β-Diketonate Cr³⁺ Chelates. Stereochemistry and Electrochemistry of Complexes with Two Different Ligands

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Abstract

The synthesis, separation, characterization and electrochemical reduction of Cr^{3+} β-diketonates of the series $Cr(C_6H_5COCHCOCH_3)_n(CH_3COCHCOCH_3)_{3-n}$ are reported. Complete separation of all compounds and their stereoisomers (no stereoisomers for $n = 0$ and 1, three stereoisomers for $n = 2$, and two for $n = 3$) was achieved, using preparative thin layer chromatography on silica gel. No attempt was made to separate optical isomers which exist for each single stereoisomer.

The electrochemical studies of all complexes were done using ac polarography, with Fast Fourier Transform Faradaic Admittance Measurements. Heterogeneous electron transfer rates have been measured in *N,N*-dimethylformamide with 0.1 M Et_4NI as supporting electrolyte (at 298 K). Three one-electron reduction steps were observed, and the heterogeneous electron transfer rates are reported for all compounds. There is a correlation between the stereostructure and the electron transfer kinetics.

Introduction

Octahedral complexes with two different bidentate ligands, of the general formula $M(CD)_n(AA)_{3-n}$, where M is a metal atom, CD an unsymmetrical bidentate ligand and AA is a symmetric bidentate ligand, have geometric isomers for $n = 2, 3$ [1–6].

In this work the series of compounds $Cr(C_6H_5COCHCOCH_3)_n(CH_3COCHCOCH_3)_{3-n}$ is presented (Fig. 1). The following abbreviations will be used: $acac^-$ is the anion of 2,4-pentanedione and $bzac^-$ is the anion of 1-phenyl-1,3-butanedione. Thus the above series will be abbreviated $Cr(bzac)_n(acac)_{3-n}$. To separate the compound mixture, preparative TLC has been used. This technique was used in the past [7–9], together with column chromatography [1], but the separation of geometrical isomers, in some cases, was not complete or not achieved at all. This separation method was successfully applied for
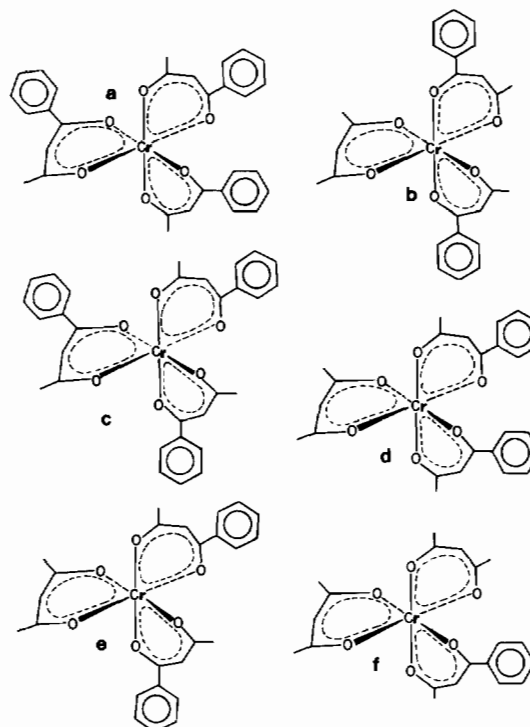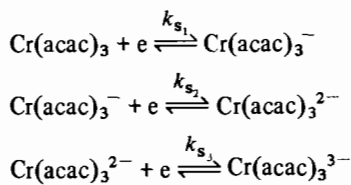

Fig. 1. Geometrical isomers of the series $Cr(bzac)_n(acac)_{3-n}$. a through f indicate elution order. g is $Cr(acac)_3$.

separation of a similar Co^{3+} series in this laboratory [4]. Electrochemical studies of chromium(III) β-diketonates are very limited, and only $Cr(acac)_3$ and $Cr(hfacac)_3$ have been studied [10–12].

The reduction of $Cr(acac)_3$ was found to be reversible in DMF [13]. A three step mechanism was proposed (Scheme 1).

$$Cr(acac)_3 + e \xrightleftharpoons{k_{s_1}} Cr(acac)_3^-$$

$$Cr(acac)_3^- + e \xrightleftharpoons{k_{s_2}} Cr(acac)_3^{2-}$$

$$Cr(acac)_3^{2-} + e \xrightleftharpoons{k_{s_3}} Cr(acac)_3^{3-}$$

Scheme 1.

No electron transfer rate constants were reported for any of the reduction steps. A reexamination of the reduction mechanism is presented here, together with data for all the other compounds of the series of interest.

The SYDAGES-based computerized fast Fourier transform faradaic admittance measurement (FFT-FAM) device has been used [14]. This method has been proven as a powerful one for the elucidation of mechanisms, and measurement of the electron transfer rates with fast redox reactions [15].

Experimental

Syntheses

All reagents used were of commercial grade. 2,4-Pentanedione (Aldrich) was distilled. The first fraction up to 139 °C was discarded, together with an additional 25 ml of distillate at 139 °C; the fraction used was collected between 139 and 140 °C. 1-Phenyl-1,3-butanedione (Aldrich) was used without further purification. $CrCl_3 \cdot 6H_2O$ and urea (Mallinckrodt, analytical grade) were used as received. The series of complexes $Cr(bzac)_n(acac)_{3-n}$ was obtained by using a mixture of the two β-diketones in the known method for synthesis of $Cr(acac)_3$ [16]. The total yield was 90% based on $CrCl_3 \cdot 6H_2O$. Separation of the product mixture has been described elsewhere [4].

Electrochemical Measurements

All the procedures used were the same as in a previous report from this laboratory [4]. The supporting electrolyte here was tetraethylammonium iodide (TEAI) 0.1 M ('electrometric grade', Southwestern Analytical Chemicals Inc.). It was recrystallized five times from doubly distilled methanol.

Results and Discussion

Relative Yield and Chromatography

Among the complexes synthesized of particular interest are those where $n = 2, 3$. (The nomenclature used is that proposed by Fay et al. [1].) For $n = 3$ the statistical yield of the cis isomer is 25%. The relative yield of this isomer, in this study, was lower, indicating a higher stability of the trans isomer [2, 17]. However, for $n = 2$ the yield of the three isomers was statistical, getting a ratio of 1:1:2 in favor of the cis cis isomer. The product was separated by preparative thin layer chromatography on silica. The elution order is presented in Table 1. Generally it depends on the number of the bzac ligands, but there is also significance to the relative position of the phenyl groups. The latter effect causes the trans isomer of $Cr(bzac)_3$ to be eluted first, and the second compound to be eluted is the trans-cis-$Cr(bzac)_2(acac)$. Only these two compounds have two phenyl groups in a relative trans position [4, 18].

Electrochemical Studies

An important problem to be solved is to eliminate the ohmic resistance and the double layer capacitance from the total cell admittance, and thus extract the faradaic admittance components [15, 19]. It is particularly important when high resistance non-aqueous solvents are used (1.0–1.5 kΩ in DMF; 0.1 M TEAI at Hg). The faradaic response contains the in phase and out of phase components [20], which can be transformed to yield, admittance magnitude and cot φ responses [14, 19]. The latter components are used to determine the heterogeneous charge transfer kinetic parameters.

The values of the apparent heterogeneous electron transfer rate constant were calculated from the slope of the cot φ versus $\omega^{1/2}$ linear plot, using eqn. (1) [21]

$$\cot \phi = 1 + \left(\frac{D\omega}{2} \right)^{1/2} \Big/ k_s^{ap} \qquad (1)$$

where k_s^{ap} is the apparent rate constant. Diffusion coefficients were calculated from the dc polarographic limiting currents and the Koutecky-Levich expanding sphere eqn. (2) [22]

TABLE 1. Analytical Data and Melting Points

Compound[a]		Calculated (%)			Found (%)			Melting point (°C)
		C	H	O	C	H	O	
trans-$Cr(bzac)_3$	(a)	67.28	5.08	17.92	66.91	4.92	18.60	232–233
trans-cis-$Cr(bzac)_2(acac)$	(b)	63.41	5.32	20.28	63.11	5.48	20.71	222–224
cis-$Cr(bzac)_3$	(c)	67.28	5.08	17.92	67.61	5.41	17.61	197–198
cis-trans-$Cr(bzac)_2(acac)$	(d)	63.41	5.32	20.28	62.98	5.27	20.01	180–182
cis-cis-$Cr(bzac)_2(acac)$	(e)	63.41	5.32	20.28	63.69	5.49	20.05	189–190
$Cr(bzac)(acac)_2$	(f)	58.39	5.64	23.33	59.00	5.89	22.92	116–117
$Cr(acac)_3$	(g)	51.57	6.06	27.48	51.48	6.04	27.23	216

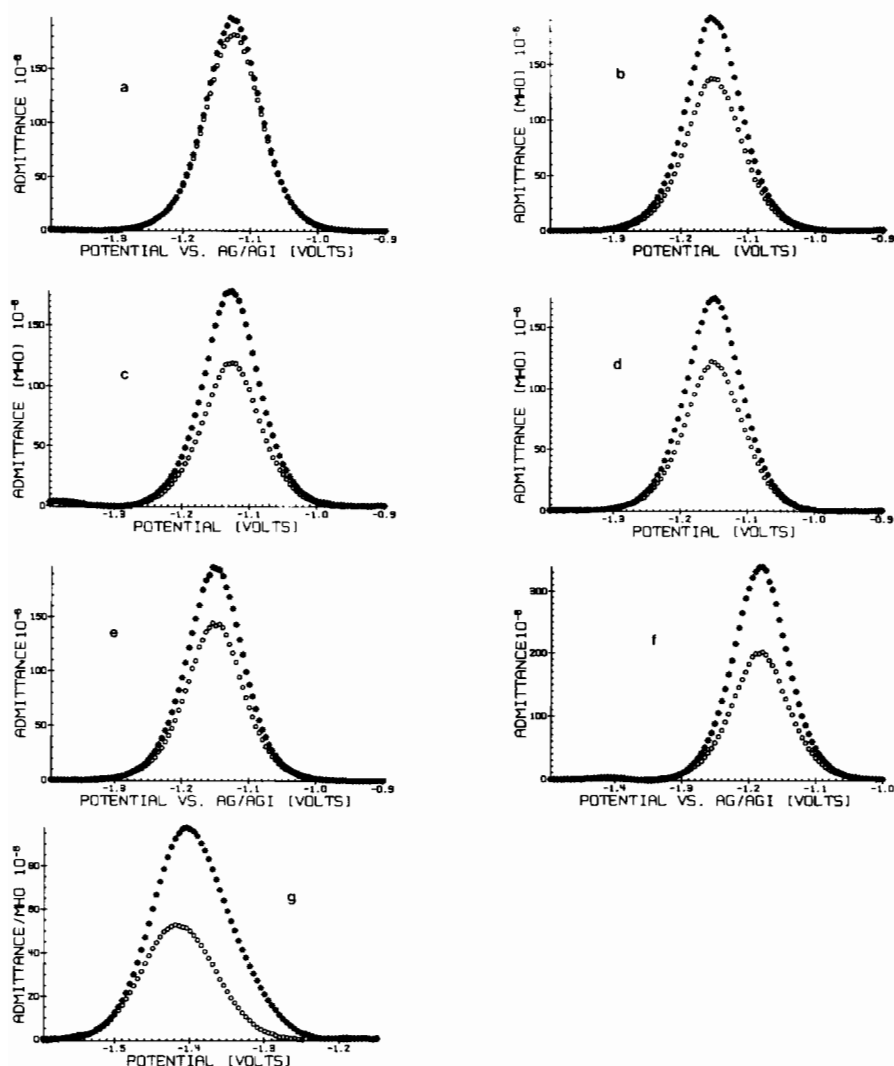[a]Compounds presented according to their elution order.

Fig. 2. a.c. Polarograms of all compounds studied in 0.1 TEAI–DMF at 25 °C, 1 s drop time, 10 averages, f = 97.6 Hz: (*) in-phase component of admittance; (○) quadrature component of admittance. First reduction step Cr(β-diketonate)$_3$ + e $\rightleftarrows$ Cr(β-diketonate)$_3^-$.

$$i_d = nFAC_o^*(7D_o/3\pi\tau)^{1/2}[1 + 39.6(D_o^{1/2}\tau^{1/6}/m^{1/3})]$$

(2)

where τ is the mechanically controlled mercury drop life. D_o and C_o^* are the oxidized species diffusion coefficient and its bulk concentration, respectively. The flow rate of the mercury was determined at the faradaic admittance peak potential for each compound, for the first and second reduction steps.

Since there is good resolution between the reduction steps, it is possible to study each charge transfer step separately [21]. For each heterogeneous electron transfer, there was no evidence of a coupled homogeneous chemical reaction. For all compounds studied, linear plots of cot ϕ *versus* $\omega^{1/2}$ were obtained, with an intercept close to the theoretical value of unity,

at the peak potential (Figs. 3 and 5). The small shoulder which shows at the negative side of the second reduction peak of *cis*-Cr(bzac)$_3$ (Fig. 4a, c), is believed to be an impurity. All the data presented here (Figs. 2–5) are an average of 10 potential scans, where each scan involved about 20 different frequencies.

The correction of the apparent heterogeneous rate constants, k_s^{ap}, for the double layer effect, has been done using the assumption that the outer Helmholz plane (OHP) is the plane where the reaction takes place ($\phi_2 = \phi_{OHP}$). The apparent rate constant k_s^{ap} is related to the corrected one, k_s^{cr}, by eqn. (3) [23]

$$k_s^{ap} = k_s^{cr} \exp[(\alpha n - z)F\phi_2/RT]$$

(3)
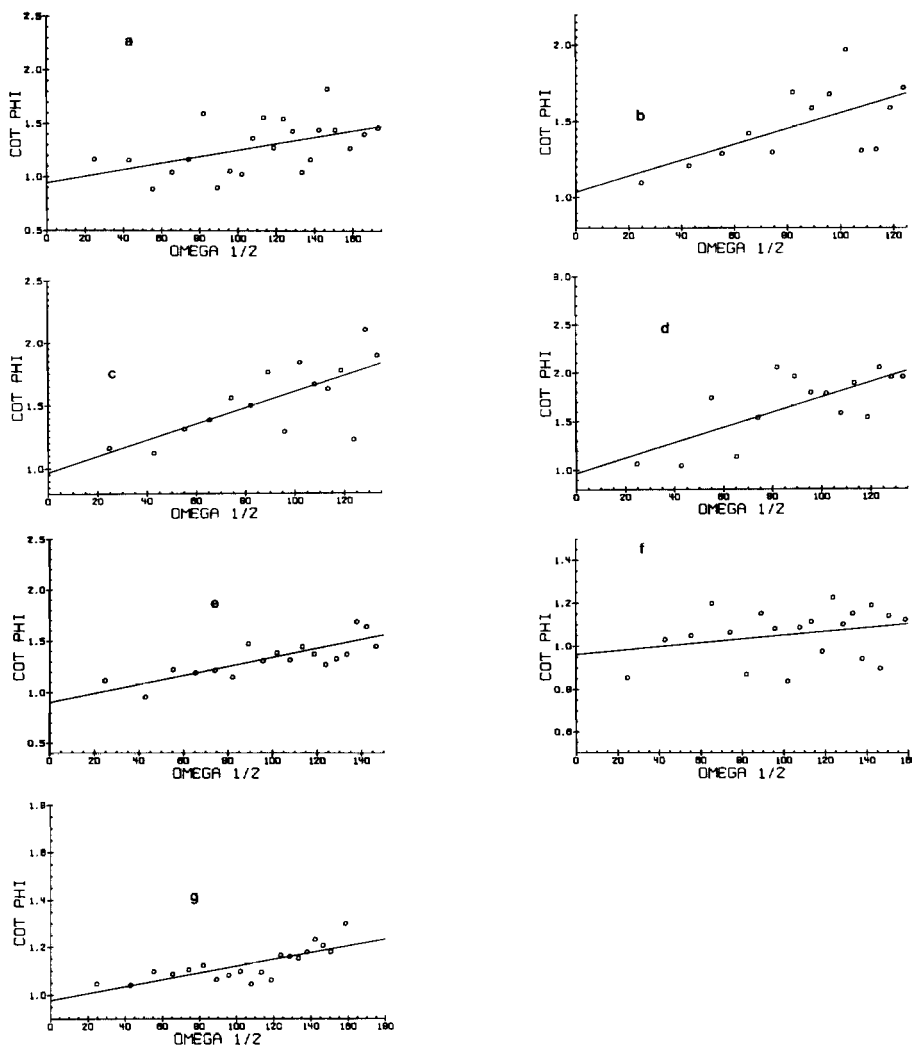
Fig. 3. cot ϕ spectra for Fig. 2.

where z is the charge of the reactant. The ϕ_2 potential was calculated using the diffuse double layer theory [16], in the same way it was done in this laboratory previously [15] according to eqns. (4) and (5)

$$\phi_2 = (2RTz_b F) \sin h^{-1} [q_m (8RT\epsilon\epsilon_o c)^{1/2}] \qquad (4)$$

$$q_m = \int_{E_{pzc}}^{E} C_{dl} dE \qquad (5)$$

where z_b is the bulk electrolyte charge, assuming $z_+ = z_-$. c is the bulk concentration of the supporting electrolyte, ϵ is the dielectric constant of bulk solvent and ϵ_o is the permittivity of free space. The double layer capacity, C_{dl}, and potential of zero charge, E_{pzc}, were obtained as described by Smith *et al.* [15].

As was mentioned earlier in this paper the reduction mechanism of $Cr(acac)_3$ in DMF was studied elsewhere. In this paper it is confirmed that the reduction mechanism follows Scheme 1. However, the calculation of rate constants for the charge transfer was possible mainly for the first two electron transfer steps. In most cases it was difficult to get a reasonable value for the third charge transfer, since it was too close to medium reduction. This difficulty may explain the two step reduction of $Cr(acac)_3$ observed in DMF previously [10]. Figure 7 shows clearly that there are two reduction steps for $Cr(acac)_3$ in the more negative range. Figure 6 shows the third reduction step for $Cr(acac)_2 bzac$ and *trans-cis*-$Cr(bzac)_2 acac$. The third electron transfer was too close to medium reduction to allow a reasonable calculation of the heterogeneous charge transfer rate constant.
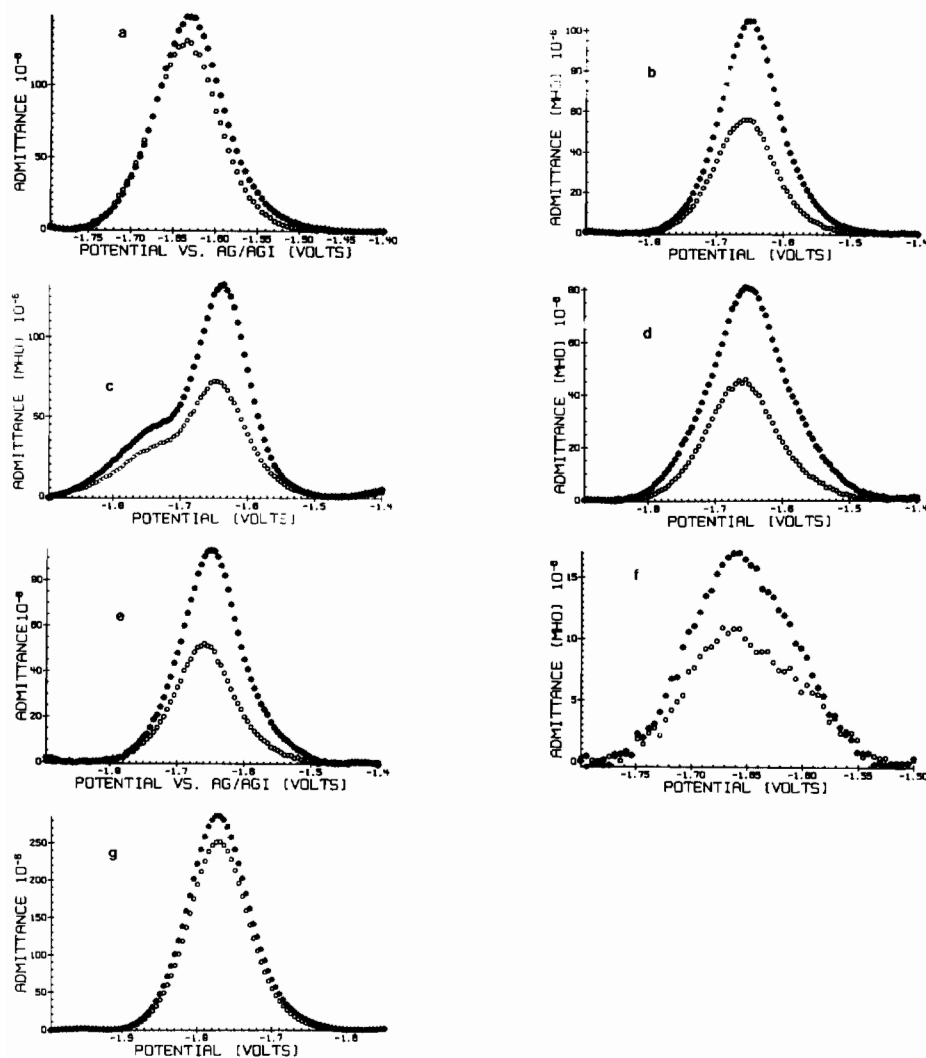
Fig. 4. a.c. Polarograms for second reduction step. Cr(β-diketonate)$_3^-$ + e $\rightleftarrows$ Cr(β-diketonate)$_3^{2-}$. f = 97.6 Hz.

The a.c. polarogram of Cr(acac)$_2$bzac had a fourth reduction step (Fig. 6), with E_p at -2.09 V. It is not clear whether the reduction product is Cr(acac)$_3^{4-}$ or a reduction of a dissociated ligand.

The redox processes investigated here were quasi reversible electron transfers. (The width of the in phase component at half-height is slightly larger than the theoretical value of 90 mV for a single reversible electron transfer [21].) All the charged species generated during the reduction steps [Cr(β-diketonate)$_3^-$, Cr(β-diketonate)$_3^{2-}$, Cr(β-diketonate)$_3^{3-}$], proved to be stable in this medium, and no free ligand was detected at constant potential coulometry.

Looking on the heterogeneous rate constant data for the first reduction step (Table 2), there are two phenomena to notice. The more significant one is the decrease in k_2 with the growing number of bzac

ligands. Increasing the number of bzac ligands causes more steric hindrance while the complex is reduced at the mercury—solution interface. This results in a high value of k_{s1} for the less sterically hindered Cr(acac)$_3$ -21.243 cm/s, and lower values for the rest of the complexes. Reducing the number of phenyl groups causes reduction of the quasi-aromatic stabilization of the β-diketonate—metal ring, and thus leads to a higher k_{s1} value. However, there is a noticeable importance to the relative position of the phenyl groups. Two groups in a *trans* (facial) position cause a higher k_{s1} value, as is seen from Table 2 for the *trans*-Cr(bzac)$_3$, which has a larger k_{s1} value than the *cis* isomer. It is even more significant when comparing the *trans*-Cr(bzac)$_3$ k_{s1} value to the k_{s1} values of the Cr(bzac)$_2$(acac) isomers, where all three isomers have lower electron transfer rates. The same '*trans*' behav-
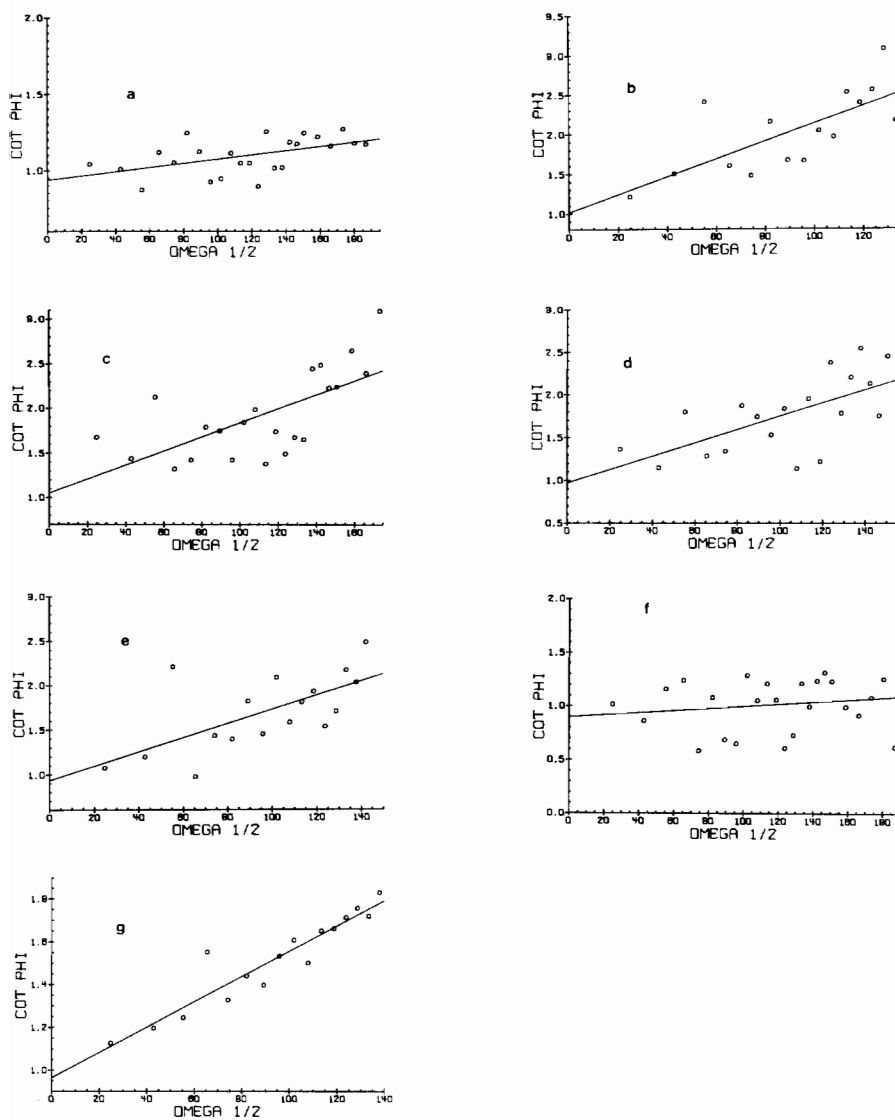
Fig. 5. cot ϕ spectra for Fig. 4.

iour has been outlined in a Co^{3+} β-diketonate series [4].

Another aspect of this study is the actual site of the electron transfer. It is possible to exclude the phenyl ring as an electron transfer site, since such an assumption will lead to a conclusion that the more bzac ligands are in a complex, the higher the k_{s1} value should be. It is believed that the electron is transferred through the chelating ring to the central atom or even directly to the metal atom.

Looking on the data of the second electron transfer rate constant k_{s2} (Table 3), there is again a general trend of larger k_{s2} value with less steric hindrance. There is, however, a distinct exception for both isomers of $Cr(bzac)_3$ which have the largest k_{s2} value of the series. The *trans* isomer has a larger k_{s2} than the *cis* one, which is in agreement with the previous assumption of the relative *trans* position of two phenyl groups. The unusually high value of k_{s2} for both isomers of $Cr(bzac)_3$ is not yet fully understood. It may arise from the perturbance of the 18 electron quasi-aromatic structure during the first charge transfer, and restabilization of the structure by the second electron transfer, thus yielding a relatively large k_{s2} value.

This work has shown a correlation between the stereochemistry and electrochemistry of the compounds studied. This type of study has been the subject of a number of recent publications from various groups [24—26], and it is certain that further investigation will reveal a more detailed picture of these redox reactions.
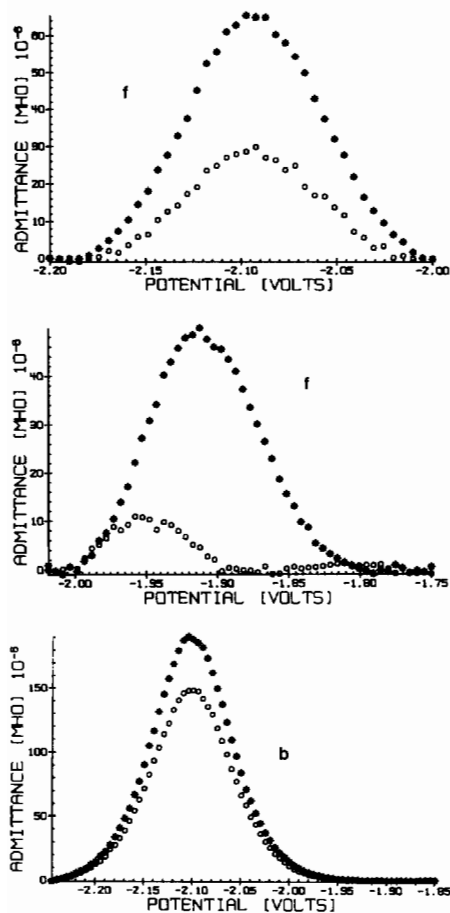
Fig. 6. Third and fourth charge transfer for Cr(acac)₂bzac (f) and third reduction step for *trans-cis*-Cr(bzac)₂acac (b). $f = 97.6$ Hz.

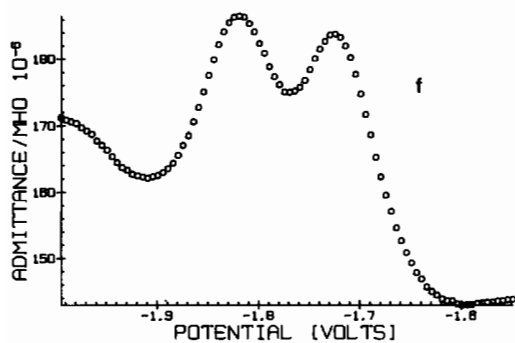Fig. 7. Out of phase component (raw data) for Cr(acac)₃ second and third electron transfer. $f = 97.6$ Hz.

Acknowledgement

TABLE 2. Data for the First Reduction Step

	E_p (V)[a]	k_{s1}^{ap} (cm s⁻¹)[bc]	ϕ_2 (V)	k_{s1}^{cr} (cm s⁻¹)
trans-Cr(bzac)₂	−1.129	0.2263	−0.0927	1.378
cis-Cr(bzac)₃	−1.124	0.1093	−0.0925	0.663
trans-cis-Cr(bzac)₂(acac)	−1.154	0.1343	−0.0935	0.830
cis-trans-Cr(bzac)₂(acac)	−1.149	0.0902	−0.0930	0.552
cis-cis-Cr(bzac)₂(acac)	−1.149	0.1588	−0.0930	0.972
Cr(bzac)(acac)₂	−1.185	0.748	−0.0942	4.688
Cr(acac)₃	−1.404	2.773	−0.1045	21.243

[a]Determined as the total admittance peak at 97.6 Hz.   [b]Calculated assuming $\alpha = 0.5$.   [c]The values presented are the average of three freshly prepared solutions.

TABLE 3. Data for the Second Reduction Step

	E_p (V)[a]	k_{s2}^{ap} (cm s⁻¹)[bc]	ϕ_2 (V)	$10^2 \times k_{s2}^{cr}$ (cm s⁻¹)
trans-Cr(bzac)₃	−1.634	0.5049	−0.107	8.875
cis-Cr(bzac)₃	−1.634	0.08822	−0.107	7.470
trans-cis-Cr(bzac)₂(acac)	−1.649	0.06218	−0.108	1.071
cis-trans-Cr(bzac)₂(acac)	−1.654	0.0643	−0.109	0.769
cis-cis-Cr(bzac)₂(acac)	−1.649	0.0878	−0.108	0.758
Cr(bzac)(acac)₂	−1.662	0.637	−0.110	1.097
Cr(acac)₃	−1.774	0.8507	−0.116	6.278

[a]Determined as the total admittance peak at 97.6 Hz.   [b]Calculated assuming $\alpha = 0.5$.   [c]The values presented are the average of three freshly prepared solutions.

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