On the Planar Structure of the Bis(dimethylglyoximato)cobalt(I) Complex

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The bis(dimethylglyoximato)cobalt(III) complexes with a trans-configuration cited below have all been found to be reduced to the cobalt(I) state in non-aqueous solvents such as a DMSO (dimethyl sulfoxide); no further reduction to the metal takes place over the potential range between 0 and −2.70 V (*vs.* SCE): $H[CoCl_2(dgH)_2]$,1) $Na[Co(NO_2)_2(dgH)_2]\cdot H_2O$, $H[Co(NCS)_2(dgH)_2]$, $H[Co(CN)(dgH)_2Cl]\cdot 4H_2O$, $(NH_4)_2[Co(CN)(dgH)_2(SO_3)]\cdot 4H_2O$, $[Co(CN)(dgH)_2(OH_2)]\cdot 3H_2O$,2) $[Co(CN)(dgH)_2(NH_3)]\cdot \frac{1}{2}H_2O$, $[Co(dgH)_2(NH_3)_2]ClO_4$, $[Co(dgH)_2(py)(NH_3)]$,1) $[Co(dgH)_2(OH_2)_2]ClO_4$,2) $[Co(dgH)_2(OH_2)(NH_3)]OCOCH_3$, $[CoX(dgH)_2(NH_3)]$ (X=I, Br, Cl, F2)), $Na[Co(CN)_2(dgH)_2]\cdot 2H_2O$.

The most striking feature of this result is that the liberation of the fifth and the sixth ligand occurs at the cobalt(I) state during the reduction, except for the case of cyanide ligands. The anodic wave of free ligand ions released from the complex was detected to exist by using a Kalousek commutator. Therefore, it seems likely that the contribution of the two ligands located above and below the $[Co(dgH)_2]$structure need not be accounted for in determining whether or not the cobalt(I) state can exist during the reduction. That is, the resulting cobalt(I) complex would take a planar structure of the $[Co^I(dgH)_2]$ type with a pair of hydrogen bonds, as is indicated in the following;

$$trans\text{-}[Co^{III}X_2(dgH)_2]^{n-} \xrightarrow{2e} [Co^I(dgH)_2]^- + 2X^{m-}.$$

In contrast to this behavior with a trans-configuration, the tris(dimethylglyoximato)cobalt(III) complex3) was found to be reduced to the metal *via* the cobalt(II) complex in the DMSO containing 0.1 M $[(C_2H_5)_4N]ClO_4$ at the dropping mercury electrode:

$$[Co^{III}(dgH)_3] \xrightarrow{e} [Co^{II}(dgH)_3]^- \xrightarrow{2e} Co(\textit{metal}).$$

No cobalt(I) state was found upon the reduction. This is consistent with the prediction that the $[Co^I(dgH)_2]^-$ anion with a planar structure could not be formed from the reduction of the cobalt(III) complexes with a *cis*-configuration, since it is not likely that the rearrangement of ligands, *viz.*, the isomerization, takes place in DMSO. Inversely, this result can be invoked to emphasize the importance of the planarity of the bis(dimethylglyoximato)cobalt(I) complex from the standpoint of the electronic structure.

Figure 1 illustrates the current-potential curves for the *trans*-$[Co^{III}F(dgH)_2(NH_3)]$ and $[Co(dgH)_3]\cdot 2.5H_2O$ complexes measured under the same experimental conditions. In the figure, the wave-height is approximately proportional to the number of electrons participating in the electrode processes, since the limiting current of both the waves is diffusion-controlled.

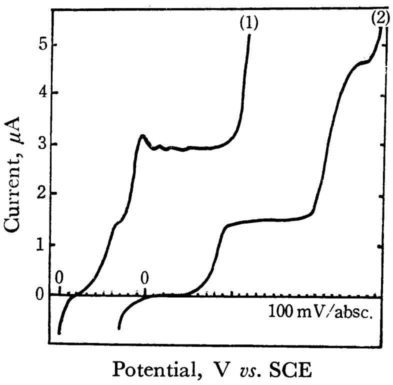

Fig. 1. Typical current-potential curves obtained at the concentration of 10^{-3}M under the same conditions (25°C): (1) *trans*-$[CoF(dgH)_2(NH_3)]$; (2) $[Co(dgH)_3]\cdot 5/2\ H_2O$ in the DMSO containing 0.1M$[(C_2H_5)_4N]ClO_4$.

Table 1. Half-wave potentials of *trans*- and *cis*-bis(dimethylglyoximato)cobalt(III) complexes in DMSO containing 0.1M$[(C_2H_5)_4N]ClO_4$(25°C)

Compound	1st Wave	2nd Wave
trans-$[CoF(dgH)_2(NH_3)]$	−0.59 $(Co^{III}\rightarrow Co^{II})$	−0.81 $(Co^{II}\rightarrow Co^{I})$
trans-$[CoCl(dgH)_2(NH_3)]$	−0.58 $(Co^{III}\rightarrow Co^{II})$	−0.81 $(Co^{II}\rightarrow Co^{I})$
trans-$H[CoCl_2(dgH)_2]$	——a) $(Co^{III}\rightarrow Co^{II})$	−0.81 $(Co^{II}\rightarrow Co^{I})$
trans-$[Co(dgH)_2(NH_3)_2]ClO_4$	−0.74 $(Co^{III}\rightarrow Co^{I})$	
$[Co(dgH)_3]\cdot 5/2H_2O$	−0.81 $(Co^{III}\rightarrow Co^{II})$	−2.11 $(Co^{II}\rightarrow Co^{0})$
cis-$[Co(dgH)_2en]ClO_4\cdot 1/3H_2O$	−0.87 $(Co^{III}\rightarrow Co^{II})$	−2.29 $(Co^{II}\rightarrow Co^{0})$
cis-$[Co(dgH)_2(NH_3)_2]ClO_4\cdot 7H_2O$	−0.82 $(Co^{III}\rightarrow Co^{II})$	−2.04 $(Co^{II}\rightarrow Co^{0})$

a) The 1st wave lies at positive region of potential. V *vs.* SCE

Table 1 presents some examples of the electrode processes and their half-wave potentials. Thus, the cis- *vs.* trans-distinction has been clearly demonstrated polarographically with regard to the stability of the cobalt(I) complex in DMSO; a similar differentiation was shown to be possible for the *cis*- and *trans*- tetracyano cobalt(III) complexes in aqueous solutions.4) This method of distinguishing steric isomers is more promising than that based on the spectra,5) because the latter is more complicated; its interpretation and assignment is based on the infrared spectra.

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1) Abbreviations used: $dg=CH_3\cdot C(NO)C(NO)\cdot CH_3$; py=pyridine.

2) Novel complexes, which have not yet been reported.

3) A. Nakahara, This Bulletin, **27**, 560 (1954).

4) N. Maki and K. Yamamoto, This Bulletin, **43**, 2450 (1970).

5) R. D. Gillard and G. Willkinson, *J. Chem. Soc.*, **1963**, 6041.