Studies on Dimethylglyoximato cobalt (III) Complexes. III. Direct Evidence for the Planar Coördination of Two Dimethylglyoximate Ions in Bis-(dimethylglyoximato)-cobalt (III) Complexes

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In the former papers[1,2] the author discussed on the high stability of bis-(dimethylglyoximato)-cobalt (III) complexes. Then, an elucidation was suggested that the most important origin of the high stability is attributable to the O-H-O hydrogen bonds in the complex radical. However, the strong hydrogen bonds of this kind will be reasonably expected only when the two dimethylglyoximate ions coördinate to a cobalt atom with planar configuration. On the other hand, there has never been found any paper which dealt with the direct evidence for the planar coördination of two dimethylglyoximate ions in bis-(dimethylglyoximato)-cobalt (III) complexes. Thus, it seems to be desirable to afford not chemical but direct evidence for the above configuration. In this work, therefore, the author measured infrared absorption spectra of the so-called Feigl-Rubinstein's bis-(dimethylglyoximato)-cobalt (III)-derivative[3,4] and the tris-(dimethylglyoximato)-cobalt (III)[1,5], confirming the planar coördination of two dimethylglyoximate ions in the former compound.

Experimental

Materials

Hydrogen Dichloro-bis-(dimethylglyoximato)-cobaltate (III), (Feigl-Rubinstein's complex), $H[Co(DH^{*})_2Cl_2]$[3,4]. — The method of Cambi et al.[4] was applied in preparing the compound. To a concentrated aqueous solution of cobaltous acetate was added a slight excess of dimethylglyoxime, and the solution was oxidized by passing air through it. On adding concentrated hydrochloric acid, the compound was precipitated in dark green rhombs. It was recrystallized from aqueous solution by adding concentrated hydrochloric acid. For optical measurements the crystal had to be freed from accompanying moisture and hydrochloric acid.

Tris-(dimethylglyoximato)-cobalt (III), $[Co(DH)_3]$[1,5]. —The compound was prepared according to the previously described procedure[1,5].

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[1] A. Nakahara, This Bulletin, 27, 560 (1954).

[2] A. Nakahara, This Bulletin, 28, 207 (1955).

[3] F. Feigl and H. Rubinstein, *Ann.*, 433, 183 (1923).

[4] L. Cambi and C. Coriselli, *Gazz. Chim. ital.*, 66, 81 (1933).

[5] A. Nakahara and R. Tsuchida, *J. Am. Chem. Soc.*, 76, 3103 (1954).

* The following symbols are used: the ion of dimethylglyoxime (DH), $H_3CC(NO)C(NOH)CH_3$; the undissociated molecule of dimethylglyoxime (DH_2), $H_3CC(NOH)C(NOH)CH_3$.

The pure product was heated on a water bath under reduced pressure in order to remove the water molecules of crystallization.

Dimethylglyoxime, DH_2.—The compound was recrystallized from 94%-ethanol, and dried in a vacuum desiccator over calcium chloride.

Measurements

The infrared absorption spectra were obtained with a Perkin-Elmer Model 21 Recording Spectrophotometer using sodium chloride prisms and a Nujol suspension of the compound in question.

Results

The results of the measurements are shown in Fig. 1 and Fig. 2. There is also inserted, in Fig. 1, the curve of bis-(dimethylglyoximato)-nickel (II), (d), which was obtained by Rundle and Parasol[6], for the purpose of comparison with the present results. As is clear from those Figures, the curve of bis-(dimethylglyoximato)-cobalt (III)-derivative, (a), is quite similar to that of the bis-(dimethylglyoximato)-nickel (II), (d). On the contrary, the curve of tris-(dimethylglyoximato)-cobalt (III), (b), differs to a considerable degree from those of (a) and (d). The difference between those two types of curves can be found, for instance, in the region from 3600 to 3300 cm⁻¹ or from 1800 to 1670 cm⁻¹. Especially, the band found at 1725 cm⁻¹ on the curve of (a) shows a very important meaning as discussed below.

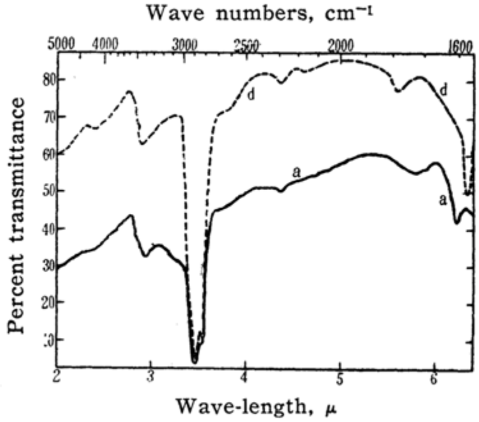

Fig. 1. Infrared absorption spectra of : (a), $H[Co(DH)_2Cl_2]$; (d), $[Ni(DH)_2]$.

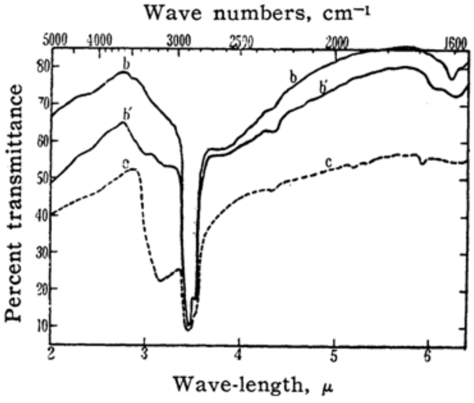

Fig. 2. Infrared absorption spectra of: (b), $[Co(DH)_3]$; (b′), $[Co(DH)_3]\cdot 2.5H_2O$; (c), Dimethylglyoxime.

Discussion

Recently Rundle and his co-workers[6,7,8] have presented trustworthy data concerning the crystal structure of bis-(dimethylglyoximato)-nickel (II).

According to their X-ray analysis, the complex molecule is planar and contains four five-membered rings as shown in Fig. 3. Of special interest was the very short O-H-O hydrogen bond, 2.44Å, shorter than any O-H-O hydrogen bond, heretofore reported. Furthermore, it was noteworthy that the O-H stretching frequency for this hydrogen bond is only 1775 cm⁻¹, about half the normal 3500 cm⁻¹, and that spectroscopic arguments have been presented indicating that the hydrogen lies symmetrically between the two oxygens in this case.

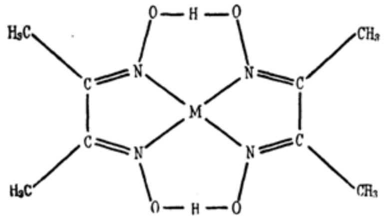

Fig. 3. The structure of planar bis-(dimethylglyoximato)-metal complex with O-H-O hydrogen bonds.

As can be seen in Fig. 1, the curve, (a), has a strong resemblance to the curve, (d), of the above bis-(dimethylglyoximato)-nickel (II) in the region from 5000 to 1670 cm⁻¹, suggesting the planar coördination of the two dimethylglyoximate ions about a cobalt atom in the bis-(dimethylglyoximato)-cobalt (III)-complex. This interpretation is supported by the fact that the curve, (b), of tris-(dimethylglyoximato)-cobalt (III) in which the planar coördination of two dimethylglyoximate ions could not be expected differs to a considerable extent from those of (a) and (d). In addition to that, the O-H stretching frequency for the above hydrogen bond can be found on (a) at 1725 cm⁻¹, and not on (b). This is

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6) R. E. Rundle and M. Parasol, *J. Chem. Phys.*, **20**, 1487 (1952).

7) L. E. Godycki, R. E. Rundle, R. C. Voter and C. V. Banks, ibid., **19**, 1205 (1951).

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

the direct evidence for the planar coördination of the two dimethylglyoximateions in the bis-(dimethylglyoximato)-cobalt(III)-derivative, since the existence of such a kind of hydrogen bond as described above could not be expected with any other configuration except the planar coördination. The appearance of the O-H stretching band on the curve, (a), is, however, somewhat broad and shifted a little towards a longer wave-length compared with the case of nickel (II)-complex, (d). This may be perfectly understandable by taking into consideration the action of an additional proton which is contained only in the Feigl-Rubinstein's bis-(dimethylglyoximato)-cobalt(III)-complex, H[*]$[Co(DH)_2Cl_2]$, and not in the bis-(dimethylglyoximato)-nickel (II). It coincides also with Rundle's opinin[9] that there are indications that very broad bands, characteristic of strong hydrogen bonds, become sharper as the O-H-O bond becomes symmetric. But the difference between the ionic radii of nickelous- and cobaltic-ion may be also concerned with the above facts. At any rate, it can be said that the O-H-O hydrogen bond in bis-(dimethylglyoximato)-cobalt(III)-complexes has been proved to be the same kind of the nature as established in the bis-(dimethylglyoximato)-nickel(II).

Rundle and Parasol[5] have also discussed the relation between the bond length and the stretching frequency for O-H-O hydrogen bonds. If it be applied their investigation to the present O-H stretching frequency, 1725 cm^{-1}, the bond length of below 2.5 Å a very short hydrogen bond, will be forecasted.

As is seen in Fig. 1 and Fig. 2, some other differences between the curves of bis- and tris-(dimethylglyoximato)-complex can be also found. But the assignments of those bands are very difficult without more detailed research. The author is, at present, investigating the fruits which are obtained by the substitution of deuterium for hydrogen atom concerned with the above O-H-O hydrogen bond[9].

Summary

Infrared absorption spectra of bis- and tris-(dimethylglyoximato)-cobalt(III)-complex were measured. Some discussions concerning the O-H stretching band of the former complex were given, and they reached the conclusion that the band at 1725 cm^{-1}. corresponds to the band at 1775 cm^{-1} of the bis-(dimethylglyoximato)nickel (II) and is characteristic of the planar bis-(dimethylglyoximato)-complexes.

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[*] Although the hydrogen atom has been written conventionally as the external cation of the comeplex anion, it is highly probable that the real structure of the complex should be considered to be "dichloro-dimethylglyoximato-dimethylglyoxime-cobalt (III)" molecule, $[Co(DH_2)(DH)Cl_2]$. If this proves to be the case, it seems to be most probable that the proton attaches to an oxygen atom.

[9] To be submitted later.