Studies on Dimethylglyoximato-cobalt (III) Complexes. IV. Intramolecular O-H-O Hydrogen Bonds in Bis-(dimethylglyoximato)-cobalt (III)-complexes[*]

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Introduction

It has been well-known for the last two decades that two dimethylglyoximate ions usually tend to coördinate to a metal atom with planar configuration[1,2]. The origin of this tendency, however, remained unclarified till last year[3]. In the former papers of this series[3,4], one of the present authors elucidated the tendency by taking intramolecular O-H-O hydrogen bonds into consideration. As far as the dimethylglyoximato-cobalt (III)-complexes are concerned, there has never been found any paper which dealt with direct confirmations of such hydrogen bonds. Although the first description of the subject was already published in the preceding paper[5], it seems to be desirable to perform further investigations in order to clear up some ambiguity which was concerned with the assignment of the infrared absorption band at $1725\ \text{cm}^{-1}$. In this work, we have measured infrared absorption spectra of hydrogen dichloro-bis-(dimethylglyoximato)-cobaltate (III) preparing with both normal and deuterated dimethylglyoxime and of several other dimethylglyoximato-cobalt (III)-complexes. Consequently, we have succeeded not only in justifying our previous conclusion but also in finding out a series of very short and symmetric O-H-O hydrogen bonds.

Experimental

Materials. Normal and Deuterated Dimethylglyoxime.—A convenient method was applied to prepare the deuterated dimethylglyoxime, dgD_2.

First of all, normal dimethylglyoxime was converted into dipotassium salt, dgK_2, by the action of an excessive amount of potassium hydroxide. 5g of dipotassium dimethylglyoximate which was perfectly free from moisture was mixed with 10 ml. of heavy water, and to this 10 ml. of concentrated deuterium chloride was added. After vigorous shaking of the mixture the insoluble

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[*] Although in the former papers of this series the symbols, DH_2 and DH, were used for dimethylglyoxime and its ion, respectively, in the present paper the symbols, dgH_2 and dgH, are preferably chosen for the convenience of discrimination from deuterated dimethylglyoxime, dgD_2, and its ion, dgD.

[1] L. Cambi and C. Coriselli, *Gazz. chim. ital.*, **66**, 91 (1936).

[2] Y. Nakatsuka and H. Iinuma, This Bulletin, **11**, 48 (1936).

[3] A. Nakahara, ibid., **27**, 560 (1954).

[4] A. Nakahara, ibid., **28**, 207 (1955).

[5] A. Nakahara, ibid., **28**, 473 (1955).

deuterated dimethylglyoxime was separated from liquor. It was heated to 110° in order to remove the moisture and adsorbed deuterium chloride. Pure normal dimethylglyoxime, dgH_2, was purified by the same procedure using normal water and hydrochloric acid instead of heavy water and deuterium chloride.

Normal and Deuterated Hydrogen Dichloro-bis-(dimethylglyoximato)-cobaltate (III).—The normal complex, $H[Co(dgH)_2Cl_2]$, was prepared by the method of Cambi et al.[6] as described in the former paper[4]. Deuterated complex, $D[Co(dgD)_2Cl_2]$, was prepared according to the following direction: 0.6 g of cobalt (II) chloride hexahydrate which was perfectly free from nickel (II) ion was dehydrated by heating until the color changed from red to blue. Instantly, it was dissolved in 10 ml. of heavy water and to this 0.6 g of deuterated dimethylglyoxime was added. The mixture was heated on a water bath and oxidized by a few drops of hydrogen peroxide. Then, the reaction mixture was filtered by suction. Dark green microscopic crystals of deuterated complex were precipitated from the filtrate by adding excess of concentrated deuterium chloride. On the other hand, partly deuterated complex, $H[Co(dgD)_2Cl_2]$, was obtained from the aqueous solution of the residual by adding excess of concentrated hydrochloric acid.

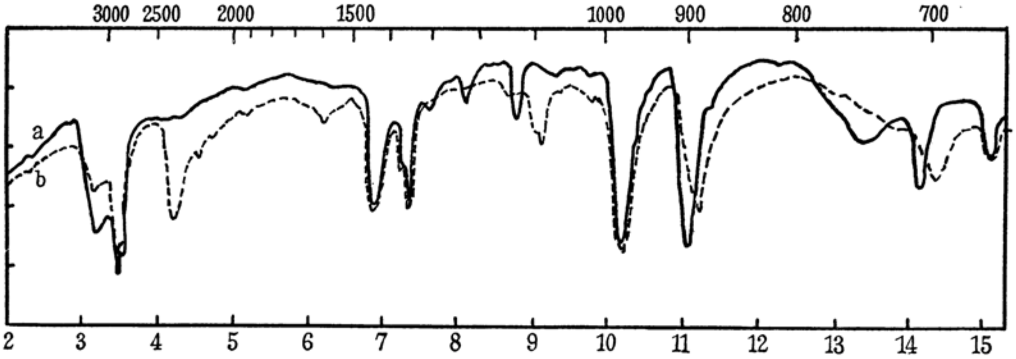

Fig. 1. Infrared absorption spectra of dimethylglyoxime: dgH_2, (a); dgD_2, (b).

Concentrated solution of deuterium chloride was obtained by passing hydrogen chloride through **heavy water**, (specific weight $d_4^{20}=1.1049$) which was produced by Norsk Hydro Elektrisk Kvaelstofaktieselskab.

Hydrogen Dibromo-bis-(dimethylglyoximato)-cobaltate (III), $H[Co(dgH)_2Br_2]$; Hydrogen Dinitro-bis-(dimethylglyoximato)-cobaltate(III), $H[Co(dgH)_2(NO_2)_2]$; Sodium Dinitro-bis-(dimethylglyoximato)-cobaltate (III), $Na[Co(dgH)_2(NO_2)_2]$; Nitro-bis-(dimethylglyoximato)-aquo-cobalt (III), $[Co(OH_2)(dgH)_2(NO_2)]$; Nitro-bis-(dimethylglyoximato)-ammine-cobalt (III), $[Co(NH_3)(dgH)_2(NO)_2]$; Chloro-bis-(dimethylglyoximato)-ammine-cobalt (III), $[Co(NH_3)(dgH)_2Cl]$; Bis-(dimethylglyoximato)-diammine-cobalt (III) Chloride, $[Co(NH_3)_2(dgH)_2]Cl$; Hydrogen dinitro-bis-(mono-O-methyl-dimethylglyoximato)-cobaltate (III), $H[Co(dgCH_3^*)_2(NO_2)_2]$; Tris-(dimethylglyoximato)-cobalt (III), $[Co(dgH)_3]$.—These complexes were prepared by the direction described in the former paper[4].

Bis-(dimethylglyoximato)-nickel (II), $[Ni(dgH)_2]$.—This was recrystallized from chloroform solution as long acicular crystals.

Measurements. The spectra were obtained with a Perkin-Elmer Model 21 spectrophotometer using sodium chloride prisms and Nujol suspensions of the compounds. For optical measurements all the samples were freed from accompanying moisture including their own water of crystallization.

Results and Discussion

The Infrared Absorption Spectra of Normal and Deuterated Dimethylglyoxime.—The results of the measurements are shown in Fig. 1. Among many differences between the two curves, the one in the region from 3300 to 2300 cm^{-1} is the most significant, so far as this study is concerned.

In that region normal dimethylglyoxime, (a), has a strong absorption band at about 3170 cm^{-1}, which corresponds to the O-H fundamental stretching vibration frequencies. On the other hand, the curve of deuterated dimethlyglyoxime, (b), shows a rather weak band at the same wave-length in compensation for a new strong band at about 2360 cm^{-1}, which is characteristic of O-D stretching vibration. This is the clear evidence for the success in substituting deuterium for hydrogen atom. Rundle et al.[7] obtained the deuterated dimethylglyoxime by recrystallizing the parent compound from heavy water. But the present method may be more effective than theirs.

The Spectra of Normal and Deuterated Hydrogen Dichloro-bis-(dimethylglyoximato)-cobaltate (III).—The spectra of normal

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[6] L. Cambi and C. Coriselli, *Gazz. chim. ital.*, 66, 81 (1936).

[7] L.E. Godycki, R.E. Rundle, R.C. Voter and C.V. Banks, *J. Chem. Phys.*, 19, 1205 (1951).

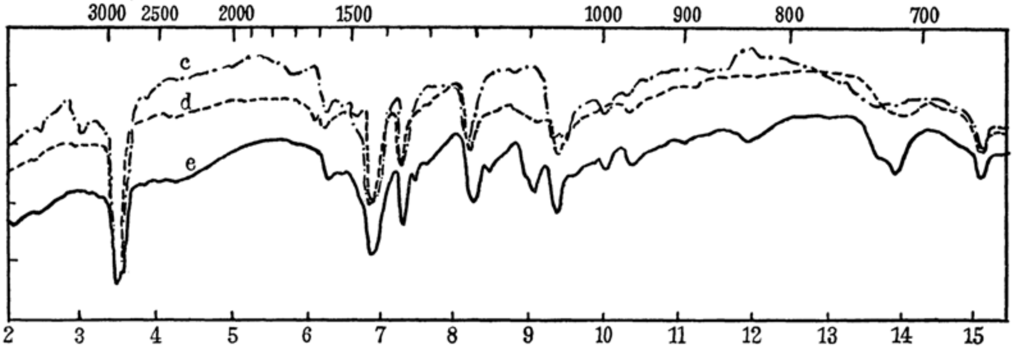

Fig. 2. Infrared absorption spectra of: (c), $H[Co(dgH)_2Cl_2]$; (d), $H[Co(dgD)_2Cl_2]$; (e), $D[Co(dgD)_2Cl_2]$.

complex, (c), partly deuterated complex, (d), and completely deuterated complex, (e), are shown in Fig. 2. In the former paper[5] the band at 1725 cm^{-1} on the curve of normal complex, $H[Co(dgH)_2Cl_2]$, was assigned to the O-H stretching frequency under the formation of strong intramolecular O-H-O hydrogen bond. (See, Fig. 3.) But the assignment was less reliable on account of the lack of decisive evidence. Now this ambiguity is perfectly swept off by the fact that the concerned band at about 1700 cm^{-1} have not been recognized on the curve of corresponding deuterated complexes, (b) and (e), as is clear from Fig. 2.

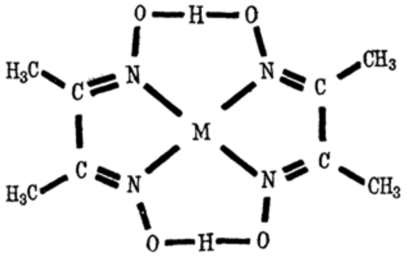

Fig. 3. Planar configuration of two dimethylglyoximate ions in bis-(dimethylglyoximato)-cobalt (III)-complexes.

Thus, there is nodoubt in the conclusion that the absorption band at 1725 cm^{-1} of hydrogen dichloro-bis-(dimethylglyoximato)-cobaltate (III) is attributable to the O-H stretching frequency under the formation of intramolecular O-H-O hydrogen bonds.

Furthermore, it is also of interest to compare the curve of partly deuterated complex, $H[Co(dgD)_2Cl_2]$, with that of completely deuterated complex, $D[Co(dgD)_2Cl_2]$. The former complex was prepared, as described in the experimental part, through a procedure in which deuterated complex was dissolved in ordinary water. Nevertheless, there cannot be recognized on the curve, (d), any indication of such O-H stretching band as can be seen in the normal complex, (c). It is, therefore, clear that the deuterium atom in the complex is hardly affected by hyrogen atom of the solvent. It may be supposed that the deuterium atom situated between the two oxygen atoms is as hard to replace as that of hydrogen.

Spectra of Other Bis-(dimethylglyoximato)-cobalt (III)-complexes.—The infrared absorption spectra of several other complexes are shown in Fig. 4, not about the whole aspect but only about the concerned region.

Fig. 4. Infrared absorption spectra of: (f), $H[Co(dgH)_2Br_2]$; (g), $H[Co(dgH)_2(NO_2)_2]$; (h), $Na[Co(dgH)_2(NO_2)_2]$; (i), $[Co(OH_2)(dgH)_2(NO_2)]$; (j), $[Co(NH_3)(dgH)_2(NO_2)]$; (k), $[Co(NH_3)(dgH)_2Cl]$; (l), $[Co(NH_3)_2(dgH)_2]Cl$.

All the bis-(dimethylglyoximato)-cobalt(III)-complexes show their respective O-H stretching band at about 1700 cm^{-1}. While in some

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* $dgCH_3=H_3C\cdot C(NOCH_3)\cdot C(NO)\cdot CH_3$

complexes the stretching bands are rather high in frequency and comparatively distinct in appearance, in other complexes they are the opposite. (Table I).

TABLE I

O-H STRETCHING FREQUENCIES OF BIS-(DIMETHYLGLYOXIMATO)-COBALT (III)-COMPLEXES

Complexes	O-H stretching frequencies cm^{-1}
$H[Co(dgH)_2Cl_2]$	1725
$H[Co(dgH)_2Br_2]$	1686
$H[Co(dgH)_2(NO_2)_2]$	1725
$Na[CO(dgH)_2(NO_2)_2]$	1740
$[Co(dgH)_2(NH_3)_2]Cl$	1695
$[Co(OH_2)(dgH)_2(NO_2)]$	1770
$[Co(NH_3)(dgH)_2Cl]$	1760
$[Co(NH_3)(dgH)_2(NO_2)]$	1766

But the relations between those absorption bands and the chemical structures are probably complicated matters. At any rate, those data shown in Fig. 4 and Table I are a series of the same examples of O-H-O hydrogen bond as those of hydrogen dichloro-bis-(dimethylglyoximato)-cobaltate (III) and Bis-(dimethylglyoximato)-nickel (II). There are some reports of both theoretical and experimental investigations concerning the relation between the oxygen-oxygen distance and the fundamental optical vibration frequency of the hydrogen atom of an O-H-O hydrogen bond[7,8,9,10]. According to Rundle et al., the O-H-O hydrogen bond in bis-(dimethylglyoximato)-nickel (II) is a kind of very short and symmetric hydrogen bond. If it be the case, *there might be expected the same kind of examples of very short O-H-O hydrogen bonds in the series of above bis-(dimethylglyoximato)-cobalt (III)-complexes.*

The Spectra of Hydrogen Dinitro-bis-(mono-O-methyl-dimethylglyoximato)-cobaltate(III), $H[Co(dgCH_3)_2(NO_2)_2]$, Tris-(dimethylglyoximato)-cobalt (III), $[Co(dgH)_3]$, and bis-(dimethylglyoximato)-nickel (II), $[Ni(dgH)_2]$.—The results of the measurements are shown in Fig. 5. The above described O-H stretching band at about 1700 cm^{-1} can be recognized neither on the curve of the first complex, (m), nor on that of the second complex, (n).

This fact may certify the previous conclusion[5)] that the band at about 1700 cm^{-1} is characteristic of the bis-(dimethylglyoximato)-metal-complexes in which the two dimethylglyoximate ions coördinate to a metal atom with planar configuration. The infrared absorption spectrum of bis-(dimethylglyoximato)-nickel (II), (o), which was newly measured in the present work shows the characteristic band at 1775 cm^{-1}, agreeing with the results of the measurement by Rundle et al.

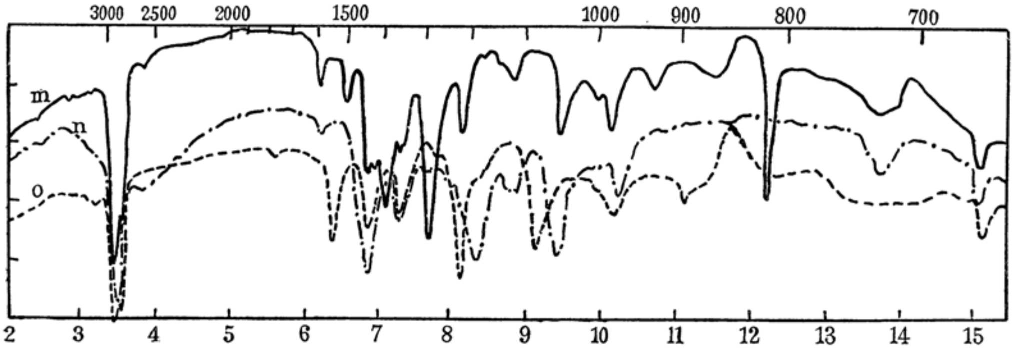

Fig. 5. Infrared absorption spectra of: (m), $H[Co(dgCH_3)_2(NO_2)_2]$, (n), $[Co(dgH)_3]$; (o), $[Ni(dgH)_2]$.

Summary

Infrared absorption spectra of hydrogen dichloro-bis-(dimethylglyoximato)-cobaltate (III) prepared from both normal and deuterated dimethylglyoxime and of several other dimethylglyoximato-cobalt (III)-complexes were measured. It has been ascertained through the data of deuterated complexes that the absorption band at 1725 cm^{-1} of hydrogen dichloro-bis-(dimethylglyoximato)-cobaltate (III) is attributable to the O-H stretching frequency under the formation of intramolecular O-H-O hydrogen bonds.

All the bis-(dimethylglyoximato)-cobalt (III)-complexes show similar O-H stretching bands in the same region. It has been forecast that a series of examples of the very short and symmetric O-H-O hydrogen bond may be expected in the bis-(dimethylglyoximato)-cobalt (III)-complexes.

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8) R.E. Rundle and M. Parasol, *J. Chem. Phys.*, **20**, 1487 (1952); L.E. Godycki and R.E. Rundle, *Acta Cryst.*, **6**, 487 (1953).

9) R.C. Lord and R.E. Merrifield, *J. Chem. Phys.*, **21**, 166 (1953).

10) A.N. Baker, Jr., ibid., **22**, 1625 (1954).

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