

Ligand Field, Electronic and Solvent Effects in the Non-aqueous Electrochemistry of Tris(β -dionato)chromium(III) Chelates

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Abstract

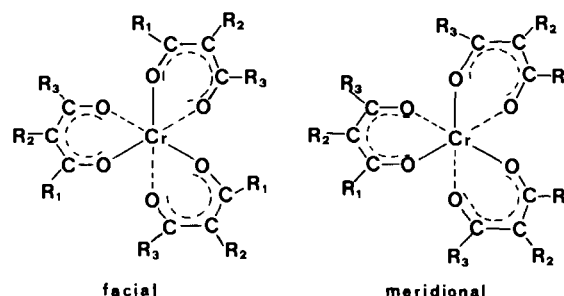
The electrochemical behaviour of a series of tris(β -dionato)chromium(III) chelates has been investigated in acetone and acetonitrile. Reduction proceeds in one electron steps involving the chromium ion. Solvent effects are less important than the influence of substituents within the β -dionato moiety. Potentials range from -2.15 to -0.89 V and a linear correlation exists between $E_{1/2}$ and the sum of Hammett σ functions of the substituents. Comparison with similarly structured complexes indicates that electronic configuration, ionization potentials and ligand field effects influence the reduction potentials. The paramagnetic complexes behave differently from the diamagnetic ones.

Introduction

Electrochemical studies involving coordination compounds have contributed significantly to the understanding of multistep redox processes and of relevant topics such as catalysis of redox reactions, photochemical conversions, electrocatalysis and biological electron transfer reactions [1–6]. The abundance of oxidation states and variability of coordination numbers of transition metals make them particularly suitable for electrochemical investigations of redox series since the redox properties of the transition metal complexes are normally associated with the metal orbitals [7, 8].

The complexes of β -diones and related ligands have attracted a lot of attention [9]. Their ease of preparation and their solubility in a wide variety of solvents have enabled the study of various aspects of their properties and reactivity. Several electrochemical studies have been carried out and relationships were sought to correlate electronic structure with redox potentials [10–16]. Data regarding the influence of groups other than organic radicals on the electro-

chemical properties of substituted β -diketonates are sparse [15]. In order to augment the existing information [12], 22 tris(β -dionato)chromium(III) chelates were prepared, the majority of them having substituents in the methinic carbon atom of the β -dionato moiety. The compounds having different groups attached to the carbonyl carbon atoms ($R_1 \neq R_3$) exist in facial (I) and meridional (II) isomers. Preliminary investigations indicated that there was no meaningful difference in the half-wave reduction potential of the isomers and the subsequent measurements were made in mixtures of the isomers. The complexes employed are listed in Table I. Their electrochemical behaviour was investigated in acetonitrile and acetone solutions by conventional polarography and cyclic voltammetry.



Experimental

Preparation of the Complexes

The ligands Hacac, Htfac, Hbzac, Hbztfac, Hdbm, Hhfac, Hhfod and Hdpm (see Table I) were purchased from Aldrich. The sodium salt Nabda was prepared by the Claisen condensation as described by Collman and coworkers [17] and the complexes $\text{Cr}(\beta\text{-diko})_3$ were prepared by established literature methods [17, 18]. Purification was accomplished by column chromatography on Al_2O_3 with benzene as eluent and repeated recrystallization from CH_3CN . When feasible they were purified by sublimation under vacuum. The observed melting points are given in Table I.

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TABLE I. Names, Abbreviations and Melting Points of the Chromium(III) Complexes Investigated

Compound	R ₁	R ₂	R ₃	Name	Melting point (°C)	
					Found	Literature
Cr(bda) ₃	CH ₃	H	H	tris(1,3-butanedionato)chromium(III)	170–171	171 ^a
Cr(acac) ₃	CH ₃	H	CH ₃	tris(2,4-pentanedionato)chromium(III)	214–215	216 ^a
Cr(Cl-acac) ₃	CH ₃	Cl	CH ₃	tris(3-chloro-2,4-pentanedionato)chromium(III)	203–204	204 ^a
Cr(Br-acac) ₃	CH ₃	Br	CH ₃	tris(3-bromo-2,4-pentanedionato)chromium(III)	224–226	228 ^a
Cr(NO ₂ -acac) ₃	CH ₃	NO ₂	CH ₃	tris(3-nitro-2,4-pentanedionato)chromium(III)	254–255	255 ^a
Cr(SCN-acac) ₃	CH ₃	SCN	CH ₃	tris(3-thiocyano-2,4-pentanedionato)chromium(III)	195–197	191 ^a
Cr(CN-acac) ₃	CH ₃	CN	CH ₃	tris(3-cyano-2,4-pentanedionato)chromium(III)	289–290	290 ^b
Cr(tfac) ₃	CF ₃	H	CH ₃	tris(1,1,1-trifluoro-2,4-pentanedionato)chromium(III)	149–150	150 ^a
Cr(bzac) ₃	C ₆ H ₅	H	CH ₃	tris(1-phenyl-1,3-butanedionato)chromium(III)	216–218	215 ^a
Cr(Br-bzac) ₃	C ₆ H ₅	Br	CH ₃	tris(2-bromo-1-phenyl-1,3-butanedionato)chromium(III)	189–190 ^c	245 ^a
Cr(NO ₂ -bzac) ₃	C ₆ H ₅	NO ₂	CH ₃	tris(2-nitro-1-phenyl-1,3-butanedionato)chromium(III)	244–245	245 ^a
Cr(SCN-bzac) ₃	C ₆ H ₅	SCN	CH ₃	tris(2-thiocyano-1-phenyl-1,3-butanedionato)chromium(III)	171–172	172 ^a
Cr(bztfac) ₃	C ₆ H ₅	H	CF ₃	tris(4,4,4-trifluoro-1-phenyl-1,3-butanedionato)chromium(III)	148–150	150 ^a
Cr(dbm) ₃	C ₆ H ₅	H	C ₆ H ₅	tris(1,3-diphenyl-1,3-propanedionato)chromium(III)	280	300 ^a
Cr(Br-dbm) ₃	C ₆ H ₅	Br	C ₆ H ₅	tris(2-bromo-1,3-diphenyl-1,3-propanedionato)chromium(III)	251–253	254 ^a
Cr(NO ₂ -dbm) ₃	C ₆ H ₅	NO ₂	C ₆ H ₅	tris(2-nitro-1,3-diphenyl-1,3-propanedionato)chromium(III)	217–218	219 ^a
Cr(SCN-dbm) ₃	C ₆ H ₅	SCN	C ₆ H ₅	tris(2-thiocyano-1,3-diphenyl-1,3-propanedionato)chromium(III)	265–266 ^c	265–266 ^c
Cr(dpm) ₃	(CH ₃) ₃ C	H	(CH ₃) ₃ C	tris(2,2,6,6-tetramethyl-3,5-heptanedionato)chromium(III)	227–229	229 ^a
Cr(Cl-dpm) ₃	(CH ₃) ₃ C	Cl	(CH ₃) ₃ C	tris(4-chloro-2,2,6,6-tetramethyl-3,5-heptanedionato)chromium(III)	270–271 ^c	270–271 ^c
Cr(NO ₂ -dpm) ₃	(CH ₃) ₃ C	NO ₂	(CH ₃) ₃ C	tris(4-nitro-2,2,6,6-tetramethyl-3,5-heptanedionato)chromium(III)	228–229 ^c	228–229 ^c
Cr(hfac) ₃	CF ₃	H	CF ₃	tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)chromium(III)	82–84	84 ^a
Cr(hfod) ₃	C ₃ F ₇	H	(CH ₃) ₃ C	tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)chromium(III)	101–103	103 ^a

^aTaken from ref. 17. ^bTaken from ref. 18. ^cThis work.

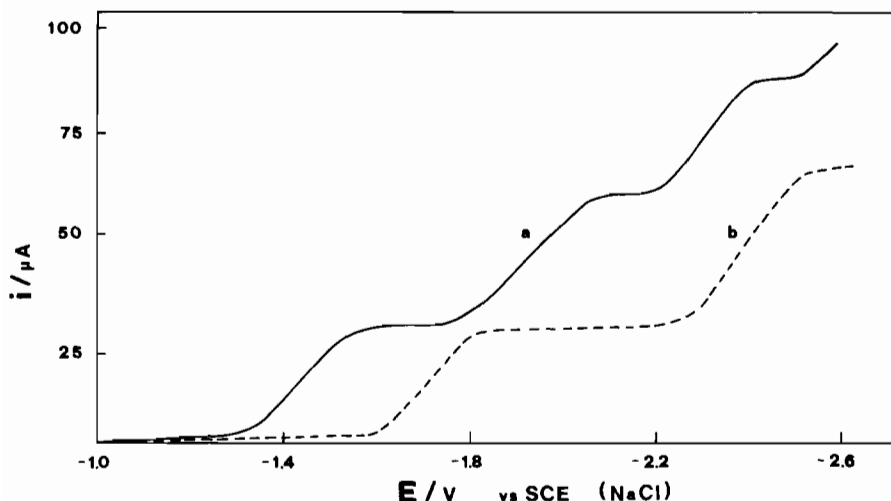


Fig. 1. Typical polarograms of the $\text{Cr}(\beta\text{-diko})_3$ series; (a) $\text{Cr}(\text{dbm})_3$ in acetone with 0.1 M TEAP as supporting electrolyte; (b) $\text{Cr}(\text{bzac})_3$ in acetonitrile with 0.1 M TEAP as supporting electrolyte.

Apparatus and Electrochemical Measurements

The techniques of conventional DC polarography and cyclic voltammetry (CV) were employed in the present study. The apparatus used and the electrode arrangement have been previously described [14, 15].

The solvents, acetonitrile (Aldrich) and acetone (Merck), were sufficiently pure and were used without further treatment. The supporting electrolyte tetraethylammonium perchlorate (TEAP, special for polarography), was purchased from Carlo Erba. Prior to its use TEAP, $[\text{Et}_4\text{NClO}_4]$, was recrystallized twice from ethanol and was dried overnight under vacuum. The solutions were 0.1 M with respect to the supporting electrolyte whereas the concentration of the chromium(III) chelate varied from 0.5×10^{-3} M to 1.0×10^{-3} M. When bulky groups were present, e.g. $-\text{C}(\text{CH}_3)_3$, the complexes were poorly soluble and the maximum concentration attained in saturated solutions was in the order of 10^{-4} M. Oxygen was excluded by purging the solution with pre-purified nitrogen which was pre-saturated with solvent vapour.

Typical polarograms are shown in Fig. 1. The solutions were examined for solvolysis or decomposition by recording the electronic spectra before and after the electrochemical measurements. A slight deterioration was observed in aged solutions of complexes having fluorinated ligands and for this reason all measurements were made immediately after dissolution.

The values given in the voltammograms refer to a hanging Hg electrode of 3.5 mm^2 surface area and were obtained against a calomel electrode saturated with NaCl (SCE).

Results and Discussion

The preparation and purification of the chromium(III) chelates under investigation proceeded smoothly

since most of the compounds are known to the literature. The conditions for electrophilic substitution reactions have diligently been described by Collman and coworkers [17]. In the case of tris(2,2,6,6-tetramethyl-3,5-heptanedionato)chromium(III), $[\text{Cr}(\text{dpmo})_3]$, the substitution reactions proceed slowly and the products were obtained in low yields (20%) probably due to steric inhibition caused by the bulky tert-butyl groups. $[\text{Cr}(\text{CN-acac})_3]$ was prepared as described by Fackler [18]. Attempts to apply the method to 1-phenyl-1,3-butanedione, Hbzac, were only partly successful apparently because of the low solubility of the β -diketone in ethanol. 2-cyano-1-phenyl-1,3-butanedione (melting point (m.p.) $69\text{--}72^\circ\text{C}$) was obtained in very low yields and in insufficient quantities for complex formation. The product was identified by elemental analysis and the strong absorption band of the cyano group at 2205 cm^{-1} .

Electrochemical investigations related to the behaviour of the best known member of the series, $[\text{Cr}(\text{acac})_3]$, have revealed that the number and reversibility of polarographic waves depend on the solvent, the supporting electrolyte and on the electrodes [5, 12, 19–23]. Murray and Hiller [19] investigated the behaviour of $[\text{Cr}(\text{acac})_3]$ in acetonitrile in closely similar conditions to the present study and observed two one-electron reduction waves. We also found that the values of diffusion currents indicate acquisition of one-electron at each step.

Substituents within the β -dionato moiety, as it is known, induce large shifts in the redox potential [10]. Electron-repelling groups impede reduction whereas electron-attracting ones have the opposite effect. For instance replacement of a methyl group by a trifluoromethyl one shifts appreciably the first

TABLE II. Reduction Potentials, Cyclovoltammetric Anodic and Cathodic Peak Values of the First Wave, Spectral Data and Hammett $\Sigma\sigma_x$ Functions for Tris(β -dicarbonylato)chromium(III) Chelates

Compound	$E_{1/2}^1$ (V)	$E_{1/2}^2$ (V)	$E_{1/2}^3$ (V)	P_c (V)	P_a (V)	$(P_c + P_a)/2$ (V)	$P_c - P_a$ (V)	$10Dq$ (μm^{-1})	$\Sigma\sigma_x$
Cr(bda) ₃	-1.68	-1.90						1.79	-0.17
Cr(acac) ₃	-1.94	-2.40						1.79	-0.34
Cr(Cl-acac) ₃	-1.57	-1.88		-1.62	0.00	-0.81	-1.62	1.76	+0.03
Cr(Br-acac) ₃	-1.58	-1.90		-1.63	-0.30	-0.97	-1.33	1.75	+0.05
Cr(NO ₂ -acac) ₃	-1.15	-1.73	-2.10	-1.15	+0.35	-0.40	-1.50	1.79	+0.37
Cr(SCN-acac) ₃	-1.21	-1.90		-1.17	-0.63	-0.90	-0.54	1.79	(+0.28) ^a
Cr(CN-acac) ₃	-1.21	-1.86		-1.26	-1.20	-1.23	-0.06	1.82	+0.34
Cr(tfac) ₃	-1.06	-1.56	-1.75					1.76	+0.38
Cr(bzac) ₃	-1.69	-2.40		-1.71	-1.65	-1.68	-0.06	1.77	-0.16
Cr(Br-bzac) ₃	-1.28	-1.88		-1.24	-0.12	-0.68	-1.12	1.72	+0.23
Cr(NO ₂ -bzac) ₃	-1.00	-1.86		-1.09	+0.45	-0.32	-1.54	1.78	+0.55
Cr(SCN-bzac) ₃	-1.02	-1.75		-1.05	-0.51	-0.78	-0.54	1.78	(+0.46) ^a
Cr(bztfac) ₃	-0.89	-1.50	-1.94	-0.90	-0.84	-0.87	-0.06	1.77	+0.56
Cr(dbm) ₃	-1.63	-2.13		-1.65	-1.59	-1.62	-0.06	1.76	+0.02
Cr(Br-dbm) ₃	-1.18	-1.93						1.72	+0.41
Cr(NO ₂ -dbm) ₃	-0.81	-1.11						1.76	+0.73
Cr(SCN-dbm) ₃	-0.70	-1.88						1.79	(+0.64) ^a
Cr(dpm) ₃	-2.15							1.78	-0.40
Cr(Cl-dpm) ₃	-1.61	-2.16						1.74	-0.03
Cr(NO ₂ -dpm) ₃	-1.21							1.79	+0.31
Cr(hfac) ₃	-0.20	-0.86	-1.50					1.75	+1.10
Cr(hfod) ₃	-1.13							1.78	(+0.41) ^b

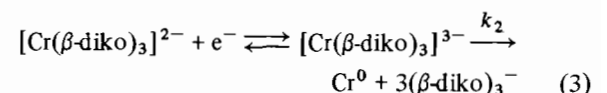
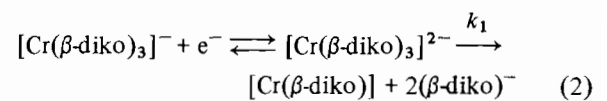
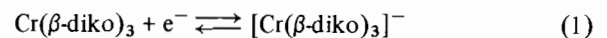
^aCalculated using $\sigma_m = +0.62$ for -SCN.^bCalculated using $\sigma_p = +0.61$ for -C₃F₇.

reduction potential to a more positive value and for [Cr(tfac)₃] $E_{1/2}$ becomes -1.06 V (Table II). As a consequence of the shifts to more positive values, certain complexes give a third reduction wave (Fig. 1). The slope of E against $\log[i/(i_a - i)]$ for each of the three waves in Cr(bztfac)₃ is very nearly the theoretical value of 59 mV for a reversible one-electron process. Substituents other than alkyls or aryls may affect the reversibility of the processes. For instance, the presence of -CN in the 2-position results in enhanced reversibility while the halogens and the nitro group have the opposite effect.

The informations regarding the mechanism of electron transfer are enhanced by the cyclic voltammograms. The average of the cathodic P_c and the corresponding anodic peak potential P_a , $(P_c + P_a)/2$, agrees well with the polarographic $E_{1/2}$ value (Table II) although their difference ΔE_p ($\Delta E_p = P_c - P_a$) is not always 60 mV, the value expected for thermodynamically reversible electron transfer. In fact ΔE_p is approximately 60 mV regardless of scan rate only in chelates bearing hydrogen or the -CN group in the 2-position (Table II). This suggests that in these chelates the stereochemistry of the species [Cr(β -diko)₃] and [Cr(β -diko)₃]⁻ is grossly similar and the similarity also encompasses the charged species [Cr(β -diko)₃]²⁻ and [Cr(β -diko)₃]³⁻. Examination of the ratio (i_{pa}/i_{pc}) indicates that the chemical stability of the charged species diminishes with increasing charge

(Fig. 2). Murray and Hiller [19] carrying out electrochemical studies of metal acetylacetonates found that acquisition of two electrons results in partial decomposition of the charged species [M(acac)₃]²⁻. Plots of (i_{pa}/i_{pc}) against the logarithm of the scanning rate made by Lung and others [5] indicate that [Cr(acac)₃]²⁻ gives up two ligands to form [Cr(acac)].

The cyclic voltammograms of some free β -diketones and their tetrabutylammonium salts, Bu₄N-(β -diko), show that reduction takes place at more negative potential than the corresponding [Cr(β -diko)₃] complexes. For instance the reduction of Bu₄Nacac occurs outside the range of the working electrode while the first reduction wave of [Cr(acac)₃] gives $E_{1/2} = -1.94$ V. These observations confirm earlier suggestions that the electron-transfer processes are metal centered chemically reversible and that the equations (1)–(3) are the most likely expressions of the reactions taking place.



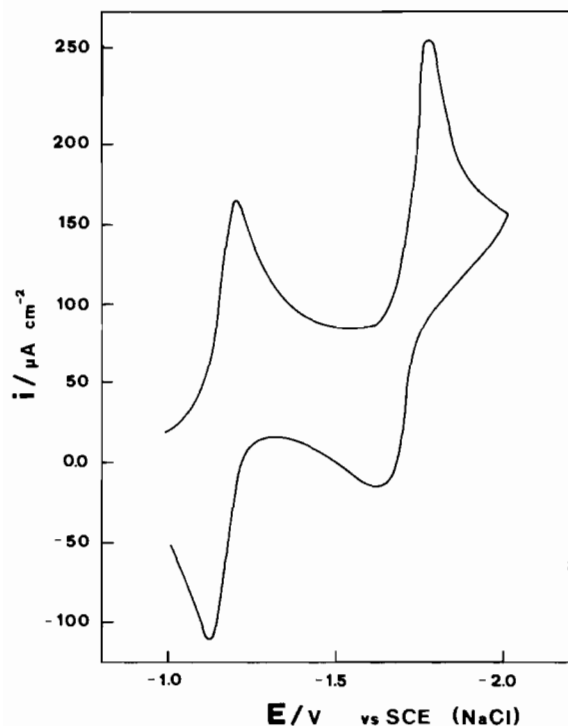


Fig. 2. Cyclic voltammogram of $\text{Cr}(\text{bztfac})_3$ in acetonitrile with 0.1 M TEAP as supporting electrolyte.

The formation of metallic chromium was detected as described by Lemoine and coworkers [24].

Information relevant to the $\text{Cr}(\beta\text{-diko})_3$ compounds is abundant [9] while only inferences may be made regarding the $[\text{Cr}(\beta\text{-diko})_3]^-$ species. Thus, although more than one reduction wave is obtained, the discussion is restricted to the first one. The shifts in the reduction potential clearly originate from the substituents within the β -dionato moiety. Handy and Lintvedt [12] determined the reduction potentials of a series of $[\text{Cr}(\beta\text{-diko})_3]$ complexes in $(\text{CH}_3)_2\text{SO}$ and dioxane–water mixtures and established that the electronic effects are polar in nature. They found that the inductive effect of the substituents attached to the carbonyl carbon atoms is best described by the appropriate σ_p parameter although their position in the chelate ring is *meta* relative to chromium(III). For alkyl or aryl groups attached to the methinic carbon atom the σ_m parameter is applicable. Their results establish linear dependence of $E_{1/2}$ on the sum of Hammett σ functions [25, 26] and are expressed by the equation

$$E_{1/2} (\text{V}) = -1.40 + 0.92 \sum \sigma_x \quad (4)$$

Linear relationship is also found for the present series (Fig. 3). This is expected since substituents within the β -dionato moiety other than alkyl or aryl groups also exert polar effects and should affect the reduction potential. However the regression line for the present

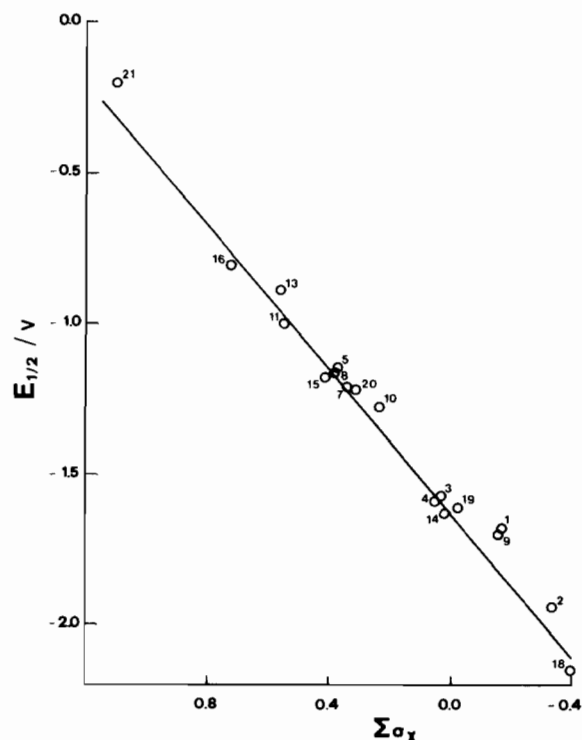


Fig. 3. Correlation of $E_{1/2}$ with the sum of the Hammett σ functions of the $\text{Cr}(\beta\text{-diko})_3$ series.

data in acetone and acetonitrile is different and obeys the equation

$$E_{1/2} (\text{V}) = -1.62 + 1.14 \sum \sigma_x \quad (5)$$

which can also accommodate the data of McMillin and coworkers [27] obtained in CH_2Cl_2 .

It emerges that the susceptibility of the electron-transfer process to the total polar effects of substituents depends on the solvent (eqns. (4) and (5)). Interestingly enough the present regression line (eqn. (5)) runs parallel to those obtained for the $\text{Ru}(\beta\text{-diko})_3$ and the $\text{Fe}(\beta\text{-diko})_3$ series [11, 15] in acetonitrile, *i.e.*

$$E_{1/2} = -0.39 + 1.14 \sum \sigma_x \quad (6)$$

Equations (5) and (6) suggest that the reaction constant is independent of the central ion. The latter, however, has an important effect on the reduction potential. The differences that are due to the central atom may be better understood by relating them to the factors influencing the reduction potential of a coordinated ion and, consequently, the change in free energy ΔG° . These are given in eqn. (7) [16]

$$-\Delta G^\circ = FE_{\text{red}}^\circ = I_p - \Delta G_f^\circ - \Delta G_s^\circ + C \quad (7)$$

where F is the Faraday, I_p is the p^{th} free energy of ionization of the free atom, ΔG_f° is the difference between the free energy of formation of the species $\text{ML}_n^-(\text{g})$ and $\text{ML}_n(\text{g})$, ΔG_s° is the difference of the

TABLE III. Variation of Reduction Potentials and Contribution of the Spherical Field to the Enthalpy of the Reaction

Compound	$\Delta E_{1/2}$ (V)			$\Delta(\Delta H_f^\circ)$ (kJ mol ⁻¹)		
	Cr(β -diko) ₃	Fe(β -diko) ₃ ^a	Co(β -diko) ₃ ^b	Cr(β -diko) ₃	Fe(β -diko) ₃ ^a	Co(β -diko) ₃ ^b
M(bda) ₃	-0.05	+0.05	-0.19	+4.82	-4.83	+18.34
M(acac) ₃	-0.31	-0.13	-0.21	+29.92	+12.55	+20.27
M(Cl-acac) ₃	+0.06	+0.17	-0.01	-5.79	-16.41	+0.97
M(CN-acac) ₃	+0.42	+0.58	+0.14	-40.53	-55.97	-13.51
M(NO ₂ -acac) ₃	+0.48	+0.65	+0.16	-46.32	-62.73	-15.44
M(bzac) ₃	-0.06	-0.06	-0.08	+5.79	+5.79	+7.72
M(tfac) ₃	+0.57	+0.53	+0.18	-55.01	-51.15	-17.37
M(bztfac) ₃	+0.74	+0.57	+0.38	-71.41	-55.01	-36.67
M(dpm) ₃	-0.52	-0.36	-0.27	+50.18	+34.74	+26.06
M(dbm) ₃	0.00	0.00	0.00	0.00	0.00	0.00

^aTaken from ref. 13. ^bTaken from ref. 15.

free energy of solvation of the aforementioned species, and C a constant contributed by the reference half-cell.

For the simple case in which only the ligands are modified, e.g. the Cr(β -diko)₃ series, eqn. (7) is reduced to

$$-F\Delta E^\circ = \Delta(\Delta G_f^\circ) = \Delta(\Delta H_f^\circ) - T\Delta(\Delta S_f^\circ) = \Delta(\Delta H_f^\circ) \quad (8)$$

since $T\Delta(\Delta S_f^\circ)$ is rather negligible [28]. ΔH_f° comprises the spherical part of the ligand field, ΔH_{LF}° , and the ligand field stabilization energy, $\Delta H_{LF}'^\circ$, i.e.

$$-F\Delta E^\circ = \Delta(\Delta H_f^\circ) = \Delta(\Delta H_{LF}^\circ) + \Delta(\Delta H_{LF}'^\circ) \quad (9)$$

For the Cr³⁺/Cr²⁺ couple ΔH_{LF}° amounts to $12Dq^{\text{III}} - 6Dq^{\text{II}} = 7Dq^{\text{III}}$ on the assumption [29] that $Dq^{\text{III}}/Dq^{\text{II}} = 1.3$. The crystal field parameter Dq is directly related to the ligand field by the equation

$$10Dq = g_{(\text{metal})} \times f_{(\text{ligand})} \quad (10)$$

Substituents in β -diketones alter [14, 30] the $f_{(\text{ligand})}$ function only marginally, and therefore $\Delta(\Delta H_{LF}^\circ)$ may be considered negligible within a given series. Under these conditions eqn. (9) in conjunction with eqn. (4) gives

$$-F\Delta E^\circ = \Delta(\Delta H_{LF}'^\circ) = -1.14F\Delta(\Sigma\sigma_x) \quad (11)$$

This suggests that on going from [Cr(bda)₃] to [Cr(tfac)₃], i.e. by inserting the -CF₃ group in the 1-position, the change in the spherical ligand field is as high as 80 kJ mol⁻¹ (Table III). Equation (11) is valid for the paramagnetic complexes mentioned so far, regardless of whether they are [30–32] high-spin (iron) or low-spin (ruthenium). It is worth considering the results [14] for the diamagnetic species Co(β -diko)₃, for which the reaction constant is different (Fig. 4). The transmission of polar effects is seemingly influenced by the electronic configuration of the central atom.

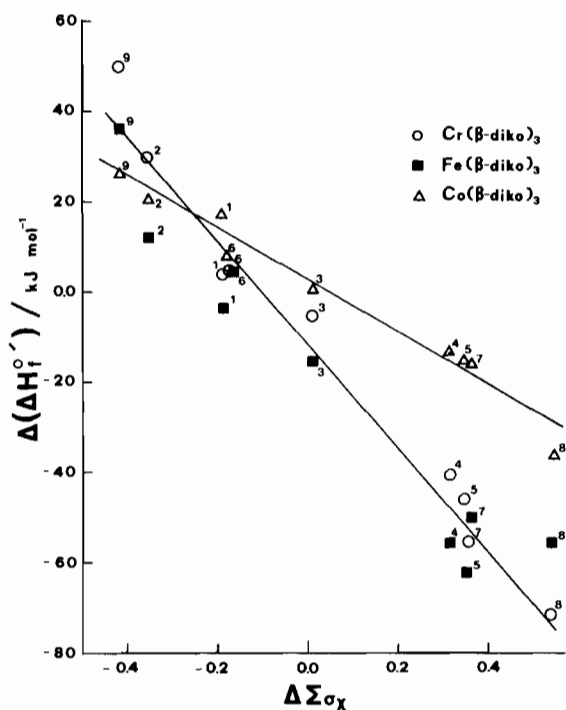


Fig. 4. Dependence of the spherical part of the ligand field ΔH_f° on the sum of the Hammett σ functions and the central ion.

Equation (7) enables the assessment of each factor appearing in it. Considering the Cr(β -diko)₃ and Fe(β -diko)₃ series, eqn. (7) is reduced to

$$F\Delta E^\circ = \Delta I_p - \Delta(\Delta H_f^\circ) = \Delta I_p - \Delta(\Delta H_{LF}^\circ) \quad (12)$$

where each quantity refers to the appropriate iron–chromium couple. ΔI_p is -29.6 kJ mol⁻¹ [33] and from eqns. (5) and (6) $F\Delta E^\circ$ assumes the value of 119 kJ mol⁻¹. As pointed out earlier, the reaction constant under the circumstances is the same in both

cases and so $\Delta(\Delta H_f^\circ)$ should be nil. This implies that $\Delta(\Delta H_{LF}^\circ)$ is about -150 kJ mol^{-1} . This value may be compared with that obtained from spectral data. $\Delta(\Delta H_{LF}^\circ)$, according to Rock [31] comprises the sum of crystal field stabilization energies incurred upon electron acquisition from respective complexes. For the appropriate iron and chromium couples it amounts to

$$\Delta(\Delta H_{LF}^\circ) = -4Dq_{Fe^{II}} - 7Dq_{Cr^{III}} \quad (13)$$

The crystal field parameters $Dq_{Fe^{II}}$ and $Dq_{Cr^{III}}$ may be obtained from the spectral data [30, 34] for $[\text{Fe}(\text{acac})_2]_n$ and the $[\text{Cr}(\beta\text{-diko})_3]$ series in conjunction with the f values of the β -dionato ligands [14]. The agreement is quite reasonable. The present findings suggest that if the validity of eqn. (7) is general it might constitute a means of correlating redox potentials with electronic spectra and *vice versa*.

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