# *Studies on Dimethylglyoximato-cobalt (III)* Complexes. II. Absorption Spectra of Bis-(dimethylglyoximato)-and Bis-(mono-O-methyl-dimethylglyoximato)-cobalt (III) Complexes*

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In the previous papers[1] the author discussed on the strong tendency of two dimethylglyoximate ions to form planar configuration about a cobalt atom, and attributed its origin to the formation of O–H–O hydrogen bonds in the complex radical. The successful synthesis of the tris-(dimethylglyoximato)-cobalt (III) reported in the same papers strongly supports the above conclusion. In order to confirm the conclusion, it might be suitable to compare properties of bis-(dimethylglyoximato)-cobalt (III) derivatives which have the O–H–O hydrogen bonds and bis-(mono-O-methyl - dimethylglyoximato) - cobalt (III) derivatives, in which the hydrogen bonds cannot be anticipated.

In this work, bis-(mono-O-methyl-dimethylglyoximato)-diammine-cobalt (III) chloride and hydrogen dinitro-bis-(mono-O-methyl-dimethylglyoximato)-cobaltate (III) were newly synthesized, and investigated spectrochemically. Absorption spectra of some bis-(dimethylglyoximato)-cobalt (III) complexes were

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* The word "dimethylglyoximo-" was used in the former paper, but the above nomenclature seems to be better.

[1] A. Nakahara, This Bulletin, **27**, 560 (1954); A. Nakahara and R. Tsuchida, *J. Am. Chem. Soc.*, **76**, 3103 (1954).

also investigated in relation to the above complexes of O-methyl-substituted dimethylglyoxime.

## Experimental

**Materials.- Bis-(mono-O-methyl-dimethylglyoximato)-diammine-cobalt (III) chloride, $[Co(NH_3)_2(DCH_3)_2{}^{**}]\ Cl\cdot 1.5\ H_2O$.**[2] —This compound was prepared as reddish brown plates or prisms by the following method: 5 g. of purpureo cobalt (III) chloride, 5.2 g. of dimethylglyoxime-monomethylether and 0.5 g. of charcoal were added to a mixture of 60 ml. of alcohol and 30 ml. of water, boiled for 10–15 hours on a water-bath, and then filtered. Alcohol was distilled off from the filtrate. The residual aqueous solution was evaporated and dried on a water-bath. The residue was washed once with chloroform and dissolved in alcohol. In this procedure only the objective complex was dissolved, and ammonium chloride was removed by filtration. When this dark brown filtrate was condensed in a vacuum desiccator on calcium chloride, the compound crystallized gradually. Analyses and other experiments for identification were already reported.[2]

**Hydrogen dinitro-bis-(mono-O-methyl-dimethylglyoximato)-cobaltate (III), $H\ [Co(DCH_3)_2(NO_2)_2]$.**—This new compound was quantitatively precipitated from a hot solution of sodium hexanitrito-cobaltate (III) by careful addition of dimethylglyoxime-mono-methylether. The precipitate was almost pure after having been washed several times with hot water and alcohol. The compound did not show any reaction characteristic of sodium ion contrary to that showed by the dimethylglyoximato-complex obtained in the same procedure.[3] Found: C, 29.19; H, 4.61; N, 20.59, Calculated for $H\ [Co(DCH_3)_2(NO_2)_2]$: C, 29.27; H, 4.66; N, 20.48%. In order to determine the valency of cobalt, the magnetic susceptibility of the compound in solid state was measured, and it was necessarily concluded that cobalt should be tervalent since the compound proved to be diamagnetic. The compound appeared as orange, rhombic crystals. It is almost insoluble in water and alcohol, but dissolves a little in concentrated acetic acid. It explodes suddenly and burns on action of concentrated sulfuric acid.

**Bis-(dimethylglyoximato)-diammine-cobalt (III) chloride, $[Co(NH_3)_2(DH)_2]\ Cl\cdot 5H_2O$.**—This yellowish brown compound was prepared according to the direction of Nakatsuka and Iinuma.[4] As was already reported,[5] the crystal is of special interest in relation to its peculiar habit and unusual optical property.

**Hydrogen dichloro-bis-(dimethylglyoximato)-cobaltate (III), $H\ [Co(DH)_2Cl_2]$.**[6] —The method of Cambi et al.[7] 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 the aqueous solution by adding concentrated hydrochloric acid.

**Hydrogen dibromo-bis-(dimethylglyoximato)-cobaltate (III), $H[Co(DH)_2Br_2]$.**—The compound was precipitated in a similar way as the above described procedure from the reaction mixture by adding concentrated hydrobromic acid.

**Chloro-bis-(dimethylglyoximato)-ammine-cobalt (III), $[Co(NH_3)(DH)_2Cl]$; Ammonium dinitro-bis-(dimethylglyoximato)-cobaltate(III), $NH_4[Co(DH)_2(NO_2)_2]\cdot H_2O$; Nitro-bis-(dimethylglyoximato)-aquo-cobalt (III), $[Co(H_2O)(DH)_2(NO_2)]$; Nitro-bis-(dimethylglyoximato)-ammine-cobalt (III), $[Co(NH_3)(DH)_2(NO_2)]$; Hydrogen dinitro-bis-(dimethylglyoximato)-cobaltate(III), $H[Co(DH)_2(NO_2)_2]$.**—These complexes were prepared according to the direction of Tschugaeff.[3][8]

**Dimethylglyoxime-mono-methylether.** — Although there are some established methods concerning the syntheses of the compound,[9][10][11] a new method was adopted in this work: 7 g. of caustic soda and 20 g. of dimethylglyoxime were added to a mixture of 100 ml. of water and 200 ml. of alcohol, stirred and dissolved entirely on a water-bath. Into the mixture 25 g. of methyliodide was poured drop by drop during about half an hour with continuous stirring. The reaction mixture was boiled on the water-bath for two hours. Then alcohol was distilled off. On cooling the residual solution a white crystalline powder was deposited, which was filtered by suction, and purified by steam distillation. Thus 8.3 g. of pure dimethylglyoxime-mono-methylether (m.p. 104°C) was yielded, and 8.7 g. of unreacted dimethylglyoxime was recovered. By adding a large quantity of water to the distilled alcohol, dimethylglyoxime-dimethylether (m.p. 44°C) was also isolated.

**Measurements.** — Absorption spectra of the above compounds in solution were measured in the region from 40 to $135\times10^{13}$/sec. by a Beckman DU quartz spectrophotometer. The formal extinction coefficient $\varepsilon$ is given by the equation $I=I_0\times10^{-\varepsilon cd}$, where $c$ is the concentration of the complex in mol. or gram-ion per liter and $d$ the thickness of the layer in cm. The concentrations used were $1/10^3-1/10^5$ and $1/10^2-1/10^4$ mol./l., in complexes and ligands, respectively. Absorption spectra of dichloro- and dibromo-complex were observed in water, as well as in methanol containing hydrochloric- and hydrobromic acid, respectively. Those of hydrogen dinitro-bis-(dimethylglyoximato)- and hydrogen dinitro-bis-(mono-

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** $DCH_3=H_3CC(NOCH_3)C(NO)CH_3$; $DHCH_3=H_3CC(NOCH_3)C(NOH)CH_3$. $DH=H_3CC(NOH)C(NO)CH_3$; $DH_2=H_3CC(NOH)C(NOH)CH_3$.

2) A. Nakahara, Y. Yamamoto and R. Tsuchida, *J. Chem. Soc. Japan*, **74**, 1021 (1953).

3) L. Tschugaeff, *Ber.*, **41**, 2228 (1908).

4) Y. Nakatsuka and H. Iinuma, This Bulletin, **11**, 48 (1936).

5) Y. Saito, A. Nakahara and H. Kuroya, *J. Inst. Polytech.*, Osaka City Univ., **1**, No. 2, Ser. C, 15 (1950).

6) F. Feigl and H. Rubinstein, *Ann.*, **433**, 183 (1923).

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

8) L. Tschugaeff, *Z. anorg. Chem.*, **46**, 144 (1905); *Ber.*, **39**, 2692 (1906); **40**, 3498 (1907); **41**, 2226 (1908).

9) G. Charrier, *Gazz. chim. ital.*, **37**, 145 (1907).

10) L. Avogadro and G. Tavola, ibid., **55**, 329 (1925).

11) E. Thilo, *Ber.*, **62**, 869 (1929).

O-methyl-dimethylglyoximato)-cobaltate (III) were also measured in 50% acetic acid, since they are almost insoluble in water as already mentioned. Absorption spectra of ligands, dimethylglyoxime and its methylether, were observed in alcohol. In cases other than the above, aqueous solutions were used.

## Results and Discussion

**Absorption Spectra of $[Co(NH_3)_2(DH)_2]Cl$, $[Co(NH_3)(DH)_2Cl]$ and $H[Co(DH)_2Cl_2]$.** — The results of the measurements are shown in Fig. 1 and Table I. The three absorption curves are quite similar to each other except for the isolated maximum in the longer wavelength region on the curve of dichloro-complex, (c). As far as the absorption spectra of cobalt (III) complexes are concerned, there are, in general, two absorption maxima in the visible and near ultraviolet region.[12] The one in the visible has been designated as the "first absorption band", and the other in the near ultraviolet as the "second absorption band". According to Tsuchida, the first band is due to the electronic transitions in the unsaturated transition shell of the central ion and the second band is attributed to the transitions of the coördination electrons.[12][13] In the above complexes, however, the second bands are completely concealed by large absorption bands presumed to be the "specific absorption bands" which are due mainly to the dimethylglyoximate ions in coördination. Only the vestiges of the first bands remain slightly as inflations at $60\sim70\times10^{13}$/sec. in (a) and (b). The origin of dark or brownish colors which is characteristic of all Tschugaeff's dimethylglyoximato-complexes is attributed to the above mentioned facts. From this standpoint Feigl-Rubinstein's compound, $H[Co(DH)_2Cl_2]$,[6][7] having green color is a quite rare type of cobaltic complexes with dimethylglyoxime. Namely, the first band of this complex, (c), is nearly isolated from the specific band, showing its maximum at $\nu=53.9\times10^{13}$/sec. The difference between (a), (b) and (c), however, is quite natural, considering the "spectrochemical series", an empirical rule found by Tsuchida.[12][13] Since the chloride ion is by far a more bathochromic ligand than the ammonia molecule in the series, the first band should be shifted bathochromically by substitution of the ammonia molecules by the chloride ions. On the other hand, Yamada and Tsuchida[14] recently presented another empirical rule, the "hyperchromic series" which is concerned with the intensity of the absorption of complexes. In the series, the ammonia molecule precedes the chloride ion, i.e., ammonia is a more hyperchromic ligand than the chloride ion. According to this rule, therefore, the relation between the first absorption bands of the three complexes can be explained also

TABLE I

ABSORPTION MAXIMA OF BIS-(DIMETHYLGLYOXIMATO)-COBALT (III) COMPLEXES

| Notation | Complex radical | Solvent | First absorption band | | Specific absorption band | | Other bands | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | $\nu$, $10^{13}$/sec. | log ε | $\nu$, $10^{13}$/sec. | log ε | $\nu$, $10^{13}$/sec. | log ε | assignment |
| (a) | $[Co(NH_3)_2(DH)_2]^+$ | water | — | — | 123.0 | 4.41 | — | — | — |
| (b) | $[Co(NH_3)(DH)_2Cl]$ | water | — | — | 122.0 | 4.38 | — | — | — |
| (c) | $[Co(DH)_2Cl_2]^-$ | $CH_3OH$-HCl | 53.9 | 1.65 | 116.5 | 4.49 | — | — | — |
| (d) | $[Co(DH)_2Cl_2]^-$ | water | — | — | 121.0 | 4.36 | — | — | — |
| (e) | $[Co(DH)_2(NO_2)_2]^-$ | water | — | — | 122.0 | 4.44 | 87.6 | 3.86 | nitro-groups |
| (f) | $[Co(NH_3)(DH)_2(NO_2)]$ | water | — | — | 123.0 | 4.40 | — | — | — |
| (g) | $[Co(H_2O)(DH)_2(NO_2)]$ | water | — | — | 121.5 | 4.41 | — | — | — |
| (h) | $[Co(DH)_2Br_2]^-$ | $CH_3OH$-HBr | 52.1 | 1.79 | 118.8 | 4.22 | 99.8 | 4.27 | third band |

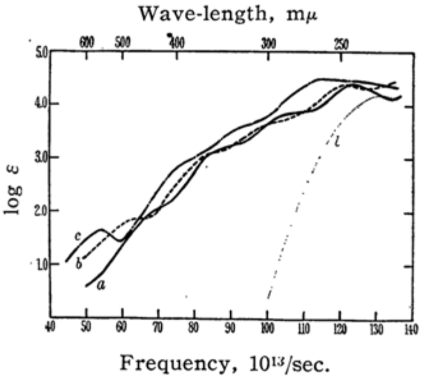

Fig. 1. Absorption spectra of: (a), $[Co(NH_3)_2(DH)_2]Cl$ in water; (b), $[Co(NH_3)(DH)_2Cl]$ in water; (c), $H[Co(DH)_2Cl_2]$ in 4% HCl-methanol.

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[12] See, for example, R. Tsuchida and M. Kobayashi, "The Colours and the Structures of Metallic Compounds" (in Japanese), (Zoshindo, Osaka, Japan, 1944).

[13] R. Tsuchida, This Bulletin, 13, 388 (1938).

[14] S. Yamada and R. Tsuchida, This Bulletin, 26, 15 (1953).

with respect to their intensities.

In the ultraviolet region, there can be recognized two inflations and one maximum. These may be considered to be the above mentioned specific absorption bands, since they are truly characteristic of dimethylglyoximato-complexes. Above all, in (a) and (b) the appearances of the absorption curves in the region are quite similar to each other, suggesting the same configuration of two dimethylglyoximate ions in each complex radical. As is clear from Table I, however, the maximum on the curve of dichloro-complex, (c), is shifted bathochromically, to a considerable degree. For this phenomenon some origins may be considered: (1) the effect of the two chloride ions coördinated in trans-positions*; (2) the solvent effect in methanol-hydrochloric-acid solution. It would probably be supposed that both the two effects are concerned in the above phenomenon. Further discussion will be given in the later section concerning the origins which contribute to the specific band.

**Absorption Spectra of $NH_4[Co(DH)_2(NO_2)_2]$, $[Co(NH_3)(DH)_2(NO_2)]$ and $[Co(H_2O)(DH)_2(NO_2)]$.**—The results of the measurements are shown in Fig. 2 and Table I. Absorption curves of these three complexes are quite similar to one another. Only the maximum at $\nu=87.6\times10^{13}$/sec. on the curve of dinitro-complex, (e), is conspicuous. This is the specific absorption band which is due to the nitro-groups in coördination.[15] Also on the curves, (f) and (g), the inflations higher than those of other complexes are recognized in this region. But they are not so remarkable as that of the dinitro-complex. This is due to the number of nitro-groups contained in the complex radical, since the specific absorption band usually changes hyperchromically with increasing number of the concerned ligands.[16] In the longer wave-length region, the vestiges of the first bands are almost unrecognized. But this may be understood by taking into consideration the above described intense specific band originating from the nitro-groups along with the hypsochromic shift of the first bands, which is also caused by the nitro-groups, one of the most hypsochromic ligand in the spectrochemical series. So far as the maxima in the shorter wave-length are concerned, there cannot be recognized any particular difference from the curves, (a) and (b), as is clear from Table I.

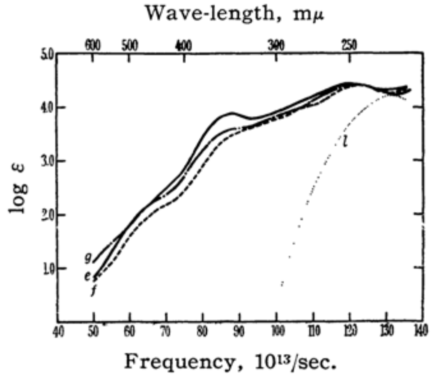

Fig. 2. Absorption spectra of aqueous solution of: $NH_4[Co(DH)_2(NO_2)_2]$, (e); $[Co(NH_3)(DH)_2(NO_2)]$, (f); $[Co(H_2O)(DH)_2(NO_2)]$, (g).

**Absorption Spectra of $H[Co(DH)_2Br_2]$ and $H[Co(DH)_2(OH)Cl]$.**—In Fig. 3 absorption curves of the above two compounds are illustrated. In the measurement of the former, (h), methanol-hydrobromic-acid solution was used, while in the case of the latter, (d), was adopted aqueous solution of the Feigl-Rubinstein's dichloro-complex, $H[Co(DH)_2Cl_2]$. It is because the dichloro-complex has been known to change itself into the above described chloro-hydroxo-complex in aqueous solution.[17] Although the valency of cobalt in the Feigl-Rubinstein's complex was considered previously to be bivalent, it is quite sure, by the investigation of Cambi et al[7]., that it must be tervalent. Therefore, the above change should be elucidated according to the following scheme:

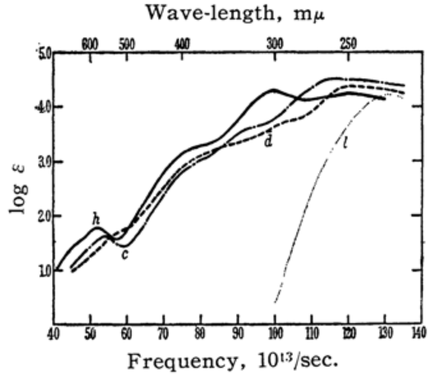

Fig. 3. Absorption spectra of: (d), $H[Co(DH)_2Cl_2]$ in water; (h), $H[Co(DH)_2Br_2]$ in 5% HBr-methanol.

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* It has been well-known that the third absorption band should appear readily when a central ion of a complex radical involves two anions in trans-positions. (Ref. 12). Consequently, there may be expected an overlapping of the third-and specific-band. In this case, such a bathochromic shift as above mentioned is very probable.

15) H. Kuroya and R. Tsuchida, *J. Chem. Soc. Japan*, 59, 1142 (1938).

16) R. Tsuchida and M. Kobayashi, This Bulletin, 13, 474 (1938).

17) "*Gmelins Handbuch d. anorg. Chem.*", 8 Aufl., 58 B, p. 21 (1930).

$$H[Co(DH)_2Cl_2]+H_2O \rightleftarrows H[Co(DH)_2(OH)Cl]+HCl$$

As shown in Fig. 3 the curve, (d), is quite different from (c), suggesting the substitution of a ligand as presented in the above equation. Since the change is, however, in an equilibrium in aqueous solution, further discussion would be impossible without more detailed researches.

As for the absorption spectrum of the dibromo-complex, (h), all the explanations described in the case of the dichloro-complex, (c), can be applied. An important fact is that the bromide ion is a more bathochromic ligand than the chloride ion. In the present case, however, there can be recognized clearly a new maximum at $\nu=100\times10^{13}$/sec. This may be considered to be the third absorption band which is due to the two bromide ions coördinated in *trans*-positions, as is known in the absorption spectrum of *trans*-dibromo-bis-(ethylenediamine)-cobalt (III)-complex.[18]

**Absorption Spectra of $[Co(NH_3)_2(DCH_3)_2]Cl$ and $H[Co(DCH_3)_2(NO_2)_2]$ in Relation to Those of $[Co(NH_3)_2(DH)_2]Cl$ and $H[Co(DH_2)(NO_2)_2]$.**—The results of the measurements are shown in Fig. 4. The absorption curve of bis-(mono-O-methyl-dimethylglyoximato)-diammine-cobalt (III) chloride, (i), resembles, as a whole, that of the corresponding dimethylglyoximato-complex, (a), but the former is considerably bathochromic to the latter.

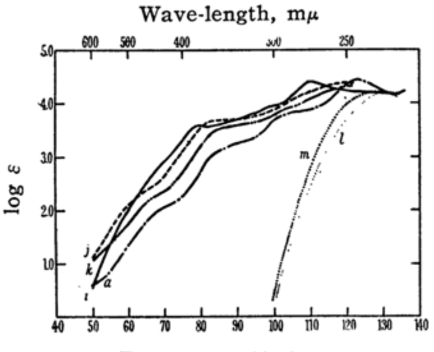

Fig. 4. Absorption spectra of: (i), $[Co(NH_3)_2(DCH_3)_2]$ Cl in water; (j), $H[Co(DCH_3)_2(NO_2)_2]$ in 50% acetic acid; (k), $H[Co(DH)_2(NO_2)_2]$ in 50% acetic acid; (1), dimethylglyoxime in alcohol; (m), dimethylglyoxime-mono-methylether in alcohol.

Since dimethylglyoxime and its methylether are closely related in their electronic structures, it may be expected quite naturally that the curve, (i), would have a strong resemblance to the curve, (a). In fact, notwithstanding a little difference between the absorption maxima of the two ligands, (l) and (m), there is brought about a considerable difference when they are in coördination. (Table II). This can be understood by taking the origin of the specific bands into consideration.

TABLE II

SPECIFIC BANDS OF $[Co(NH_3)_2(DH)_2]Cl$ AND $[Co(NH_3)_2(DCH_3)_2]Cl$

| | νmax, $10^{13}$/sec. | log ε | ν max(complex) ~ ν max(ligand) |
|---|---|---|---|
| $[Co(NH_3)_2(DH)_2]Cl$ | 123.0 | 4.41 | 7.4 |
| ligand, $DH_2$ | 130.4 | 4.20 | |
| $[Co(NH_3)_2(DCH_3)_2]Cl$ | 110.3 | 4.37 | 17.9 |
| ligand, $DHCH_3$ | 128.2 | 4.21 | |

That is, the specific bands are the results of the polarizing deformation of the concerned ligands in the complex radical. While the two strong O-H-O hydrogen bonds are, as discussed in the previous paper,[1] expected in the bis-(dimethylglyoximato)-cobalt (III)-complexes, there could not be expected such hydrogen bonds in the corresponding bis-(mono-O-methyl-dimethylglyoximato)-complexes. Therefore, the degree of the polarizing deformation is anticipated to be larger in the latter than in the former. As for the reason of the above presumption, there may be supposed defying action of protons against the polarizing deformation of the concerned ligands under the effect of the cobalt (III) ion. In other words, the difference between the absorption spectra of $[Co(NH_3)_2(DCH_3)_2]Cl$ and $[Co(NH_3)_2(DH)_2]Cl$ supports the conclusion that the O-H-O hydrogen bonds play an important role in the determination of the electronic structure of bis-(dimethylglyoximato)-cobalt (III)-complex. The relation between the absorption curves of $H[Co(DCH_3)_2(NO_2)_2]$ and $H[Co(DH)_2(NO_2)_2]$ are similar to that between (a) and (i).

**The Stabilities of Bis-(dimethylglyoximato)-complexes.**—In the previous paper, it was concluded that the high stability of the bis-(dimethylglyoximato)-cobalt(III)-complexes, in which the two dimethylglyoximato ions coördinate to a cobalt atom with planar configuration, is attributed to the O-H-O hydrogen bonds in the complex radical. In this work, the above conclusion was confirmed by the other chemical evidence. Although bis-(mono-O-methyl-dimethylglyoximato)-diammine-cobalt (III) chloride can be prepared from purpureo cobalt (III) chloride according to the almost similar direction to that of the corresponding dimethylglyoximato-complex, the

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[18] M. Linhard and M. Weigel, *Z. anorg. Chem.*, **271**, 101 (1952).

reaction for preparing the former is caused by the aid of charcoal and is finished less rapidly than that for preparing the latter. This indicates the fact that the bis-(dimethylglyoximato)-complex is by far more stable than bis-(mono-O-methyldimethylglyoximato)-complex. With respect to many other reactions for preparing bis(mono-O-methyl-dimethylglyoximato)-derivatives and corresponding dimethylglyoximato-derivatives, the above described conclusion is also supported. Such a distinct difference, which is originated from the substitution of the hydrogen atom by the methylradical will verify a remarkable contribution of O-H-O hydrogen bonds in the bis-(dimethylglyoximato)-complex radical towards the stabilization of the compounds. *Being united through the two O-H-O hydrogen bonds, the two dimethylglyoximate ions in the complex must be considered as one quadridentate group.*

## Summary

Two new compounds, $[Co(NH_3)_2(DCH_3)_2]Cl$ and $H[Co(DCH_3)_2(NO_2)_2]$ have been synthesized as the first examples of tervalent-cobalt complexes of dimethylglyoxime-mono-methylether. Absorption spectra of the compounds and several bis-(dimethylglyoximato)-cobalt (III)-complexes in solution have been measured.

The absorption curves of bis-(dimethylglyoximato)-cobalt (III)-complexes, generally, consist of three inflations and one maximum. The inflation in the visible region is the vestige of the first absorption band, and the two other inflations and one maximum in the ultraviolet region are the specific absorption bands which are due mainly to the dimethylglyoximate ions in coördination.

As for the first absortion bands, the results of the measurements can successfully be elucidated on the basis of the spectrochemical- and hyperchromic-series found by Tsuchida et al. For $NH_4[Co(DH)_2(NO_2)_2]$, is also the specific band originated from the nitro-groups in coördination remarkable.

The isolated maxima on the curves of $H[Co(DH)_2Cl_2]$ and $H[Co(DH)_2Br_2]$ in the longer wave-length region are nothing but the first absorption bands which are shifted towards red owing to the bathochromic effect of the two halogenide ions.

In the dibromo-complex, the third absorption band is conspicuous. It has never been recognized clearly in the other complexes with dimethylglyoxime.

The absorption curves of bis-(mono-O-methyl-dimethylglyoximato)-complexes, as a whole, resemble those of corresponding dimethylglyoximato-complexes, but the bathochromic shift of the specific absorption bands from that of free ligand molecule amounts to a considerable degree in comparison with the cases of dimethylglyoximato-complexes. And this phenomenon is elucidated in connexion with the O-H-O hydrogen bonds.

From comparison of the reactions for preparing the bis-(mono-O-methyl-dimethylglyoximato)- and bis-(dimethylglyoximato)-complexes, the high stability of the latter was discussed.

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