectra recorded at 60 MHz in dichloromethane and referenced to TMS as an internal standard. [b] Temperature at which DH–CH_3 resonance of dimer first shows asymmetry. [c] Temperature measurements were made using a methanol standard and checked against an iron–constantan thermocouple. [d] Resonance too broad to measure or unobserved. [e] Resonance observed as a triplet ($J_{^1H-^{19}F}$ = 54.5 Hz) in CH_2Cl_2-d_2 at 220 MHz and referenced to internal TMS.

the difluoromethyl compound did not permit accurate line-shape analysis. The spectra observed at −70° for all compounds represent the slow-exchange limit, as lower temperatures failed to produce additional line narrowing. Half-intensity widths at −70° were used to estimate T_2.

The observation of four distinct signals for the DH–CH_3 protons as well as two separate O–H–O bridging resonances in the low-temperature spectra of ligand-free alkylcobaloximes is in accord with a dimer structure formed through cobalt–oxygen linkages, as previously suggested.[4,9] The shift of the O–H–O proton signals to higher fields with increased electron-withdrawing character of the σ-bonded axial alkyl group is the opposite trend from that expected on the basis of inductive effects. It probably arises from weakening of the hydrogen-bond interaction. The axial alkyl group bonded to the cobalt in $[CH_3Co(DH)_2]_2$ and $[CH_2ClCo(DH)_2]_2$ exhibits a single sharp resonance at τ 9.43 and 6.58, respectively, throughout the observed temperature range. In $CHF_2Co(DH)_2$ the C–H signal at τ 4.64 is split into a triplet by geminal ^{19}F coupling, with $J_{^1H-^{19}F}$ = 54.5 Hz.

Adducts of the alkylcobaloximes with 1,4-thioxane (TOX) were prepared and the ^1H nmr spectra recorded. The TOX signals are complex multiplets appearing near the free-ligand values, and are not reported here in detail. Accurate measurement of the chemical shifts is complicated by the fact that the resonance of the $-CH_2$ group lying closest to the sulfur atom is shifted considerably upfield from its position in the uncoordinated ligand and is partially obscured by the DH–CH_3 resonance. This signal is shifted from its value in the free ligand almost twice as much as the absorption arising from the methylene groups adjacent to the oxygen atom.[14] The similarity of the nmr spectra of $CH_2ClCo(DH)_2TOX$ and $CHF_2Co(DH)_2TOX$ to that of $CH_3Co(DH)_2TOX$, in which TOX is presumed to bind through the sulfur,[4] suggests that TOX in these complexes is exclusively sulfur bound, although the oxygen and sulfur are equally available for coordination. In spite of the increased electron-withdrawing character of the σ-bonded haloalkyl groups, the cobalt moiety binds to the sulfur of TOX, thus exhibiting a preference for the more polarizable base.

Discussion

The asymmetrical collapse of the ligand methyl signal in the exchange-broadened region of the spectrum as

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(14) The chemical shifts of ligand protons can be separated into "sulfur" and "oxygen" resonances depending on the adjacent heteroatom.[15] Protons adjacent to the coordination center should exhibit the largest difference in chemical shift from the free ligand value.

(15) J. Bradshaw, S. Eardley, and A. G. Long, *J. Chem. Soc. A*, 801 (1968).

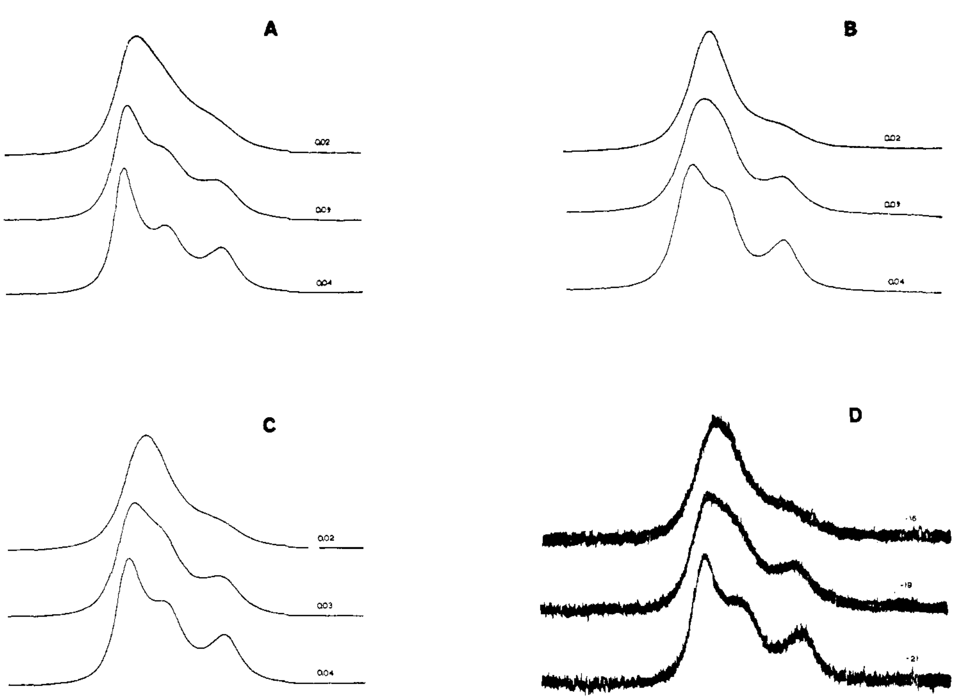

Figure 3. A comparison of the calculated and observed DH–CH_3 region of the ^1H nmr spectra of $[CH_3Co(DH)_2]_2$ in the critical exchange-broadened region. Calculated line shapes are a function of the mean preexchange lifetime and the kinetic exchange matrix: (A) random, (B) sequential, (C) best fit, (D) observed.

depicted in Figure 2 provides a means of distinguishing between alternative mechanisms for the exchange. The theoretical nmr spectral line shape for exchange between magnetically nonequivalent sites may be calculated using an appropriate kinetic transfer matrix (K) which specifies the details of the relative rates of transfer of magnetization between sites.[12,13] Thus, nmr spectra are produced when the matrices are substituted into the appropriate full line-shape function which gives the relative intensity of absorption at each point in the spectrum. The similarity of the the temperature dependence of the ^1H nmr spectra in the intermediate-exchange region suggests that DH–CH_3 groups become equivalent by the same process for all three dimers. In fact, the identical kinetic exchange matrix gives calculated spectra which exactly fit the experimental spectra for $[CH_3Co(DH)_2]_2$ and $[CH_2ClCo(DH)_2]_2$. Only methylcobaloxime dimer will be discussed in detail, but analogous arguments hold for $[CH_2ClCo(DH)_2]_2$ and probably for $[CHF_2Co(DH)_2]_2$.[16]

The kinetic exchange matrices I–III and the spectra generated from them (Figure 3) are discussed for three plausible limiting cases. The simplest, designated as a 1, 2 shift, describes exchange between two sites (matrix I). This exchange scheme, which does not allow all four DH–CH_3 groups to become equivalent, produces a two-line spectrum in the fast-exchange region. The sequential matrix, II, allows for an equal probability of transfer into two other sites and a zero probability of transfer into the remaining one. The sequential process is not likely *a priori* to describe the observed exchange. Examination of models reveals that exchange of a given methyl group with the two nearest methyl groups in the plane of the dimethylglyoximato ligands is not likely to occur with equal probability, by any kind of nondissociative twist mechanism which might be proposed. The random matrix, III, provides transfer between any of the nonequivalent sites with equal probability. Random exchange is applicable to a dissociative process, in which all four planar methyl groups become equivalent.

$$\mathrm{I} = \begin{bmatrix} -1 & 0 & 0 & 1 \\ 0 & -1 & 1 & 0 \\ 0 & 1 & -1 & 0 \\ 1 & 0 & 0 & -1 \end{bmatrix}$$

$$\mathrm{II} = \begin{bmatrix} -1 & 0 & 0.5 & 0.5 \\ 0 & -1 & 0.5 & 0.5 \\ 0.5 & 0.5 & 1 & 0 \\ 0.5 & 0.5 & 0 & -1 \end{bmatrix}$$

$$\mathrm{III} = \begin{bmatrix} -1 & 1/3 & 1/3 & 1/3 \\ 1/3 & -1 & 1/3 & 1/3 \\ 1/3 & 1/3 & -1 & 1/3 \\ 1/3 & 1/3 & 1/3 & -1 \end{bmatrix}$$

Although the random and sequential processes produce the same limiting spectra in the fast- and slow-exchange limits, they produce different line shapes in the intermediate-exchange region. In applying the sequential exchange matrix, it is necessary to make some assumption about which magnetic sites are sequentially related. Since the four methyl resonances observed in the slow-exchange region cannot be unequivocally assigned *a priori* to the four nonequivalent positions in the dimer, Figure 1, it was necessary to examine all the possible combinations. In Figure 3 are shown the line shapes in the intermediate-exchange region for the random (A) and sequential (B) exchanges. The latter

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(16) The limited solubility of $[CHF_2Co(CH)]_2$ in noncoordinating solvents precluded detailed line-shape analysis.

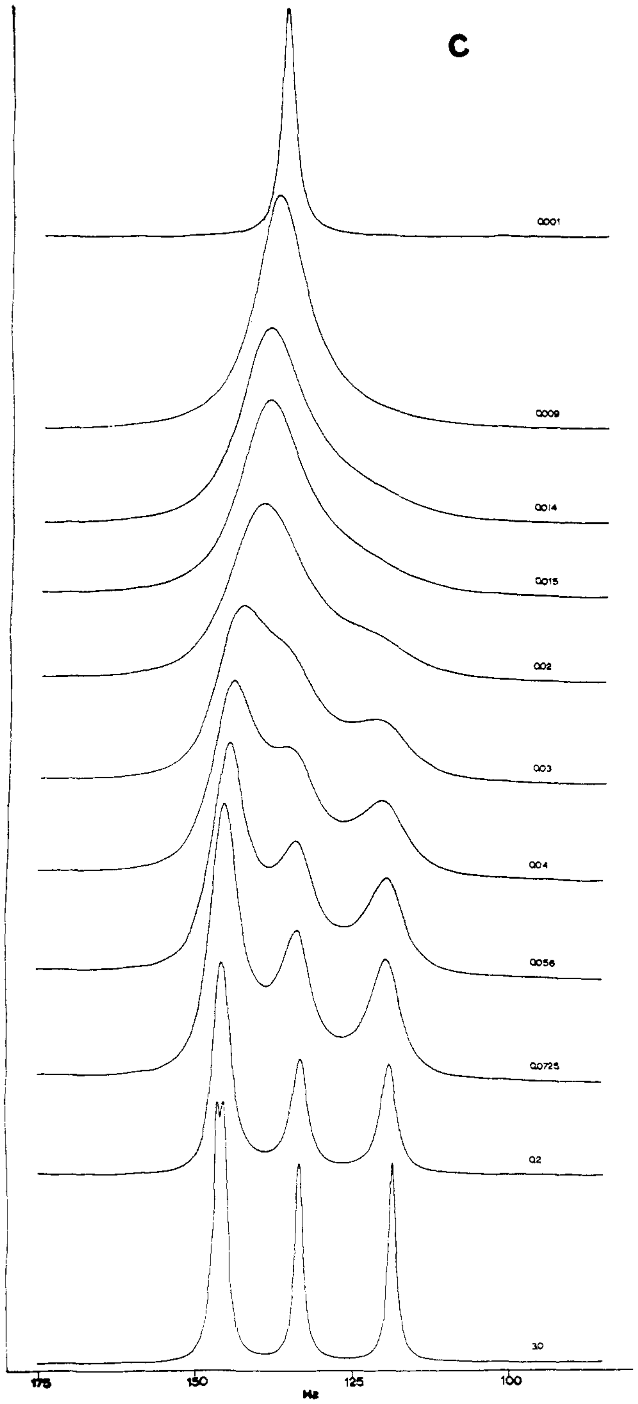

Figure 4. Calculated spectra as function of τ for exchange matrix IV, which provides a best fit with the observed spectra.

correspond to the assignment of sequentially related resonances which most closely resembles the observed spectra. It is evident upon comparing these limiting theoretical exchange models with the observed spectra, D, that neither process fits the observed results exactly. Furthermore, no weighted mixture of the random and sequential processes serves to improve the fit with experimental results. On the basis of several trial and error experiments, it was found that the exchange matrix IV leads to an essentially exact fit to the experimental results, as seen in the comparison of the calculated spectra, C, and observed spectra, D, in Figure 3. The spectra calculated from IV over the entire exchange region are depicted in Figure 4, for comparison with the observed spectra shown in Figure 2.

$$\mathrm{IV} = \begin{bmatrix} -1 & 0.2 & 0.2 & 0.6 \\ 0.2 & -1 & 0.6 & 0.2 \\ 0.2 & 0.6 & -1 & 0.2 \\ 0.6 & 0.2 & 0.2 & -1 \end{bmatrix}$$

Matrix IV consists of approximately equal weights of matrices I and III, corresponding to the 1, 2 and random exchanges, respectively. A 1, 2 shift might be considered to result from an exchange in and out of the bridging position of the two oxygens which form a particular OHO bond. Examination of models shows that such an exchange, which would require concurrent switching of bridging oxygens on each cobalt, cannot occur without a very considerable opening of the cobalt–oxygen distances, because of severe steric interactions. Steric interactions would appear to preclude *any* exchange process, sequential or concerted, which does not involve essentially complete rupture of the dimer bonding. The fact that the nonrandom and random components lead to essentially the same exchange rates also suggests that they must have essentially the same energetics. If there were a pathway for exchange possessing an enthalpy of activation significantly less than that for the dissociative pathway, it would be expected to dominate the exchange kinetics. The fact that the exchanges in both the CH_3– and CH_2Cl dimers involve the same proportion of random and nonrandom character is further support for the idea that the nonrandom component is due to a process which is essentially dissociative in terms of its energetics, but in which the two halves of the dimer do not completely separate before recombining. The exchange of bridging positions between the two oxygens which form a given OHO system involves the least motion of the separated halves of the dimer. It thus appears reasonable to regard the overall exchange process as consisting of essentially a dissociation of the dimer in terms of the energetics involved, but with some retention of orientation between "monomers," so that the exchange is not entirely random. As we have already noted,[5] the kinetics of exchange between $[CH_3Co(DH)_2]_2$ and $CH_3Co(DH)_2L$ suggest that "intramolecular" exchange within the dimer is significantly faster than the exchange involving the adducts, even when adduct dissociation is rapid. The 1, 2 shift component in the dimer exchange is in our view a particular manifestation of the cage effect. Clearly, if all dissociations led to solvent separation of the monomers, there would be no nonrandom component in the exchange matrix. The 1, 2 shift component reflects the fact that the monomers are constrained by the solvent from fully separating.

The 1, 2 shift exchange matrix which is contained in matrix IV involves exchange between the highest and lowest methyl resonances, and between the two resonances which lie inside these. It is worth considering whether the resonances between which the 1, 2 shift is occurring can plausibly be assigned to the appropriate methyl groups (See Figure 1). The major contributions to the chemical shift separations among the methyl groups probably arise in the electronic effects of the bridging O–H–O system, perturbed by coordination of an oxygen methyl atom to the neighboring cobalt atom, or in the positioning of the methyl groups with respect

Table III. Quasithermodynamic Parameters for Exchange in $CH_3Co(DH)_2$ and $CH_2ClCo(CH)_2$

Dimer	E_a, kcal/mol[a]	k_r,[b] sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol[c]	$\Delta S^{\ddagger}$, eu[c]
$[CH_3Co(DH)_2]_2$	13.7 ± 0.9	1.88×10^3	13.1	25.4
$[CH_2ClCo(DH)_2]_2$	14.2 ± 1.4	1.95×10^2	13.6	25.1

[a] The activation energies were taken from the slope of the line obtained from a least-squares fit of the data at a 99% confidence limit. [b] Apparent first-order rate constant at 25°, $k_r = 1/\tau$. [c] At 25°.

to the π-bonding system of the neighboring $Co(DH)_2$. The methyl group closest to the cobalt-oxygen bond is assigned to the lowest field peak. The methyl group closest to the other oxygen of that OHO pair can most reasonably be assigned to the highest field resonance on the basis of its proximity to the N=C bond of the other $Co(DH)_2$ unit. The two methyl groups adjacent to the O-H-O system not involved in dimer bonding are also nonequivalent; one is trans to a bridging oxime oxygen, the other trans to a "free" oxygen. They are also nonequivalent because of their geometrical relationship to the π-bonding system of the neighboring $Co(DH)_2$. Of the two remaining resonances, the lower is assigned the $-CH_3$ group lying closest to the coordinated oxygen and neighboring π system and the higher to the group trans to the coordinated oxime oxygen.

This particular assignment of the resonances, in conjunction with the 1, 2 shift exchange matrix, leads to the fit with observed spectra. While it is obviously empirical, it does lead to agreement with the experimental results and is not an unreasonable assignment, based on examination of the locations of the various methyl groups relative to the bridging oxygens and the C=N bonds of the opposite $RCo(DH)_2$ unit.[10] The exchange matrix for the random process is, of course, independent of the assignments of methyl groups to particular resonances.

Superposition of calculated and observed spectra in the temperature range between the fast- and slow-exchange limits permits estimates of the mean pre-exchange lifetime, τ, and thus of the first-order rate constant $k_e = 1/\tau$. τ was determined as a function of temperature for both the CH_3 and CH_2Cl compounds, to provide data for the Arrhenius plots shown in Figure 5. The least-squares slopes for these graphs correspond to Arrhenius energies of 13.7 ± 0.9 and 14.2 ± 1.4 kcal for the CH_3 and CH_2Cl compounds, respectively. The uncertainties given are 99% confidence limits, based on least-squares analysis. Systematic errors in the line shape analyses, *e.g.*, a temperature dependence in the chemical shift separations between sites, could, however, lead to systematic errors in these results. The quasithermodynamic parameters for the exchange are listed in Table III.

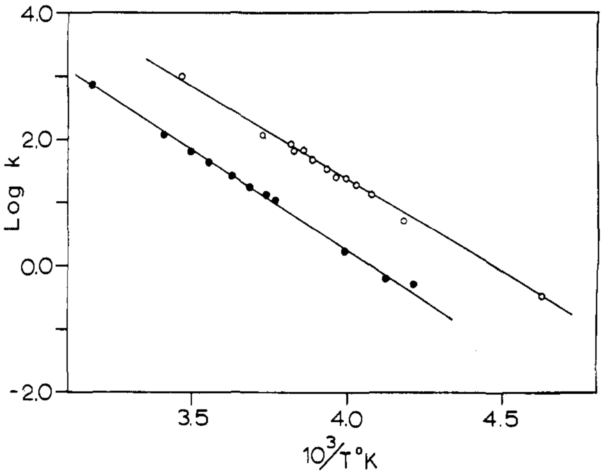

Figure 5. Arrhenius plot for dimer equivalence where $k = 1/\tau$: ○, $CH_3Co(DH)_2$; ●, $CH_2ClCo(DH)_2$.

While it is evident from the nmr spectra that the free energy of activation is larger for the CH_2Cl than for the CH_3 derivative, the enthalpies of activation do not differ by very much. Such difference as might exist, however, is in the expected direction, since the more electron-withdrawing CH_2Cl ligand should lead to a stronger acidity at the cobalt.

The large, positive entropies of activation are consistent with the view that the exchange process is essentially dissociative. If it is assumed that formation of the dimer from the monomers does not require a significant enthalpy of activation, the enthalpies of activation determined here are essentially estimates of the enthalpies of dissociation. Within the limits of this assumption, the nmr data thus provide a basis for relating enthalpies of reaction between various ligands L and the dimer, as in eq 2, to the enthalpy change for reaction of a $CH_3Co(DH)_2$ or $CH_2ClCo(DH)_2$ monomer with L to form the adduct.

Acknowledgment. We thank Professor George M. Whitesides for the use of his program NMRCTL for calculating and plotting line shapes.