CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY,
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Hydrogen Bonding in Some Copper(II) and Nickel(II) *vic*-Dioximes[1]

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The infrared spectra of bis(2,3-butanedionedioximato-N,N′)copper(II) [$\mathrm{Cu(DMG)_2}$], bis(2,3-butanedionedioximato-N,N′)-nickel(II) [$\mathrm{Ni(DMG)_2}$], bis(2,3-pentanedionedioximato-N,N′)nickel(II) [$\mathrm{Ni(EMG)_2}$], and their deuterated analogs were investigated. The spectra of $\mathrm{Ni(DMG)_2}$ and $\mathrm{Cu(DMG)_2}$ in solution were also determined. The hydrogen bonding in the copper chelate was found to be much stronger in solution than in the solid. On the basis of the infrared spectra and the reactivity with dimethyl sulfate, phenyl isocyanate, and acetic anhydride, it is concluded that the hydrogen bonding in $\mathrm{Cu(DMG)_2}$ rearranges upon solution so that it is quite similar to the hydrogen bonding of the two nickel chelates in the crystalline state. Thus, a shortening of the O–O distances in the copper chelate is predicted upon solution. Finally, this study indicates the possibility that symmetrical hydrogen bonds occur for both nickel chelates in the crystalline state and that all three chelates have symmetrical hydrogen bonds in solution.

Introduction

The presence of very strong hydrogen bonds in bis(2,3-butanedionedioximato-N,N′)nickel(II) [$\mathrm{Ni(DMG)_2}$] in an organic solvent was very early indicated by the lack of reactivity of the hydroxyl groups with phenyl isocyanate,[2] acetic anhydride,[3] methylmagnesium iodide in amyl ether,[4] and dimethyl sulfate.[5] In an organic solvent bis(2,3-butanedionedioximato-N,N′)copper(II) [$\mathrm{Cu(DMG)_2}$] appears to behave in a similar manner because, according to Fleischer,[6] Tirpak found that the hydroxyl groups in this chelate did not react with methylmagnesium iodide.

Subsequent determination of the crystal structure of $\mathrm{Ni(DMG)_2}$[7,8] revealed the O–O distances in the molecule to be very short (2.40 A); thereby indicating that the inertness of hydroxyl hydrogens was due to very strong hydrogen bonding. On the other hand, the crystal structure of $\mathrm{Cu(DMG)_2}$[9] showed this chelate to exist in the crystal as a dimer joined by two Cu–O bonds. Consequently, there are two different O–O distances (2.53 and 2.70 A) in solid $\mathrm{Cu(DMG)_2}$ indicating that in the crystalline state the hydrogen bonding in this chelate is weaker than that in solid $\mathrm{Ni(DMG)_2}$. Knowing that the solubilities and enthalpies of solution were quite similar for these two chelates in an inert solvent, Rundle and Banks[10] predicted that the hydrogen bonds in $\mathrm{Cu(DMG)_2}$ rearrange to much stronger hydrogen bonds upon solution. This rearrangement was required to provide the necessary energy for $\mathrm{Cu(DMG)_2}$ to have a solubility similar to $\mathrm{Ni(DMG)_2}$ in an inert solvent.

The present investigation was undertaken to establish and characterize any rearrangement of the hydrogen bonds in $\mathrm{Cu(DMG)_2}$ upon solution. It was necessary to use $\mathrm{Ni(EMG)_2}$ [bis(2,3-pentanedionedioximato-N,N′)nickel(II)] instead of $\mathrm{Ni(DMG)_2}$ as a control and comparison for many of the studies of $\mathrm{Cu(DMG)_2}$ in solution, because $\mathrm{Ni(DMG)_2}$ was not soluble enough in the appropriate solvents. Although $\mathrm{Ni(EMG)_2}$ has a greater solubility than $\mathrm{Ni(DMG)_2}$ in a great variety of solvents,[11] it has an analogous molecular structure with an even shorter O–O distance (2.33 A)[12] indicating that the hydrogen bonding in these two chelates is quite similar and probably very strong.

Experimental Section

Preparations.—The metal chelates were prepared by the methods outlined in a previous paper.[11]

The deuterium-substituted compounds were prepared in a drybox with a dry nitrogen atmosphere. The hydroxyl hydrogens on dimethylglyoxime were exchanged for deuterium by the dissolution of dimethylglyoxime in boiling deuterium oxide. The infrared spectrum indicated that the exchange was essentially complete after one such recrystallization. Nevertheless, to ensure complete exchange this process was carried out three successive times. The product of these recrystallizations was dissolved in hot deuterium oxide and combined with the proper amount of anhydrous copper(II) or nickel(II) chloride. The amount of anhydrous sodium carbonate needed to neutralize the liberated acid was then added. The mixture was digested over low heat for at least 2 hr. The chelates were collected by gravity filtration and kept under a dry atmosphere until they had been prepared for the determination of the infrared spectra.

$\mathrm{Ni(EMG)_2}$ was prepared in the deuterated form in a manner analogous to that described for $\mathrm{Ni(DMG)_2}$ and $\mathrm{Cu(DMG)_2}$.

Spectra.—A Beckman IR-7 spectrophotometer was used to record the infrared spectra between 4000 and 600 $\mathrm{cm^{-1}}$. Spectra in the range between 800 and 33 $\mathrm{cm^{-1}}$ were recorded on a Beckman IR-11 spectrophotometer. Attenuated total reflectance (ATR) spectra were obtained for the 4000–600-$\mathrm{cm^{-1}}$ region using a Barnes Engineering Co. free-reflection ATR attachment on the Beckman IR-7.

Media for spectra of the crystalline compounds were Nujol mull, Halocarbon oil mull, and KBr disks. Halocarbon oil mulls gave the best spectra in the 4000–1300 $\mathrm{cm^{-1}}$ range, and the oil itself had no bands in this region. Nujol mulls yielded the best spectra in the region below 1300 $\mathrm{cm^{-1}}$. Spectra of samples

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[3] M. F. Barker, *Chem. News*, **130**, 99 (1925).

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[5] E. Thilo and H. Friedrich, *Ber.*, **62**, 2990 (1929).

[6] D. Fleischer, Ph.D. Thesis, University of Pittsburgh, 1959, pp 67–68. University Microfilms 59-2396, Ann Arbor, Mich.

[7] L. E. Godycki and R. E. Rundle, *Acta Cryst.*, **6**, 487 (1953).

[8] D. E. Williams, G. Wohlauer, and R. E. Rundle, *J. Am. Chem. Soc.*, **81**, 755 (1959).

[9] E. Frasson, R. Bardi, and S. Bezzi, *Acta Cryst.*, **12**, 201 (1959).

[10] R. E. Rundle and C. V. Banks, *J. Phys. Chem.*, **67**, 508 (1963).

[11] J. E. Caton and C. V. Banks, *Talanta*, **13**, 967 (1966).

[12] E. Frasson and C. Panattoni, *Acta Cryst.*, **13**, 893 (1960).

in KBr disks were made for the entire region between 4000 and 600 cm^{-1}, and in all cases these spectra were identical with those obtained by the mull techniques. Extra grinding of the crystalline samples greatly improved the quality of the spectrum obtained in the 2800–2000-cm^{-1} region. For Cu(DMG)$_2$, best results were obtained when the crystals were first dissolved in 95% ethyl alcohol with the solvent then being rapidly evaporated to yield a finely powdered Cu(DMG)$_2$ sample. This powdered sample was then subjected to extra grinding and handled in the usual manner for the mull or disk technique.

The ATR spectra of Ni(DMG)$_2$ and Ni(EMG)$_2$ were obtained by pressing the powdered sample against the face of a KRS-5 crystal. However, adequate contact between the face of the crystal and Cu(DMG)$_2$ could not be obtained by the above technique; therefore, Cu(DMG)$_2$ was grown on the KRS-5 crystal by the evaporation of a solution of Cu(DMG)$_2$ in ethanol on the crystal face.

Spectra in solution were obtained for the 4000–1000-cm^{-1} region. Matched 0.2-mm cells with potassium bromide windows were used. The solvent for Ni(EMG)$_2$ was reagent grade quality chloroform obtained from Allied Chemical Co. This chloroform was dried over silica gel and distilled before using. Deuterated Ni(EMG)$_2$ [Ni(EMG)$_2$-d_2] was dissolved in deuteriochloroform obtained in 99.5% purity from Bio-Rad Laboratories.

To obtain spectra of Cu(DMG)$_2$ in solution, the chloroform was made 0.1 M in Fisher Certified Reagent *n*-butylamine. The *n*-butylamine increases the solubility of Cu(DMG)$_2$ by adduct formation.[6,11,13,14]

In the case of deuterated Cu(DMG)$_2$ [Cu(DMG)$_2$-d_2], the solvent was prepared by first equilibrating 0.4 ml of *n*-butylamine with 10 ml of deuterium oxide. The *n*-butylamine was extracted into 10 ml of deuteriochloroform. The deuteriochloroform was equilibrated with an equal volume of fresh deuterium oxide three additional times. Each equilibration consisted of shaking the two-phase mixture for 1 hr and then recovering the deuteriochloroform phase. This solvent was dried by adding several pellets of molecular sieves. (The procedure described for the preparation of this solution was first carried out on identical volumes of *n*-butylamine, water, and chloroform. A nonaqueous titration on the final chloroform solution revealed the *n*-butylamine concentration to be approximately 0.1 M.) The infrared spectrum of the dried solution showed that the amine hydrogens had been exchanged. This solution was then saturated with Cu(DMG)$_2$-d_2, and the infrared spectrum of the resulting solution was obtained.

Reactivity.—For testing the reactivity of the solid chelates, about 10 mg of the solid was placed in a small test tube, and the sample was covered with about 20 drops of phenyl isocyanate, acetic anhydride, or dimethyl sulfate. Any immediate reaction was noted, then the test tube was placed in a desiccator and any later reaction was noted. The reactivity of saturated solutions of the chelates in benzene was checked by adding 5 drops of the above reagents to 1 ml of the benzene solutions. Any color change was noted.

Discussion

Infrared Spectra.—Previously, there has been some doubt as to whether the OH stretching vibrations for metal *vic*-dioximes were located in the 1600–1900-cm^{-1} region[15-19] or in the 2300-cm^{-1} region.[20] The spectrum of Ni(DMG)$_2$ shown in Figure 1 indicates without doubt that there is a band at 2322 cm^{-1}. When Ni(DMG)$_2$ is deuterated [Ni(DMG)$_2$-d_2], this 2322-cm^{-1} band disappears as indicated in Figure 1, and a new band appears at 1530 cm^{-1}. Thus, it is apparent that the OH stretching vibration for Ni(DMG)$_2$ occurs in the 2300-cm^{-1} region.

Table I indicates the location of the OH and OD bands for all the compounds studied. The data in this table appear to present some difficulty in interpretation. In the first place the more strongly hydrogen-bonded OHO group in Cu(DMG)$_2$ (O–O distance = 2.53 A) has approximately the same OH stretching frequency as the OHO groups in Ni(DMG)$_2$ and Ni(EMG)$_2$ which have significantly shorter O–O distances in the crystalline state. A possible explanation for this behavior follows from the work of Lippincott and Schroeder,[21] who calculated that the increase in OH frequency shift as the O–O distance decreased should have a maximum. This maximum, which Lippincott and Schroeder calculated to occur at an O–O distance of 2.45 A, corresponds to the case of symmetrical hydrogen bonding. It seems logical that as the O–O distance decreased beyond this symmetrical point, one should expect the frequency of the OH stretching vibration to increase, because the OH bond should then decrease in length and become stronger. Therefore, a plausible explanation for OH stretching bands located in the vicinity of 2300 cm^{-1} for Ni(DMG)$_2$, Ni(EMG)$_2$, and Cu(DMG)$_2$, despite the differences in O–O distance, is that the 2.53-A O–O distance of Cu(DMG)$_2$ falls on one side of the maximum found by Lippincott and Schroeder;[21] whereas the shorter O–O distances of the nickel chelates occur at a corresponding point on the opposite side.

TABLE I

FREQUENCY OF OH AND OD BANDS

Chelate	State[a]	R[b]	ν_{OH}[c]	ν_{OD}[c]	δ_{OH}[d]	δ_{OD}[d]	Ref[e]
Cu(DMG)$_2$	C	2.70	2650	1977	1492	1175	8
	C	2.53	2382	2370	1640[f]	1262	8
	S	...	2375	1675	1640	1274	...
Ni(EMG)$_2$	C	2.33	2388	1515	1784	1209	11
	S	...	2350	1512	1715	1253	...
Ni(DMG)$_2$	C	2.40	2322	1530	1790	1275	7

[a] C is solid or crystalline state; S indicates in solution. [b] R is OHO distance in A. [c] ν is stretching frequency in cm^{-1}. [d] δ is bending frequency in cm^{-1}. [e] Reference for OHO distance. [f] The ATR spectra were of great value in establishing the presence of this band. There is a blunt shoulder at 1640 cm^{-1} in the infrared spectrum of Cu(DMG)$_2$; however, it is difficult to see the difference between the infrared spectrum of Cu(DMG)$_2$ and that of Cu(DMG)$_2$-d_2 in the 1640-cm^{-1} region. The ATR spectra inserted into Figure 3 left little doubt that a band existed at 1640 cm^{-1} for Cu(DMG)$_2$ but not for Cu(DMG)$_2$-d_2.

As one would expect from the crystal structure of Cu(DMG)$_2$, there are two OH stretching bands for the solid (2650 and 2382 cm^{-1}); however, upon solution only one OH stretching band remains (2375 cm^{-1}) [see Figure 2]. These data support the prediction of Rundle and Banks[10] that the Cu–O bonds in Cu(DMG)$_2$ are broken and the chelate exists as a monomer upon solution.

An insignificant shift occurs for the 2382-cm^{-1} band in crystalline Cu(DMG)$_2$ upon deuteration (Figure 3).

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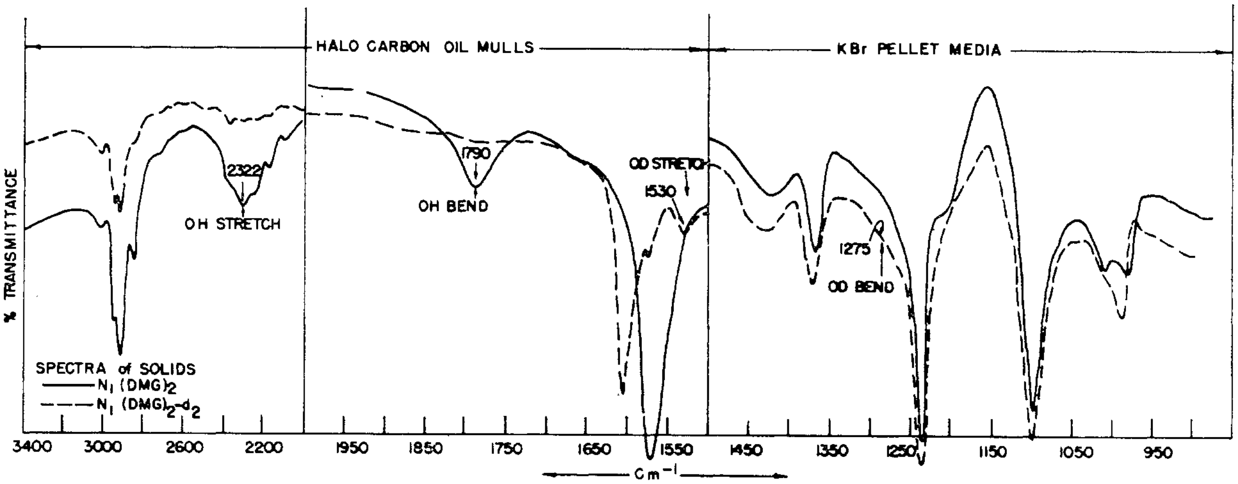

Figure 1.—Infrared spectra of crystalline Ni(DMG)$_2$ and Ni(DMG)$_2$-d_2.

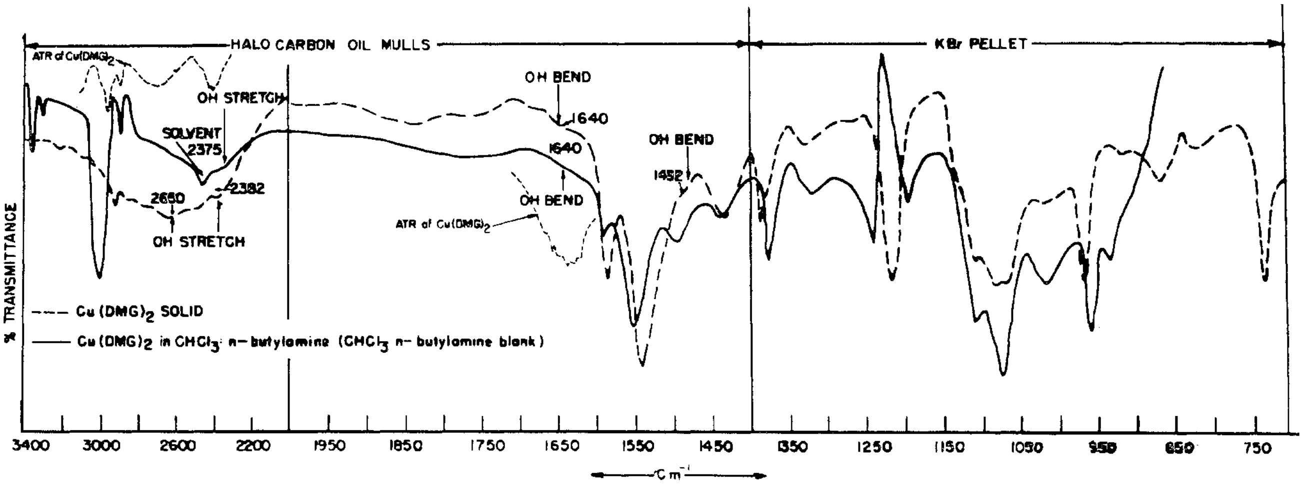

Figure 2.—Infrared spectra of Cu(DMG)$_2$ in the crystalline state and in solution.

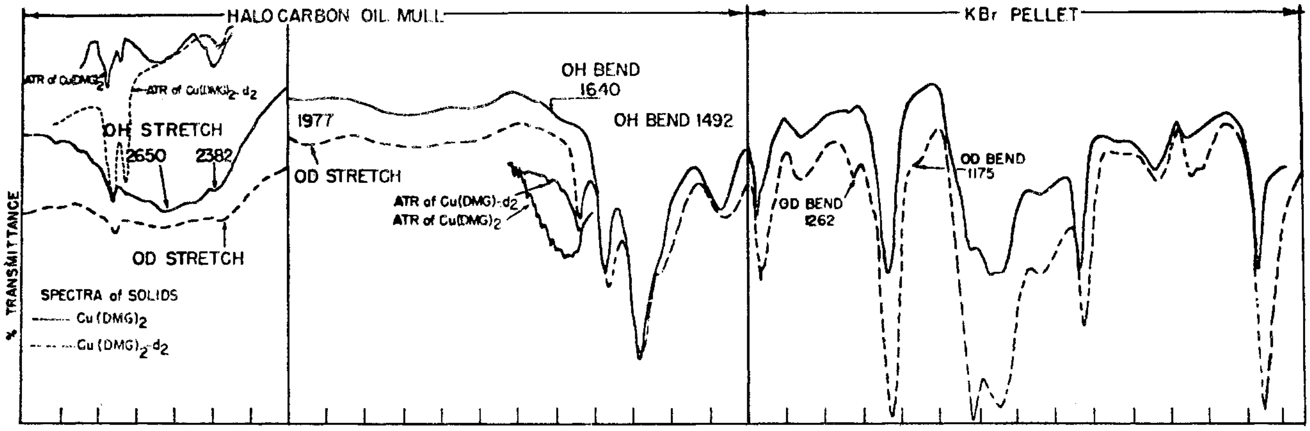

Figure 3.—Infrared spectra of crystalline Cu(DMG)$_2$ and Cu(DMG)$_2$-d_2.

This band arises from the OH stretching vibration in the 2.53-A OHO bond. The extremely small shift caused by deuteration of such an OHO bond is not without precedent. Snyder and Ibers[22] observed similar behavior for chromous acid [HCrO$_2$] which has an OHO distance of 2.49 A and an ODO distance of 2.55 A.[22] The X-ray and infrared studies of Snyder and Ibers on chromous acid quite convincingly indicate that the OHO bond in chromous acid is symmetric, whereas the ODO bond is asymmetric. According to Rundle[23] the "abnormal isotope effect" (ODO distance > OHO distance) is to be expected for O–O distances around

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(22) R. G. Snyder and J. A. Ibers, *J. Chem. Phys.*, **36**, 1356 (1962).

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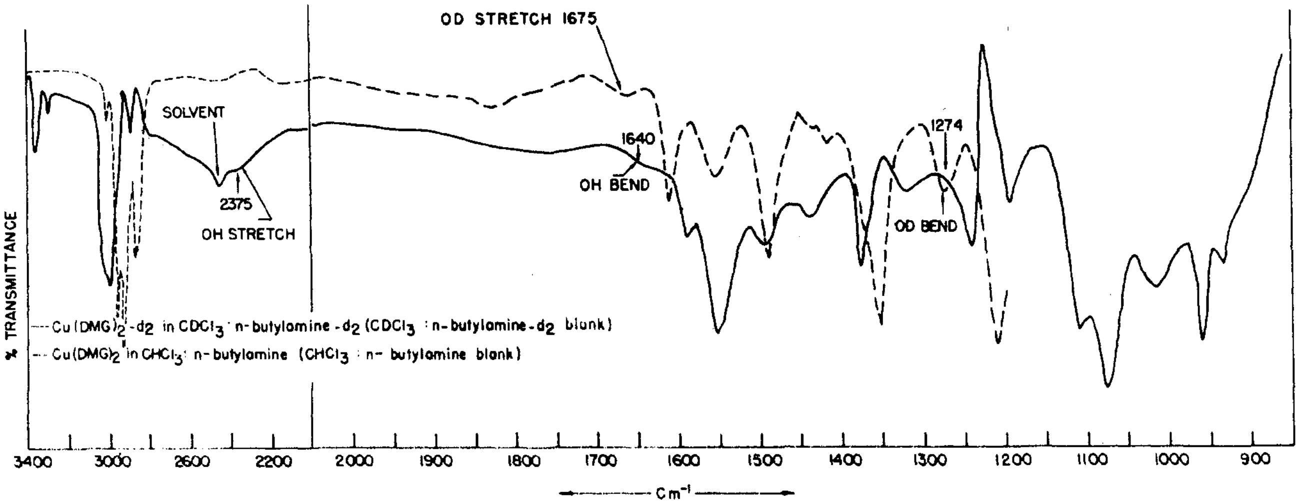

Figure 4.—Infrared spectra of Cu(DMG)$_2$ and Cu(DMG)$_2$-d_2 in solution.

2.50 A. In the region of the "abnormal isotope effect" hydrogen is presumed to be in a symmetric arrangement in the OHO bond, whereas deuterium remains in an asymmetric arrangement. Thus, when the O–O distance is about 2.5 A, one encounters the unique situation where the deuterium may be more strongly associated with one of the oxygen atoms than is the hydrogen. The resulting OD bond is then stronger than the corresponding OH bond and the increased bond strength would tend to nullify the decrease in stretching frequency expected from the higher reduced mass of the ODO. Therefore, the small shifts observed in the frequency upon deuteration of the 2.53-A OHO bond in Cu(DMG)$_2$ are not surprising. Based on the work of Rundle[23] and the infrared data, it could be speculated that the 2.53-A O–O distance in Cu(DMG)$_2$ becomes slightly longer when deuterium is substituted for hydrogen. Thus, it is the authors' intention to check the ODO distance in Cu(DMG)$_2$-d_2 in the near future.

For Cu(DMG)$_2$ in solution the band in the 2300-cm^{-1} region does shift upon deuteration (Figure 4) in the manner one would expect from reduced mass considerations. This shift is quite similar to that observed for Ni(EMG)$_2$ in solution. Thus, in solution the OHO bond in Cu(DMG)$_2$ is apparently longer or shorter than the range of distances where Rundle[23] predicted the "abnormal isotope effect" to occur. It appears likely that these OHO bonds are shorter because Fleischer[6] has reported that Tirpak observed no reaction between Cu(DMG)$_2$ in solution and methylmagnesium iodide. Thus, the hydrogens in the OHO bonds of Cu(DMG)$_2$ are apparently very strongly bound. This then indicates that the OHO bonds in Cu(DMG)$_2$ apparently do rearrange upon solution.

The 2.70-A O–O distance in Cu(DMG)$_2$ is longer than the range of distances where Rundle[23] says the "abnormal isotope effect" should occur. In this region both hydrogen and deuterium are expected to be in asymmetrical arrangements and the frequency shift upon deuteration should be approximately that expected by the change in reduced mass. The data in Table I indicate that this is true for the band arising from the 2.70-A OHO bond in Cu(DMG)$_2$.

For O–O distances shorter than the range where the "abnormal isotope effect" occurs [such as those in Ni(DMG)$_2$ and Ni(EMG)$_2$], the hydrogen and the deuterium are both expected to be in symmetrical arrangements between the oxygen atoms and the shift in frequency upon deuteration should approximate that predicted by the change in reduced mass. A glance at Table I will show that such is indeed the case for Ni(DMG)$_2$ and Ni(EMG)$_2$.

There is very little difference between the spectra of the chelates in their hydrogen form and the deuterium-substituted chelates in the 500–100-cm^{-1} range (Figures 5–7). If the lowest vibrational energy level of the OH bond had been split owing to proton tunneling in an asymmetrical OHO bond, one might have expected a band in this region to have disappeared upon deuteration.[24] Therefore, the behavior of the far-infrared spectrum is consistent with the presence of symmetrical OHO bonds; however, it should be pointed out that the far-infrared spectra alone do not constitute any evidence for symmetrical OHO bonds.

Reactivity.—The current investigation indicated, in agreement with Barker,[3] that acetic anhydride did not affect Ni(DMG)$_2$. This reagent dissolves significant amounts of Ni(EMG)$_2$ as do other organic solvents such as chloroform and benzene,[11] but acetic anhydride does not appear to react with or decompose Ni(EMG)$_2$. However, the brown Cu(DMG)$_2$ crystals react upon contact with acetic anhydride and a blue precipitate is formed. When acetic anhydride was added to benzene solutions of the three chelates, no color change or evidence of reaction was observed.

Phenyl isocyanate was observed to decompose Cu(DMG)$_2$ partially (as evidenced by the appearance of some blue color), but this reagent did not appear to react with solid Ni(DMG)$_2$ and Ni(EMG)$_2$ or with any

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(24) D. Hadzi, *J. Chem. Phys.*, **34**, 1445 (1961).

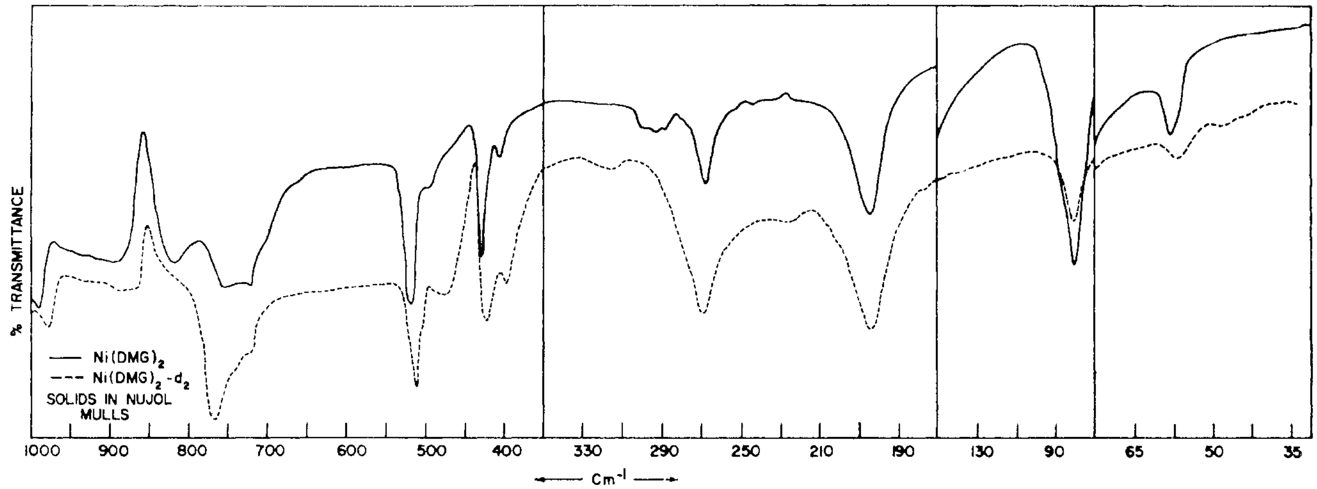

Figure 5.—Far-infrared spectra of crystalline $Ni(DMG)_2$ and $Ni(DMG)_2$-d_2.

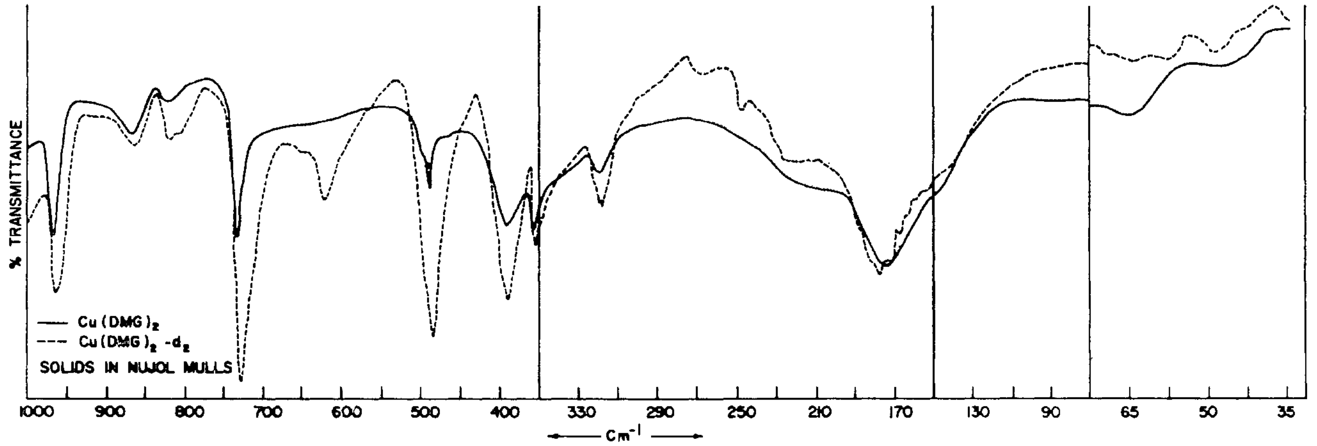

Figure 6.—Far-infrared spectra of crystalline $Cu(DMG)_2$ and $Cu(DMG)_2$-d_2.

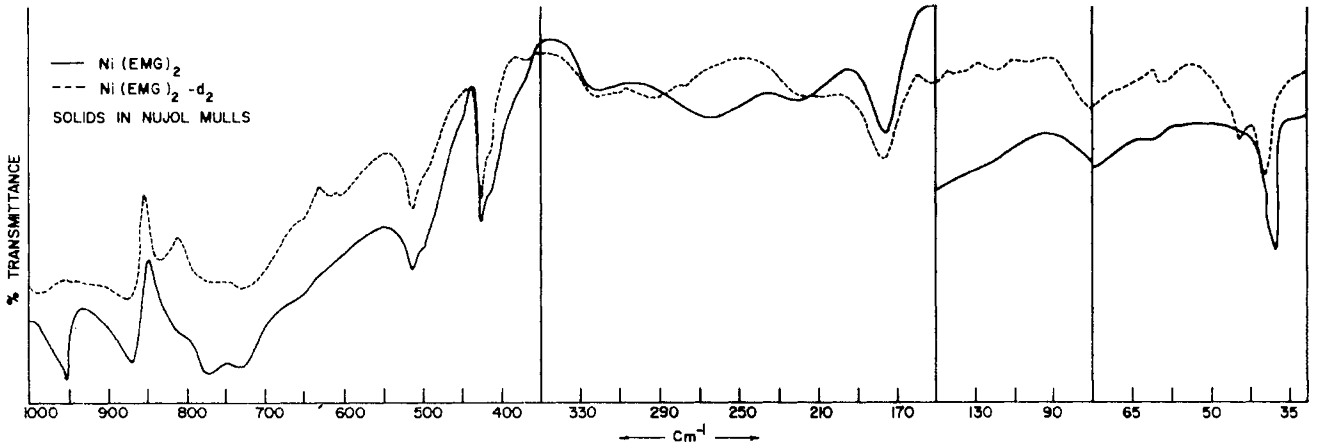

Figure 7.—Far-infrared spectra of crystalline $Ni(EMG)_2$ and $Ni(EMG)_2$-d_2.

of the three chelates in benzene solution. Tschugaeff[2] also found no reaction between phenyl isocyanate and $Ni(DMG)_2$.

Dimethyl sulfate was found to react immediately with solid $Cu(DMG)_2$ yielding a green solution and a green precipitate. Both $Ni(DMG)_2$ and $Ni(EMG)_2$ reacted slowly with dimethyl sulfate. The former chelate slowly lost its scarlet color leaving a white precipitate while the $Ni(EMG)_2$ dissolved completely forming a colorless solution. This reaction between dimethyl sulfate and the nickel chelates required several days, whereas similar amounts of the reagent and $Cu(DMG)_2$ brought about the described decomposition of the copper chelate in a matter of minutes. In benzene solution all three chelates appear to decompose slowly in the presence of dimethyl sulfate. Since these observations are in disagreement with those of Thilo and Friedrich,[5] who could not find any reaction between Ni(DMG)$_2$ and dimethyl sulfate, the slow decomposition observed might be due to slow decomposition of the dimethyl sulfate to more acidic products.

Brady and Muers[4] have shown that Ni(DMG)$_2$ did not yield methane with methylmagnesium iodide in amyl ether, and in organic solution[6] Cu(DMG)$_2$ does not react with methylmagnesium iodide.

All these data on reactivity of the three chelates seem to indicate first, that the hydroxyl groups in solid Cu(DMG)$_2$ are more reactive than those in Ni (EMG)$_2$ or Ni(DMG)$_2$ and, second, that in solution Cu(DMG)$_2$ is less reactive than in the solid and appears to be much like the crystalline nickel chelates. All three chelates appear to have similar strong hydrogen bonds in solution.

Nature of the OHO Bond.—The data on reactivity, coupled with the infrared evidence, would seem to give very substantial support to the prediction of Rundle and Banks[10] that the OHO bonds in Cu(DMG)$_2$ rearrange upon solution to become more strongly hydrogen bonded. The infrared data interpreted in terms of the "abnormal isotope effect"[23] indicate that solid Ni(DMG)$_2$ and Ni(EMG)$_2$ have symmetrical OHO and ODO bonds. Concerning the two different O–O bonds in solid Cu(DMG)$_2$, it is believed that both hydrogen and deuterium have asymmetrical arrangements in the longer O–O bond; whereas, hydrogen has a symmetrical and deuterium has an asymmetrical arrangement in the shorter O–O bond. Upon solution both OHO bonds in Cu(DMG)$_2$ appear to become identical, and the infrared data coupled with the unreactivity of the hydroxyl groups would seem to indicate that both deuterium and hydrogen exist in symmetrical arrangements. Thus, it would be expected that the O–O distance of Cu(DMG)$_2$ in solution should be significantly shorter than either of the O–O distances in the crystal and should be approximately the same as the O–O distances found in crystalline Ni(DMG)$_2$ and Ni(EMG)$_2$.

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Low-Frequency Infrared Studies of Some Tin(IV) Halide Adducts[1]

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The infrared spectra of the complexes $SnCl_4 \cdot 2L$ (L = CH_3CN, CH_2CHCN, C_6H_5CN), $SnBr_4 \cdot 2CH_3CN$, $SnX_4 \cdot$dipy (X = Cl, Br, I), and $SnX_4 \cdot 2DMF$ (X = Cl, Br) have been investigated in the 500–140-cm^{-1} region. The SnN stretching frequencies for the $SnCl_4 \cdot 2$(nitrile) and $SnX_4 \cdot$dipy adducts have been observed below the CsBr region. The SnCl stretching frequencies of all adducts occur in the 275–370-cm^{-1} region, whereas those of SnBr are located in the 195–250-cm^{-1} region. The assignments made in this investigation reverse those made recently by other workers for the SnCl and SnN stretching frequencies for the nitrile adducts and the SnCl and ligand vibrations for the DMF derivatives. Some special features of the spectra of $SnCl_4 \cdot 2CH_2CHCN$ in the NaCl region, particularly the observed crossover of the vinyl twist and wag frequencies, are discussed.

Introduction

Several papers have appeared in the past few years dealing with the low-frequency spectra of some nitrile adducts of stannic chloride.[2–5] Considerable controversy has arisen over the assignments of the bands below 500 cm^{-1} in the spectrum of $SnCl_4 \cdot 2CH_3CN$. Brown and Kubota[2] originally assigned the bands around 400 cm^{-1} as SnCl stretching modes, whereas those bands occurring between 350 and 300 cm^{-1} were assigned to the asymmetric and symmetric SnN stretching vibrations. Beattie, *et al.*,[3] however, showed that the assignments of Brown and Kubota were incorrect; they assigned the bands around 400 cm^{-1} as ligand vibrations (NCC bending modes) and the lower frequency bands as SnCl stretching vibrations. On the basis of a simple valence force field calculation, Beattie and Rule[4] predicted that the SnN stretching frequency for $SnCl_4 \cdot 2CH_3CN$ would occur below 265 cm^{-1}.

We have examined the low-frequency spectra of acetonitrile and acrylonitrile derivatives of M(CO)$_6$ (M = Cr, Mo, W) and showed that for the acetonitrile derivatives, the NCC bending modes occur in the 390–400-cm^{-1} region,[6] in agreement with the assignments of Beattie, *et al.*[3]

However, Aggarwal and Singh,[5] on the basis of the low-frequency infrared spectra of some amide, urea, and aminobenzoic acid adducts of Sn(IV) halides, have reversed the assignments and support those of Brown and Kubota[2] for $SnCl_4 \cdot 2CH_3CN$. It was this paper which prompted us to design some definitive experi-

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(3) I. R. Beattie, G. P. McQuillan, L. Rule, and M. Webster, *J. Chem. Soc.*, 1514 (1963).

(4) I. R. Beattie and L. Rule, *ibid.*, 3267 (1964).

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