Nature of the Hydrogen Bond in 1,2-Bis(*vic*-dioximo-*N,N'*)Nickel(II) Compounds

Infrared Spectrophotometric Study

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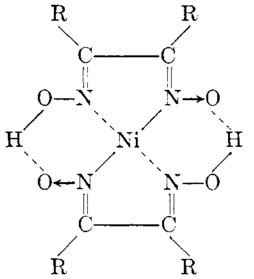
Although the various *vic*-dioximes have been widely used in the analytical chemistry of nickel and palladium, a more complete knowledge of the constitution of the inner-complex compounds thus formed should facilitate the extension of the scope of their application and the development of new organic analytical reagents. It has long been assumed that the decreased reactivity of the remaining oxime hydrogens in the inner-complex compounds formed by the reaction of the *vic*-dioximes with nickel or palladium ions was caused by hydrogen bonding between these oxime hydrogens and the proximate oxygens of the nitrone-form oxime groups. In this paper, infrared spectrophotometric evidence is presented to show that in the nickel inner-complex compounds of several *vic*-dioximes, the characteristic absorption maxima normally attributed to O—H bonds are not detected in the usual region. These maxima, shifted slightly to lower frequencies because of intermolecular association, are noted in the spectra of the corresponding solid *vic*-dioximes. The conclusion is drawn that the oxime hydrogens of the metal derivatives are present in an O—H—O structure unlike that observed in normal hydrogen bonds.

FEIGL (*10*) has emphatically stressed the importance to applied analytical chemistry of a clear understanding of the constitution of the metallo-organic complexes that are employed as the bases of analytical procedures. The whole process of developing new organic analytical reagents and of extending the scope of applicability of existing reagents depends upon exhaustive studies that will lead to a more complete knowledge of the structures of these complexes. While previous papers in this series have dealt mainly with the preparation and analytical application of various *vic*-dioximes (*11, 12, 14, 23–25, 29–31*), this investigation was undertaken to attempt to determine, by an infrared spectrophotometric study, the nature of the hydrogen bond in 1,2-bis-(*vic*-dioximo-*N,N'*)nickel(II) compounds.

The gross features of the structure of the inner-complex compounds formed by the reaction of the *anti*-form of the *vic*-dioximes with nickel(II) ions are well established. The general formula, commonly written for convenience as



was originally proposed by Pfeiffer (*20, 21*) on the basis of a study of analogous complexes. Sugden (*7, 27*) isolated and identified geometric isomers corresponding to the cis- and trans- configurations of the nickel derivatives of several unsymmetrically substituted *vic*-dioximes. This evidence for the planar structure of these molecules has been confirmed by magnetic measurements (*6, 7, 16, 27*). The nickel derivatives of several *vic*-dioximes have been found to be diamagnetic, indicating the existence of bond orientation of the dsp^2 type. Added proof for the structure of these chelate compounds has been established by means of x-ray analyses (*17, 18, 26*). In this connection Rundle and Godycki (*26*) have shown that the inner-complex compound of nickel(II) ions and 2,3-butanedionedioxime possesses a planar configuration with an atomic arrangement in general agreement with that shown above.

It has long been assumed (*3*) that hydrogen bonding occurs between the remaining oxime hydrogens and the proximate oxygens of the nitrone-form oxime groups. Chemical evidence indicating a lack of reactivity or, at least, greatly decreased reactivity of these hydrogens has been plentiful. Tschugaeff (*28*) early reported that these complex compounds would not react with phenyl isocyanate. Barker (*2*) found that 1,2-bis(2,3-butanedionedioximo-*N,N'*)nickel(II) was not acted upon by acetic anhydride. Under the same conditions the parent dioxime is very readily acetylated. Brady and Muers (*3*) found that this same inner-complex compound gave no methane with methylmagnesium iodide in amyl ether. Additional evidence that the acidity and, consequently, the reactivity of the oxime hydrogens have been greatly reduced upon forming an inner-complex compound with nickel(II) or palladium(II) ions lies in the fact that the parent *vic*-dioximes will dissolve in very dilute basic solutions while the inner-complex compounds will precipitate from strongly basic solutions.

Published reports of infrared spectroscopic examinations of *vic*-dioximes have not been found. However, Buswell, Rodebush, and Roy (*5*) conducted infrared absorption studies on several symmetrical monoketoximes in carbon tetrachloride solution in varying concentrations. With low oxime concentrations they observed absorption maxima at 2.76 microns indicative of "free" O—H vibration frequencies. As the oxime concentrations were increased, the molal absorption due to free O—H decreased and absorption maxima at about 3.0 microns increased in molal absorption. The assignment of these latter maxima to intermolecularly associated O—H was consistent with the behavior expected of these groups in more concentrated solutions.

Buswell, Dietz, and Rodebush (*4*) were among the first to show that O—H absorption maxima are shifted to longer wave lengths with the formation of hydrogen bonds by the O—H hydrogens. Badger (*1*) found that a definite relation existed between the energy of the hydrogen bond and the shift of the O—H absorption maxima which accompanies the formation of the hydrogen bond. The absorption maxima for the fundamental O—H vibration frequencies are found in the range of approximately 2.7 microns for free O—H groups and up to 4.0 microns for strongly associated O—H groups (*22*, p. 6). In this study, it was

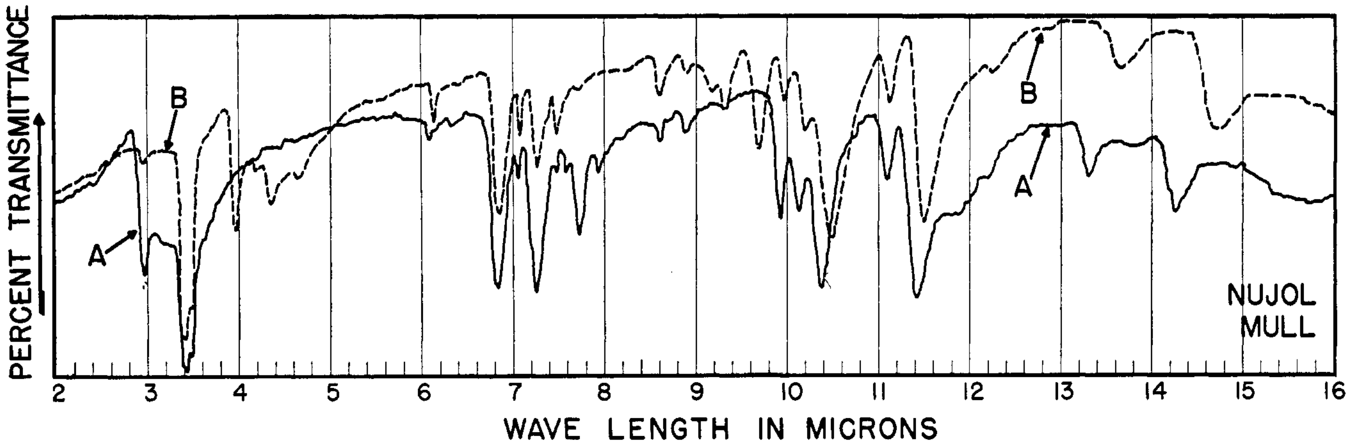


Figure 1. Infrared Absorption Spectra

A. 1,2-Cyclohexanedionedioxime
B. 1,2-Cyclohexanedionedioxime-d_2

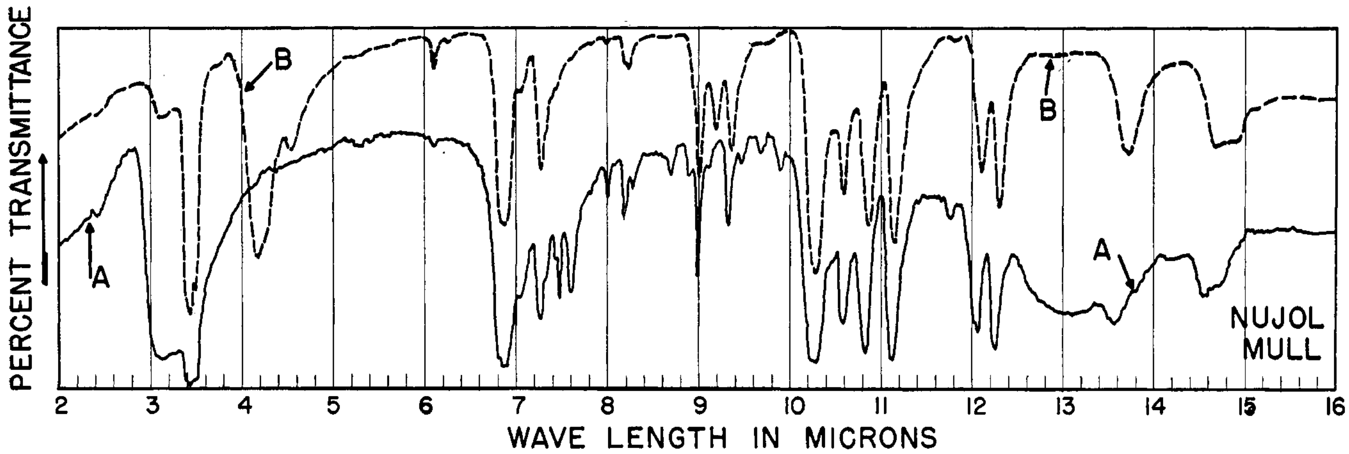


Figure 2. Infrared Absorption Spectra

A. 1,2-Cycloheptanedionedioxime
B. 1,2-Cycloheptanedionedioxime-d_2

assumed that by observing the position of the O—H absorption maxima in the various nickel(II) *vic*-dioxime inner-complex compounds compared to those for free O—H absorption maxima, at least a qualitative measure of the strength of the hydrogen bonds could be obtained.

The names employed for the inner-complex compounds are based on the suggestions of Fernelius, Larsen, Marchi, and Rollinson (*13*) for a uniform system of nomenclature of coordination compounds. The general name, *vic*-dioxime, was adopted for the parent compounds (in preference to such names as 1,2-dioximes, *o*-dioximes, or α-dioximes) to emphasize the presence of two vicinal oxime groups rather than to imply structural features.

APPARATUS AND MATERIALS

The spectra were recorded on a Baird Model B double-beam infrared recording spectrophotometer. Sodium chloride and potassium bromide prisms and standard cell plates were employed. The instrument was calibrated by means of known absorption maxima of polystyrene and carbon dioxide.

The *vic*-dioximes, 1,2-cyclohexanedionedioxime (obtained from the Hach Chemical Co., Ames, Iowa), 1,2-cycloheptanedionedioxime (prepared in this laboratory, *29*), and 2,3-butanedionedioxime (Mallinckrodt reagent grade) were recrystallized from dry benzene to remove last traces of water that might be present.

The nickel derivatives of these *vic*-dioximes were prepared by adding the reagent solutions to very dilute nickel chloride solutions in a manner similar to that prescribed for the determination of nickel with the respective *vic*-dioximes (*9*, *30*, *31*).

1,2-Cyclohexanedionedioxime-d_2, 1,2-cycloheptanedionedioxime-d_2, and 2,3-butanedionedioxime-d_2 were prepared by recrystallizing the respective *vic*-dioximes from heavy water obtained through the Atomic Energy Commission from the Stuart Oxygen Co., San Francisco, Calif. Its purity was claimed to be 99.8% D_2O. All operations with heavy water were carried out in a dry box. Fresh portions of this liquid were used for each individual operation.

1,2-Bis(1,2-cyclohexanedionedioximo-*d*-*N*,*N*′)nickel(II), 1,2-bis(1,2-cycloheptanedionedioximo-*d*-*N*,*N*′)nickel(II), and 1,2-bis(2,3-butanedionedioximo-*d*-*N*,*N*′)nickel(II) were prepared by adding heavy water solutions of the respective deuterio *vic*-dioximes to hot solutions of anhydrous nickel chloride in heavy water. In the case of the latter inner-complex compound it was necessary to add a small amount of anhydrous sodium carbonate to the reaction solution in order to raise the pH to a value where complete precipitation was obtained. The solutions were digested briefly before filtration. The precipitates were dried at 110° C. for 1 hour. All compounds were stored in a desiccator.

Nujol (heavy mineral oil, U.S.P., Stanco, Inc.) and perfluorokerosene (Du Pont FCX-330) were employed as media for preparing the mulls for infrared examination.

EXPERIMENTAL

The various *vic*-dioximes and the inner-complex compounds were prepared for infrared examination by the mull technique. No reference cell plate was used. When thick pastes were necessary in order to bring out weak absorption bands, the loss in transmitted radiation of the sample beam was compensated for by closing down the shutter in front of the reference beam.

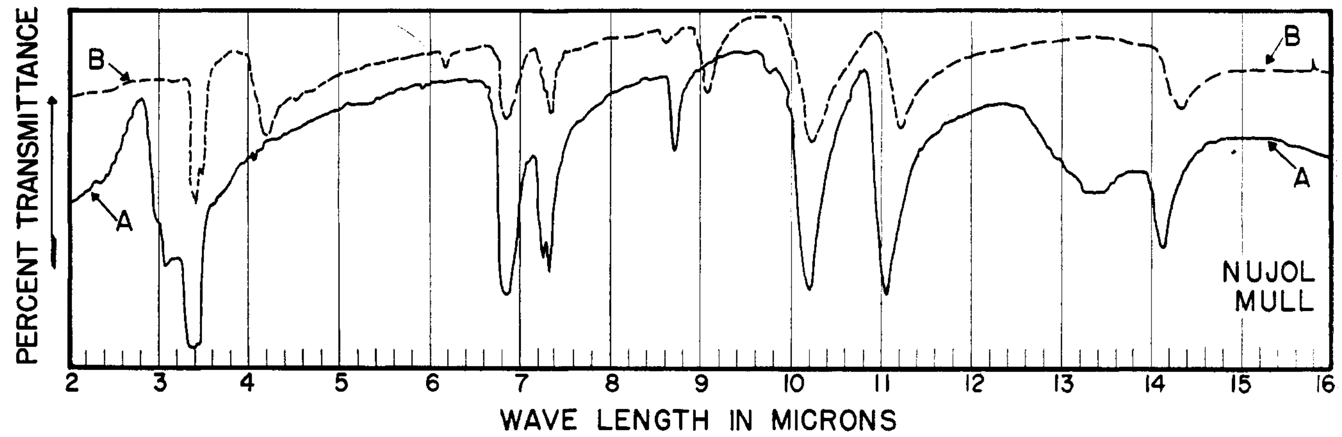


Figure 3. Infrared Absorption Spectra

A. 2,3-Butanedionedioxime
B. 2,3-Butanedionedioxime-d_2

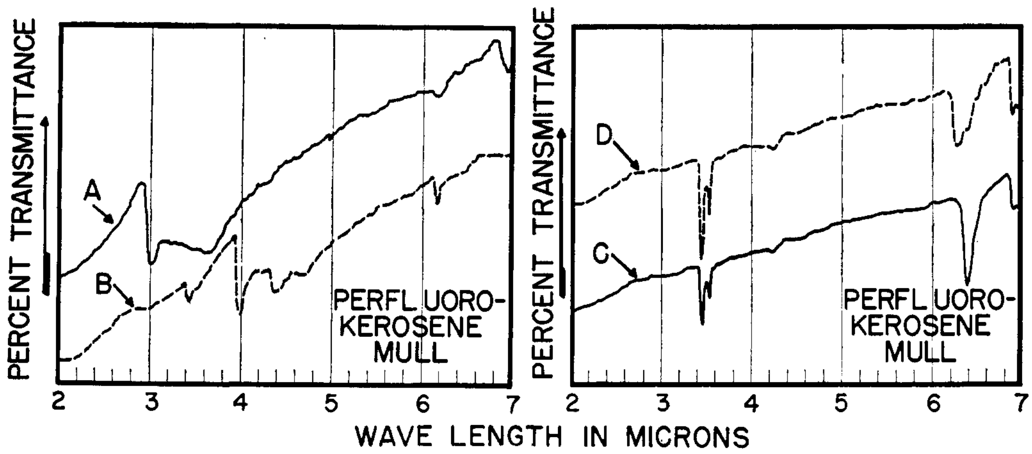


Figure 4. Infrared Absorption Spectra

A. 1,2-Cyclohexanedionedioxime
B. 1,2-Cyclohexanedionedioxime-d_2
C. 1,2-Bis(1,2-cyclohexanedionedioximo-*N,N'*)nickel(II)
D. 1,2-Bis(1,2-cyclohexanedionedioximo-*d*-*N,N'*)nickel(II)

The mull technique was employed for this investigation because suitable solvents for the various compounds were not found. Solvents, such as pyridine, which dissolved the inner-complex compounds were known to change their identity (*33*). By the nature of this work such structural alterations could not be tolerated.

The absorption spectra of 1,2-cyclohexanedionedioxime, 1,2-cycloheptanedionedioxime, and 2,3-butanedionedioxime in Nujol and perfluorokerosene (in the range 2 to 7 microns) are shown in Figures 1 to 6. Absorption maxima attributed to O—H vibration frequencies are found at 2.98, 3.11, and 3.13 microns, respectively. The O—D absorption maxima in 1,2-cyclohexanedionedioxime-d_2, 1,2-cycloheptanedionedioxime-d_2, and 2,3-butanedionedioxime-d_2 occurred at 3.99, 4.18, and 4.19 microns, respectively. The relatively weak O—H absorption maxima compared to the strong O—D absorption maxima exhibited by the spectra of the deuterio compounds gave an indication of the high degree of exchange of deuterium for hydrogen effected by the experimental procedure. Evidence that a partial exchange of deuterium for hydrogen attached to carbon had taken place was shown by the existence in the 1,2-cycloheptanedionedioxime-d_2 and 2,3-butanedionedioxime-d_2 spectra of weak absorption maxima at 4.53 and 4.54 microns, respectively (*22*, p. 20). A very weak absorption maximum, appearing as a shoulder on a stronger absorption maximum, at this wave length was detected for 1,2-cyclohexanedionedioxime-d_2 in perfluorokerosene (Figure 4).

The absorption spectra of 1,2-bis(1,2-cyclohexanedionedioximo-*N,N'*)nickel(II), 1,2-bis(1,2-cycloheptanedionedioximo-*N,N'*)nickel(II), and 1,2-bis(2,3-butanedionedioximo-*N,N'*)nickel(II) and the respective deuterio compounds (Figures 4 through 9) did not exhibit absorption maxima that could be assigned to associated O—H or O—D vibration frequencies in the region in which these maxima normally occur.

It was assumed that absorption maxima shifts that were common to the three pairs of inner-complex compounds (which differed only in the substitution of deuterium for hydrogen) might be of value in drawing conclusions as to the disposition of the O—H absorption maxima. In the Nujol mulls weak absorption maxima were found at 5.68, 5.61, and 5.62 microns, respectively, for 1,2-bis(1,2-cyclohexanedionedioximo-*N,N'*)nickel(II), 1,2-bis(1,2-cycloheptanedionedioximo-*N,N'*)nickel(II), and 1,2-bis(2,3-butanedionedioximo-*N,N'*)nickel(II). In each of the corresponding deuterio derivatives these maxima do not appear.

Strong absorption maxima that occur at 6.38, 6.38, and 6.37 microns, respectively, in the nickel derivatives of 1,2-cyclohexanedionedioxime, 1,2-cycloheptanedionedioxime, and 2,3-butanedionedioxime in both the Nujol and perfluorokerosene mulls

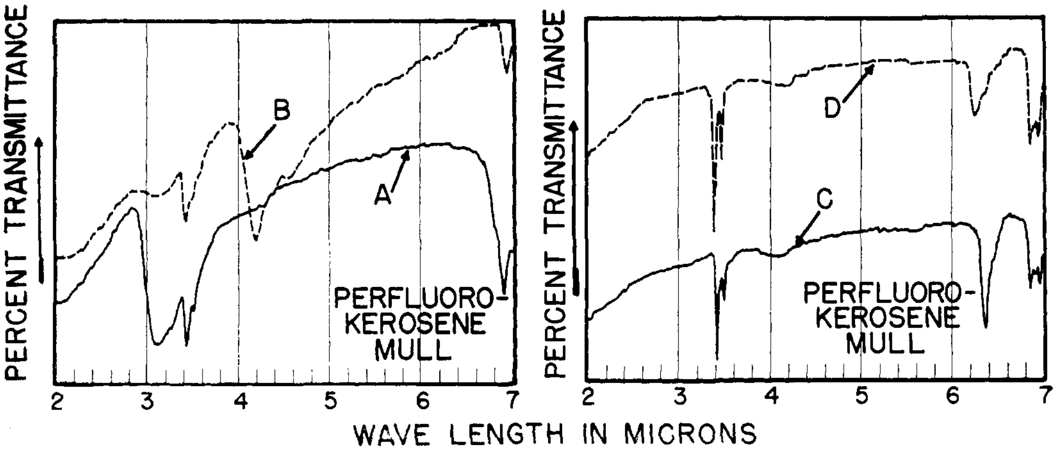


Figure 5. Infrared Absorption Spectra

A. 1,2-Cycloheptanedionedioxime
B. 1,2-Cycloheptanedionedioxime-d_2
C. 1,2-Bis(1,2-cycloheptanedionedioximo-*N*,*N'*)nickel(II)
D. 1,2-Bis(1,2-cycloheptanedionedioximo-*d*-*N*,*N'*)nickel(II)

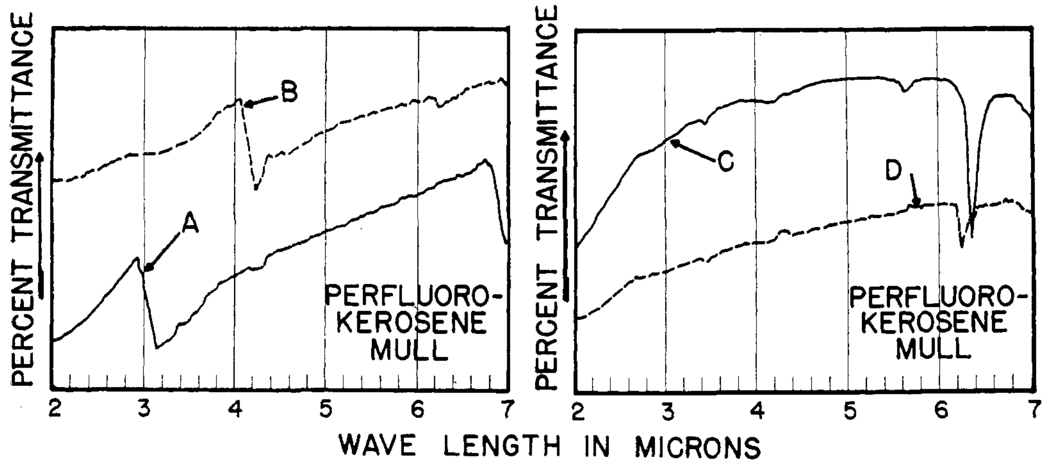


Figure 6. Infrared Absorption Spectra

A. 2,3-Butanedionedioxime
B. 2,3-Butanedionedioxime-d_2
C. 1,2-Bis(2,3-butanedionedioximo-*N*,*N'*)nickel (II)
D. 1,2-Bis(2,3-butanedionedioximo-*d*-*N*,*N'*)nickel(II)

appeared to be shifted to the shorter wave lengths of 6.25, 6.27, and 6.24 microns in the respective deuterio compounds with an accompanying decrease in intensity. These maxima, which appear less intense in the spectra of the corresponding *vic*-dioximes, fall in the region of C=N stretching vibrations. It appears reasonable to attribute this intensity increase to a change in the dipole moment of this atom pair upon inner-complex formation.

The last consistent difference involved the strong, broad absorption maxima appearing at 13.2 microns in 1,2-bis(1,2-cyclohexanedionedioximo-*d*-*N*,*N'*)nickel(II) and at 13.0 microns in the other two deuterio inner-complex compounds. Well-defined absorption maxima are not exhibited at these wave lengths in the normal compounds. The curves for these compounds in Nujol using the potassium bromide prism and window plate in this wave-length region are the same as those observed above for each compound, except that the maxima are shifted slightly because of experimental error apparently caused by a change in prisms.

DISCUSSION

The absorption maxima attributed to fundamental O—H stretching vibration frequencies in the three *vic*-dioximes studied are found at wave lengths that are indicative of intermolecular hydrogen bonding (*5*). Similar observations are made for the fundamental O—D absorption maxima in the three deuterio compounds. On the basis of these data, it is not possible to state whether the hydrogen bonding is to oxygen or nitrogen (O—H- - -O or O—H- - -N) or both of another *vic*-dioxime molecule.

The absence in the usual wave-length regions of absorption maxima due to fundamental O—H and O—D stretching vibration frequencies in the respective inner-complex compounds indicates that the *vic*-dioxime O—H and O—D groups have greatly changed their identity upon forming the inner-complex compounds with nickel(II) ions.

In normal OHO hydrogen bonds the O—H- - -O distances vary between 2.5 and 2.9 A. (*19*, p. 289). The equilibrium position of the hydrogen atom from one oxygen atom is approximately 1.0 A. and from 1.5 to 1.9 A. from the other. Pauling (*19*, p. 311) states that 2.54 A. is the smallest O—H- - -O bond distance known. No subsequent reports in the literature have been found that would invalidate this statement.

As O—H absorption maxima are observed in cases of normal hydrogen bonding, the question arises as to the nature of the O—H groups in these inner-complex compounds. If the O—H- - -O distance in these compounds is greater than 2.5 A. it appears reasonable to expect the O—H absorption maxima to be present in the usual wave-length regions. An O—H- - -O distance greater than that normally assigned in hydrogen bonding should give rise to O—H absorption maxima characteristic of free O—H groups. The logical alternative involves the possibility that this distance is somewhat less than 2.5 A. The infrared spectroscopic evidence coupled with chemical evidence for the lack of reactivity of the O—H hydrogens suggests the presence of an O—H—O structure unlike that observed in normal hydrogen bonding involving these atoms.

The studies of Westrum and Pitzer (*32*) on the nature of the hydrogen bond in crystalline potassium hydrogen fluoride may provide valuable information concerning the character of this O—H—O structure. Infrared absorption maxima arising from free F—H fundamental vibration frequencies occur at approximately 2.4 microns and from F—H frequencies in $(HF)_n$ polymers at approximately 2.9 microns (*32*). In these polymers the F—H- - -F distance has been determined to be about 2.55 A., while in the potassium hydrogen fluoride crystals this distance is very close to 2.26 A. Ketelaar (*15*) obtained infrared spectral data for these crystals as well as for potassium deuterium fluoride. Strong absorption maxima at 6.9 and 9.6 microns have been attributed to the F—H and F—D fundamental stretching vibration frequencies, respectively, indicating a considerable shift from the position of the maxima in the common F—H- - -F (and presumably F—D- - -F) hydrogen bonds. From thermodynamic, dielectric, and spectra data, Westrum and Pitzer have decided that the potential curve for the proton in this F—H—F bond has a single minimum located midway between the two fluoride atoms. Calculations of the "hydrogen bond" energy in F—H—F bonds have yielded values ranging from 30 to 50 kg.-cal. (*8*, *15*).

The possibility of an O—H—O bond in the inner-complex compounds which is less than 2.5 A. in length and which has the same general characteristics as the F—H—F bond in potassium hydrogen fluoride crystals does not seem unreasonable in view of the evidence for the chemical unreactivity of the O—H hydrogens, the symmetry of the molecules, and the spectral data presented herein. While three consistent maxima shifts have been detected, it appears unwise at this time to make definite statements concerning the possible disposition of any absorption maxima due to O—H and O—D fundamental frequencies.

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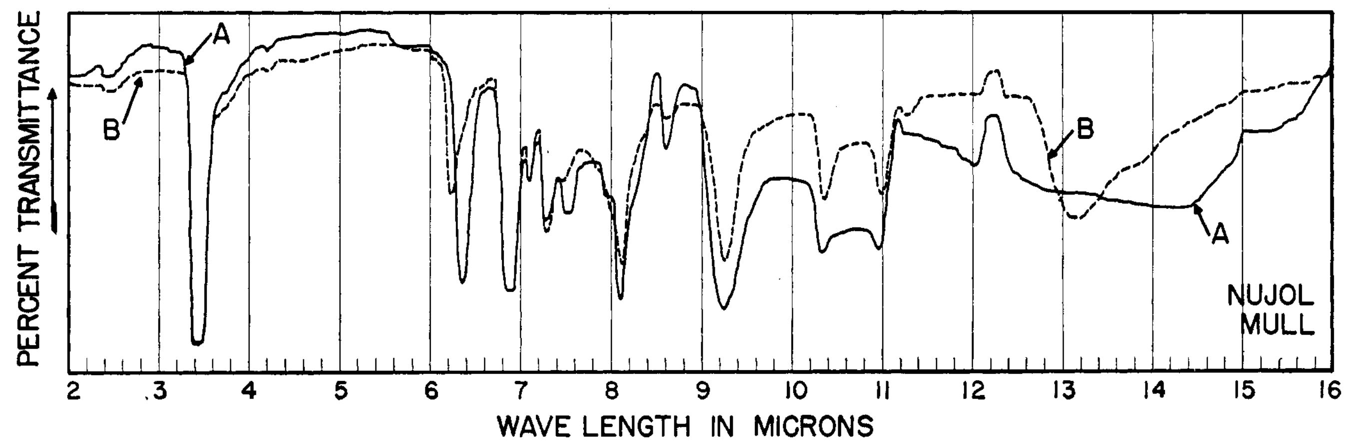

Figure 7. Infrared Absorption Spectra

A. 1,2-Bis(1,2-cyclohexanedionedioximo-*N*,*N'*)nickel(II)
B. 1,2-Bis(1,2-cyclohexanedionedioximo-*d*-*N*,*N'*)nickel(II)

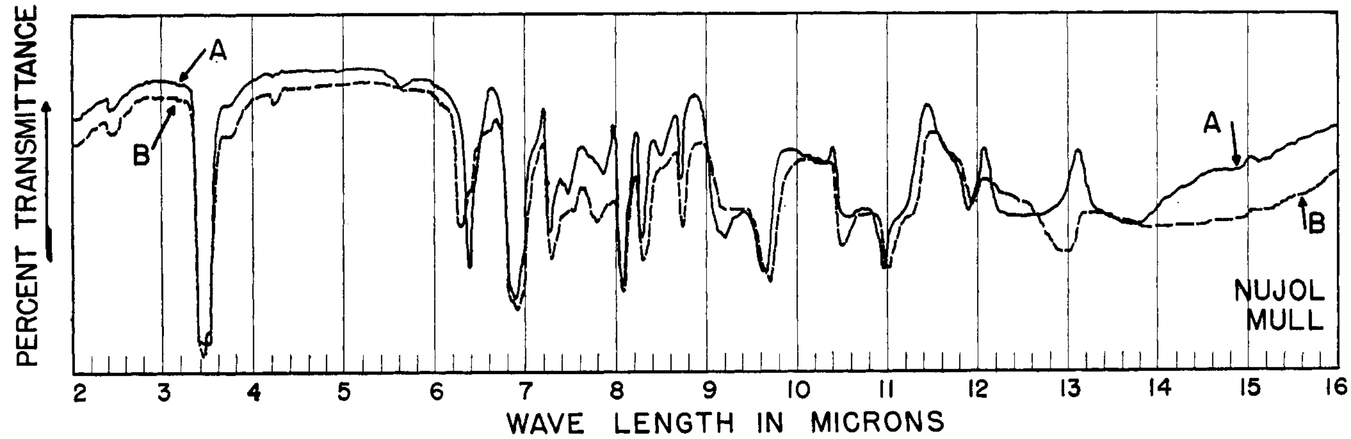

Figure 8. Infrared Absorption Spectra

A. 1,2-Bis(1,2-cycloheptanedionedioximo-*N*,*N'*)nickel(II)
B. 1,2-Bis(1,2-cycloheptanedionedioximo-*d*-*N*,*N'*)nickel(II)

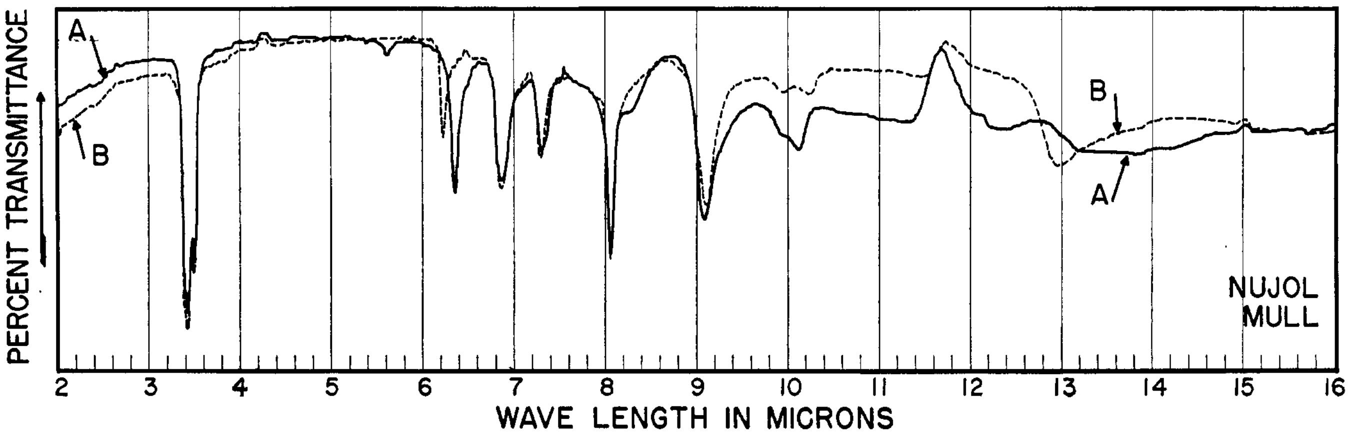

Figure 9. Infrared Absorption Spectra

A. 1,2-Bis(2,3-butanedionedioximo-*N*,*N'*)nickel(II)
B. 1,2-Bis(2,3-butanedionedioximo-*d*-*N*,*N'*)nickel(II)

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Mass Spectrometric Determination of Molecular Weights of Components of a Mixture

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PRESENT methods of qualitative analysis using the mass spectrometer are dependent on the availability of a catalog of spectra for all compounds that are to be identified (*7*). The rapidly growing literature dealing with mass spectrometer analysis affords a reasonably extensive compilation for such comparative studies, but in certain fields of application such data are decidedly incomplete; thus there remains some difficulty associated with identification of unknown compounds or a mixture of unknown compounds. The desirability of procedures that would supplement the usual methods is apparent. This paper describes a procedure for determining the molecular weight of unidentified components by the use of mass spectrometric data.

It has long been known that the rate of effusion of a gas is inversely proportional to the square root of the molecular weight—a relationship first accurately formulated by Graham (*2*). The hydrodynamic properties of the molecular beam in the mass spectrometer inlet system have been described in detail by Honig (*3*) and recently this diffusion property has been used by Friedel and Sharkey (*1*) to determine the concentration of D^+ in the spectrum of HD containing an appreciable concentration of hydrogen. In fact, it is standard practice to use the diffusion rate of *n*-butane as a means of calibrating the mass spectrometer (*8*). The inlet system of the mass spectrometer at the authors' disposal is equipped with a gold foil containing two holes approximately 0.043 mm. in diameter. Generally, the pressure on the high pressure side of the orifice is initially maintained at 40 microns. With this magnitude of pressure and considering the