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Electrochemical Reduction of Some Tris(β-diketonato)ruthenium(III) Complexes in Acetonitrile and Interaction of the Reduced Anions with Lithium and Sodium Ions

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In tetraethylammonium perchlorate-acetonitrile solution, $[Ru(R_1\text{-}CO\text{-}CR_2\text{-}CO\text{-}R_3)_3]$ (R_1,R_3=-CH_3, -CF_3, -C_6H_5, -$C(CH_3)_3$; R_2=-H, -C_6H_5) was reversibly reduced at a dropping mercury electrode to the corresponding univalent anion. A linear relationship was found between the half-wave potential and the sum of the Hammett constants of the substituents of ligands. In some cases, the polarogram and the cyclic voltammogram were shifted to more positive potentials in the presence of lithium or sodium ions. This effect was explained quantitatively by the two-step association between the reduction product, $[Ru(R_1\text{-}CO\text{-}CR_2\text{-}CO\text{-}R_3)_3]^-$, and alkali metal ions. The association constants were calculated. The K_2 values were appreciable and the K_1 values were much larger than expected for a simple electrostatic interaction. Furthermore, the K_1 values were linearly related to the sum of the Hammett constants of the substituents of the ligands. These results suggest the importance of the local charge distribution on the complex anions. In the presence of lithium ion, $[Ru(acac)_3]^-$ forms $Li[Ru(acac)_3]$ which is insoluble in acetonirile.

The polarographic behavior of acetylacetonato complexes is affected by the properties of solvents and by the addition of perchlorate of alkali metal or alkaline earth metal. Murray and Hiller[1)] first studied in detail the mechanism of polarographic reduction of $[Fe(acac)_3]$ in lithium perchlorate–acetonitrile solutions. They found that the reduction potential of $[Fe(acac)_3]$ was shifted to more positive potentials by the addition of $LiClO_4$. They have shown that the effect is caused by a coordinative relaxation reaction of the reduction product, $[Fe(acac)_3]^-$, in which an acetylacetonato ligand becomes transferred to lithium ion. Heineman *et al.*[2)] have confirmed this interaction by means of the optically transparent thin-layer electrode. Misumi *et al.*[3)] also examined this effect in *N*,*N*-dimethylformamide (DMF) and obtained similar results. Recently, Kalinowski and Ćmiel[4)] investigated solvent effects on the interaction between $[Fe(acac)_3]^-$ and Li^+, Na^+, or K^+ and discussed them in terms of the donor-acceptor concept. The coordinative relaxation reaction was also observed in the systems of $[Cu(acac)_2]^-$–Li^+ (in acetonitrile)[5)] and $[Eu(acac)_3]^-$–Li^+, Mg^{2+} (in DMF).[3)] In the reduction of $[Mn(acac)_3]$,[6)] the potential shifts were also observed on the addition of perchlorate of Li^+, Na^+, or K^+ in many nonaqueous solvents. These effects were qualitatively explained in terms of the ion-pair formation between $[Mn(acac)_3]^-$ and alkali metal ions. This explanation, however, appears to lack quantitative corroboration.

In the course of a polarographic study of tris(acetylacetonato)ruthenium(III) in aqueous and acetonitrile solutions,[7)] we came to notice that the reduction step in acetonitrile is shifted to more positive potentials in the presence of sodium ions.

The present paper deals with the interaction of lithium and sodium ions with eight kinds of tris(β-diketonato)ruthenate(II) ions which are produced by the polarographic reduction of the corresponding Ru^{III} complexes. Effects of the substituents of the ligands are also discussed.

Experimental

Preparation of the Complexes.† Among the eight complexes, $[Ru(pfm)_3]$ and $[Ru(paa)_3]$ are new compounds. They were synthesized as described below. $[Ru(bzac)_3]$ and $[Ru(acac)_3]$ were prepared according to the published methods (Refs. 8 and 7, respectively). For the other complexes, see the appendix.

[Ru(pfm)₃]: Hydrated ruthenium trichloride (1 g, *ca.* 4 mmol as Ru), 3.3 g (17 mmol) of Hpfm and 0.5 g (5 mmol) of potassium hydrogencarbonate were refluxed at 120 °C for 10 h. An additional 1.2 g (12 mmol) of potassium hydrogencarbonate was added, and the reflux was continued at 150 °C for 20 h. The mixture was then extracted with dichloromethane several times. The extracts were combined and this mixture was washed in a separatory funnel successively with 2% potassium hydrogencarbonate solution, 2% HCl solution, and water. Removal of the solvent from extracts left an oily red material, which was steam-distilled. The first 5 cm^3 portion of the distillate being discarded, the distillate containing drops of red liquid was collected and left to stand overnight, during which the drops solidified. The solid was dried under vacuum and then ground to powder, which was again vacuum-dried at room temperature. Found: C, 42.5; H, 4.5%. Calcd for $RuC_{24}H_{30}O_6F_9$: C, 42.0; H, 4.40%.

[Ru(paa)₃]: A portion of ruthenium(III) chloride solution (5 mmol as Ru, dissolved in 40 cm^3 of 1 mol dm^{-3} HCl) was reduced with ethanol to the bivalent state, and the mixture was evaporated nearly to dryness on a water bath. The blue residue was dissolved in 50 cm^3 of water and the pH of the solution was adjusted to about 2 with 1 mol dm^{-3} NaOH solution. The solution was then refluxed on a water bath with 4 g (23 mmol) of Hpaa and 200 cm^3 of ethanol under nitrogen atmosphere. After 4 h, the pH

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† The following ligand abbreviations will be used in this paper (in the order of Table 1): Hbzfa, 1,1,1-trifluoro-4-phenyl-2,4-butanedione; Hfac, 1,1,1-trifluoro-2,4-hexanedione; Hpfm, 1,1,1-trifluoro-5,5-dimethyl-2,4-pentanedione; Hdbm, 1,3-diphenyl-1,3-propanedione; Hbzac, 1-phenyl-1,3-butanedione; Hacac, 2,4-pentanedione; Hpaa, 3-phenyl-2,4-pentanedione; Hdpm, 2,2,6,6-tetramethyl-3,5-heptanedione.

Table 1. Polarographic data for RuL_3 ($L=R_1$-CO-CR_2-CO-R_3^-) in 0.1 mol dm^{-3} TEAP acetonitrile solution at 25 °C

Complex		[R_1-CO-CR_2-CO-R_3]$^-$			$E^\circ_{1/2}$/V$^{a)}$	Reciprocal slope/mV
		R_1	R_2	R_3		
1	[Ru(bzfa)$_3$]	-CF_3	-H	-C_6H_5	−0.29	−64.5
2	[Ru(fac)$_3$]	-CF_3	-H	-CH_3	−0.36	−57.0
3	[Ru(pfm)$_3$]	-CF_3	-H	-$C(CH_3)_3$	−0.47	−61.7
4	[Ru(dbm)$_3$]	-C_6H_5	-H	-C_6H_5	−0.86	−65.0
5	[Ru(bzac)$_3$]	-C_6H_5	-H	-CH_3	−0.96	−64.0
6	[Ru(acac)$_3$]	-CH_3	-H	-CH_3	−1.08	−61.0
7	[Ru(paa)$_3$]	-CH_3	-C_6H_5	-CH_3	−1.17	−65.8
8	[Ru(dpm)$_3$]	-$C(CH_3)_3$	-H	-$C(CH_3)_3$	−1.39	−64.0

a) Against a silver-silver ion electrode (0.01 mol dm^{-3} $AgNO_3$ in acetonitrile).

of the solution was readjusted to about 2, and the reflux was continued for *ca.* 10 h, when the color of the solution turned to reddish purple. The pH of the solution was then adjusted to about 6, and further refluxing was continued for 5 h. After removal of the solvent, the residue was extracted into several portions of benzene. The combined benzene solution was passed through a column of Merck Alminiumoxid 90 (Aktivitätsstufe II—III). The eluent was concentrated, and the complex was precipitated by adding ethanol. A red powdery material was obtained, which was dried under vacuum at room temperature. Found: C, 63.3; H, 5.5%. Calcd for $RuC_{33}H_{33}O_6$: C, 63.3; H, 5.3%.

Complexes **1**, **2**, **3**, and **5** have geometrical isomers, and each of the complexes has optical isomers. The isomeric mixtures were used, since the precision of the present method seemed too low to detect any difference among the isomers. Indeed, in the case of [Ru(bzac)$_3$], the half-wave potentials of the *mer*- and *fac*-isomers were identical in both TEAP and $NaClO_4$ solutions.[9]

Other Chemicals: Tetraethylammonium perchlorate (TEAP) and tetrabutylammonium perchlorate (TBAP) were of special polarographic grade purchased from Nakarai Chemicals, Ltd. Anhydrous $LiClO_4$ of ICN Pharmaceutical, Inc., was dried under vacuum at 130 °C. Anhydrous $NaClO_4$ of guaranteed reagent grade of Kanto Chemical Co., Inc., was dried under vacuum at 120 °C. Purification of acetonitrile has been described previously.[7]

Measurement. All the potentials were measured against a silver-silver ion electrode (Ag/0.01 mol dm^{-3} $AgNO_3$ in acetonitrile), and all the electrochemical measurements were carried out at (25.0±0.1) °C. Deoxygenation of solutions was carried out with argon gas which had been passed through two wash bottles containing acetonitrile kept at 25 °C. Electrochemical measurement was carried out mainly by using a Fuso Polarograph Model 312 with a Fuso Potential Scanning Unit Model 321 and a Riken Denshi X-Y Recorder Model F-42CP. An H-type electrolytic cell with a glass frit was used. A dropping mercury electrode (DME) and a counter electrode of spiral platinum wire were both placed in one compartment and the reference electrode was connected to the other compartment through a bridge filled with 0.1 mol dm^{-3} TEAP solution. The DME had a flow rate of mercury of 1.38 mg s^{-1} under a mercury head of 50 cm. Cyclic voltammetry was carried out as previously described,[7] except that the silver-silver ion reference electrode was used and both compartments were filled with the supporting electrolyte solution. A Hitachi Model 200-20 Spectrophotometer was used for recording absorption spectra. An NEC PC 8001 Personal Computer was used for data processing. Elemental analyses of C, H, and N were carried out by means of a Shimadzu Seisakusho Ltd. CHN Analyzer CHN-1A. Lithium was determined by means of a Seiko SAS 740 Atomic Absorption/Flame Spectrophotometer. Ruthenium was determined spectrophotometrically according to the ruthenate method.[10]

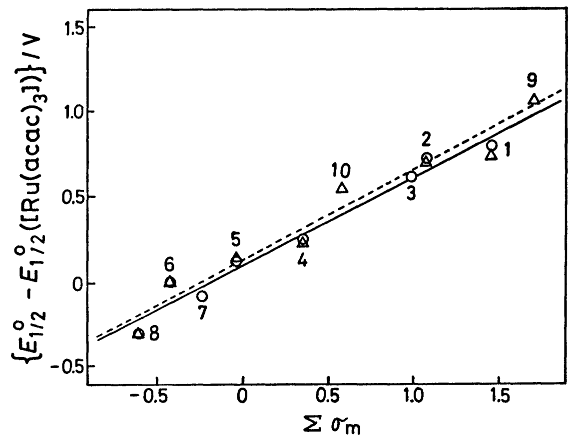

Fig. 1. Relationship between relative half-wave potential and the sum of the Hammett constants in 0.1 mol dm^{-3} TEAP at 25 °C. —○—, this work (in acetonitrile); ---△---, Patterson and Holm[11] (in DMF). Complexes are numbered as in Table 1 except for **9** ([Ru(acac)(hfac)$_2$] and **10** ([Ru(acac)$_2$(hfac)]) (Hhfac, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione).

Results and Discussion

TEAP Systems. In 0.1 mol dm^{-3} TEAP solution, every complex listed in Table 1 showed a reduction step with diffusion-controlled limiting current, which corresponded to Nernstian one-electron reduction to the univalent anion. The half-wave potentials ($E^\circ_{1/2}$) and the reciprocal slopes of the logarithmic plots of the reduction steps are presented in Table 1.

Patterson and Holm[11] investigated in DMF the substituent effect on the $E^\circ_{1/2}$ of a series of tris(β-diketonato)ruthenium(III) complexes including six of the present ones. In the present case, too, the plot of $E^\circ_{1/2}$ *vs.* the sum of the Hammett constant ($\Sigma\sigma_m$ or $\Sigma\sigma_p$) was a straight line. In Fig. 1, this relationship is represented in terms of the half-wave potentials relative to that of $[Ru(acac)_3]$ and along with these authors' data, where $\Sigma\sigma_m$ is calculated by using the values given by Murov.[12] The agreement between the two sets of data is remarkable. This is not surprising since the relative permittivities of the two solvents are almost the same (ε_r(acetonitrile)$=38$ and ε_r(DMF)$=37$ at 25 °C[13]), if there is little specific solute-solvent interaction. Patterson and Holm[11] explained this linear relationship qualitatively as follows. Since Ru^{III} has the low spin, d^5 electronic configuration, the d electrons are localized in the t_{2g} metal orbital. The t_{2g} metal orbital which is a $d\pi$ orbital, forms a π molecular orbital with a π ligand orbital, and in the redox process the electron will be added to or subtracted from this molecular orbital. The substituents affect the eletron density of σ and π molecular orbitals. The Hammett constant is a measure of the electron-accepting character of the substituent. The more electron-accepting is the substituent, the more stabilized is the reduced form with respect to the oxidized form, hence the more positive is $E^\circ_{1/2}$.

A linear correlation between $E^\circ_{1/2}$ and the Hammett constant is known in many systems of organic substances.[14–16] For benzene derivatives, azo dyes,[16] and some heterocylic compound derivatives,[15] slopes ranging from $+0.02$ V to $+0.37$ V were observed. The slope of *ca.* $+0.5$ V obtained in the present case is somewhat larger, probably reflecting the more immediate influence of the substituents on the orbital energies of the metal chelate.

$LiClO_4$ and $NaClO_4$ Systems. In the presence of $LiClO_4$, the polarogram and cyclic voltammogram of $[Ru(acac)_3]$ were shifted to more positive potentials; but their shapes were so distorted by the presence of maxima, apparently owing to the formation of insoluble film, that no quantitative analyses of the waves were possible. When the large scale reduction at a mercury pool electrode was carried out in 0.1 mol dm^{-3} $LiClO_4$ with enforced stirring of the mercury surface, a brown precipitate was obtained. The precipitate was collected by the filtration and washed with deoxygenated acetonitrile under argon atmosphere. In the presence of atmospheric oxygen, the precipitate redissolved instantly to give the tervalent species. It was fairly stable when dry and was subjected to elemental analysis. The results were in good agreement with the calculated values for $Li[Ru(acac)_3]$. Found: Ru, 24.0; C, 44.2; H, 5.2; Li, 1.6%. Calcd for $Li[Ru(acac)_3]$: Ru, 24.9; C, 44.4; H, 5.2; Li, 1.7%. On reduction in the presence of lithium ions, therefore, the reduction product, $[Ru(acac)_3]^-$, forms the lithium salt, which is insoluble in acetonitrile.

In the presence of $NaClO_4$, the polarogram and the cyclic voltammogram of $[Ru(acac)_3]$ were also shifted to more positive potentials, as shown in Fig. 2, without changing the Nernstian characteristics (Table 2). The $E_{1/2}$ was independent of the depolarizer concentration at a given sodium perchlorate concentration. The addition of small amounts of water did not affect the $E_{1/2}$. When the $[Ru(acac)_3]$ was partially reduced at a mercury pool electrode in 0.1 mol dm^{-3} $NaClO_4$, a single redox step appeared at the same $E_{1/2}$. When the cathodic diffusion currents recorded intermittently in the course of the electrolytic reduction were plotted against the quantity of electricity, the magnitude of the former decreased and that of the latter increased linearly. The plots indicate that the process is a one-electron reduction, without any complication owing to subsequent chemical reactions. The UV-visible spectra of $[Ru(acac)_3]$ were the same in both 0.1 mol dm^{-3} $NaClO_4$ and 0.1 mol dm^{-3} TEAP. It follows that the shift of $E_{1/2}$ is attributable to a specific interaction of sodium ions with $[Ru(acac)_3]^-$, not with $[Ru(acac)_3]$. The spectra of the reduced forms, in fact, were different in the two media.

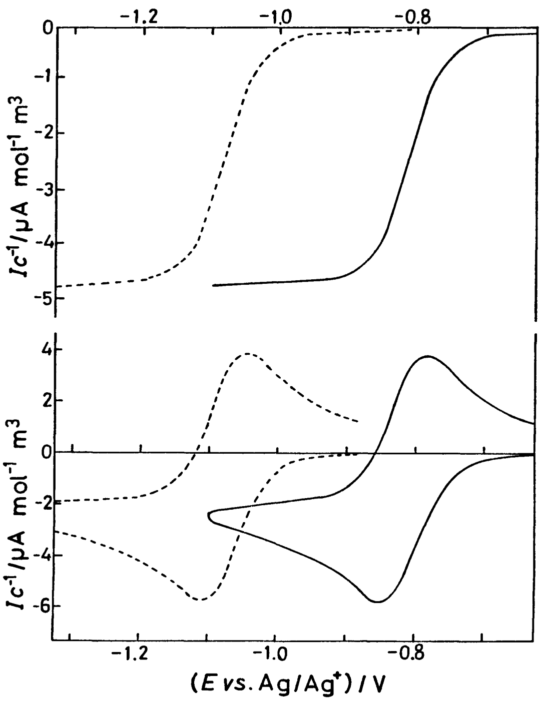

Fig. 2. DC polarograms and cyclic voltammograms of $[Ru(acac)_3]$ in acetonitrile. ----, in 0.1 mol dm^{-3} TEAP; ——, in 0.1 mol dm^{-3} $NaClO_4$; scan rate for CV$=0.1$ V s^{-1}, 25 °C.

TABLE 2. THE DEPENDENCE OF $\Delta E_{1/2}$ OF $[Ru(acac)_3]$ ON THE CONCENTRATION OF DISSOCIATED SODIUM IONS IN ACETONITRILE AT 25 °C

$[Na^+]$/mol m^{-3}	$\Delta E_{1/2}$/mV[a)]	Reciprocal slope/mV
0	(0)	-61.0
6.9	151	-60.7
13.7	187	-62.5
20.6	207	-60.1
34.3	232	-59.7
48.0	246	-61.5
68.4	269	-59.6

a) Against a silver-silver ion electeode (0.01 mol dm^{-3} $AgNO_3$ in acetonitrile). Concentration of $[Ru(acac)_3]$ is 1 mol m^{-3}.

Consequently, the shift of $E_{1/2}$ is interpreted in terms of the association equilibria between sodium or lithium ion (M^+) and $[Ru(acac)_3]^-$ subsequent to the electron transfer:

$$[\mathrm{Ru(acac)_3}] + \mathrm{e}^- \rightleftharpoons [\mathrm{Ru(acac)_3}]^- \tag{1}$$

$$[\mathrm{Ru(acac)_3}]^- + \mathrm{M}^+ \rightleftharpoons \mathrm{M}[\mathrm{Ru(acac)_3}]$$

$$\mathrm{M}[\mathrm{Ru(acac)_3}] + \mathrm{M}^+ \rightleftharpoons \{\mathrm{M_2}[\mathrm{Ru(acac)_3}]\}^+ \tag{2}$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$\{\mathrm{M}_{n-1}[\mathrm{Ru(acac)_3}]\}^{(n-2)+} + \mathrm{M}^+ \rightleftharpoons \{\mathrm{M}_n[\mathrm{Ru(acac)_3}]\}^{(n-1)+}.$$

When the electron transfer is Nernstian and the subsequent reactions are reversible and the large excess of M^+ is present, this relation holds:[17)]

$$E = E^{\circ\prime} + (RT/F)\ln(\bar{D}_\mathrm{R}/D_\mathrm{O})^{1/2} + (RT/F)\ln(1+\sum_{i=1}^{n}\beta_i[\mathrm{M}^+]^i) + (RT/F)\ln[(I_\mathrm{d}-I)/I], \tag{3}$$

with

$$\beta_i = \prod_{j=1}^{i} K_j, \tag{4}$$

where D_O is the diffusion coefficient of $[\mathrm{Ru(acac)_3}]$, and $\bar{D}_\mathrm{R}$ is the mean diffusion coefficient of the reduced form, the other symbols having the usual meanings. K_j is the conditional stepwise formation constant of the jth associate in terms of amount-of-substance concentration:

$$K_j = C_j/[\mathrm{M}^+]C_{j-1}, \tag{5}$$

where C_j is the concentration of $\{\mathrm{M}_j[\mathrm{Ru(acac)_3}]\}^{(j-1)+}$. Hence the half-wave potential is given by

$$E_{1/2} = E^\circ_{1/2} + (RT/F)\ln(\bar{D}_\mathrm{R}/D_\mathrm{R})^{1/2} + (RT/F)\ln(1+\sum_{i=1}^{n}\beta_i[\mathrm{M}^+]^i), \tag{6}$$

where D_R is the diffusion coefficient of $[\mathrm{Ru(acac)_3}]^-$ and $E^\circ_{1/2}$ is the half-wave potential at $[\mathrm{M}^+]=0$. Since $\bar{D}_\mathrm{R}$ and D_R are expected to be almost the same,

$$\Delta E_{1/2} = E_{1/2} - E^\circ_{1/2} = (RT/F)\ln(1+\sum_{i=1}^{n}\beta_i[\mathrm{M}^+]^i). \tag{7}$$

The β_i values were calculated by analysing the dependence of $\Delta E_{1/2}$ on $[\mathrm{M}^+]$ according to the method presented by Momoki *et al.*[18)] For this purpose the values of $[\mathrm{M}^+]$ were calculated from the analytical concentration of the perchlorate by using the association constants of TEAP (7.3 $\mathrm{mol^{-1}\,dm^3}$) and $\mathrm{MClO_4}$ (4.0 $\mathrm{mol^{-1}\,dm^3}$ for M=Li and 6.8 $\mathrm{mol^{-1}\,dm^3}$ for M=Na at 25 °C) reported by Fujinaga *et al.*[19)] Although those values are thermodynamic association constants, they were used in the present calculation without correction for the ionic strength, because their values were found to have little effect on the results of the following numerical analysis. It is assumed that the association between $[\mathrm{Ru(acac)_3}]^-$ and tetraethylammonium ions is negligible; this assumption seems legitimate in view of the fact that the $E^\circ_{1/2}$ remained unchanged when the concentration of TEAP was changed from 0.05 mol $\mathrm{dm^{-3}}$ to 0.1 mol $\mathrm{dm^{-3}}$ or TEAP was replaced by TBAP. The total electrolyte concentration was, therefore, kept constant at 0.1 mol $\mathrm{dm^{-3}}$ with TEAP.

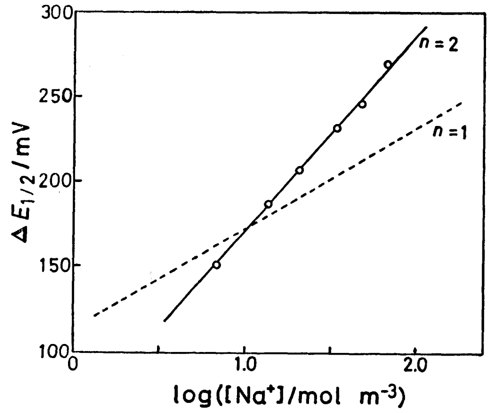

Fig. 3. $\Delta E_{1/2}$ *vs.* log ($[\mathrm{Na^+}]/\mathrm{mol\,m^{-3}}$) plot for $[\mathrm{Ru(acac)_3}]^-$–$\mathrm{Na^+}$ system in acetonitrile. ○, observed values; ----, calculated line for $n=1$; ——, calculated line for $n=2$. Total concentration of $\mathrm{NaClO_4}$ = 0.01 – 0.1 mol $\mathrm{dm^{-3}}$, 25 °C.

TABLE 3. THE CONDITIONAL STEPWISE FORMATION CONSTANTS OF TRIS(β-DIKETONATO)RUTHENATE(II) IONS WITH $\mathrm{Li^+}$ AND $\mathrm{Na^+}$ IN ACETONITRILE AT 25 °C, ELECTROLYTE CONCENTRATION = 0.1 mol $\mathrm{dm^{-3}}$

	Complex anion	log ($K_1/\mathrm{mol^{-1}\,dm^3}$)		log ($K_2/\mathrm{mol^{-1}\,dm^3}$)	
		$\mathrm{Li^+}$	$\mathrm{Na^+}$	$\mathrm{Li^+}$	$\mathrm{Na^+}$
1	$[\mathrm{Ru(bzfa)_3}]^-$	—	—	—	—
2	$[\mathrm{Ru(fac)_3}]^-$	—	—	—	—
3	$[\mathrm{Ru(pfm)_3}]^-$	—	—	—	—
4	$[\mathrm{Ru(dbm)_3}]^-$	1.7	2.6	1.2	1.1
5	$[\mathrm{Ru(bzac)_3}]^-$	2.3	2.8	1.0	1.6
6	$[\mathrm{Ru(acac)_3}]^-$	♯	3.8	♯	3.1
7	$[\mathrm{Ru(paa)_3}]^-$	♯	♯	♯	♯
8	$[\mathrm{Ru(dpm)_3}]^-$	4.7	4.1	1.4	1.2

—, not detectable ($\log(K/\mathrm{mol^{-1}\,dm^3}) <$ *ca.* 0.5); ♯, not measurable.

The maximum number of the bound cations, n, has to be known to carry out the calculation. For $n=1$, no reasonable fitting was obtained (Fig. 3); for $n=3$, β_3 resulted in a negative value. It was therefore decided that the association of up to two sodium ions per complex anion was meaningful under the experimental conditions. The $\Delta E_{1/2}$ values calculated on the basis of the β values for $n=2$ are in very good agreement with the experiment (Fig. 3).

The other tris(β-diketonato)ruthenate(II)–$\mathrm{Li^+}$, $\mathrm{Na^+}$ systems were analyzed in the same way, since the electrochemical behavior was quite similar except for $[\mathrm{Ru(paa)_3}]^-$, of which the polarograms were distorted in the presence of $\mathrm{Na^+}$ or $\mathrm{Li^+}$ and the analysis was impossible.

In Table 3, the results are presented in terms of K_1 and K_2; for the first three cases, no shift of $E_{1/2}$ was detectable. These formation constants reveal that the interaction is not simply electrostatic ion-pairing.

First, the K_2 values are appreciable. It is reported that the anion radicals of a number of *p*-quinones produced by the one-electron reduction in DMF react with lithium or barium cations to form 2-cations-to-1-anion associates.[20,21)] To the author's knowledge, the present systems are the first examples of 2 to 1 association for univalent anions of a metal complex.

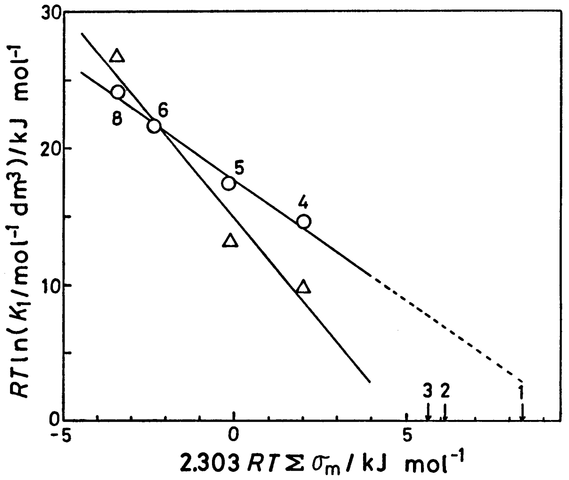

Fig. 4. Relationships between K_1 and the sum of the Hammett constants. —○—, Na^+ system; —△—, Li^+ system. Complex anions are numbered as in Table 3.

Second, the K_1 values are much larger than expected for simple ion-ion electrostatic attraction. For example, the Fuoss theory,[22] which can well explain the association constants of $LiClO_4$ and $NaClO_4$, predicts about 7 mol^{-1} dm^3 when the ion-ion distance is assumed to be 0.6 nm in the case of $[Ru(acac)_3]^-$–Na^+ system (crystallographic radius of $[Ru(acac)_3]$ molecule is *ca.* 0.5 nm[23]). Inversely, an unreasonably small value (*ca.* 0.1 nm) for the ion-ion distance would be required for a formation constant of 5.8×10^3 mol^{-1} dm^3 (experimental value in $[Ru(acac)_3]^-$–Na^+ system). Examination of the K_1 values indicates that the local charge distribution on the complex anion plays an important role. The K_1 seems to be independent of the bulkiness of the complex anion, since the diffusion current constants ($I_d/c\,m^{2/3}\,t^{1/6}$) of the complex were experimentally in the order of **4**, **5**, **8**, **6**. However, the value of K_1 depends on $E^\circ_{1/2}$: the more negative is $E^\circ_{1/2}$, the larger becomes K_1. $E^\circ_{1/2}$ is in turn linearly dependent on the sum of the Hammett constants of the substituents of the ligand, as mentioned earlier. The relationships between K_1 and $\Sigma\sigma_m$ for Li^+ and Na^+ systems are presented in Fig. 4, where the two quantities are expressed in energetic terms. The two straight lines can be explained as follows. When the substituents on the ligand are stronger electron acceptors, the electron density on the chelate rings will decrease. This decrease in the electron density, on one hand, will make the reduction of the neutral complex molecule easier (more positive $E^\circ_{1/2}$) and on the other hand will make it less easy for the cation to attach to the reduced complex anion. This picture implies that the association is attributable mainly to the chelate rings. There are similar cases: Kalinowski and Galazka[24] pointed out the possibility of interaction between Li^+ and the π electron system of the ligands of $[Cu(acac)_2]$ in some aprotic solvents, and Steinbach and Burns[25] found that $[M(acac)_3]$ (M=Fe^{III}, Al^{III}, or Cr^{III}), when recrystallized from chloroform, incorporated two solvent molecules to form the chloroformate and inferred that the hydrogen atom of chloroform was possibly attracted to the oxygens of the acetylacetonate. If the association accompanies desolvation of the cation, the stability will be determined by the balance of two antagonistic factors: the energy loss in desolvation and the energy gain in association. The former depends mainly on the cation size, and the latter on both the cation size and the density of the local negative charge on the ligand system. A high local negative charge will favor the association with a smaller cation, since the energy gain in association offsets the larger desolvation energy. When the local negative charge is low, however, the desolvation energy becomes predominant and a small cation will associate less easily. The two straight lines in Fig. 4 seem to reflect qualitatively this situation, although the examples are too few to allow a quantitative interpretation.

In connection with the present study only the effects of magnesium ion were studied, for potassium, rubidium, and caesium perchlorates were too sparingly soluble in acetonitrile. Magnesium ion does react with the complex anions. But the electrode process was complicated by rapid decomposition subsequent to the association. Besides, a small amount of water had a pronounced effect, making the situation more complicated experimentally. Some results of this study will be reported separately.

Appendix

Preparation of the Complex. *[Ru(bzfa)$_3$]*: "Hydrated ruthenium trichloride" (0.5 g, ca. 2 mmol as Ru), 0.4 g (4 mmol) of potassium hydrogencarbonate, 3.9 g (18 mmol) of Hbzfa were ground together in an agate motar. The resulting muddy solid was extracted with a few portions of carbon tetrachloride. After removal of the solvent, the residue was dissolved in ethanol, and the solution was passed through a column of Merck Alminiumoxid 90 (Aktivitätsstufe II—III). A red material obtained after removal of the solvent from the eluent was dried under vacuum at room temperature. Found: C, 49.3; H, 3.0%. Calcd for $RuC_{30}H_{18}O_6F_9$: C, 48.7; H, 2.6%.

[Ru(fac)$_3$]: A blue residue was obtained, as in the case of $[Ru(paa)_3]$, starting from 0.5 g of ruthenium(III) chloride (2.4 mmol as Ru, dissolved in 40 cm^3 of 1 mol dm^{-3} HCl); it was dissolved in 50 cm^3 of water. The pH was adjusted to about 3 with 1 mol dm^{-3} KOH solution, and then the solution was refluxed on a water bath with 5 g (33 mmol) of Hfac and 20 cm^3 of ethanol for 8 h. After being cooled, the solution was filtered, and the residue was extracted with ethanol. The ethanol solution was concentrated until small crystals began to appear on the surface. Crude $[Ru(fac)_3]$ was obtained on cooling. The product, after being washed with water, was recrystallized from ethanol and dried under a vacuum at room temperature. Found: C, 33.0; H, 2.1%. Calcd for $RuC_{15}H_{12}O_6F_9$: C, 33.8; H, 2.3%.

$[Ru(dbm)_3]$: This complex was prepared by the method of Wolf *et al.*[26] with slight modifications. $[Ru(acac)_3]$ (1.6 g, 4 mmol) and 5.4 g (24 mmol) of Hdbm were dissolved in 50 cm^3 of ethyl benzoate. The solution was refluxed at 160 °C for 12 h under nitrogen atmosphere. Then, 1.2 g of potassium hydrogencarbonate was added to the solution and the reflux was continued for 6 h. After removal of solvent, the residue was extracted with methanol. The black crystalline material obtained by concentration of the extract was recrystallized from benzene and dried under vacuum at room temperature. Found: C, 70.6; H, 4.5%. Calcd for $RuC_{45}H_{33}O_6$: C, 70.1; H, 4.3%.

[Ru(dpm)$_3$]: "Hydrated ruthenium trichloride" (1.5 g, 7 mmol as Ru), 1.0 g (10 mmol) of sodium hydrogencarbonate, and 10 g (54 mmol) of Hdpm were refluxed for 6 h at 160 °C on an oil bath. An additional amount (2.0 g) of sodium hydrogencarbonate was introduced, and the reflux was continued for 18 h at 210 °C. Excess Hdpm and water were removed under reduced pressure, and the residue was extracted into carbon tetrachloride. After removal of the solvent, the residue was dissolved in benzene. This solution was passed through a column of Merck Alminiumoxid 90 (Aktivitätsstufe II—III) and the eluent was concentrated to about 5 cm^3. Acetonitrile and a small amount of water were added to the solution to precipitate the complex. Orange crystals collected by filtration were dried under vacuum. Found: C, 61.0; H, 8.6%. Calcd for $RuC_{33}H_{57}O_6$: C, 60.9; H, 8.8%.

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