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Structure and Homogeneous Chemical Equilibria of Lithium β-Diketonates in Dimethyl Sulfoxide

Yoshinori ARAKI,[†] Akio IWASE, Setsuko KUDO,* Toshishige M. SUZUKI, and Toshiro YOKOYAMA
Department of Chemistry, Faculty of Science, Yamagata University, Kojirakawa-machi, Yamagata 990
[†] Traffic Control Materials Laboratory, Yamagata 3M Ltd., Ohaza Osanagi, Higashine 999-37

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The structure and the homogeneous chemical equilibria of lithium β-diketonates (LiL), viz., Li(dbm), Li(bzac), and Li(acac), in dimethyl sulfoxide (DMSO) were studied by means of ^{13}C NMR, IR spectral measurements, and rotating disk voltammetry, where dbm$^-$, bzac$^-$, and acac$^-$ indicate the enolate anions of dibenzoylmethane, benzoylacetone, and acetylacetone, respectively. It was found by the ^{13}C NMR and IR spectral measurements that LiL existed mainly as Li(uni-L) in DMSO, where uni- means that the ligand coordinates to the metal as unidentate. Since it is known that LiL dissociates slightly into ions in DMSO, LiL is involved in the following homogeneous chemical equilibrium:

$$\mathrm{Li(uni\text{-}L)} \rightleftharpoons \mathrm{Li^+ + L^-}$$

Furthermore, the apparent dissociation constant ($\log K_{\mathrm{app}}$) of LiL was obtained by rotating disk voltammetry in DMSO containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate (TBAP), i.e., Li(dbm): -3.0 ± 0.1, Li(bzac): -2.7 ± 0.1, and Li(acac): -2.0 ± 0.1, respectively. It was noted that the homogeneous chemical equilibria shifted more to the right in 0.1 mol dm^{-3} TBAP–DMSO than in DMSO alone. The behavior can be explained mainly in terms of the interaction between the π-electron system of Li(uni-L) and the cations of TBAP.

In previous papers,[1–5] the homogeneous chemical equilibria of ten bis(β-diketonato)nickel(II) complexes in DMSO were investigated by means of conductivity, electronic spectral measurements, cryoscopy, polarography, and cyclic voltammetry. For instance, it was found polarographically that three complexes, viz., Ni(dbm)$_2$,[2] Ni(bzac)$_2$,[1] and Ni(acac)$_2$,[5] were involved in the following homogeneous chemical equilibria:

(a) Ni(dbm)$_2$ and Ni(bzac)$_2$

$$\begin{tikzcd}[row sep=small, column sep=small] \mathrm{Ni(bi\text{-}L)_2} \arrow[r, phantom, "\rightleftharpoons"] & \mathrm{Ni(bi\text{-}L)(uni\text{-}L)} \\ \arrow[r, phantom, "\rightleftharpoons"] & \mathrm{Ni(bi\text{-}L)^+ + L^-} \arrow[d, shift left] \\ & \mathrm{Ni(uni\text{-}L)^+} \arrow[u, shift left] \end{tikzcd}$$

(b) Ni(acac)$_2$

$$\begin{tikzcd}[row sep=small, column sep=small] \text{Polymeric species} \arrow[r, phantom, "\rightleftharpoons"] & \mathrm{NiL_2} \\ \arrow[r, phantom, "\rightleftharpoons"] & \mathrm{Ni(bi\text{-}L)^+ + L^-} \arrow[d, shift left] \\ & \mathrm{Ni(uni\text{-}L)^+} \arrow[u, shift left] \end{tikzcd}$$

where bi- means that the ligand coordinates to the metal as bidentate and L$^-$ indicates the enolate anion of the β-diketone. Because the polarographic measurements in the previous research were based on the reduction of the metal base of the complexes, they do not provide detailed information on the ligands.

The present paper deals with the structure and the homogeneous chemical equilibria of Li(dbm), Li(bzac), and Li(acac) in DMSO by use of ^{13}C NMR and IR spectral measurements, and in 0.1 mol dm^{-3} TBAP–DMSO by means of rotating disk voltammetry based on the oxidation of the ligand base. Since LiL is a simple compound, it was expected that this research would provide more direct information regarding the bond between the metal and the ligand, and more quantitative information with respect to homogeneous chemical equilibria for metal β-diketonates in DMSO.

Experimental

Reagents. Lithium dibenzoylmethanate [Li(dbm)] was prepared as follows: To 5 mmol of Aldrich Chemicals' dibenzoylmethane (98%) in 50 mL of methanol was added 5 mmol of Nakarai Chemicals' lithium hydroxide monohydrate (99%) in 150 mL of methanol. The resulting solution was evaporated and a small amount of diethyl ether was added to the concentrated solution. The solution was permitted to stand for a minimum of 2 h in an ice bath and then was filtered. The salt was recrystallized once with methanol–diethyl ether. Then, the salt was dried in vacuo at 105±5 °C for ca. 6 h. The yield of the salt was 30.5%. Found: C, 77.74; H, 5.01%. Calcd for $C_{15}H_{11}O_2Li$: C, 78.26; H, 4.82%. Lithium benzoylacetonate [Li(bzac)] and lithium acetylacetonate [Li(acac)] were synthesized by the same method as Li(dbm). Found: C, 71.11; H, 5.66%. Calcd for $C_{10}H_9O_2Li$: C, 71.43; H, 5.41%. Found: C, 55.74; H, 6.44%. Calcd for $C_5H_7O_2Li$: C, 56.62; H, 6.67%.

Tetrabutylammonium dibenzoylmethanate [n-Bu$_4$N(dbm)], tetrabutylammonium benzoylacetonate [n-Bu$_4$N(bzac)], and tetrabutylammonium acetylacetonate [n-Bu$_4$N(acac)] were obtained according to the method described by Buchta et al.[6] Found: C, 79.50; H, 10.10; N, 2.67%. Calcd for $C_{31}H_{47}O_2N$: 79.93; H, 10.19; N, 3.01%. Found: C, 76.92; H, 11.32; N, 3.00%. Calcd for $C_{26}H_{45}O_2N$: C, 77.35; H, 11.26; N, 3.47%. Found: C, 73.87; H, 13.01; N, 3.95%. Calcd for $C_{21}H_{43}O_2N$: C, 73.82; H, 12.71; N, 4.10%. These salts were stored in the dark under nitrogen.

The dimethyl sulfoxide and TBAP used in rotating disk voltammetry were the same as described previously.[7]

Apparatus and Procedures. ^{13}C NMR spectra were obtained with a Varian VXR-300 spectrometer at room temperature. Test solutions were prepared as 0.4 mol dm^{-3} LiL in methanol-d_4 (CD$_3$OD) and dimethyl-d_6 sulfoxide (DMSO-d_6). Chemical shifts were reported in ppm units, relative to internal tetramethylsilane.

IR spectra were recorded on a Hitachi 270-50 infrared spectrophotometer. Samples were prepared as 1% LiL dispersion in KBr pellets and 10 mmol dm^{-3} solutions in DMSO. The solutions were measured with a calcium fluoride cell of 0.5 mm optical length at room temperature.

Rotating disk voltammograms were obtained with a Nikko Keisoku DPGS-1 dual potentiogalvanostat, a Nikko Keisoku NFG-3 function generator, and a Watanabe WX 4421 X-Y plotter. A disk electrode was rotated by means of a Nikko Keisoku SC-4 motor speed controller and a Nikko Keisoku RRDE-1 rotating ring-disk electrode apparatus. Current–potential curves were measured with a three-electrode system at 25.0±0.2 °C. A platinum rotating disk electrode (surface area: 0.071 cm^2) was used as a working electrode, with a platinum wire as a counter electrode and an aqueous saturated calomel electrode (SCE) as a reference electrode. The rotation speed of the disk electrode ranged from 51 to 890 rad s^{-1}. Voltammograms were recorded at 20 mV s^{-1} scan rate. All test solutions were deaerated for ca. 30 min with nitrogen gas before measurements. As a supporting electrolyte, 0.1 mol dm^{-3} TBAP was used.

Results and Discussion

1. In DMSO. ^{13}C NMR Spectra: The data for the ^{13}C NMR chemical shift of LiL are summarized in Table 1. Each resonance was a singlet, except methylene carbon of Li(bzac) and Li(acac), measured in CD_3OD. Only one carbonyl carbon resonance was obtainted for Li(dbm) and Li(acac), while Li(bzac) gave two carbonyl carbon resonances, due to $-CH_3$ and -Ph substituents at ^{1}C and ^{3}C positions, which were assigned from the chemical shifts of acetone and acetophenone.[8] The Table shows that the carbonyl and methylene carbon resonances indicate drastic upfield shifts in DMSO-d_6, in comparison with the resonances in CD_3OD.

The differences between the chemical shifts in the two solvents used are also presented in Table 1, where

$$d_i = C_i(\text{in } CD_3OD) - C_i(\text{in DMSO-}d_6)\ (i = 1\text{—}3) \quad (1)$$

The d_1 and d_3 values suggest that the structure of LiL in DMSO-d_6 is different from that in CD_3OD.

Raban et al. reported that Li(acac) existed almost completely in the chelated form in CD_3OD.[9] As described in section 2 of the present paper, Li(dbm) and Li(bzac) are more stable than Li(acac); therefore, they also tend to exist in the chelated form in CD_3OD. On the other hand, since LiL is strongly solvated in DMSO-d_6, it may be expected that the lithium-oxygen bond will tend to break in DMSO-d_6.

Shibata et al. studied ^{13}C NMR chemical shifts of various β-diketones in DMSO-d_6 and chloroform-d.[8] According to that paper, carbonyl carbon resonances indicated drastic upfield shifts in DMSO-d_6, in comparison with the resonances in chloroform-d, i.e., d=2.7—5.5 ppm. The results led to the conclusion that DMSO-d_6 broke the intramolecular hydrogen bond of the β-diketone and that the upfield shift was caused by the contribution of the free carbonyl carbon which was not influenced by the intramolecular hydrogen bond.

In addition, ^{13}C NMR chemical shifts of the carbonyl carbon for n-Bu_4NL were obtained in DMSO-d_6, viz., n-Bu_4N(dbm) showed 180.5 ppm and n-Bu_4N(bzac) indicated 190.9 and 179.8 ppm at ^{1}C and ^{3}C positions.[10] These findings suggest that the structure of LiL is analogous to that of n-Bu_4NL in DMSO-d_6. However, dissociation of Li(dbm) is negligible in DMSO-d_6 under the conditions used in this study, as discussed below.

The present research demonstrates that LiL does not take the chelated form in DMSO-d_6 (Scheme 1) because the behavior of LiL is very similar to that of the β-diketones reported by Shibata et al., and the carbonyl carbon resonances for LiL appear at the similar positions of those for n-Bu_4NL in DMSO-d_6. Therefore, it is found that the upfield shifts of LiL in DMSO-d_6 are

Table 1. ^{13}C NMR Chemical Shifts of LiL in CD_3OD and DMSO-d_6

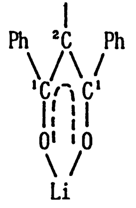
Compound	Solvent	Chemical shift of carbonyl carbon/ppm				Chemical shift of methylene carbon/ppm	
		C_1	d_1[a]	C_3	d_3[b]	C_2	d_2[c]
Li(dbm)	CD_3OD	187.4				95.3	
	DMSO-d_6	182.5	4.9			91.1	4.2
Li(bzac)	CD_3OD	192.6		186.2		97.1[d]	
	DMSO-d_6	189.3	3.3	180.3	5.9	94.1	3.0
Li(acac)	CD_3OD	191.3				99.3[d]	
	DMSO-d_6	186.8	4.5			97.4	1.9

a) d_1=C_1(in CD_3OD)−C_1(in DMSO-d_6)

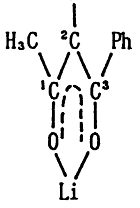
b) d_3=C_3(in CD_3OD)−C_3(in DMSO-d_6)

c) d_2=C_2(in CD_3OD)−C_2(in DMSO-d_6)

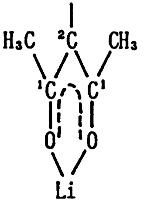
d) Triplet



Li(dbm)

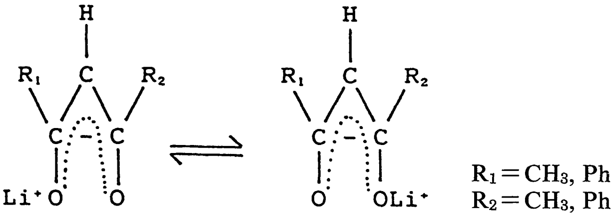


Li(bzac)



Li(acac)

in CD_3OD



Scheme 1.

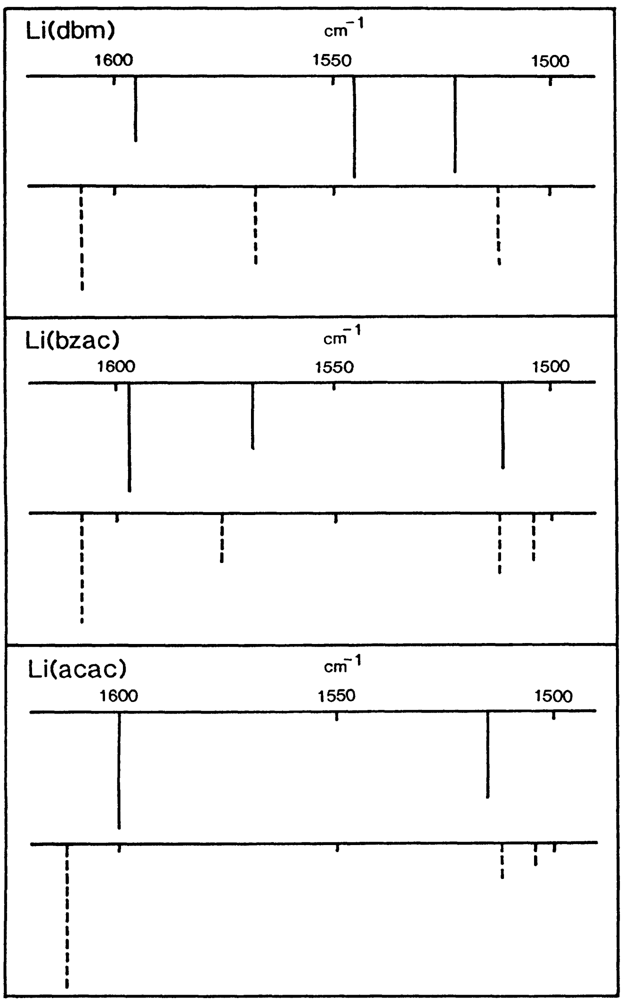


Fig. 1. IR spectra of LiL in the solid state (solid line) and in DMSO (broken line).

caused by the contribution of the free carbonyl carbon. As shown in Scheme 1, the two species contribute to the upfield shifts; however, it was not possible to separate the two species, and it was also impossible to differentiate between the free carbonyl carbon and the other within the NMR time scale. The mixture of the two species is represented as Li(uni-L) below.

IR Spectra: IR spectra of LiL in the solid state and in DMSO are diagrammed in Fig. 1. Each characteristic band of $\nu(\mathrm{C}\cdots\mathrm{O})$[11,12] of Li(dbm), Li(bzac), and Li(acac) appears at 1595, 1597, and 1600 cm^{-1} in the solid state and at 1608, 1608, and 1612 cm^{-1} in DMSO, respectively. In addition, $\nu(\mathrm{C}\cdots\mathrm{O})$ of n-Bu$_4$N(dbm) was 1611 cm^{-1} in the solid state and 1612 cm^{-1} in DMSO. These findings suggest that the structure of Li(dbm) in DMSO is similar to that of n-Bu$_4$N(dbm). However, the degree of dissociation for Li(dbm) in DMSO is very minimal, as described below. Although it is thought that the shifts of $\nu(\mathrm{C}\cdots\mathrm{O})$ in DMSO are caused by the solvent effect, it is more plausible that LiL takes the unidentate structure because of the conclusion in the ^{13}C NMR study.

Chemical Equilibria: Arnett et al. reported that the dissociation constant ($\log K_\mathrm{D}$) of Li(dbm) was -5.86 ± 0.01 in DMSO.[13] By using this datum, it is possible to calculate the degrees of dissociation for the prepared concentration in the ^{13}C NMR and IR spectral measurements. Thus, the calculated degree of dissociation is 0.2% for 0.4 mol dm^{-3} in the ^{13}C NMR study, while it is 1.2% for 10 mmol dm^{-3} in the IR study. Since these degrees of dissociation are very minimal, the dissociated species in Scheme 2, i.e., Li$^+$ and L$^-$, are negligible for the both measurements. Therefore, the main species in DMSO is Li(uni-L), and the fact is consistent with the result in ^{13}C NMR and IR studies.

2. In TBAP-DMSO. Rotating Disk Voltammetry: Typical rotating disk voltammograms of LiL and n-Bu$_4$NL are shown in Fig. 2. In general, a limiting current is shown by the Levich equation[14] under convective-diffusion controlled conditions, as follows:

$$i_\mathrm{L}=0.620nFAD^{2/3}\,\omega^{1/2}\,\nu^{-1/6}C \qquad (2)$$

where i_L is the limiting current, n is the number of

$$\mathrm{Li(uni\text{-}L)} \xrightleftharpoons{K_\mathrm{D}} \mathrm{Li^+ + L^-}$$

Scheme 2.

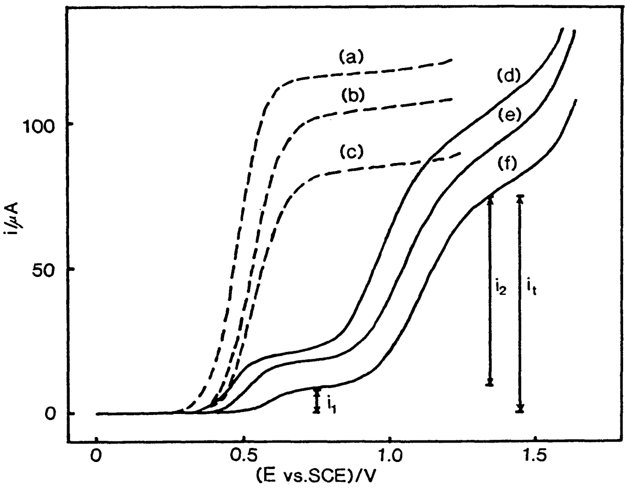


Fig. 2. Rotating disk voltammograms of 2 mmol dm^{-3} (a) n-Bu$_4$N(acac), (b) n-Bu$_4$N(bzac), (c) n-Bu$_4$N(dbm), (d) Li(acac), (e) Li(bzac), and (f) Li(dbm) at 775 rad s^{-1} rotation speed in 0.1 mol dm^{-3} TBAP-DMSO.

transferred electrons, F is the Faraday constant, A is the surface area of the disk electrode, D is the diffusion coefficient, ω is the rotation speed of the disk electrode, ν is the kinematic viscosity, and C is the bulk concentration. The limiting currents for LiL (i_t) and for n-Bu$_4$NL in Fig. 2, are proportional to the square root of ω. The plots of i_t at a constant rotation speed vs. C for LiL give a straight line in the concentration range from 1 to 10 mmol dm^{-3}.

VandenBorn et al. reported that n-Bu$_4$N(dbm) existed as the enolate anion in DMSO containing 0.1 mol dm^{-3} tetraethylammonium perchlorate and that controlled potential coulometry gave the n value of 0.98±0.03.[15] Therefore, the observed limiting current for n-Bu$_4$NL in Fig. 2 is consistent with a one-electron oxidation process; and i_t for LiL also corresponds to a totally one-electron oxidation process.

The first wave (i_t) in Fig. 2 contains a kinetic current due to a preceding chemical reaction. Figure 3 shows the correlation between i_1/i_2 and ω. As seen in Fig. 3, i_1/i_2 decreases as ω increases and it remains constant above 670 rad s^{-1}. Consequently, i_1 contains no kinetic current under the latter conditions.

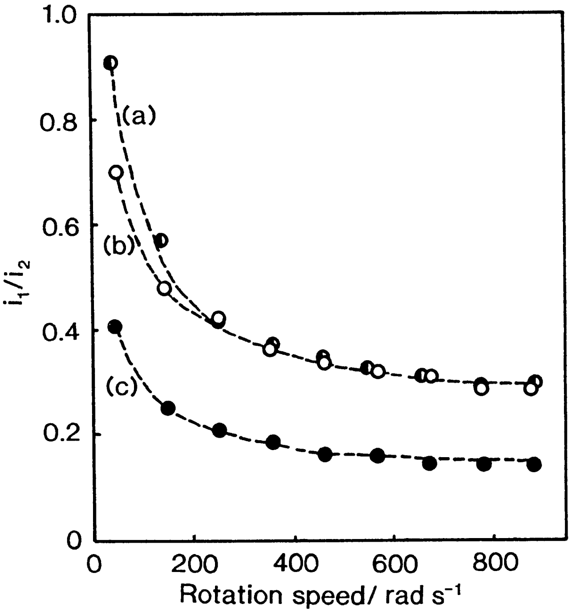


Fig. 3. Plots of i_1/i_2 vs. rotation speed for rotating disk voltammograms of 2 mmol dm^{-3} (a) Li(acac), (b) Li(bzac), and (c) Li(dbm) in 0.1 mol dm^{-3} TBAP-DMSO.

The rotating disk voltammetric data on the oxidation of LiL and n-Bu$_4$NL at ω=775 rad s^{-1} are summarized in Table 2. The half-wave potential and slope of i_1 for Li(bzac) and Li(acac) are almost equal to those for n-Bu$_4$N(bzac) and n-Bu$_4$N(acac) with errors of ±0.01 V and ±5 mV, respectively. While the half-wave potential of i_1 for Li(dbm) is a little different from that for n-Bu$_4$N(dbm), the first wave for Li(dbm) indicated the following findings:

(a) The first wave involved the kinetic current resulting from the preceding chemical reaction below ω=670 rad s^{-1}, as mentioned above.

(b) When a small amount of lithium perchlorate was added to the solution, i_1 decreased and i_2 increased under the conditions of ω=775 rad s^{-1}.

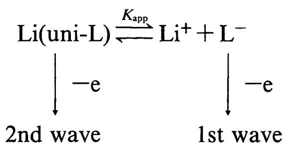
These experimental findings suggest that the first wave should be assigned to the oxidation of the enolate anion arising from the dissociative reaction; the second wave corresponds to the oxidation of Li(uni-L), on the basis of the results described in section 1 (Scheme 3).

The diffusion coefficient (D) of the enolate anion of n-Bu$_4$NL is calculated from the slope of the plots of limiting current vs. the square root of ω in terms of Eq. 2. The data are also presented in Table 2. The datum for n-Bu$_4$N(dbm) agrees with that reported VandenBorn et al.[15]

It is possible to determine the concentration of L$^-$ (Scheme 3) in 0.1 mol dm^{-3} TBAP-DMSO in terms of Eq. 3,[14]

$$1/i_L = 1/i_K + 1/0.620nFAD^{2/3}\,\omega^{1/2}\,\nu^{-1/6}C \qquad (3)$$

where i_K represents the current in the absence of any



Scheme 3.

Table 2. Rotating Disk Voltammetric Data on the Oxidation of 2 mmol dm^{-3} LiL and n-Bu$_4$NL at 775 rad s^{-1} Rotation Speed in 0.1 mol dm^{-3} TBAP-DMSO

Compound	($E_{1/2}$ vs. SCE)/V	Slope/mV	$i_j^{a)}$/μA	$i_t^{a)}$/μA	D/cm^2 s^{-1}
Li(dbm)	0.60	93	8.2		
	1.10	147	59.5	67.7	
Li(bzac)	0.51	95	16.6		
	1.04	147	60.3	76.9	
Li(acac)	0.46	93	19.6		
	0.97	147	67.6	87.2	
n-Bu$_4$N(dbm)	0.54	104		80.4	2.3×10^{-6}
n-Bu$_4$N(bzac)	0.53	103		101	3.3×10^{-6}
n-Bu$_4$N(acac)	0.48	96		114	3.8×10^{-6}

a) The meanings of i_j and i_t are shown in Fig. 2, where j=1—2.

Table 3. Apparent Dissociation Constant ($\log K_{app}$) of LiL at Different Concentration in 0.1 mol dm^{-3} TBAP-DMSO

Compound	C/mmol dm^{-3}	$\log K_{app}$
Li(dbm)	1.0	—[a]
	2.0	−2.9
	5.0	−3.1
Li(bzac)	1.0	−2.7
	2.0	−2.7
	5.0	−2.6
Li(acac)	1.0	−2.0
	2.0	−2.1
	5.0	—[a]

a) It was impossible to obtain these data because of a lack of fit for the plots.

mass transfer effects. The plots of $1/i_L$ for the first wave vs. $1/\omega^{1/2}$ showed straight lines at 0.6, 0.7, and 0.8 V vs. SCE. From the slope of the line, the concentration of L^-, i.e., C, was calculated by using the D for n-Bu_4NL in Table 2 and $\nu=0.01828$ cm^2 s^{-1}. Then, the apparent dissociation constant ($\log K_{app}$) of LiL in 0.1 mol dm^{-3} TBAP–DMSO was obtained, as shown in Table 3.

The values decrease in the following order: Li(acac)>Li(bzac)>Li(dbm). This order agrees with that of the dissociation constants ($\log K_d$) of β-diketones, measured in the aqueous 75 vol% dioxane, namely Hacac>Hbzac>Hdbm, which are −12.70, −12.85, and −13.75, respectively.[16] The $\log K_{app}$ of Li(dbm) is −3.0±0.1 in 0.1 mol dm^{-3} TBAP–DMSO; however, the $\log K_D$ of Li(dbm) is −5.86±0.01 in DMSO.[13] It was found that the homogeneous chemical equilibrium (Scheme 2) for Li(dbm) shifted more to the right in 0.1 mol dm^{-3} TBAP–DMSO than in DMSO alone.

The TBAP effect on the homogeneous chemical equilibrium for Li(dbm) can be considered first from the standpoint of the ionic strength of the solution. Libuš et al. reported conductometric and spectrophotometric results of copper(II) trifluoroacetate [$Cu(CF_3COO)_2$] in DMSO.[17] That paper indicated that the association constant of $CuCF_3COO^+$ in DMSO derived from the spectrophotometric results, after making activity corrections, agreed with that derived from conductometric data. If the dissociation constant of Li(dbm), after making activity corrections, is defined as K_I, the following equation is set up:

$$\log K_I = \log K_D - \log Y_{Li} - \log Y_{dbm} \quad (4)$$

where Y_{Li} and Y_{dbm} are the activity coefficients of Li^+ and dbm^-, respectively. Thus, $\log K_I \approx -5.6$ is obtained by using $\log K_D = -5.86$[13] and $\log Y_{Li} = \log Y_{dbm} = -0.12$[18] at I (ionic strength)=0.1 in 0.1 mol dm^{-3} TBAP–DMSO. However, the $\log K_I \approx -5.6$ is still different from the $\log K_{app} = -3.0 \pm 0.1$.

It was described in a previous paper[19] that the dissociation of bis(benzoyltrifluoroacetonato)nickel(II), bis(2-furoyltrifluoroacetonato)nickel(II), and bis(2-thenoyltrifluoroacetonato)nickel(II) complexes in DMSO was enhanced by the presence of one of the supporting electrolytes and that it was considered that such promotion of the dissociation was caused by an interaction between the π-electron system of the complex and the cations of the electrolyte. Although it is impossible to discuss the difference between the $\log K_{app} = -3.0 \pm 0.1$ and the $\log K_D = -5.86 \pm 0.01$ quantitatively, the difference can be explained mainly in terms of the interaction between the π-electron system of Li(uni-dbm) and the cations of TBAP. It is thought that a similar interaction also takes place in the case of Li(bzac) and Li(acac).

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