that each deprotonation site generates its own conjugate base. This was not observed. In view of the mechanism found for the ammoniation of the azido and isothiocyanato complexes, it is remarkable that there are no indications for rate-limiting deprotonation on base hydrolysis of these compounds.[25]

Acknowledgment. This work has benefited much from preliminary studies in which Dr. W. E. Renkema and Dr. H. J. A. M. Kuipers have participated.

Registry No. *trans*-$[Co(en)_2(N_3)Cl]ClO_4$, 30051-75-3; *trans*-$[Co(en)_2(N_3)Br]ClO_4$, 82704-31-2; *trans*-$[Co(en)_2(N_3)(Me_2SO)](ClO_4)_2$, 82768-63-6; *trans*-$[Co(en)_2(NCS)Cl]ClO_4$, 13820-98-9; *trans*-$[Co(en)_2(NCS)Br]ClO_4$, 88510-77-4; NH_3, 7664-41-7; Cl_2, 7782-50-5; Br_2, 7726-95-6; Me_2SO, 67-68-5.

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[25] We observed that *trans*-$[Co(en)_2N_3Cl]^+$ exchanges its protons in ^2H_2O before base hydrolysis.

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Electrochemistry of Bis(dibenzoylmethanato)cobalt(II) in Dimethyl Sulfoxide

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The homogeneous chemical equilibria and the electrochemical behavior of bis(dibenzoylmethanato)cobalt(II) in dimethyl sulfoxide were studied by molar mass, conductivity, and ultraviolet spectral measurements, polarography, and cyclic voltammetry with a platinum electrode. It was found that $Co(dbm)_2$ was involved in the following equilibria in the solution: $Co(bi\text{-}dbm)_2 \rightleftharpoons Co(bi\text{-}dbm)(uni\text{-}dbm) \rightleftharpoons Co(dbm)^+ + dbm^-$; $Co(dbm)_2 + dbm^- \rightleftharpoons Co(dbm)_3^-$. In the above formulas, bi- and uni- mean that the ligand coordinate to the metal as bidentate and unidentate, respectively. Two waves at less negative potentials were explained as due to the two-electron reduction of different species, followed by the dissociation reactions; the first wave is mainly due to the reduction of Co(bi-dbm)(uni-dbm) and the second wave to that of $Co(bi\text{-}dbm)_2$.

Introduction

Much attention is being given to the metal complexes with β-diketones in both the pure and applied chemistry fields. In previous papers,[2-4] the voltammetric studies of bis(β-diketonato)nickel(II) complexes in dimethyl sulfoxide solutions provided useful information regarding the homogeneous chemical equilibria.

Matschiner et al.[5] studied the electrochemical behavior of bis(β-diketonato)cobalt(II) complexes of $Co(bzac)_2$, $Co(dbm)_2$, and $Co(acac)_2$[6] in nonaqueous solvents such as *N,N*-dimethylformamide and a mixed solvent of tetrahydrofuran-acetonitrile. According to the results, the electrochemical reduction mechanism of $Co(bzac)_2$ and $Co(dbm)_2$ was presented as

$$CoL_2 \overset{e^-}{\rightleftharpoons} CoL_2^- \overset{e^-}{\rightleftharpoons} CoL_2^{2-}$$

$$CoL_2^{2-} \rightarrow Co^0 + 2L^-$$

$$2CoL_2 + 2L^- \rightleftharpoons 2CoL_3^-$$

On the other hand, $Co(acac)_2$ was found to be irreversibly reduced in one step; however, the electrode reaction was not studied in detail.

This paper presents an investigation on the electrochemistry of bis(dibenzoylmethanato)cobalt(II) in dimethyl sulfoxide.

Experimental Section

Reagents. Dimethyl sulfoxide (Me_2SO) was the same as described previously.[7] Me_2SO was stored in a taped solvent bottle fitted with an automatically zeroing buret in a room with a low percentage of humidity. The Nakarai Chemicals tetrabutylammonium perchlorate (TBAP) purified for polarographic measurements was recrystallized once from ethanol, followed by drying in vacuo at room temperature for a minimum of 24 h. After cobalt(II) perchlorate hexahydrate was prepared by the reaction of cobalt(II) carbonate with perchloric acid,[8] it was brought to a constant weight in a desiccator over magnesium perchlorate.[9]

Bis(dibenzoylmethanato)cobalt(II) ($Co(dbm)_2$) was obtained as the monohydrate by the method available in the literature.[10]

Tris(dibenzoylmethanato)cobalt(III) ($Co(dbm)_3$) was synthesized by the same method as tris(acetylacetonato)cobalt(III).[11]

Tetrabutylammonium dibenzoylmethanate (n-$Bu_4N(dbm)$) was prepared according to the method of Buchta and Evans.[12] The salt was stored in the dark under dried nitrogen.

Apparatus and Procedures. Dc and differential-pulse (DP) polarograms were obtained with a Yanagimoto P-1000 voltammetric analyzer and a Watanabe WX-4404 X-Y recorder. The electrolysis cell for polarographic measurements reported previously[7] was modified in order to keep test solutions strictly away from atmospheric moisture. The capillary for the dropping-mercury electrode had an m value of 0.890 mg s^{-1} and a drop time, t_d, of 6.60 s at -1.0 V vs. SCE when measured in an air-free 0.05 mol dm^{-3} TBAP-Me_2SO solution at a mercury reservoir height of 50 cm. The mean current, $\bar{i}$, was measured in the case of dc polarography.

Cyclic voltammograms were obtained with a Hokuto Denko LS-1C linear scanner or an Iwatsu Denshi FG-330 function generator, a Nikko Keisoku DPGS-1 dual potentiogalvanostat, and a Riken Denshi F-32 X-Y plotter. Current-potential curves for scan rates higher than 500 mV s^{-1} were checked with an Iwatsu Denshi SS-5100 synchroscope. A Pt-button electrode (surface area 0.080 cm^2) was used as the working electrode for cyclic voltammetry. The electrolysis cell was similar to one described by Nawi and Riechel.[13]

Current-potential curves were measured with the three-electrode system at 25.0 ± 0.2 °C except for temperature-effect experiments. All the test solutions were deaerated for ca. 30 min with nitrogen gas in a thermostat before measurements. An aqueous saturated calomel electrode (SCE) was used as a reference electrode. As for the supporting electrolyte, 0.05 mol dm^{-3} TBAP was used unless otherwise stated.

Controlled-potential electrolysis was performed on a Yanagimoto VE-8 controlled-potential electrolyzer and a Nikko Keisoku NDCM-2 digital coulometer at a mercury-pool cathode at room temperature under a nitrogen atmosphere.

Conductivities were measured with a Yanagimoto MY-8 conductivity outfit at 25.00 ± 0.05 °C. The bright platinum electrode was used.

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(1) Present address: Chemical Laboratory, Yamagata Building Service Co., Ltd., Iizuka-machi, Yamagata 990, Japan.
(2) Kudo, S.; Iwase, A.; Tanaka, N. *Bull. Chem. Soc. Jpn.* **1982,** *55,* 1416.
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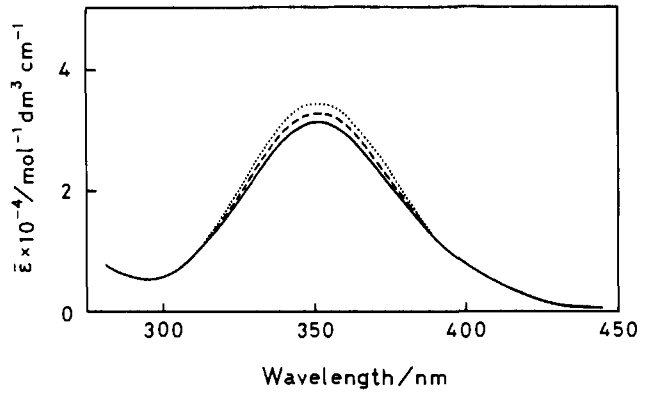

Figure 1. UV spectra of $Co(dbm)_2$ in Me_2SO. Concentrations (mmol dm^{-3}): (···) 0.01; (--) 0.1; (—) 0.7.

Table I. Polarographic Data for the Reduction of $Co(dbm)_2$, Hdbm, and *n*-Bu_4N(dbm) in 0.05 mol dm^{-3} TBAP–Me_2SO

compd	($E_{1/2}$ vs. SCE)/V	slope/mV	$\bar{i}_j/\bar{i}_t$[a]
$Co(dbm)_2$	-1.59	53	0.47
	-1.78	65	0.53
	~-2.4		
	-2.74		
Hdbm[b]	-1.37	68	
	-1.69		
	-2.27	50	
	-2.68		
n-Bu_4N(dbm)[b]	-2.27	50	
	-2.68		

[a] The $\bar{i}_j/\bar{i}_t$ ratios for $Co(dbm)_2$ were obtained at a concentration of 1 mmol dm^{-3} at a controlled drop time. The meanings of $\bar{i}_j$ and $\bar{i}_t$ are shown in Figure 2, where j = 1, 2. [b] Reference 3.

Electronic spectra were recorded on a Schimadzu UV-240 spectrophotometer at 25.0 ± 0.5 °C by using quartz cells of 0.1- and 1.0-cm optical lengths.

The molar mass of the complex in Me_2SO was determined by cryoscopy, with tris(acetylacetonato)cobalt(III) as the standard material.

Results

Molar Mass, Conductance, and Electronic Spectral Measurements. The molar mass of the complex in Me_2SO corresponded to that of $Co(dbm)_2{\cdot}2Me_2SO$–$Co(dbm)_2{\cdot}3Me_2SO$.

The molar conductivities of $Co(dbm)_2$ solutions were 0.8–0.5 S cm^2 mol^{-1} in the concentration range 0.01–2 mmol dm^{-3}. On the assumption of the simple dissociation of $Co(dbm)_2$ to the corresponding ions for the 1,1-valency type electrolyte, a 2–1% degree of dissociation would be expected for the above concentrations.

The electronic spectrum of $Co(dbm)_2$ in the visible region was independent of the concentration in the range 2–20 mmol dm^{-3} and was not influenced by the addition of 0.05 mol dm^{-3} TBAP. As shown in Figure 1, however, the apparent molar absorption coefficient ($\bar{\varepsilon}$) of the $\pi \rightarrow \pi^*$ transition in the near-ultraviolet region increased with a decrease in the concentration of the complex, indicating the existence of equilibria in the solution. It was found that $Co(dbm)_2$ resembled $Ni(bzac)_2$ and $Ni(dbm)_2$ in the concentration dependence of $\bar{\varepsilon}$ values of UV spectra; the latter complexes were involved in the following equilibria:[2,3]

$$\mathrm{Ni(bi\text{-}L)_2} \rightleftharpoons \mathrm{Ni(bi\text{-}L)(uni\text{-}L)} \rightleftharpoons \mathrm{Ni(bi\text{-}L)^+} + \mathrm{L^-} \rightleftharpoons \mathrm{Ni(uni\text{-}L)^+} + \mathrm{L^-}$$

where bi- and uni- mean that the ligands coordinate to the metal as bidentate and unidentate, respectively. Furthermore, the addition of 0.05 mol dm^{-3} TBAP to 0.1–0.7 mmol dm^{-3} $Co(dbm)_2$ solutions induced a small increase in the $\bar{\varepsilon}$ value of UV spectra.

Polarography. The data for the polarographic reduction of $Co(dbm)_2$, Hdbm, and n-Bu_4N(dbm) are summarized in Table I. The electrochemical behavior of Hdbm[12] and *n*-Bu_4N(dbm)[12,14] was discussed previously. $Co(dbm)_2$ gave four reduction waves, of which two waves at more negative potentials were considered as due to the reduction of the ligand on the basis of a comparison of the half-wave potential ($E_{1/2}$) of the complex with that of Hdbm or *n*-Bu_4N(dbm). Therefore, the two waves of $Co(dbm)_2$ appearing at less negative potentials will hereinafter be noted.

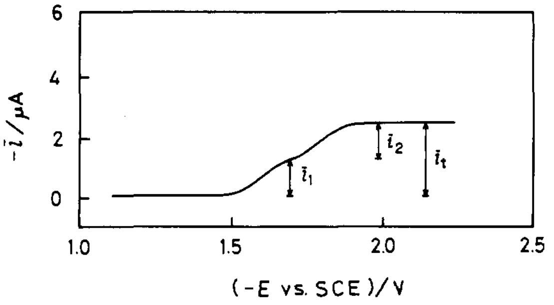

Figure 2. Dc polarogram of 1 mmol dm^{-3} $Co(dbm)_2$ in 0.05 mol dm^{-3} TBAP–Me_2SO.

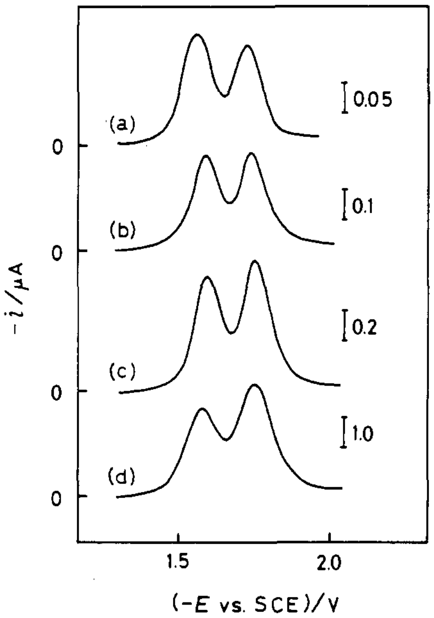

Figure 3. DP polarograms of $Co(dbm)_2$ in 0.05 mol dm^{-3} TBAP–Me_2SO. Concentrations (mmol dm^{-3}): (a) 0.26; (b) 0.45; (c) 1.1; (d) 5.3. Modulation amplitude = 25 mV; pulse interval = 1.0 s.

A typical dc polarogram of $Co(dbm)_2$ is presented in Figure 2. The first limiting current ($\bar{i}_1$) at the least negative potential was diffusion controlled, judging from the dependence of $\bar{i}_1$ on $h_c^{1/2}$, where h_c is the effective height of the mercury reservoir corrected for back-pressure. The total limiting current ($\bar{i}_t$) was also diffusion controlled and was proportional to the concentration of $Co(dbm)_2$ over the range 0.2–10 mmol dm^{-3}. The diffusion current constant obtained from the $\bar{i}_t$ value was approximately equal to that of the two-electron-reduction wave of the solvated Co^{2+}.[9] The ratio $\bar{i}_1/\bar{i}_2$ was independent of temperature (25–50 °C), but it increased with decreasing concentration of $Co(dbm)_2$. Such a concentration dependence of the cathodic current ratio is clearly illustrated by the DP polarograms shown in Figure 3. This finding indicates that the electrode reaction does not correspond to a consecutive one-electron-transfer process. In addition, the ratio of $\bar{i}_1/\bar{i}_2$ increased to some extent with an increase in the concentration of TBAP (0.05–0.20 mol dm^{-3}). Although the slopes of the log $[\bar{i}/(\bar{i}_d - \bar{i})]$ vs. E plots of $Co(dbm)_2$ were close to the theoretical value for a reversible one-electron-transfer process, that is 59 mV (Table I), the half-wave potentials of two waves shifted to more negative potentials with a decrease in t_d. On the basis of a DP polarographic diagnosis,[15] the electrode reaction

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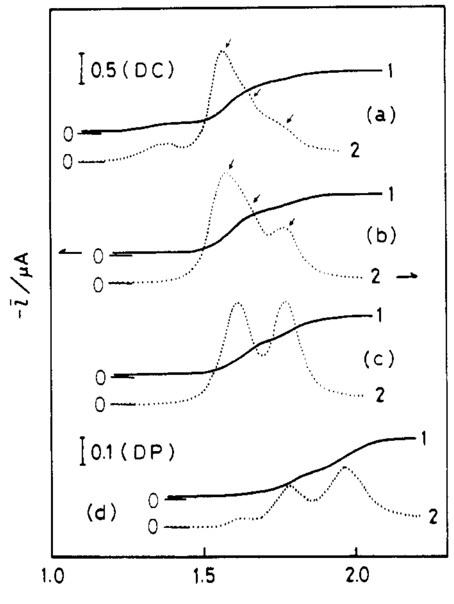

Figure 4. Dc (1) and DP (2) polarograms of Co(II)–dbm complexes in 0.05 mol dm^{-3} TBAP–Me_2SO solutions containing the ligand at different concentrations and 0.5 mmol dm^{-3} $Co(ClO_4)_2$. Concentrations (mmol dm^{-3}) of n-Bu_4N(dbm): (a) 0.50; (b) 0.65; (c) 1.0; (d) 2.0. Conditions: (1) t_d = 1.0 s; (2) modulation amplitude = 25 mV; pulse interval = 1.0 s.

was decided to be not reversible. Thus, the two waves for Co$(dbm)_2$ appearing at less negative potentials are due to a consecutive irreversible two-electron reduction of different species involved in an equilibrium in the solution but for which the rate of reestablishment of the equilibrium is slow.[16,17]

By the addition of n-Bu_4(dbm) to a solution of $Co(dbm)_2$, the $\bar{i}_1$ value decreased and a new wave (the third wave) appeared at ca. −2.0 V. Under such conditions, the ratio $\bar{i}_2/\bar{i}_3$ decreased with a decrease in t_d (4.0–0.5 s). These findings suggest the formation of $Co(dbm)_3^-$ in the bulk solution.

The dc and DP polarograms of the solutions containing 0.5 mmol dm^{-3} $Co(ClO_4)_2$ and n-Bu_4N(dbm) at different concentrations were measured in order to know the reduction potentials for the species which might be formed in the Co(II)–dbm$^-$ system (Figure 4). The mole ratios (dbm/Co) of solution giving curves a–d in Figure 4 are 1.0, 1.3, 2.0, and 4.0, respectively. The polarograms of curves c agreed with those of 0.5 mmol dm^{-3} $Co(dbm)_2$. In curve a, the wave (or peak) at the least negative potential is due to the reduction of Co^{2+} not bound to dbm$^-$, because it coincides in reduction potential with the free Co$(Me_2SO)_6^{2+}$ obtained from a solution containing $Co(ClO_4)_2$.[9,18] On the basis of a comparison of dc and DP polarograms, it is apparent that the waves at ca. −1.6 V of dc polarograms in curves a(1) and b(1) are composite ones. The peaks at −1.57 V of DP polarograms in curves a(2) and b(2) seem to be due to the reduction of $Co(dbm)^+$, though the plot of peak current (i_p) vs. mole ratio (dbm/Co) is difficult to interpret without a separation of overlapping peaks. As will be explained later with the results given in Figure 7, this assignment is supported by the cyclic voltammetry of a solution containing 1 mmol dm^{-3} $Co(ClO_4)_2$ and 0.5 mmol dm^{-3} n-Bu_4N(dbm). The wave (or peak) at the most negative potential of curves d is the same one as obtained by the addition of n-Bu_4N(dbm) to a solution of $Co(dbm)_2$. It is, therefore, reasonable to consider that $Co(dbm)_2$ exists as two dissolved species of the bis complex.

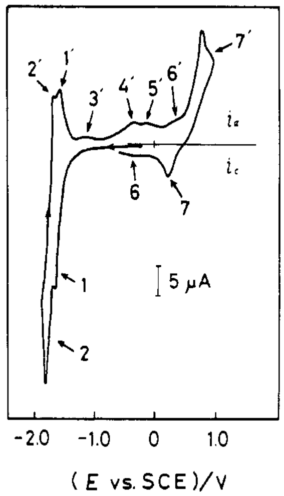

Figure 5. Cyclic voltammogram of 5 mmol dm^{-3} $Co(dbm)_2$ in 0.05 mol dm^{-3} TBAP–Me_2SO. Scan rate = 25 mV s^{-1}.

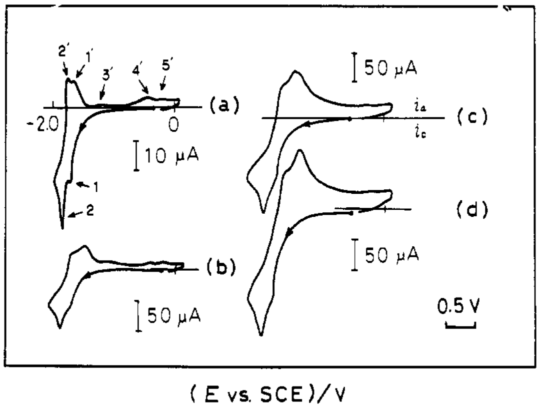

Figure 6. Cyclic voltammograms of 5 mmol dm^{-3} $Co(dbm)_2$ in 0.05 mol dm^{-3} TBAP–Me_2SO. Scan rates (mV s^{-1}): (a) 25; (b) 200; (c) 670; (d) 1320.

Table II. Cyclic Voltammetric Data Based on the Reduction of $Co(dbm)_2$ in 0.05 mol dm^{-3} TBAP–Me_2SO[a]

	(E_p vs. SCE)/V		
peak[b]	E_{pc}	E_{pa}	$\Delta E_p/V$[c]
1/1′	−1.66	−1.52	0.14
2/2′	−1.81	−1.66	0.15
3′		−1.15	
4′		−0.40	
5′		−0.15	

[a] Scan rate = 25 mV s^{-1}. [b] See Figure 5. [c] $\Delta E_p = E_{pa} - E_{pc}$.

Table III. Cyclic Voltammetric Data Based on the Oxidation of $Co(dbm)_2$ in 0.05 mol dm^{-3} TBAP–Me_2SO[a]

	(E_p vs. SCE)/V		
peak[b]	E_{pa}	E_{pc}	$\Delta E_p/V$[c]
6′/6	+0.35	∼−0.5	0.8–0.9
7′/7	+0.73	+0.20	0.53

[a] Scan rate = 25 mV s^{-1}. [b] See Figure 5. [c] $\Delta E_p = E_{pa} - E_{pc}$.

Cyclic Voltammetry. A typical cyclic voltammogram of Co$(dbm)_2$ is shown in Figure 5. Reduction peaks 1 and 2 were observed on an initial negative scan, corresponding to the polarographic ones. Oxidation peaks 1′, 3′, 4′, and 5′ were obtained after cathodic scanning of reduction peak 1, while oxidation peak 2′ was obtained only after cathodic scanning of reduction peak 2. In addition, oxidation peaks 6′ and 7′ appeared on an initial positive scan and reduction peaks 6 and 7 were observed only after anodic scanning of peaks 6′ and 7′, respectively. The peak currents $(i_p)_{6'}$ and $(i_p)_{7'}$ were proportional to $v^{1/2}$, where v means the po-

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(16) Vlček, A. A. *Prog. Inorg. Chem.* **1963**, *5*, 211.
(17) The term "slow" means that the reaction proceeds so slowly that its occurrence practically can be neglected in the vicinity of the electrode surface during electrolysis.
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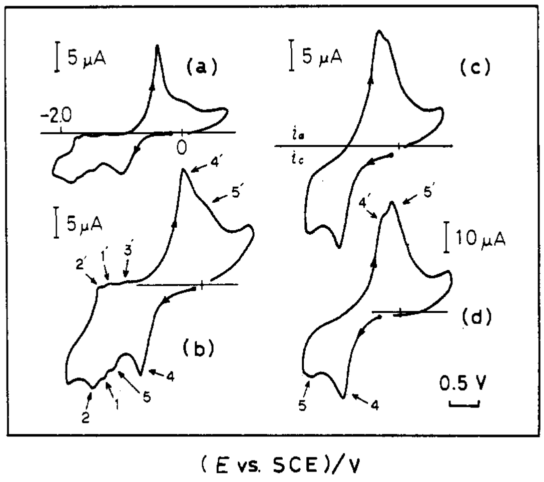

Figure 7. Cyclic voltammograms of Co(II)–dbm complexes in 0.05 mol dm^{-3} TBAP–Me_2SO solution containing 1 mmol dm^{-3} $Co(ClO_4)_2$ and 0.5 mmol dm^{-3} n-$Bu_4N(dbm)$. Scan rates (mV s^{-1}): (a) 50; (b) 200; (c) 200; (d) 510.

tential scan rate. For scan rates higher than 500 mV s^{-1}, it was confirmed that cyclic voltammograms recorded with an X-Y plotter were identical with those obtained with a synchroscope. As the scan rate increased, the peak potentials (E_p) of peaks 1 and 2 shifted to more negative potentials and those of peaks 6′ and 7′ shifted to more positive potentials. Such a scan rate dependence of peak potentials indicates that both the reduction and the oxidation of $Co(dbm)_2$ are irreversible. The cyclic voltammetric data of the complex are summarized in Tables II and III. Figure 6 represents the influence of scan rates on the cyclic voltammograms of 5 mmol dm^{-3} $Co(dbm)_2$. The following results were obtained.

(1) The voltammetric peak current ratio $(i_p)_{1'}/(i_p)_{2'}$ was dependent on the scan rate, but it was not appreciably varied at high scan rates as seen in curves c and d.

(2) Peaks 3′, 4′, and 5′ substantially disappeared at high scan rates as seen in curves c and d, indicating that they mainly correspond to the separate steps occurring after the reduction. The electroreduction of $Co(dbm)_2$ followed by the dissociation reactions is verified by the appearance of peak 4′ coinciding with an anodic stripping peak of Co^0 at low scan rates as seen in curves a and b.

The information on oxidation peak 5′ was obtained from the cyclic voltammograms (Figure 7) of a solution containing 1 mmol dm^{-3} $Co(ClO_4)_2$ and 0.5 mmol dm^{-3} n-$Bu_4N(dbm)$. Peak 4 is due to the reduction of the solvated Co^{2+}, and peak 4′ is an anodic stripping peak of Co^0. Oxidation peak 5′ was observed after the cathodic scanning of reduction peak 5. The ratio $(i_p)_{4'}/(i_p)_{5'}$ decreased significantly with an increase in the scan rate. It follows from these that peak 5′ comes from the oxidation of $Co(dbm)^-$ and that the ligand is liberated from the species under the conditions of the experiments in Figure 7. Note the correspondence of peak 5 in Figure 7 to the peaks at −1.57 V observed in DP polarograms of curves a(2) and b(2) in Figure 4.

Two redox couples of peak 6′/peak 6 and peak 7′/peak 7 were also studied. The variation in current of these peaks was observed after the addition of n-$Bu_4N(dbm)$ to the solution of $Co(dbm)_2$ (Figure 8). The one-electron-oxidation peak of dbm^- [14] appeared at +0.55 V (peak 8′). With an increase in the ligand concentration in the solution, $(i_p)_6$ and $(i_p)_{6'}$ increased, while $(i_p)_7$ and $(i_p)_{7'}$ diminished. The potential of peak 6 coincides with that of the one-electron reduction of $Co(dbm)_3$. Thus, it seems probable that peaks 6′ and 7′ are attributed to the one-electron oxidation of $Co(dbm)_3^-$ and $Co(dbm)_2$, respectively. The one-electron-transfer process of peak 7′ was confirmed by using well-known theoretical expressions for irreversible processes,[19] when the existence of

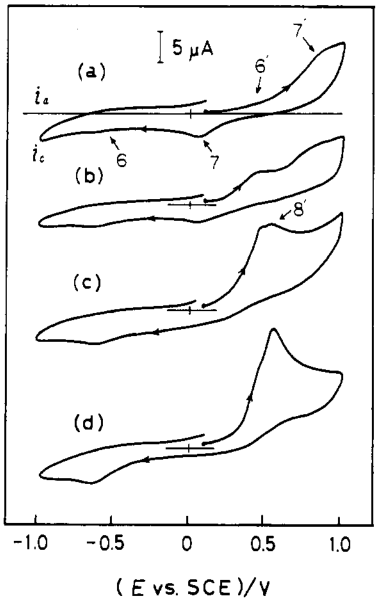

Figure 8. Effect of addition of n-$Bu_4N(dbm)$ on the cyclic voltammogram of 1 mmol dm^{-3} $Co(dbm)_2$ in 0.05 mol dm^{-3} TBAP–Me_2SO. Concentrations (mmol dm^{-3}) of n-$Bu_4N(dbm)$: (a) 0; (b) 0.5; (c) 1.0; (d) 2.0. Scan rate = 200 mV s^{-1}.

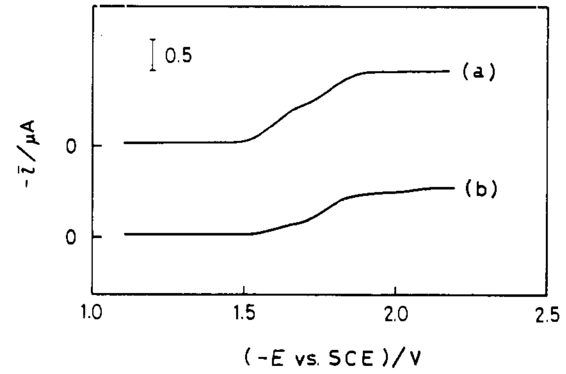

Figure 9. Dc polarograms of (a) 0.5 mmol dm^{-3} $Co(dbm)_2$ and (b) a solution after reduction of solution a at −1.70 V (280 mC) in 0.05 mol dm^{-3} TBAP–Me_2SO. The volume of electrolytic solution used was 5.0 cm^3.

$Co(dbm)_3^-$ was neglected in determining the total complex concentration because no n-$Bu_4N(dbm)$ was added. The diffusion coefficient used in the calculation of number of electrons transferred was 2.5×10^{-6} cm^2 s^{-1}, the mean value obtained from the Ilkovic equation polarographically. The peak current ratio $(i_p)_{6'}/(i_p)_{7'}$ did not seem to increase after the reduction of the main species compared with that obtained on an initial positive scan even at the slow scan rate giving curve a in Figure 6. This finding should be remembered in the discussion of the chemical reaction after the electron transfer given in the following section. The reduction peak for $Co(dbm)_3^-$ in the solution containing $Co(dbm)_2$ was detected in the DP polarogram, which was obtained at high sensitivity.

Controlled-Potential Electrolysis. As shown in Figure 9, the controlled-potential electrolysis of a solution of $Co(dbm)_2$ at −1.70 V resulted in the formation of $Co(dbm)_3^-$ and also in a decrease in the total limiting current ($\bar{i}_t$) due to the two-electron reduction of Co(II).

Discussion

Homogeneous Chemical Equilibria. $Co(dbm)_2$ exists predominantly as the monomeric bis complex in Me_2SO at concentrations not higher than 10 mmol dm^{-3}, judging from the molar mass determined by cryoscopy, the conductance, and the proportionality of $\bar{i}_t$ to the complex concentration. An increase in the $\bar{\varepsilon}$ value of the UV spectrum of $Co(dbm)_2$ with a decrease in the concentration

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(19) Sawyer, D. T.; Roberts, J. L., Jr. "Experimental Electrochemistry for Chemists"; Wiley: New York, 1974; p 339.

corresponds to an increase in the DP polarographic peak current ratio, $(i_p)_1/(i_p)_2$, as has been shown in Figure 3. Such a tendency observed for $Co(dbm)_2$ in Me_2SO and similar observations on $Ni(bzac)_2$ and $Ni(dbm)_2$ suggest the dissociation of $Co(dbm)_2$. This is explained by the distribution of $Co(dbm)_2$ to the main dissolved species $Co(bi\text{-}dbm)_2$ and Co(bi-dbm)(uni-dbm), which are reduced at −1.59 and −1.78 V, respectively at a dropping-mercury electrode (Table I). The decrease in the $\bar{i}_t$ value by the controlled-potential electrolysis of a solution of $Co(dbm)_2$ at −1.70 V also is not in conflict with this view. As can be seen from the effect of ionic strength on the ratio $\bar{i}_1/\bar{i}_2$ and that of the addition of 0.05 mol dm^{-3} TBAP on the UV spectrum of $Co(dbm)_2$, the chemical equilibria are shifted only by a relatively large amount of the electrolyte used for voltammetric measurements.

Oxidation peak 6′ in the cyclic voltammogram of $Co(dbm)_2$ revealed the existence of a small amount of $Co(dbm)_3^-$ in the bulk of the solution containing $Co(dbm)_2$. Naturally, $Co(dbm)^+$ should be recognized also as a dissolved species in the solution, though the reduction peak for $Co(dbm)^+$ is not distinguishable from those of the main species in both DP polarography and cyclic voltammety owing to its small amount and a small difference in E_p between $Co(dbm)^+$ and Co(bi-dbm)(uni-dbm).

The homogeneous chemical equilibria of $Co(dbm)_2$ in Me_2SO are

$$Co(bi\text{-}dbm)_2 \rightleftharpoons Co(bi\text{-}dbm)(uni\text{-}dbm) \rightleftharpoons Co(dbm)^+ + dbm^-$$

$$Co(dbm)_2 + dbm^- \rightleftharpoons Co(dbm)_3^-$$

where the concentration of $Co(dbm)_3^-$ is presumed to be less than ca. 4% of the total complex concentration. No information could be obtained as to whether or not $Co(uni\text{-}dbm)_2$ exists in the solution. However, the concentration of species of this type seems to be negligibly small compared to the total complex concentration, in analogy with $Ni(dbm)_2$.[3]

Redox Process. On the basis of the experimental results shown in Figures 6–8, the main peaks observed in the cyclic voltammetry of $Co(dbm)_2$ are explained as due to the reduction process followed by the dissociation reactions and the simple one-electron oxidation process.

reduction process

$$Co(bi\text{-}dbm)(uni\text{-}dbm) + 2e^- \rightarrow Co(bi\text{-}dbm)(uni\text{-}dbm)^{2-} \quad \text{peak 1}$$

$$Co(bi\text{-}dbm)_2 + 2e^- \rightarrow Co(bi\text{-}dbm)_2^{2-} \quad \text{peak 2}$$

$$Co(bi\text{-}dbm)_2^{2-} \xrightarrow{k_1} Co(bi\text{-}dbm)(uni\text{-}dbm)^{2-}$$

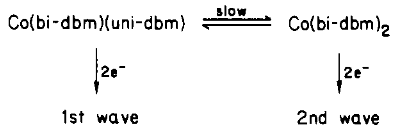
$$Co(bi\text{-}dbm)(uni\text{-}dbm)^{2-} \xrightarrow{k_2} Co(bi\text{-}dbm)^- + dbm^-$$

$$Co(bi\text{-}dbm)^- \xrightarrow{k_3} Co(uni\text{-}dbm)^-$$

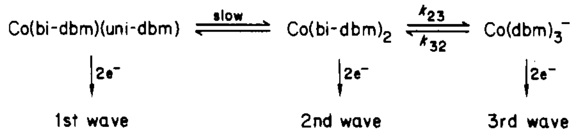
$$Co(uni\text{-}dbm)^- \xrightarrow{k_4} Co^0 + dbm^-$$

The symbols k_1, k_2, k_3, and k_4 are the rate constants of the above dissociation reactions. Since the peak current ratio $(i_p)_{6'}/(i_p)_{7'}$ did not seem to increase after the reduction of depolarizers compared with that obtained on an initial positive scan, the reaction of $Co(dbm)_2$ with dbm^- in the vicinity of the electrode surface during electrolysis could be neglected: this finding may be taken to indicate a role of Me_2SO as solvent in the chemical reaction steps after the electron transfer. In the controlled-potential electrolysis, however, the formation of $Co(dbm)_3^-$ is significant (Figure 9). No definite statement can be made at the moment concerning the assignment of peak 3′, though it may come from the oxidation of $Co(bi\text{-}dbm)^-$ produced by the liberation of dbm^- from $Co(bi\text{-}dbm)(uni\text{-}dbm)^{2-}$.

Information on the reduction process of $Co(dbm)_2$ obtained by dc and DP polarography is given below:[17]



n-$Bu_4N(dbm)$ not added



n-$Bu_4N(dbm)$ added

where k_{32} and k_{23} mean the forward and the backward rate constants, respectively, of the reaction

$$Co(dbm)_3^- \rightleftharpoons Co(bi\text{-}dbm)_2 + dbm^-$$

The dc polarographic current ratios, $\bar{i}_1/\bar{i}_t$ and $\bar{i}_2/\bar{i}_t$, in Table I represent mainly the respective molar fractions of Co(bi-dbm)(uni-dbm) and $Co(bi\text{-}dbm)_2$ for the total complex concentration of 1 mmol dm^{-3} in 0.05 mol dm^{-3} TBAP–Me_2SO:

oxidation process

$$Co(dbm)_2 \rightarrow Co(dbm)_2^+ + e^- \quad \text{peak 7}'$$

The electrochemical and the UV spectral behavior of some bis(β-diketonato)cobalt(II) complexes in Me_2SO will be reported separately. It was found from the UV spectra that a loss of the complexes by adsorption on the surface of glass vessels was remarkable in the solutions of $Co(bzac)_2$ and $Co(acac)_2$ at concentrations below 1 mmol dm^{-3} in *N,N*-dimethylformamide at 25 °C. Thus, such studies of bis(β-diketonato)cobalt(II) complexes in other solvents might be restricted.

Registry No. $Co(bi\text{-}dbm)_2$, 14405-50-6; $Co(dbm)_3^-$, 70623-37-9; $Co(dbm)_3$, 21679-34-5; $Co(ClO_4)_2$, 13455-31-7; n-$Bu_4N(dbm)$, 52894-26-5.