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Hydrogen Bonding to Metal β-Ketoenolates[1]

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An infrared spectral examination of hydrogen bonding to various neutral bis, tris, and tetrakis β-ketoenolate complexes has been carried out using deuteriochloroform, water, and methanol as the hydrogen-bonding agents. The data obtained indicate very weak or no hydrogen bonding occurs with the tetrahedral bis complexes, stronger hydrogen bonding to the planar bis and to many of the tris complexes, and a pronounced interaction of the solvent with tetrakis complexes. The hydrogen-bond interaction of water with acetylacetonatomanganese(III) and diisobutyrylmethanatomanganese(III) also has been examined. Sites available for hydrogen bonding to the complexes are discussed.

Introduction

Solvents capable of hydrogen bonding greatly perturb the visible and near-infrared spectra of manganese(III) β-ketoenolate complexes.[2] Clarke, *et al.*,[3] recently showed that the vapor pressures of halomethane solvents are dependent on the concentration of tris(acetylacetonato) metal complex in such a way that hydrogen bonding is suggested. Other recent studies have suggested solvent interaction in general[4] and hydrogen bonding in particular[5-8] may occur between certain solvents and metal β-ketoenolates.

This study characterizes the hydrogen-bond interaction between various bis, tris, and tetrakis metal β-ketoenolates and the solvents chloroform-*d*, water, and methanol. Utilizing the fact that hydrogen-bond formation perturbs the infrared spectrum of the hydrogen-bonding solvent, direct evidence for hydrogen-bond formation has been obtained.

Experimental Section

Metal complexes used in this study were prepared by well-established procedures.[8,9] The infrared spectral measurements consisted of studies described below, which employed $CDCl_3$, water, and methanol as interacting solvents. Spectra were observed with a Beckman Model IR-7 spectrophotometer.

Deuterioform.—A standard solution for the deuterioform work was prepared from 5 g. of $CDCl_3$ (Merck Sharp and Dohme) with sufficient dry, distilled CCl_4 to produce 50 ml. of solution. Samples of β-ketoenolates were weighed directly into small vials and 1 ml. of the $CDCl_3$–CCl_4 mixture was added from a syringe. Agitation was used to produce complete solution (when possible). The solution was transferred to a NaCl cavity cell and the spectrum was observed from 2200 to 2500 cm.$^{-1}$ using dry, distilled CCl_4 as a reference. The calibration of the instrument was checked with the C–D stretch of deuterioform itself.

In another study employing deuterioform, a portion of the carbonyl stretching region, 1300–1700 cm.$^{-1}$, was investigated. Very dilute solutions of $Pd(AA)_2$, $Pd(DPM)_2$, $Cu(DPM)_2$, $Cu(AA)_2$, $Be(AA)_2$, $Fe(AA)_3$, $Co(AA)_3$, $Zr(AA)_4$, and $Th(AA)_4$ in the deuterioform–CCl_4 mixture and in pure CCl_4 were examined. The purpose of the study was to determine whether changes in this region could be employed as a criterion of hydrogen bonding and also whether expected changes in certain bands would aid their assignment.

Methanol.—Because methanol hydrogen bonds with itself, a 0.005 M solution of methanol in CCl_4 was employed. The CCl_4 was distilled and stored over P_2O_5. In this way, water bands at ~3620 and ~3700 cm.$^{-1}$ often were eliminated. The cells used employed Teflon film for windows and 1-cm. Teflon spacers. Sample solutions were prepared as in the $CDCl_3$ study.

To observe the growth of the side band centered at ~3550 cm.$^{-1}$, which is attributed to the hydrogen-bonded OH stretch, solutions of increasing concentrations of thorium(IV) acetylacetonate were studied. Five samples were observed, ranging from a pure CH_3OH–CCl_4 solution to a saturated solution of the complex.

Water.—As in the experiments with methanol, a dilute solution of water in purified CCl_4 was studied in cells with 1-cm. Teflon spacers. Samples of $Mn(AA)_3$ and $Mn(DIBM)_3$ in the H_2O–CCl_4 solution were observed in the region 3300–4000 cm.$^{-1}$.

Nuclear Magnetic Resonance.—The n.m.r. spectra of two planar, diamagnetic, dipivaloylmethane complexes also were examined. Nearly saturated solutions of the nickel(II) and palladium(II) complexes in purified, dry CCl_4 were examined with and without added chloroform. The chloroform peak itself was studied as a function of the concentration of the complex, using solutions containing ~10^{-1} M $Pd(DPM)_2$ and ~10^{-2} M $CHCl_3$ in CCl_4. The chloroform was purified to remove water and ethanol. The spectra were run on a Varian Model A-60 spectrometer at ~40°. Tetramethylsilane was used as an internal standard.

Results

The infrared spectra (Tables I and II and Figures 1–3) show conclusive evidence for hydrogen-bond interaction[10] between the hydrogen-bonding solvents used in this study and metal β-ketoenolates. Infrared spectra fulfill the requirements specified by Pimentel and McClellan[11] for hydrogen-bond determination, namely evidence for bond formation and specific solvent hydrogen–solute interaction.

In deuterioform and in methanol, hydrogen bonding to tetrahedral bis complexes was either very weak or did not exist, *i.e.*, the C–D or O–H stretches were not observably perturbed (Figure 4). However, evidence

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TABLE I

HYDROGEN-BOND FORMATION OF METAL β-KETOENOLATES TO $CDCl_3$ IN CCl_4

Samples[a] (ratio)[b]	Comments
$Zn(AA)_2$ (2); $Zn(DPM)_2$ (~5); $Be(AA)_2$ (2.5); $Be(AA)_2$ (0.75); $Mn(DPM)_3$ (4.6)	C–D str. not observably perturbed
$Cu(DPM)_2$ (4); $Pd(DPM)_2$ (4); $Cr(AA)_3$ (4); $Fe(AA)_3$ (3); $Fe(AA)_3$ (1.9); $Co(AA)_3$ (2.4); $Co(AA)_3$ (1.4); $Mn(DIBM)_3$ (2.5)	Weak shoulder observed on low-energy side of the C–D str.
$Mn(DIBM)_3$ (~0.75)[c]	Developed shoulder
$Zr(AA)_4$[c]	Distinct shoulder at ~2250 cm.$^{-1}$
$Th(AA)_4$ (0.9)	Two peaks of nearly equal intensity

[a] AA = acetylacetonate anion, DPM = anion of dipivaloylmethane, DIBM = anion of diisobutyrylmethane. [b] Ratio of $CDCl_3$ to $M(A)_n$. [c] Incomplete solution.

TABLE II

HYDROGEN-BOND FORMATION OF METHANOL TO METAL β-KETOENOLATES IN CCl_4

Sample (M)[a]	Comments
$Be(AA)_2$ (0.02); $Mn(DIBM)_3$ (0.02); $Mn(DPM)_3$ (0.01); $Pd(DPM)_2$ (sat.); $Zn(DPM)_2$ (0.01)	No perturbation of OH str.
$Co(AA)_3$ (0.02)	H-bond abs. 3500–3600 cm.$^{-1}$
$Cr(AA)_3$ (0.015)	H-bond abs. 3475–3600 cm.$^{-1}$
$Mn(AA)_3$ (0.02)[b]	H-bond abs. 3500–3625 cm.$^{-1}$
$Fe(AA)_3$ (0.025)	H-bond abs. 3500–3625 cm.$^{-1}$
$Th(AA)_4$ (0.01)	H-bond abs. 3450–3620 cm.$^{-1}$

[a] Concentration of complex in parentheses. CH_3OH concentration ~0.005 M in CCl_4. [b] Water band observed near 3720 cm.$^{-1}$.

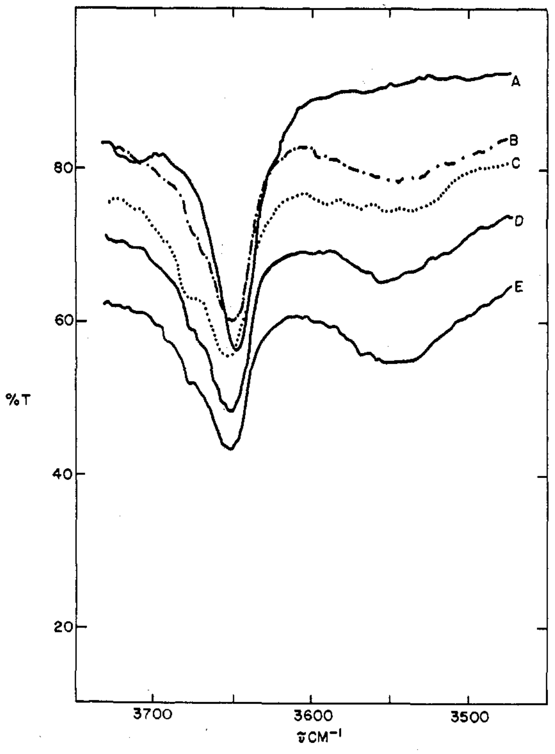

Figure 1.—Hydrogen-bond formation of methanol to thorium(IV) acetylacetonate in CCl_4: A, 0.005 M CH_3OH in CCl_4 solution; B–E, samples of thorium(IV) acetylacetonate (zero to saturated) in order of increased concentration. Curves D and E are displaced by 10% to lower transmission values for clarity.

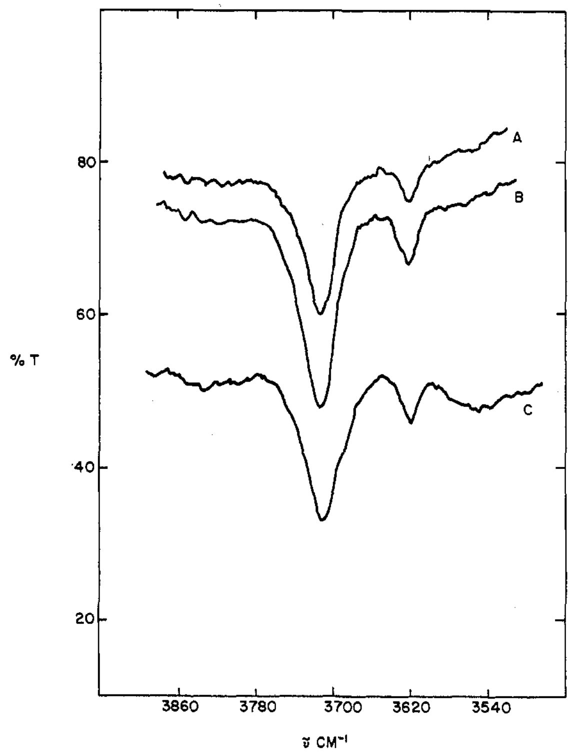

Figure 2.—Hydrogen-bond formation of water to $Mn(DIBM)_3$: A, water in purified CCl_4; B, dilute solution of $Mn(DIBM)_3$ in H_2O–CCl_4; C, same sample as B saturated with $Mn(DIBM)_3$. Note the indistinct shoulder in C near 3680 cm.$^{-1}$ and the broad band near 3540 cm.$^{-1}$.

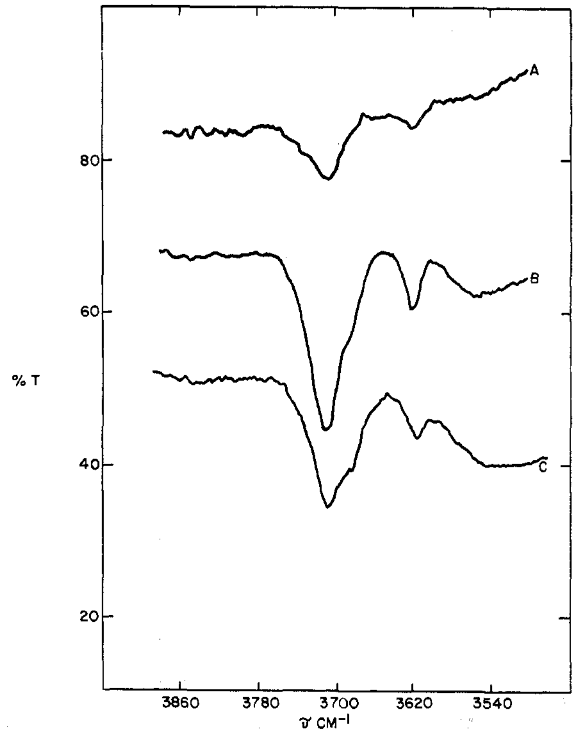

Figure 3.—Hydrogen-bond formation of water to $Mn(AA)_3$: A, water in purified CCl_4; B, a dilute solution of $Mn(AA)_3$ in H_2O–CCl_4; C, same sample as B saturated with $Mn(AA)_3$.

for the interaction of deuterioform and the planar bis complexes[9] $Cu(DPM)_2$ and $Pd(DPM)_2$ was found. For each metal tris acetylacetonate studied, interaction

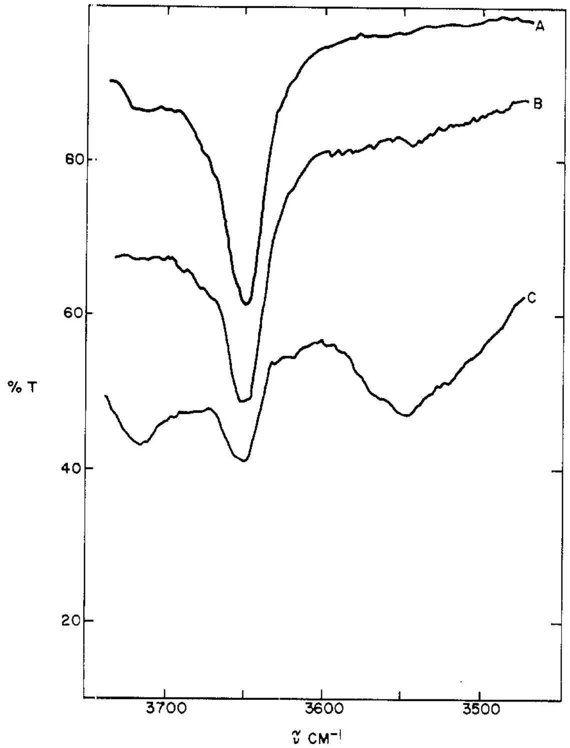

Figure 4.—Comparison of a bis and a tris complex in CH_3OH–CCl_4 solution: A, 0.005 *M* CH_3OH in CCl_4 solution; B, 0.022 *M* $Be(AA)_2$, hydrogen bonding not evident; C, 0.0185 *M* $Co(AA)_3$, strong side band (3500–3600 cm.$^{-1}$) indicates hydrogen bonding.

Figure 5.—Hydrogen bonding of methanol (A) to tris(2,4-pentanedionato)manganese(III) (B) and tris(2,4-pentanedionato)-iron(III) (C).

was observed with both deuterioform and methanol (Figure 5). However, with methanol no hydrogen bonding was detected to tris(diisobutyrylmethanato)- and tris(dipivaloylmethanato)manganese(III) at the rather low concentrations of methanol (in CCl_4) used.

The tetrakis acetylacetonate complexes studied, $Zr(AA)_4$ and $Th(AA)_4$, showed extensive interaction with deuterioform and methanol. The spectrum of the methanol O–H stretch with added $Th(AA)_4$ is reproduced in Figure 1. The growth of a broad band at ~3550 cm.$^{-1}$ with increasing $Th(AA)_4$ is clearly evident. Furthermore, the principal O–H band at ~3650 cm.$^{-1}$ is seen to move to slightly higher energies and to broaden somewhat.

Spectral evidence for hydrogen bonding of water to $Mn(AA)_3$ and $Mn(DIBM)_3$ has been found (Figures 2 and 3). With both $Mn(AA)_3$ and $Mn(DIBM)_3$ a shoulder on the low-energy side of the O–H stretch at ~3700 cm.$^{-1}$ is found along with a broad band near 3540 cm.$^{-1}$. The interaction appears to be weaker with $Mn(DIBM)_3$ than with $Mn(AA)_3$, however.

The carbonyl region (1300–1700 cm.$^{-1}$) of the spectra shows no noticeable differences between those taken in CCl_4 and those taken in the deuterioform–CCl_4 mixture.[3]

The n.m.r. spectra of the two dipivaloylmethane complexes show the two peaks expected with intensity ratios of 18:1. In the palladium complex the ring proton resonance was found at τ ~4.3 while with $Ni(DPM)_2$ it was at τ ~4.7. The *t*-butyl hydrogens appear at τ ~8.7. These peaks do not shift upon addition of $CHCl_3$. The $CHCl_3$ peak also appears to be insensitive to the presence of $Pd(DPM)_2$, at least to the concentrations attainable in this study.[12]

Discussion

It has been suggested[3,5] that a "trifurcated" bond between hydrogen-bonding solvents and tris β-ketoenolates may be formed in which the hydrogen atom presumably interacts equally with three oxygen atoms on an octahedral face of the complex. This suggestion arose from the fact that disolvates of chloroform and other hydrogen-bonding solvents were isolated.[5] However, no direct evidence for hydrogen bonding was obtained. While our studies do not support or eliminate "trifurcation"[13] of hydrogen atoms for species such as $CDCl_3$ and CH_3OH, the data clearly show that these common solvents and water do hydrogen bond to many metal β-ketoenolates.

Models indicate that molecules such as $CHCl_3$ and CH_3OH can hydrogen bond to the oxygen atoms of the chelate in bis planar, tris, and tetrakis complexes without excessive crowding. With tetrahedral bis species such as $Be(AA)_2$ or $Zn(AA)_2$, hydrogen bonding to one chelate ring may interfere with the π orbitals of the other ring, particularly if the hydrogen bond forms at an angle consistent with sp^2 (or nearly sp^2) hybridization of the oxygen. This may in part explain the lack of hydrogen-bond formation with the tetrahedral complexes studied.

The tris diisobutyrylmethane and tris dipivaloylmethane complexes of manganese(III) show no hydro-

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[12] A referee has informed us that he has found n.m.r. evidence for hydrogen bonding of $CHCl_3$ to some tris acetylacetonates.

[13] L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1948, p. 286.

gen bonding to methanol in the $CH_3OH-CCl_4$ solutions studied (Table II). This implies that the bulky isopropyl groups of the diisobutyrylmethane and the even larger *t*-butyl groups of the dipivaloylmethane can, at least in part, block the approach of methanol to the hydrogen-bonding site, presumably the chelate oxygens. However, in pure methanol the effect on the visible and near-infrared spectra[2] is very striking; even with these complexes some interaction (albeit a weak one) can occur.

It is probable that at least partial rehybridization of the orbitals of the oxygen atom will occur upon hydrogen-bond formation. There is some ultraviolet spectral evidence to suggest this as the $\pi-\pi^*$ transition[9] in certain β-ketoenolate complexes is solvent dependent. The considerable shift observed in the near-infrared band of diisobutyrylmethanatomanganese(III) in hydrogen-bonding solvents[2] shows that a perturbation of the electronic system of the chelate ring can occur upon forming hydrogen bonds.

The basicity of the oxygen atoms in β-ketoenolate complexes with their resulting availability for hydrogen bonding is apparent by the ease with which the nickel(II),[14] cobalt(II),[14] manganese(II),[15] and iron(II) acetylacetonates polymerize.[9] However, the possibility that hydrogen-bond formation may occur with the chelate ring itself, as in hydrogen-bond formation to benzene,[16] cannot be discounted, especially in view of the interesting adducts reported by Oestreich[17] between tris β-ketoenolate complexes and silver perchlorate. The lack of hydrogen-bond formation between the tetrahedral bis complexes and $CHCl_3$ or CH_3OH does suggest ring interaction is not important, however, since the rings are as available in these complexes as in the tris or tetrakis species.

In principle, shifts of the $CHCl_3$ proton on hydrogen bonding to $Pd(DPM)_2$ might have been used to decide whether the hydrogen bonding occurs with the β-ketoenolate oxygens or with the ring. Interaction with the oxygen atoms might be expected to produce a low-field shift as occurs with tertiary amines,[16] while interaction with the ring would give shifts in the opposite sense as found with benzene.[16] With the concentrations used in this work, however, the method appears to be insufficiently sensitive to give reliable results. Perhaps a detailed investigation with other complexes having higher solubilities would be more successful.[12]

The spectra showing hydrogen bonding between water and $Mn(AA)_3$ or $Mn(DIBM)_3$ can be interpreted with the following considerations. There are two types of hydrogen bonding which may be present: (1) a 1:1 complex where only one hydrogen of the water molecule is bonded, and (2) a "chelate" complex where both hydrogens are bonded, presumably to oxygens of different β-ketoenolate rings. A dilute solution of water in CCl_4 shows[18] free O–H peaks (Figures 2 and 3) at ~3700 and ~3620 cm.$^{-1}$. If a 1:1 complex were formed, a shoulder or side band should appear on the low-energy side of the 3700 cm.$^{-1}$ band, while in the "chelate" complex, no shoulder should appear. In the "chelate," as well as the 1:1 complex, a broad band from ~3600 to 3400 cm.$^{-1}$ should be found.[18]

The spectrum of water in CCl_4 with added $Mn(DIBM)_3$ and $Mn(AA)_3$ can be seen in Figures 2 and 3, respectively. In the curves labeled C, a saturated solution of the complex, some asymmetry of the 3700 cm.$^{-1}$ OH band is observed, along with the broad band at ~3540 cm.$^{-1}$. The presence of the shoulder on the low-energy side of the 3700 cm.$^{-1}$ band indicates that some of the hydrogen-bonded water is present as the 1:1 complex, since this band would be absent if both water hydrogens were involved. If no "chelate" type water were present, the shoulder should increase in intensity proportional to the growth of the 3540 cm.$^{-1}$ band. This does not appear to be true; however, the data are not sufficiently good to be conclusive on this point.

The comparison of the $H_2O-Mn(DIBM)_3$ spectrum (Figure 2) with that of $H_2O-Mn(AA)_3$ (Figure 3) indicates that, as in the case where methanol is the hydrogen-bonding solvent, steric properties of the ligands may influence the extent of the hydrogen bonding.

As we stated previously,[2] the role hydrogen-bond formation may play in perturbing the electronic properties of β-ketoenolate complexes has been determined in only a few cases. The solvents to be chosen for such studies must be picked with considerable caution, since hydrogen-bond formation in some cases may strongly perturb the electronic symmetry of the chelate ring.

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