Ligand-Exchange Kinetics in Methylatobis(dimethylglyoximato)cobalt(III) Complexes

Sir:

Bis(dimethylglyoximato)cobalt(III) (Co(DH)$_2$) complexes and related systems have recently been of interest as analogs of cobalamins.[1] In addition to the chemistry involving the Co–C bond,[2,3] these compounds can be thought of as model systems for vitamin B$_{12}$ with respect to ligation in the axial position *trans* to the alkyl. Competition for binding to cobalt at this site in vitamin B$_{12}$ is probably important in determining binding of the vitamin to peptide or protein and is involved in the action of the so-called intrinsic factor.[4] We report here a number of initial observations of the kinetics of ligand exchanges in CH$_3$Co(DH)$_2$L compounds which require a different view of the CH$_3$Co(DH)$_2$ moiety as Lewis acid than has been prevalent heretofore. In addition, a number of observations regarding the "ligand-free" compound, CH$_3$Co(DH)$_2$, are reported.

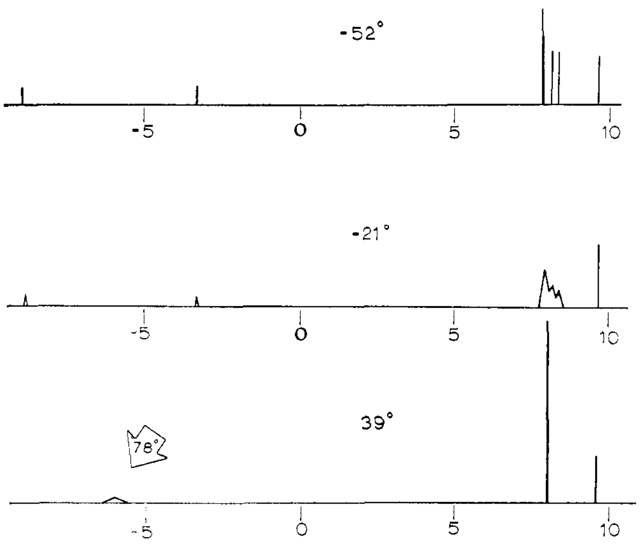

Figure 1. Schematic 60-MHz ^{1}H nmr spectra of CH$_3$Co(DH)$_2$ at various temperatures in dichloromethane.

Aquomethylcobaloxime [methylatobis(dimethylglyoximato)aquocobalt(III)], CH$_3$Co(DH)$_2$H$_2$O, can be easily dehydrated[5] to the anhydrous material, CH$_3$Co(DH)$_2$, which may be associated in solution. On the other hand, it may be five-coordinate,[6] as the ligand-free cobalt bis(salicylaldehyde)ethylenediamine and bis(acetylacetone)ethylenediamine complexes,[7,8] and also alkylcobinamides, are supposed to be.

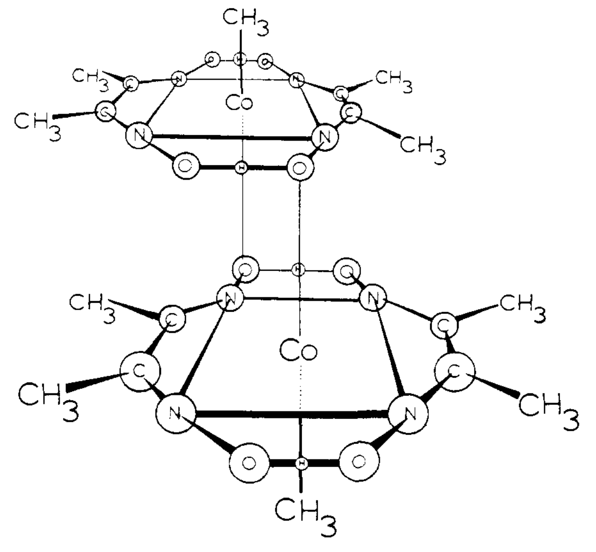

Figure 2. Proposed structure for dimeric CH$_3$Co(DH)$_2$.

We have observed that methylcobaloxime is associated in solution. The molecular weight has been determined ebullioscopically in dichloromethane and corresponds to a dimer within the limits of the experimental technique.[9] The ^{1}H nmr spectra of CH$_3$Co(DH)$_2$ at various temperatures are depicted in Figure 1. At low temperature the dimethylglyoxime methyl groups at τ 7.86 are no longer equivalent but show a pattern with areas 2:1:1.[10] Absorptions assigned to bridging O—H···O groups appear at τ −9.13 and −3.38. A single axial methyl resonance is seen at all temperatures. The nmr results are exactly in accord with a dimer structure formed through a cobalt–oxygen linkage (Figure 2). An association of this form was suggested for the solid by Schrauzer and Windgassen.[5] Similar intramolecular interaction resulting in dimeric structures have been observed for Cu(DH)$_2$,[11] the β form of copper 8-hydroxyquinolate,[12] cobalt and iron dithiolates,[13] and several salicylaldimine and β-ketoimine complexes of transition metals.[14]

The association of methylcobaloxime is readily disrupted by many coordinating ligands, forming the stable six-coordinate complexes of cobalt(III) reported by Schrauzer.[1] This may be represented as

$$[CH_3Co(DH)_2]_2 + 2L \longrightarrow 2CH_3Co(DH)_2L$$

In nearly all the cases the equilibrium lies far to the right, and only the coordinated molecule is observable. However, the diphenyl sulfoxide complex dissociates in solution to give an appreciable concentration of the dimer, as observed at low temperature in the nmr spectrum.

We have examined the temperature dependences of the nmr spectra of solutions containing excess ligand,

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

[6] (a) R. A. Firth, H. A. O. Hill, B. E. Mann, J. M. Pratt, R. G. Thorp, and R. J. P. Williams, *J. Chem. Soc., A*, 2419 (1968); H. A. O. Hill, J. M. Pratt, and R. J. P. Williams, *Discussions Faraday Soc.*, in press; (b) H. A. O. Hill, J. M. Pratt, and R. J. P. Williams, *Chem. Brit.*, **5**, 156 (1969).

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[9] Values for several trials using 0.01–0.04 *M* solutions ranged from 543 to 695, with an average molecular weight of 627 (calculated for dimer, 608). A trial using bromobenzene as a solvent (bp 156°) yielded 543 although decomposition was evident after several hours in the ebulliometer.

[10] The peak with area 2 is actually two resonances, with a separation of about 1 Hz.

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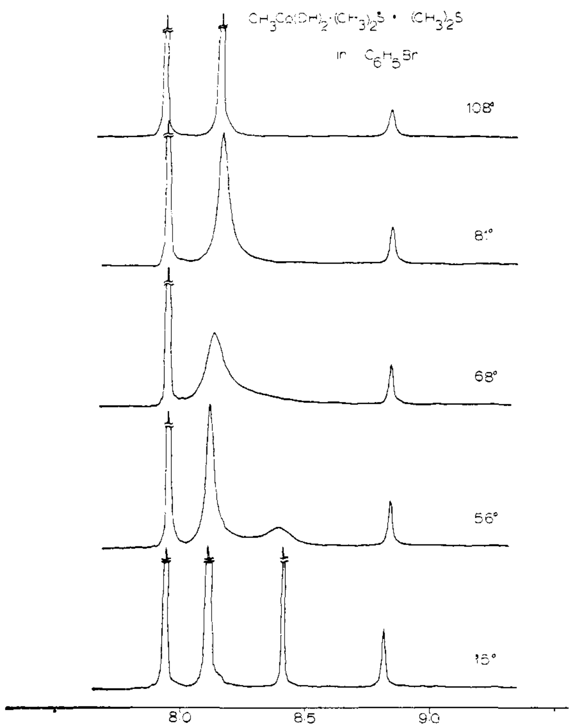

Figure 3. The 60-MHz ^1H spectra of $CH_3Co(DH)_2(CH_3)_2S$ at various temperatures in bromobenzene solution containing excess $(CH_3)_2S$.

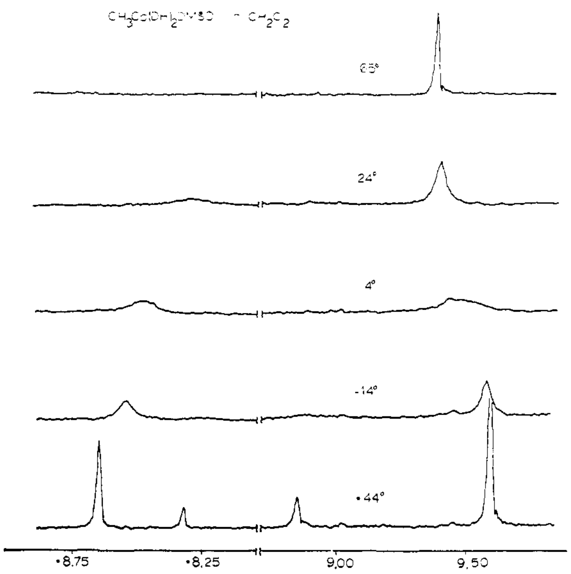

Figure 4. The 60-MHz ^1H spectra of $CH_3Co(DH)_2DMSO$ in dichloromethane showing Co—CH_3 and OH···O absorptions.

with the aim of evaluating the kinetics and mechanism of the ligand exchange reaction

$$CH_3Co(DH)_2L + \overset{*}{L} \longrightarrow CH_3Co(DH)_2\overset{*}{L} + L$$

Figure 3 depicts the nmr spectra of the $CH_3Co(DH)_2S(CH_3)_2$ + $S(CH_3)_2$ system. The methyl resonances of free and complexed sulfide, at τ = 8.11 and 8.40, respectively, are distinguishable at room temperature but coalesce at about 65°. Analogous results were also obtained for dichloromethane solutions. Similarly, the splitting of the axial CH_3 resonance by scalar coupling with coordinated ^{31}P serves in observing the kinetics of ligand exchanges for phosphine and phosphite systems. In the case of $P(OCH_3)_3$, addition of excess ligand does not significantly affect the coalescence temperature. This indicates that the rate-determining process in the exchanges is dissociation.

$$CH_3Co(DH)_2L \longrightarrow CH_3Co(DH)_2 + L$$

The rates of exchange have been compared for a number of ligands with the result that the following order of ligand exchange rates is observed: CH_3CN, DPSO, DMSO > $(CH_3)_2S$ > $S(CH_2CH_2)_2O$ (S-bonded) > $(CH_3)_3N$ > $P(OCH_3)_3$ > $P(C_6H_5)_3$. Detailed line-shape analyses now in progress will provide quantitative data on enthalpies of dissociation, etc. It is already apparent, however, that the order of ligand stabilities with respect to dissociation is characteristic for a "soft," or class b acid.[15] The marked stability of the phosphite and phosphine complexes suggests that π-bonding between cobalt and the ligand π-acceptor orbitals may be an important factor in determining the kinetics of exchange. This result is in reasonable accord with the implications based on substitutional behavior of sulfitobis(dimethylglyoximato)cobalt(III) complexes.[16] It stands, however, in contrast to conclusions that only σ-bonding effects are of importance[6b,17] in cobalamin systems. The present results are in fact the only kinetic data available on systems which can be claimed to be vitamin B_{12} analogs, and which involve a sufficiently wide range of ligand type to reveal the character of the cobalt center as a Lewis acid.

The fact that $CH_3Co(DH)_2$ behaves as a soft acid is demonstrated very nicely by the observation that DMSO exhibits coordination isomerism.[18] The low-temperature nmr spectrum indicates an equilibrium between sulfur and oxygen coordination (Figure 4). The axial methyl and O—H···O resonances split into two absorptions which have chemical shifts characteristic of sulfur and oxygen coordination[19] (relative area oxygen/sulfur = 4.48). The absorption for DMSO shows three peaks when excess ligand is present, due to free, S-bonded, and O-bonded DMSO. The $CH_3Co(DH)_2$ moiety appears to prefer sulfur coordination. In the 1,4-thioxane complex, although oxygen and sulfur possess comparable steric requirements, the complex forms with sulfur coordination.

From these results it is at least plausible to suppose that the cobalt site in alkylcobalamins should bind effectively to sulfur in proteins, as well as at oxygen and nitrogen.

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(18) B. B. Wayland and R. F. Schramm, *Inorg. Chem.*, 8, 971 (1969), report both S and O coordination in some palladium(II) complexes.

(19) As a rough rule, coordination of N or O results in a τ value for the axial CH_3 bonded to Co in the range 9.30–9.40. Coordination of S or P results in a τ value of 9.0–9.1.

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