Studies on Dimethylglyoximo-cobalt(III) Complexes. I. The Preparation and Some Properties of Tris-(dimethylglyoximo)-cobalt(III)

By Akitsugu NAKAHARA

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Introduction

Since the work of Tschugaeff[1] a number of dimethylglyoximo-cobalt(III) complexes have been prepared, but the complex compound having three ions* of dimethylglyoxime about a cobalt atom has never been described. Mann[2] has pointed out that chelating groups fall into two classes: (a) those that can fill all six co-ordination positions, e.g., ethylenediamine, oxalate radical etc.; (b) those which, while capable of filling four positions in the quadri-co-ordinate complex, cannot fill more than four-co-ordination positions when introduced into the sexa-co-ordinate complex. Dimethylglyoxime was cited by Mann as the typical example of the latter case. Thus it has been a definite opinion that the synthesis of tris-(dimethylglyoximo)-cobalt(III) cannot be reached or at least is very difficult[3]. This concept, however, has perfectly been overthrown since the present author has succeeded in preparing this pending compound by a quite simple method. The present paper deals with the method of preparation and properties of this new compound, with some discussions concerning the process of the complex formation.

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

[2] F. G. Mann, *J. Chem. Soc.*, **1933**, 412; H. J. Emeleus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," 2nd ed., George Routledge and Sons, Ltd. London, (1952), p. 125

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

* The following symbols are used: the ion of dimethylglyoxime (DH), $CH_3C(NO)C(NOH)CH_3$; the undissociated molecule of dimethylglyoxime (DH_2), $CH_3C(NOH)C(NOH)CH_3$.

Experimental

The Preparation and Identification.—The preparation of tris-(dimethylglyoximo)-cobalt(III) was performed as follows: Six grams of dimethylglyoxime was completely dissolved in 60 ml. of hot water containing 6 g. of potassium hydroxide. After the solution was cooled to 40—50°C, 5 g. of crystalline cobaltous nitrate hexahydrate was added. The mixture was shaken vigorously and thoroughly, and to this 12 ml. of 50% acetic acid was poured. Then the air was bubbled vigorously through the reaction mixture for about three hours. Beautiful orange-yellow acicular crystals gradually were deposited. The mixture was allowed to stand for several hours, and then was filtered by suction. The crude substance was recrystallized from water containing a small amount of acetic acid. Four grams of pure substance was yielded.

In place of potassium hydroxide and cobaltous nitrate in the above described procedure, sodium hydroxide and cobaltous chloride, respectively, can also be used. Therefore, it will be concluded that the resulting products have nothing to do with K^+ and Na^+ or NO^-_3 and Cl^-. In fact, the products did not show any reaction characteristic of those ions. Nevertheless, if the product were not the uncharged complex molecule, the compound would necessarily have H^+ or OH^- as the external ion of the complex radical, and the aqueous solution of the compound would have to show, similarly to the case of $H_3O^+[Co(DH)_2(NO_2)_2]^-$ or $[Co(NH_3)_2(DH)_2]^+ OH^-$, considerably strongly acidic or basic property, respectively.[4] The present compound, however, was found to be neither acidic nor basic. In consequence, it was concluded that the product is an uncharged complex molecule. The results of analyses were as follows: Co, 12.90; C, 32.51; H, 5.98; N, 18.80; H_2O, 9.75 Calcd. for $[Co(DH)_3]\cdot 2.5\ H_2O$: Co, 13.12; C, 32.08; H, 5.83; N, 18.71; H_2O, 10.02%.

Furthermore, as far as the valency of cobalt is concerned, it is reasonably considered to be tervalent since the cobaltous salts in general are very easily oxidized in the presence of glyoximes to cobaltic complexes[5].

Thus it was finally decided that the present substance surely corresponds to the tris-(dimethylglyoximo)-cobalt(III) $[Co(DH)_3]\cdot 2.5\ H_2O$.

Measurements of the Absorption Spectra.—The absorption spectra of the complex and its ligand, dimethylglyoxime, were determined at room temperature with a Beckman Model DU quartz spectrophotometer. The results are shown in Fig. 1. The concentrations used were $1/10^3$—$1/10^5$ and $1/10^2$—$1/10^4$ mol./l., in (a) and (b), respectively. While the measurement of dimethylglyoxime was made in alcoholic solution, that of the complex was made in aqueous solution for the purpose of comparison with the data obtained in bis-(dimethylglyoximo)-derivatives. Molar extinction coefficients ε were calculated from the familiar equation $\varepsilon = \frac{1}{cd} \times \log_{10}(I_0/I)$, where c is the concentration of the compound in mol./l., and d the thickness of the layer in cm.

Description of the Properties.—The clear acicular crystals of tris-(dimethylglyoximo)-cobalt (III) obtained by successful recrystallization are orange-yellow or brownish-yellow. The bright-yellow coloured opaque fibroid crystals which we very often encounter are impure. The pure crystal is quite stable in the atmosphere, and hardly ever decomposes below 200°C. It is somewhat soft to the feel in comparison with ordinary inorganic complexes. This is probably attributable to the feeble intermolecular forces, which are possible in the spherical compound surrounded by many methyl-groups. It is soluble in water, alcohol, chloroform and dioxane, and insoluble in benzene and acetone. In concentrated acetic acid, it decomposes on dissolution.

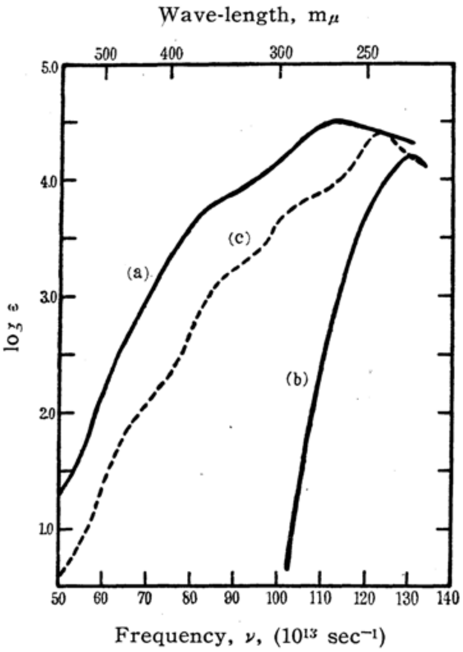

Fig. 1. Absorption spectra of: (a), tris-(dimethylglyoximo)-cobalt(III) in aqueous solution; (b), dimethylglyoxime in alcoholic solution, and (c), bis-(dimethylglyoximo)-diammine-cobaltic chloride in aqueous solution.

Discussion

The Absorption Spectra.—The absorption curve, (a), has only one maximum in the spectral region from 50 to 130×10^{13}/sec., and is quite monotonous. This will probably be due to the large and complicated specific absorption bands[6] of ligands, dimethyl-

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[4] L. Tschugaeff, *Ber.*, **41**, 2228 (1908); *J. Russ. Ges.* [chem.], **41**, 1366 (1909); **41**, 218 (1909); *Z. anorg. Chem.*, **46**, 163 (1905); Gmelins Handbuch d. anorg. Chem., 8. Auflage, **58B**, 276, 324 (1930).

[5] L. Cambi and C. Coriselli, *Gazz. chim. ital.*, **66**, 81 (1936); *Chem. Abstr.*, **30**, 8158 (1936).

[6] R. Tsuchida, and M. Kobayashi, This Bulletin, **13**, 471 (1938); R. Tsuchida, ibid., **13**, 442 (1938); **13**, 388 (1938).

glyoxime. Although bis-(dimethylglyoximo)-cobalt(III) complexes[7,8] show similar absorption curves on the whole, they differ considerably from the present curve, (a). As is clear from Table I,[8] tris-(dimethylgyloximo)-cobalt(III) has the absorption maximum at 113×10^{13}/sec., while the maxima of bis-(dimethylglyoximo)-complexes are observed in the region from 121.5 to 123×10^{13}/sec. In other words, the former is bathochromic to the latter. Also with respect to the molar extinction coefficients the former is hyperchromic to the latter as shown in Table I.

TABLE I
ABSORPTION MAXIMA FOUND IN THE SHORTER WAVE-LENGTH

Complexes	absorption maxima	
	$\nu_{max.}$	$\log \varepsilon_{max.}$
$[Co(NH_3)_2(DH)_2]Cl \cdot 5H_2O$	123.0	4.41
$[Co(NH_3)(DH)_2Cl]$	122.0	4.38
$[Co(DH)_2(NO_2)_2]NH_4 \cdot H_2O$	122.0	4.44
$[Co(NH_3)(DH)_2(NO_2)]$	123.0	4.40
$[Co(H_2O)(DH)_2(NO_2)]$	121.5	4.41
$[Co(DH)_3] \cdot 2.5\ H_2O$	113.2	4.50
Dimethylglyoxime	130.4	4.20

It has long been known that the specific absorption bands are usually shifted bathochromically and hyperchromically with an increasing number of the concerned ligands.[6] If the present absorption band is assumed to be the specific absorption band of dimethylglyoxime, the relation between the absorption maximum of tris-(dimethylglyoximo)-complex and that of bis-(dimethylglyoximo)-derivative agrees with the above mentioned empirical rule. Moreover, judging from the curve in the longer wave-length, dimethylglyoxime seems probably to precede, at least, ethylenediamine in the spectrochemical series.[6] That is to say, dimethylglyoxime is a considerably hypsochromic ligand. The details concerning the absorption spectra of the dimethylglyoximo-cobalt(III) complexes will be reported later.[8]

Stabilities of Dimethylglyoximo-complexes.—According to Nakatsuka and Iinuma,[9] two ions of dimethylglyoxime in the bis-(dimethylglyoximo)-diamine-cobalt(III) complexes generally have a strong tendency to form the planar configuration. Certainly, this opinion is supported by many chemical evidences. For instance, it is necessary to assume such a strong tendency characteristic of dimethylglyoxime, in order to elucidate the reason why any pair of geometric isomers of those complexes has never been obtained, while it is capable of isolating *cis*- and trans-isomers for the bis-ethylenediamine- or bis-oxalato-complexes. The distinguished stability of planar co-ordinated bis-(dimethylglyoximo)-derivative can be recognized also in the fact that any type of complex radical other than the bis-(dimethylglyoximo)-derivative has never been prepared for the last five decades. Although no paper concerning the origin of this characteristic has ever been published, it may be considered that O—H—O hydrogen bonds in the planar configuration as shown in Fig. 2 are necessarily concerned in the distinguished stability of those complexes.* This is probably because such a kind of hydrogen bond in bis-(dimethylglyoximo)-nickel(II) was demonstrated recently by Godycki and Rundle from the standpoint of X-ray analysis,[10] and directly by means of the measurement of infra-red absorption spectrum.[11] The existence of the above mentioned O—H—O hydrogen bonds in the cobalt(III) complexes will be expected reasonably from the evidence obtained in the nickel complex. If it proves to be the case, we can estimate this energy of hydrogen bond at several kilocalories per mol. from a large number of data.[12] Since there are two hydrogen bonds in one complex radical, the energy of at least 10—15 kilocalories will be expected per mol. On the other hand, so far as the ordinary cobalt(III) complexes are

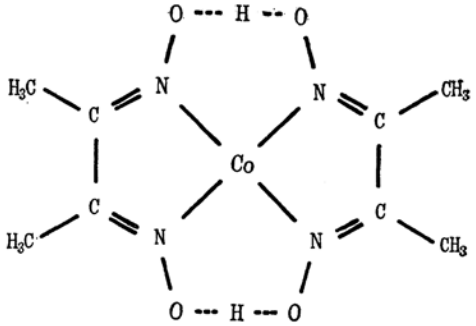

Fig. 2 Planar bis-(dimethylglyoximo)-cobalt(III)-complexes with O—H—O hydrogen bonds.

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[7] H. Kuroya, *J. Inst. Polytech.*, Osaka City Univ., **1**, No. 2, Ser. C, 11 (1950).

[8] To be published later.

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

[10] L. E. Godycki, R. E. Rundle, R. C. Voter and C. V. Banks, *J. Chem. Phys.*, **19**, 1205 (1951); L. E. Godycki and R. E. Rundle, *Acta Cryst.*, **6**, 487 (1953).

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

[12] See, for example, S. Seki, *Chem. and Chem. Ind.* (in Japanese), **6**, 2226—2227 (1953).

* On the contrary, the opinion that the origin of the tendency towards the planar configuration may be attributable to the π-electrons in the conjugated double bond system is out of the question, since tris-(dipyridyl)- or tris-(phenanthroline)-complexes generally are readily synthesized.

concerned, heats of formation are about 30—50 kcal/mol.[13] (Table II). Thus it may be supposed that the present O—H—O hydrogen bonds in the planar configuration contribute to a considerable degree towards the complex formation. The origin of the strong tendency towards the planar configuration characteristic of dimethylglyoxime will, therefore, be found in the above described O—H—O hydrogen bonds. It is then quite natural that the synthesis of tris-(dimethylglyoximo)-cobalt(III) should be very difficult in the ordinary conditions, since the planar bis-(dimethylglyoximo)-derivatives are exceedingly stable. The method of preparation of tris-(dimethylglyoximo)-cobalt (III) suggested by the present author, however, is compatible with the above conclusion. Namely, in this condition, the O—H—O hydrogen bonds are interrupted by potassium hydroxide in the process of the complex formation. In such a condition, three ions of dimethylglyoxime will be able to co-ordinate to a cobalt atom, quite similarly to the ethylenediamine or oxalate radical. And it may be supposed that the formation of the original form of the product already is finished before acetic acid is poured. This assumption is supported by the fact that the synthesis of tris-(dimethylglyoximo)-cobalt(III) is unsuccessful if acetic acid is poured on at the beginning. At any rate, the reactions adopted by many investigators differ in the starting form of dimethylglyoxime from the present method; i.e., in the former dimethylglyoxime exists as a molecule and in the latter as a bivalent anion.

TABLE II

HEAT OF FORMATION OF COBALT(III) COMPLEXES

Complex ions	Heat of formation kcal.
$[Co(NH_3)_6]^{3+}$	51.9
$[Co(NH_3)_5(NO_2)]^{2+}$	53.1
$[Co(NH_3)_5Cl)]^{2+}$	41.7
$[Co(NH_3)_5(H_2O)]^{3+}$	45.0
$[Co(NH_3)_4(NO_2)_{2\substack{(1)\\(6)}}]^{+}$	53.1
$[Co(NH_3)_4(NO_2)_{2\substack{(1)\\(2)}}]^{+}$	53.9
$[Co(NH_3)_4Cl_{2\substack{(1)\\(6)}}]^{+}$	32.0
$[Co(NH_3)_4Cl_{2\substack{(1)\\(2)}}]^{+}$	30.2
$[Co(NH_3)_4(NO_2)Cl_{\substack{(1)\\(6)}}]^{+}$	49.3
$[Co(NH_3)_4(H_2O)(NO_2)_{\substack{(1)\\(6)}}]^{2+}$	45.6
$[Co(NH_3)_4(NO_2)_4]^{-}$	47.0
$[Co(NO_2)_6]^{3-}$	28.1

Summary

Tris-(dimethylglyoximo)-cobalt(III) was newly synthesized by making use of dipotassium dimethylglyoximate. The crystals are quite stable in the atmosphere similarly to other so-called luteo-complexes, and orange-yellow in color. It is soluble in organic solvents, e.g., chloroform, alcohol and dioxane, as well as in water, but insoluble in benzene and acetone.

The absorption spectrum of this compound in aqueous solution was measured, and it was concluded that dimethylglyoxime is a considerably hypsochromic ligand.

Some discussions concerning the stabilities of bis-(dimethylglyoximo)-cobalt(III) complexes were given and they reached the following conclusions: (1) the distinguished stability of bis-(dimethylglyoximo)-derivatives is probably due to the O—H—O hydrogen bonds which are expected for the planar configuration of two dimethylglyoximic ions, and (2) the synthesis of tris-(dimethylglyoximo)-cobalt(III) can be successfully achieved only by interrupting the formation of those hydrogen bonds in the course of co-ordination of the ligands.

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Department of Chemistry, Faculty of
Science, Osaka University,
Nakanoshima, Osaka

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[13] K. B. Yatsimirski and L. L. Pankova, *J. Gen. Chem. U. S. S. R.*, **18**, 2051 (1948); **19**, 617, 623 (1949); *Chem. Abstr.*, **43**, 2355, 7805, 7806 (1949); **44**, 7701 (1950).