915. *Infrared Spectra and Hydrogen Bonding in the Nickel–Dimethylglyoxime and Related Complexes.*

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Infrared spectra of dimethylglyoxime derivatives of Ni, Pd, Pt, and Cu, of the Ni and Pd complexes of *cyclo*hexane-1 : 2-dione dioxime, and of sodium and potassium hydrogen dimethylglyoxime derivatives were investigated. Assignments have been made as follows: νOH 2300—2900, δOH 1650—1800, νC=N 1500—1600, νN–O near 1240 and 1000, γOH 820—930 cm.$^{-1}$. It is concluded that the hydrogen bond in these complexes cannot be of the symmetrical type as suggested by Rundle and Parasol.[1]

Since the spectroscopic and *X*-ray work by Rundle and Parasol [1] and Rundle and Godycki [2] have been published, it has been generally accepted that the hydrogen bonds in nickel–dimethylglyoxime and some related complexes are probably symmetrical in the sense

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[1] Rundle and Parasol. *J. Chem. Phys.*, 1952, **20**, 1487.

[2] Rundle and Godycki, *Acta Cryst.*, 1953, **6**, 487.

that the protons occupy a central position between the oxygen atoms and that they move in a single minimum potential trough. This assumption was based on the apparent centrosymmetric structure of the nickel complex, the short O–O distance (2·44 Å), and the OH stretching frequency at 1775 cm.$^{-1}$. No direct location of the protons has been carried out and the spectrum has not been analysed in detail. The band mentioned above was assigned only on the ground of its disappearance after deuteration. In view of the importance of the existence of symmetrical hydrogen bonds in general and its bearing upon the character of the metal–nitrogen linkage in the glyoximates we re-investigated this problem.

Infrared spectra of dimethylglyoxime derivatives of Ni, Pd, Pt, Cu, and of *cyclo*hexane-1 : 2-dione dioxime complexes with Ni and Pd were studied and the important bands were assigned. To facilitate the assignments, sodium and potassium hydrogen dimethylglyoxime derivatives were prepared and their spectra recorded. These two salts have not been so far described. Spectra of deuterated Ni–, Pd–, and Na–dimethylglyoxime complexes were also obtained.

RESULTS

The Bands between 2000 *and* 3000 *cm.*$^{-1}$.—All the spectra of the complexes investigated contain a band near 2340 cm.$^{-1}$ (Figs. 1, 3, 4, 6, 7, 8). It is of variable intensity, being very weak in nos. 1 and 3 but strong in no. 8, and very broad. The latter property has to be borne in mind when considering the frequencies listed in the Table. In the spectrum of the copper–dimethylglyoxime complex there is another, stronger peak at 2650 cm.$^{-1}$ and there seem to be higher-frequency weak bands also for the other complexes, although they appear only as a broadened base of the CH$_3$-bands near 2930 cm.$^{-1}$. This band should be considered in connection with the weak absorption near 1910 cm.$^{-1}$ which shows up together with the band near 1820 cm.$^{-1}$ in the spectra of deuterated nickel– and palladium–dimethylglyoxime complexes. The latter band is the deuterium analogue of the band at 2340 cm.$^{-1}$ which disappears on deuteration. The spectra of the sodium and the potassium derivative (Fig. 9; the two are very similar) contain very strong and broad bands culminating at 3000 cm.$^{-1}$.

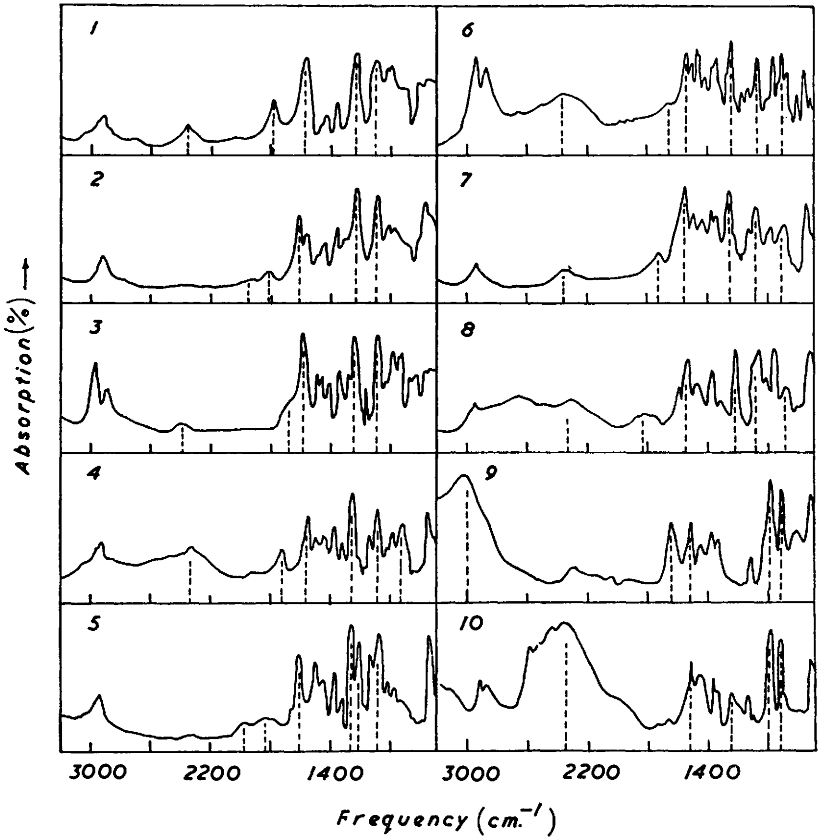
Infrared absorption frequencies (cm.$^{-1}$*) of some metal–oxime complexes and salts.*

	νOH	νOD	δOH	δOD	νC=N(H)	νC=N(D)	ν'C=N	νNO	ν'NO	γOH
Dimethylglyoxime complexes										
Ni ...	2350	1810, 1910	1780	1265(?)	1560	1600	?	1235	1100	900—950(?)
Pd ...	2340	1830, 1970	1710	1210	1550	1610	1500	1250	1090	910
Na ...	3020	2340	1650	1237	1510	1540	—	990	922	815
K	3030	—	1650	—	1490	—	—	1010	930	835
cyclo*Hexane*-1 : 2-*dione dioxime complexes*										
Ni ...	2380	—	1670	—	1570	—	?	1235	990	950(?)
Pd ...	2380	—	1650	—	1540	—	1495	1245	1065	930
Pt ...	2350	—	1720	—	1550	—	1495	1260	1090	905
Cu ...	2340, 2650	—	1820	—	1590	—	1540	1210	1060	860

The Band between 1600 *and* 1800 *cm.*$^{-1}$.—This band varies in position and intensity in different complexes. It appears as a shoulder in spectra nos. 3 and 6, but is well developed in no. 9. It is absent from the spectra of the deuterated compounds, which contain instead a new band near 1220 cm.$^{-1}$. With the deuterated nickel complex (Fig. 2) this band does not appear clearly, but it might be hidden under the base of the strong band at 1250 cm.$^{-1}$.

The Bands between 1600 *and* 700 *cm.*$^{-1}$.—Several characteristic features appear rather consistently in this region. There is one medium or very strong band between 1500 and 1570 cm.$^{-1}$ which is shifted slightly to higher frequencies on deuteration (up to 100 cm.$^{-1}$). In some complexes there is also a weaker band near 1500 cm.$^{-1}$, which is stronger after deuteration (cf. nos. 4 and 5) but is not observed for either of the nickel complexes. There are two strong bands which appear with little changed frequency in the spectra of the complexes (near 1230 and 1050 cm.$^{-1}$). A similar pair appears for the sodium and the potassium salt at lower frequencies. Finally, a very broad band should be mentioned, normally near 900 cm.$^{-1}$ but absent from the spectra of the deuterated compounds. It is difficult to locate this band for either of the nickel complexes because of the particularly strong, diffuse background absorption which extends from about 1500 cm.$^{-1}$ to the end of the region investigated. This background absorption seems to be lower for the deuterated complex, a phenomenon observed[3] in several spectra of substances containing very strong hydrogen bonds, *e.g.*, potassium dihydrogen phosphate and arsenate.

FIGS. 1—10. *Infrared spectra of some metal–oxime complexes and salts (drawings combined from mulls with Nujol and hexachlorobutadiene).*



1, Ni–dimethylglyoxime; 2, the same, but deuterated; 3, Ni–*cyclo*hexane-1 : 2-dione dioxime; 4, Pd–dimethylglyoxime; 5, the same, but deuterated; 6, Pd–*cyclo*hexane-1 : 2-dione dioxime; 7, Pt–dimethylglyoxime; 8, Cu–dimethylglyoxime; 9, Na hydrogen glyoxime derivative; 10, the same, but deuterated.

DISCUSSION

There is no doubt that the band near 2340 cm.$^{-1}$ belongs to the OH stretching vibration, as do the higher-frequency bands mentioned. The differences in the intensities of these bands seem to be connected in some way with the nature of the metal. Their weakness, particularly in the spectrum of both nickel complexes, may explain the failure of other investigators to notice them. The previous assignment[1] of the band near 1700 cm.$^{-1}$ to the OH stretching appears untenable in view of the present results. In principle the appearance of two OH bands could also be admitted and explained by the splitting of the vibrational levels due to the proton tunnelling,[4] but in the present case strong arguments

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[3] Blinc and Hadži, *Mol. Phys.*, 1958, in the press.

[4] Blinc and Hadži, " Hydrogen Bonding," Pergamon Press, London, in the press.

against the assignment of the 1700 cm.$^{-1}$ band to one of the OH stretchings can be brought. If the bands at 2340 and 1710 cm.$^{-1}$ were due to splitting of the OH vibrational levels, deuteration should strongly reduce the extent of splitting. The spectrum of the deuterated palladium–dimethylglyoxime complex shows that this is not the case. The appearance of the band near 1650 cm.$^{-1}$ in the spectra of the potassium and the sodium salt and its shift on deuteration of the latter, similar to that with the palladium complex, also provide a strong argument against this supposition. Comparison of the present spectra with those observed[3] in the series of ferroelectric compounds of the type of KH_2PO_4, where the split OH bands are due to the tunnelling, also suports the same conclusion. In KH_2PO_4, the two OH bands were found at 2750 and 2400 cm.$^{-1}$, the O–O distance[5] (2·49 Å) being only slightly longer than, *e.g.*, in the palladium–dimethylglyoxime complex. On the other hand, the shifts on deuteration from about 1700 to 1230 cm.$^{-1}$ indicate that these bands are due to OH and OD deformation vibrations. Similar frequencies for this vibration have been found[3] for KH_2PO_4 and related compounds. The very high frequency and low intensity of the band near 1820 cm.$^{-1}$ in the spectrum of the copper–dimethylglyoxime complex causes some doubt whether this band is analogous to that just discussed for other complexes: the particular intensity of the νOH band in the copper derivatives places this complex somewhat outside the group.

The band near 1550 cm.$^{-1}$ has been assigned by Rundle and Parasol[1] to the N–O stretching vibration. In organic nitroso-compounds the νN=O stretching band has been found[6] to vary in frequency within rather large limits, 1450—1600 cm.$^{-1}$, its position depending to some extent upon the double-bond character of the linkage.[7] Thus, Rundle and Parasol's assignment implies a nearly pure double band which contradicts Rundle and Godycki's *X*-ray results.[2] The bond length (1·38 Å) indicates no shortening of the N–O bond compared with, *e.g.*, that in a hydroxylamine *O*-ether[8] (1·37 Å). On the other hand, the N–O bond in the nickel–dimethylglyoxime complex seems to be much longer[9] than the N–O bond in iodonitrosobenzene (1·24 Å). Thus, we should look for the N–O stretching band at much lower frequencies. For simple oximes, it appears[10] between 930 and 960 cm.$^{-1}$. For quinone oximes[11] it is at somewhat higher frequencies, near 1000 cm.$^{-1}$, probably owing to the increase in double-bond character because of resonance. Salt formation may also increase the frequency, and the bands near 930 and 1000 cm.$^{-1}$ in the spectra of the potassium and the sodium derivative are obviously due to the νN–O vibrations. For these two salts the two N–O bonds are probably unequal, because one OH group is ionized, so that the two band frequencies appear. Salt formation enhances the resonance in the quinone oximes and we find for their salts a strong band near 1200 cm.$^{-1}$ which is apparently due to the altered N–O linkage.[11] Thus it appears reasonable to assign the bands near 1080 and 1240 cm.$^{-1}$ in the spectra of the present complexes to the N–O stretching modes. The existence of two bands may have two explanations. They may be due to two unequal N–O linkages, as have been found by Rundle and Godycki.[2] However, the difference in the bond lengths is declared insignificant by these authors and indeed it would be incompatible with the symmetry of the complex. The other explanation is very straightforward. Considering only the skeleton of the complex, consisting of four each of C, N, and O atoms and having the symmetry D_{2h}, we may expect two N–O and two C=N infrared-active vibrations of the B_{2u} and B_{3u} type,* respectively. If the bands near 1080 and 1240 cm.$^{-1}$ are assigned to the N–O stretching vibrations, the bands between 1500 and 1600 cm.$^{-1}$ are necessarily ascribed to the C=N stretching vibrations. The

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* Designated ν and ν' in the Table.

[5] Bacon and Pease, *Proc. Roy. Soc. A.*, 1953, **220**, 397.

[6] Bellamy, "The Infra-Red Spectra of Complex Molecules," Methuen, London, 1953, p. 254.

[7] Lüttke, *J. Phys. Radium*, 1954, **15**, 633.

[8] Kitaigorodskii, "Org. Kristallokhimya," Akad. Nauk S.S.S.R., Moscow, 1955, p. 9.

[9] Webster, *J.*, 1956, 2841.

[10] Palm and Werbin, *Canad. J. Chem.*, 1954, **32**, 858.

[11] Hadži, *J.*, 1956, 2725.

corresponding bands in the spectra of simple oximes appear[12] between 1620 and 1660 cm.$^{-1}$. Resonance, with consequent decrease of the double-bond character, may produce a lowering of the frequency such as is observed[11] in the quinone oxime spectra. The C=N bond lengths (1·20 and 1·25 Å) found by Rundle and Godycki[2] for the nickel–dimethylglyoxime complex are compatible with the present frequency. The shift of the νC=N band to higher frequency after deuteration is explained by interaction with the nearby δOH vibration: this vibration, being of higher frequency, " repels " the C=N frequency and when the former is removed by deuteration, the C=N frequency returns to its undisturbed value. The shift in the opposite direction upon deuteration has been observed[11] in the quinone oxime spectra, but in these the δOH had a lower frequency than the νC=N vibration.

Assignment of the band near 900 cm.$^{-1}$ presents no difficulties: its disappearance upon deuteration and original shape suggest that it is due to the γOH (out-of-plane) deformation.

Hydrogen Bonding.—The high νOH frequency seems at first glance not to accord with the short O–O distance found by Rundle and Godycki.[2] However, the usual relations between O–O distance and OH frequency hold only for straight hydrogen bonds.[13] It is very probable that the protons in the nickel–dimethylglyoxime and related complexes are not situated on the line connecting the oxygen atoms and thus their frequency does not fit these relations.

In view of the above results, it seems that the hydrogen bonds in the complexes investigated are not of the symmetrical type, in the sense that the proton does not occupy a central position between two oxygen atoms. The observed symmetry of the nickel– and the palladium–dimethylglyoxime complex may be of a statistical character, which would imply that the protons are rapidly changing their position from near one oxygen atom to near the other. The potential barrier separating the two potential minima is probably very small, so this can be considered as a tunnelling of the protons. If this were so, the vibrational levels should be split. We may assume that the hydroxyl bands at 2340 and ~2900 cm.$^{-1}$ are due to this splitting. However, the existence of the latter band is not beyond doubt, and thus the spectrum does not clearly either prove of disprove the existence of the tunnelling, although this appears very probable on general grounds.

EXPERIMENTAL

The complexes were prepared by standard methods and recrystallised from nitrobenzene. The potassium and the sodium complex were prepared by adding ethanolic potassium hydroxide and aqueous sodium hydroxide, respectively, to ethanolic dimethylglyoxime. The metal hydrogen glyoxime derivatives were precipitated immediately, and neutralisation could not be achieved even if a large surplus of alkali was used. The derivatives were recrystallised several times from ethanol. The potassium derivative was analysed for potassium. No further characterisation, other than the infrared spectrum, was undertaken. Deuteration was by dissolving the substances in boiling dioxan and adding deuterium oxide until crystallisation had set in. The crystalline precipitate was filtered off and dried, precautions being taken against contamination with atmospheric moisture. The spectra were recorded with a Perkin-Elmer Model 21 spectrophotometer, equipped with a rock-salt prism. The samples were mulls in Nujol or hexachlorobutadiene.

The authors are grateful to Misses M. Žitko and T. Berginc for the preparation of substances.

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[12] Palm and Werbin, *Canad. J. Chem.*, 1953, **31**, 1004.

[13] Lippincott and Schroeder, *J. Chem. Phys.*, 1955, **23**, 1099.