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Deprotonation of Oxime Complexes: Dimethylglyoxime-Cobalt(III) Complexes[*1]

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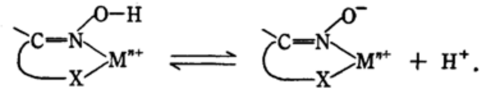
Dimethylglyoxime-Co(III) complexes with the formula $[Co(dmgH)_2A_2]^n$ (I), where dmgH is dimethylglyoximato mono-anion, A is an axial ligand such as aniline, *p*-anisidine, pyridine, γ-picoline, imidazole, NH_3, CN^-, and NO_2^-, and n is -1, 0, or $+1$, were found to change their electronic absorption spectra reversibly depending on the pH of the solution. These changes have been attributed to the dissociation of the proton from the intramolecular hydrogen bridges of the complex; the changes are accompanied by the formation of the complex $[Co(dmgH)(dmg)A_2]^{n-1}$, where dmg represents the dimethylglyoximato di-anion. The proton dissociation constants (pK_a) obtained by the spectrophotometric method indicated that the complex I is generally a weak acid of $pK_a=7.7—12.6$. With the exception of the pyridine and the γ-picoline ligand, axial ligands do not appreciably affect the pK_a values. However, axial pyridine and the γ-picoline ligand increase the tendency of the hydrogen bridges to dissociate the proton.

Some metal chelate-complexes coordinated with oxime derivatives are thought to dissociate the proton reversively depending upon the pH of the solutions. The reaction can be generally represented as follows:



This phenomenon has been observed in Fe(III) complexes of Schiff bases derived from 1,2-diketonemonoximes and amines[1] and in complexes of methyl-2-pyridyl ketoxime.[2] As for pyridine-2-aldoxime complexes of Fe(II), Fe(III), Ni(II), Pd(II), and Pt(II), proton dissociation constants (pK_a) corresponding to the above reaction have been determined.[3,4]

In the present paper an extensive investigation with respect to such proton dissociation as is described above has been made on Co(III)-dimethylglyoxime complexes of the $[Co(dmgH)_2A_2]^n$[*2] type, this investigation has revealed that the hydrogen in the intramolecular, hydrogen bridges of the complexes can be ionized as an proton depending on the pH of the aqueous solution. Moreover, the ionization constants have been expeditiously obtained by the spectrophotometric method.[5]

Experimental

Measurements. The electronic absorption spectra were measured with a Hitachi EPS-3 spectrophotometer. An aqueous complex solution was buffered to a desirable pH by adding a McIlavine or Kolthoff's buffer solution. The pH measurements of the solution was made on a glass-electrode pH meter calibrated against the standard buffer. All measurements of both the spectra and pH were carried out at room temperature from 20 to 25°C.

Complexes. *Bis(dimethylglyoximato)-di(imidazole)cobalt(III) Chloride*, $[Co(dmgH)_2(imidazole)_2]Cl\cdot 2H_2O$. This complex was newly prepared for the present study. Into an aqueous solution containing 5 g of cobalt(II) chloride hexahydrate, 5 g of dimethylglyoxime and 7 g of imidazole dissolved in ethanol were added. The subsequent passing of air through the solution for 30—40 min at room temperature resulted in the precipitation of a reddish-brown complex. This complex was recrystallized from hot water.

Found: Co, 11.66; C, 33.89; H, 5.19; N, 22.51; Cl, 6.81%. Calcd for $Co(C_{14}H_{18}N_8O_4)Cl\cdot 2H_2O$: Co, 11.86; C, 33.85; H, 5.27; N, 22.56; Cl, 6.70%.

The other complexes studied were prepared and purified according to the methods in the articles noted in Table 1.

[*1] Part of this work has been communicated: Y. Yamano, I. Masuda, K. Shinra, *Inorg. Nucl. Chem. Letters*, **4**, 581 (1968).

[1] I. Masuda, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **82**, 563, 1350 (1961).

[2] D. K. Banerjea and K. K. Tripathi, *Anal. Chem.*, **32**, 1196 (1960).

[3] G. I. H. Hanania and D. H. Irvine, *J. Chem. Soc.*, **1962**, 2745.

[4] I. Masuda and K. Shinra, *Science Reports, Osaka University*, **11**, 3 (1962).

[*2] Mono-, and di-valent dimethylglyoximato anion are abbreviated as dmgH, and dmg, respectively. "A" represents axial ligand such as amine, CN^- or NO_2^-. And "n" denotes +1, 0, or -1.

[5] W. Stenström and N. Goldsmith, *J. Phys. Chem.*, **30**, 1683 (1926).

TABLE 1. pK_a VALUES OF THE COMPLEXES ASSOCIATED WITH THE EQUILLIBRIUM (1)

Complex	pK_a	Isosbestic point (mμ)
$[Co(dmgH)_2(Aniline)_2]Cl \cdot 4H_2O$[6]	10.5	250, 347
$[Co(dmgH)_2(p\text{-Anisidine})_2]Cl \cdot H_2O$[7]	10.9	249
$[Co(dmgH)_2(Pyridine)_2]Cl \cdot H_2O$[6,8]	7.7	250
$[Co(dmgH)_2(\gamma\text{-Picoline})_2]Cl \cdot H_2O$	8.0	248
$[Co(dmgH)_2(Imidazole)_2]Cl \cdot 2H_2O$	9.9	246
$[Co(dmgH)_2(NH_3)_2]Cl \cdot 5H_2O$[6]	10.5	245
$[Co(dmgH)_2NH_3 \cdot Cl]$[8,9]	12.0	248
$K[Co(dmgH)_2(CN)_2] \cdot 1.5H_2O$[10]	12.6	242
$NH_4[Co(dmgH)_2(NO_2)_2] \cdot H_2O$[9,11]	12.6	240

Results

The complexes of the type $[Co(dmgH)_2A_2]^{n}$*2 listed in Table 1 change their electronic absorption spectra with a change in the pH in an aqueous solution. For instance, the spectrum of the aniline complex with A=aniline in an alkaline medium differs from that in an acid medium, as is shown in Fig. 1. With a change in the pH the complex undergoes a series of reversible spectrum changes, with the isosbestic points at 250 and 347 mμ, as may be seen in Fig. 2. Moreover, a plot of the absorbances at 280 mμ against the pH values gave the curve shown in Fig. 4-a. These spectral evidences seem to indicate that the complex exists in two types of structures in solutions: the type A in solutions with pH<9, and the type B in solutions with pH >11.5.

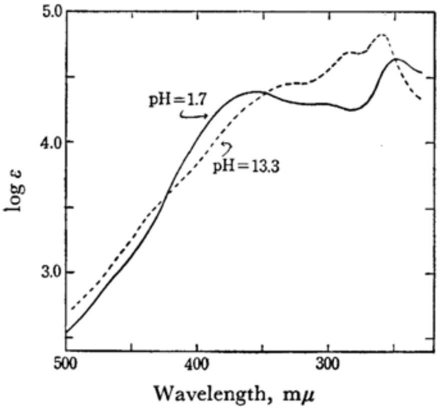


Fig. 1. Electronic spectra of $[Co(dmgH)_2(Aniline)_2]Cl \cdot 4H_2O$ in acid (pH=1.7) and alkaline (pH=13.3) solutions.

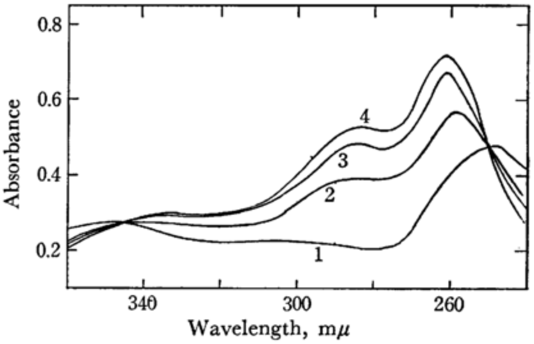


Fig. 2. Electronic spectra of $[Co(dmgH)_2(Aniline)_2]Cl \cdot 4H_2O$ in solutions of various pH.
Initial concentration: 2.18×10^{-5} M
Cell length: 1 cm.
pH: curve 1=5.4, curve 2=10.6, curve 3=11.1, curve 4=12.9

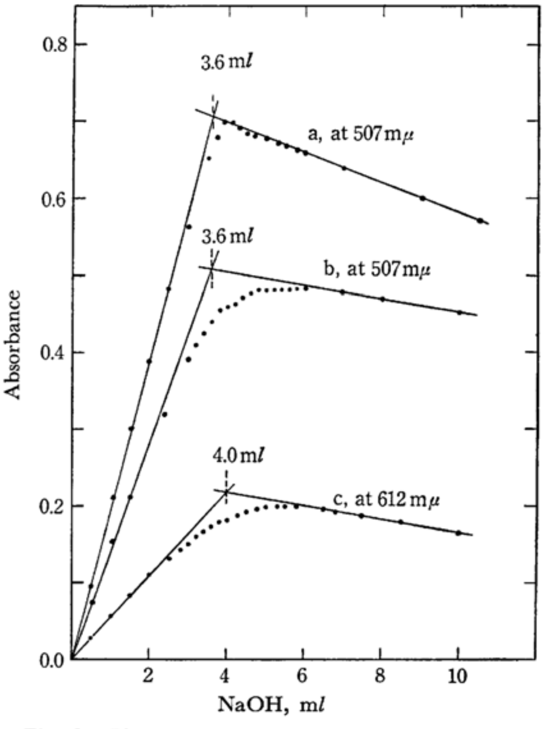


Fig. 3. Photometric titration curves of aqueous complex solutions by standard (0.0416 N) NaOH solution.

		NaOH, ml*
a:	$[Co(dmgH)_2(Pyridine)_2]Cl \cdot H_2O$, 0.160 mmol	3.8
b:	$[Co(dmgH)_2(NH_3)_2]Cl \cdot 5H_2O$, 0.160 mmol	3.8
c:	$[Co(dmgH)_2(Aniline)_2]Cl \cdot 4H_2O$, 0.168 mmol	4.1

* Calculated amount of NaOH, ml

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

7) C. Matsumoto, T. Kato and K. Shinra, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **86**, 1266 (1965).

8) L. Tschgaeff, *Ber.*, **39**, 2701 (1906).

9) H. Kuroya, *J. Institute Polytechnics, Osaka City University*, **1**, C1 (1950).

10) N. Maki, This Bulletin, **38**, 2013 (1965).

11) L. Tschgaeff, *Ber.*, **41**, 2230 (1908).

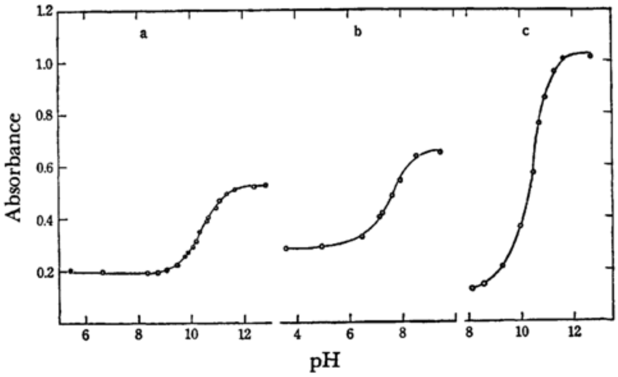

Fig. 4. Absorbance : pH curves.
a: $[Co(dmgH)_2(Aniline)_2]Cl \cdot 4H_2O$, initial concentration$=2.18\times10^{-5}$ M, $\lambda=280$ mμ
b: $[Co(dmgH)_2(Pyridine)_2]Cl \cdot H_2O$, initial concentration$=1.01\times10^{-4}$ M, $\lambda=300$ mμ
c: $[Co(dmgH)_2(NH_3)_2]Cl \cdot 5H_2O$, initial concentration$=1.00\times10^{-3}$ M, $\lambda=420$ mμ
Cell length$=1.0$ cm

The complex thus isolated, given in Table 1, has the formula $[Co(dmgH_2)(aniline)_2]Cl$; in an aqueous solution it shows a spectrum which quite agrees with that of the type A described above. Moreover, the photometric titration of this complex on an aqueous solution with a standard aqueous sodium hydroxide indicated that one mole of the complex is equivalent to one mole of sodium hydroxide, as is shown in Fig. 3.

Thus the above experimental results show that the conversion of the type A to the type B is accompanied by an proton dissociation of the complex. The ionization constants (pK_a) associated with this proton dissociation for the aniline complex was, then, spectrophotometrically obtained as 10.5 on the basis of the following relation: in the absorbance : pH curve shown in Fig. 4-a the pH value corresponding to the absorbance which is equal to $(D_A+D_B)/2$ should represent the pK_a. In this equation, D_A and D_B are the absorbances due to the complexes of the type A and of the type B respectively; they can be evaluated from the curve extrapolated according to the method of Stenström and Goldsmith.⁵⁾

All the other complexes listed in Table 1 display spectral changes analogous to those of the aniline complex. The isosbestic points of the spectral changes are shown in Table 1. Also listed in Table 1 are the pK_a values with respect to each complex determined from the absorbance : pH curves shown in Figs. 4 and 5.

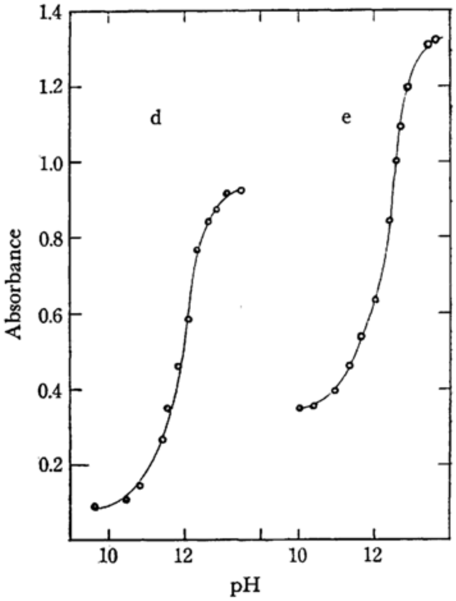

Fig. 5. Absorbance : pH curves.
d: $[Co(dmgH)_2NH_3 \cdot Cl]$, initial concentration$=1.02\times10^{-3}$ M, $\lambda=440$ mμ
e: $NH_4[Co(dmgH)_2(NO_2)_2] \cdot H_2O$, initial concentration$=1.00\times10^{-3}$ M, $\lambda=420$ mμ
Cell length$=1.0$ cm

Discussion

It has been considered on the basis of NMR[12,13] and IR[13,14] spectroscopic studies and the chemical characteristics,⁶⁾ that, in a series of cobalt(III)-dimethylglyoxime complexes with the formula $[Co(dmgH)_2A_2]^n$,*² the central cobalt ion coordinates two dimethylglyoximato radicals to form a planar configuration including stable, intramolecular hydrogen bridges and two moles of A as

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12) H. A. O. Hill, K. G. Morallee and R. E. Collis, *Chem. Commun.*, **1967**, 888; Y. Yamano, I. Masuda and K. Shinra, *Inorg. Nucl. Chem. Letters*, **4**, 581 (1968).

13) R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, **1963**, 6041.

14) A. Nakahara, J. Fujita and R. Tsuchida, This Bulletin, **29**, 296 (1956).

axial ligands. As for the ammine complex with A=NH_3, X-ray crystallography has confirmed it to have a planar chelate structure.[15)]

The electronic spectra of the complexes with A=NH_3, NO_2^-, or a halide anion have also been reported by several workers.[16)] Matsumoto[7)] has stated that the complexes with A=aniline derivatives are characterized by two intense ($\log \varepsilon \doteqdot 4$) absorption bands; one is due to the Co(III)→dmgH charge transfer observed around 300 mμ, and the other, to the axial ligand A→Co(III) charge transfer in the range of 350—410 mμ. However, there seems to have been no study which has dealt, in detail, with the spectral changes in the complexes.

As has been shown in the present study, the $[Co(dmgH)_2A_2]^n$ complexes, listed in Table 1 change their electronic spectra reversibly depending on the pH of the solution. From such spectral changes as those shown in Figs. 4 and 5, the complexes may be considered to exist in the solution in two forms, the type A in acid and neutral media and the type B in an alkaline medium. The isolated complexes with the $[Co(dmgH)_2A_2]^n$ composition show, in aqueous solutions, electronic spectra which agree with those of the corresponding A-type complex, and they consume one equivalent of an aqueous sodium hydroxide to change into a B-type complex.

From a consideration of these experimental results and in view of the structure of the complexes, it seems most reasonable to conclude that the electronic spectral changes of the $[Co(dmgH)_2A_2]^n$ are due to the proton dissociation of hydrogen in the hydrogen bridges of the complexes, as is shown in Eq. (1).

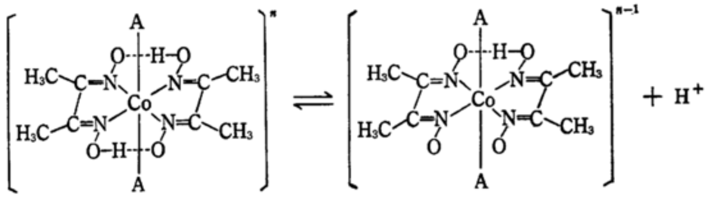
Further support for the above conclusion comes from the fact that, in the case of 1,2-cyclohexanedionedioxime (niH_2), which is analogous to the dimethylglyoxime, two types of complexes, $[Co(niH)_2(p\text{-anisidine})_2]Cl$ and $[Co(niH)(ni)(p\text{-anisidine})_2]$, have been isolated.[17)] As to α-benzildioxime(bzH_2), the complex with the $[Co(bzH)(bz)(p\text{-anisidine})_2]$ formula is also known.

The dissociation constants, pK_a(Table 1), associated with Eq. (1) indicate that the $[Co(dmgH)_2A_2]^n$ complex is generally a very weak acid. With the exception in the pyridine complex, monovalent complex-cation always shows pK_a=9.9—10.9, and the monovalent complex-anion, pK_a=12.6, while a neutral complex shows pK_a values between them (Table 1).

In the cobalt complexes with dimethylglyoxime, the tendency to form O–H–O hydrogen bonding shown in Fig. A has been considered to be very strong. In fact, the complex with the $Co(dmgH)_3$ composition, where a similar hydrogen bonding is lacking, can be synthesized only in a strong alkaline solution.[14)] However, as has been seen in the present work, the $[Co(dmgH)_2A_2]^n$ complexes (Fig. A) may be characterized as acids, though they are very weak (Table 1). As for their conjugate bases $[Co(dmgH)(dmg)A_2]^{n-1}$ (Fig. B), the remaining hydrogen bridge was not observed to dissociate the proton under the experimental conditions (pH≦13) employed. This seems to be mainly due to the stronger hydrogen bonding in the $[Co(dmgH)(dmg)A_2]^{n-1}$ than in the corresponding $[Co(dmgH)_2A_2]^n$, since the increase in the negative charges of a complex ion of this type may only slightly increase the pK_a value in 1—2, as is indicated in Table 1.

In general, an oxime group may be expected to increase its tendency to dissociate the proton when coordinated to a transition metal ion. The iron(II) complex with pyridine-2-aldoxime, $[Fe(PAO)_3H_2]^+$,*3 dissociates proton showing pK_a=3.36, and as to $[Fe(PAO)_3H]$, its pK_a=7.13; in the case of the palladium complex, $[Pd(PAO)_2H]^+$, the pK_a is 4.0, though a free pyridinealdoxime gives pK_a=10.22 referred to its oxime group.[3,4)]

In comparison with the above facts, in the case of dimethylglyoxime-Co(III) complexes, the oxime group shows a much larger pK_a value than that expected from the pK_a value of free dimethylglyoxime, which is known to be about 11.[18)] The



(1)

Fig. A

Fig. B

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15) K. S. Viswanathan and N. R. Kunchur, *Acta Cryst.*, **14**, 675 (1961).

16) A. Nakahara, This Bulletin, **28**, 207 (1955).

*3 Pyridine-2-aldoximato anion is abbreviated as PAO.

17) C. Matsumoto, I. Masuda and K. Shinra, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **88**, 46 (1967).

18) T. V. Parke and W. W. Davis, *Anal. Chem.*, **26**, 642 (1954).

larger pK_a values for the complexes may be attributable to the hydrogen bonding in the dimethylglyoxime-Co(III) complexes (Fig. A).

Finally, it is of interest to note that pyridine and γ-picoline complexes show somewhat lower pK_a values than those of the other complexes, as may be seen in Table 1; this indicates that axial pyridine derivatives tend to facilitate the proton dissociation of hydrogen bridges in the complexes. It appears that this can be understood by assuming a double bonding character between the nitrogen atom in the pyridine ring and the central cobalt, which would make easy the transmittance of an electronic effect of the axial ligand to the oximato radical. A study of this point in some detail will be presented in a subsequent paper.