β-Diketonate Co³⁺ Chelates. Stereoisomerism and Electrochemical Studies of Complexes with Two Different Ligands

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Abstract: The syntheses, separation, and characterization of Co³⁺ β-diketonates of the series Co(p-BrC₆H₄COCHCOCH₃)ₙ(CH₃COCHCOCH₃)₃₋ₙ where n = 0, 1, 2 or 3 is 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. Characterization was by elemental analyses, NMR spectroscopy, and single-crystal X-ray analysis where necessary. The electrochemical studies of all complexes were done, using ac polarography with fast Fourier transform Faradaic admittance measurements. These electrochemical measurements were done with use of the dropping mercury electrode in dimethylformamide, containing 0.1 M Et₄NBF₄ as supporting electrolyte (at 298 K). The heterogeneous electron-transfer rates of all isomers are reported. There was a good correlation between the stereostructure of the isomers and their heterogeneous electron-transfer kinetics.

Octahedral coordination complexes with two different bidentate ligands, one of which is unsymmetrical, have geometric isomers. In complexes of the general formula M(CD)₂(AA) (where M is the metal atom, CD is an unsymmetrical bidentate ligand, and AA is a symmetric bidentate ligand) there are three geometric isomers[1] (B, D, and E in Figure 1). The nomenclature used is that proposed by Fay.[1] When the complex is of the type M(CD)₃, where are only two geometrical isomers[2,3] (A and C in Figure 1). For complexes of the formula M(AA)₂(CD) (F in Figure 1) and M(AA)₃, there are no geometrical isomers. All the above mentioned complexes and their isomers also exist as a pair of optical isomers.

This work presents a study of the series of compounds Co(p-BrC₆H₄COCHCOCH₃)ₙ(CH₃COCHCOCH₃)₃₋ₙ where n is 0, 1, 2 or 3. The following abbreviations will be used: (acac)⁻ is the anion of 2,4-pentanedione and (p-Br-bzac)⁻¹ is the anion of 1-(4'-bromophenyl)-1,3-butanedione (or p-Br-Benzoylacetone), thus the above series will be abbreviated Co(p-Br-bzac)ₙ(acac)₃₋ₙ. Thin-layer chromatography was used as a separation method. This technique was used before[4–6] together with column chromatography,[1] but the separation, in some cases, of geometrical isomers of similar series was not complete or not achieved at all.

In this study the synthesis, complete separation, characterization, and heterogeneous electron-transfer observations of the above mentioned series are reported.

The one-electron reduction of Co(acac)₃ was previously investigated among other metal β-diketonates.[7–13] The reversibility of this reaction was investigated in various solvents like dimethoxyethane,[7] acetonitrile,[11,12] and acetone,[13] and different conclusions were reached depending on the solvent and polarographic method used. While this paper was in preparation additional electrochemical study of Co(III) β-diketonates was published.[30] Although stereoisomers exist for 8 out of 12 chelates studied, no attempt was made to separate these isomers, and the compounds were treated as pure. We present here a reexamination of the Co(acac)₃ reduction process in dimethylformamide, together with electrochemical data of the series of interest, using the SYD-AGES-based computerized fast Fourier transform Faradaic admittance measurement (FFT-FAM) device.[14] This method has proven itself as a powerful one for the elucidation of mechanisms of redox processes in various cases.[15–17]

Experimental Section

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-(4'-Bromophenyl)-1,3-butanedione was prepared as described in the literature.[18] The series of complexes Co(p-Br-bzac)ₙ(acac)₃₋ₙ was obtained by using a mixture of the two β-diketones in known method of synthesis for Co(acac)₃.[19] The total yield was 60% based on cobalt(II) carbonate.

Chromatography. Separation of all isomers was done on silica plates from Merck (PF²⁵⁶). About 40 mg of mixture were dissolved in 0.5 mL of dry ether and applied on a single plate. The development was with chloroform, and after 2 h complete separation of all the compounds and their isomers was achieved. (The letters A through G indicate the elution order of the isomers.) The dry silica bands were removed and washed thoroughly with ether, which was filtered and evaporated. No attempt was made to separate the pairs of optical isomers existing for each stereoisomer. The elemental analyses and melting points of each chelate are given in Table I.

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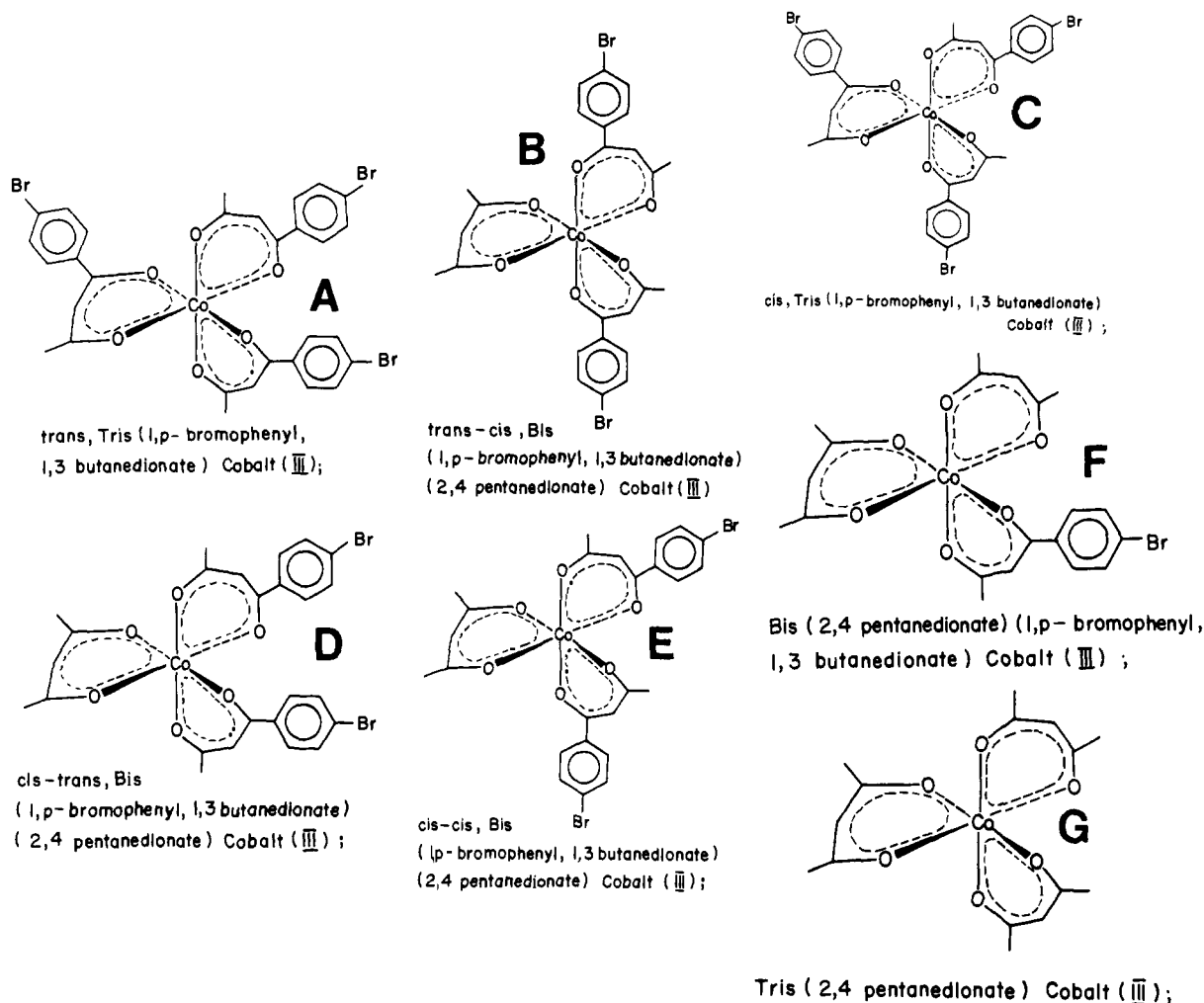‡Technion Israel Institute of Technology.
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trans, Tris (1,p- bromophenyl,
1,3 butanedionate) Cobalt ($\underline{III}$);

trans-cis, Bis
(1,p-bromophenyl, 1,3 butanedionate)
(2,4 pentanedionate) Cobalt ($\underline{III}$)

cis, Tris (1,p-bromophenyl, 1,3 butanedionate)
Cobalt ($\underline{III}$) ;

cis-trans, Bis
(1,p-bromophenyl, 1,3 butanedionate)
(2,4 pentanedionate) Cobalt ($\underline{III}$) ;

cis-cis, Bis
(1p-bromophenyl, 1,3 butanedionate)
(2,4 pentanedionate) Cobalt ($\underline{III}$);

Bis (2,4 pentanedionate) (1,p- bromophenyl,
1,3 butanedionate) Cobalt ($\underline{III}$) ;

Tris (2,4 pentanedionate) Cobalt ($\underline{III}$);

Figure 1. Geometrical isomers of the series $Co(p\text{-Br-bzac})_n(acac)_{3-n}$.

Table I. Analytical Data and Melting Points

	calculated			found			
	C	H	Br	C	H	Br	mp, °C
trans-Co(*p*-Br-bzac)$_3$ (A)	46.21	3.10	30.79	46.46	3.30	31.26	67–68
cis-Co(*p*-Br-bzac)$_3$ (C)	46.21	3.10	30.79	46.71	3.14	29.72	105–106
trans-cis-Co(*p*-Br-bzac)$_2$(acac) (B)	47.03	3.63	25.05	46.93	3.76	24.45	205–207
cis-trans-Co(*p*-Br-bzac)$_2$(acac) (D)	47.03	3.63	25.05	46.89	3.41	24.51	80–81
cis-cis-Co(*p*-Br-bzac)$_2$(acac) (E)	47.03	3.63	25.05	47.37	3.51	25.31	98–100
Co(*p*-Br-bzac)(acac)$_2$ (F)	48.15	4.42	19.57	47.75	4.50	19.95	119–120

Electrochemical Measurements. The computerized instrument used has been described in detail elsewhere.[14,20] The electrochemical cell was comprised of a dropping mercury working electrode (DME) with a mechanically controlled 1 s drop time and a flow rate of 0.24, mg/s. A platinum wire was used as the auxiliary electrode, and the reference electrode was a homemade Ag/AgI/0.10 M tetraethylammonium iodate (TEAI) electrode, in dimethylformamide (DMF), with a Vycor frit solution junction. All potential values in the paper are reported vs. this reference electrode. It's potential vs. the SCE reference electrode is –0.54 V in DMF.

DMF ("distilled in glass", Burdick and Jackson Laboratories) was passed over a column of alumina (Alcoa Company of America, dried for 12 h at 450 °C), under N$_2$. The first portion eluted from the column (about one-third) was discarded because of a possible impurity. The main portion was redistilled under vacuum, and the first portion of the distillate was discarded. The remaining solvent was stored under argon until it was used to prepare a cell solution.

The supporting electrolyte was tetraethylammonium tetrafluoroborate (TEATFB) ("electrometric grade" Southwestern Analytical Chemicals

Inc.) recrystallized five times from hot doubly distilled Methanol (Burdick and Jackson). TEAI underwent the same recrystallization process. After recrystallization the supporting electrolytes were dried in vacuo at 70 °C for 24 h.

The recrystallized TEAI and the purified DMF were used to prepare the reference electrode solution. Argon (Matheson Gas Products) was used to degas the solution in the cell. The gas was passed through two columns on the way to the cell. The first one was filled with molecular sieves and the second with an oxygen scavenger (Ridox). This was followed by a gas bubbler solvent saturator system.

All measurements were taken under a blanket of Argon at a temperature of 25.0 ± 0.5 °C.

Results and Discussion

Relative Yield. The series $Co(p\text{-Br-bzac})_n(acac)_{3-n}$ was synthesized in the usual way of preparing Co(acac)$_3$ by allowing a mixture of the two ligands to react with CoCO$_3$. In a similar series for Cr^{3+} with acac and p-NO$_2$-bzac as the ligands, it was shown that in variable ligand ratio, in the starting materials mixture, from a 1:5 ratio acac:p-NO$_2$-bzac to 5:1, respectively, there is a large preference toward the products containing the aromatic ligands, 52–98%. The total yield was 78% of products which contained the aromatic ligand, when the ratio of ligand in the

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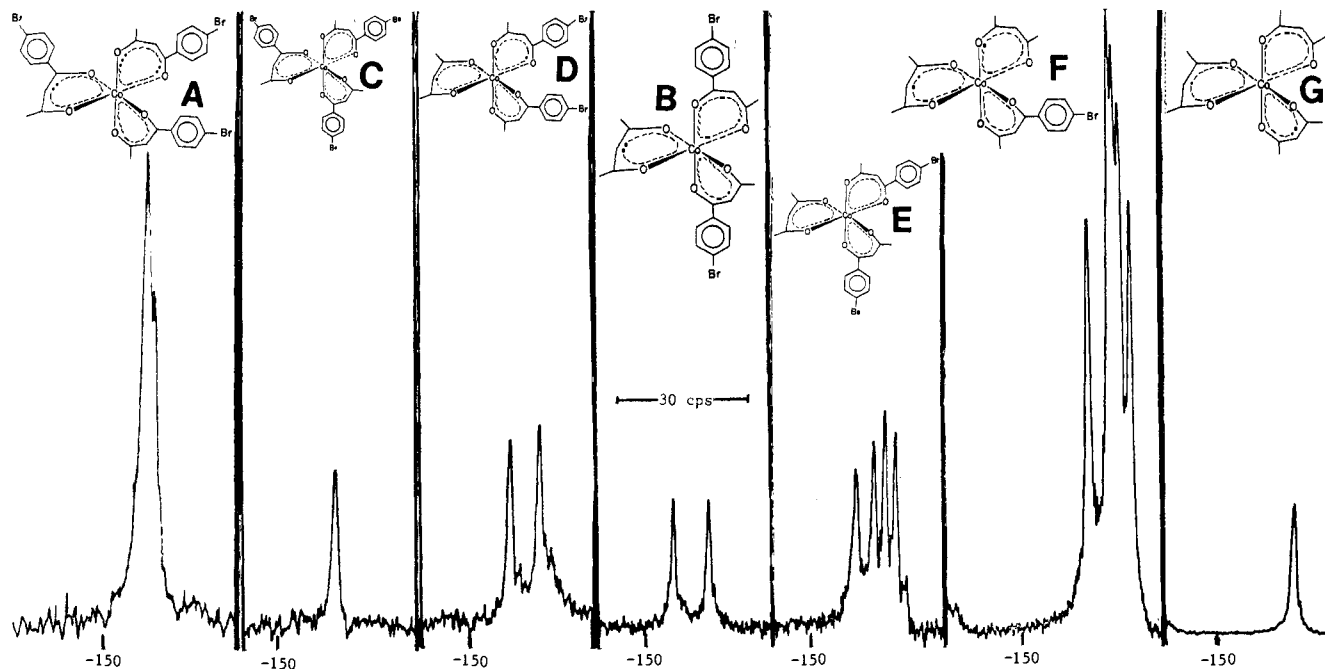
Figure 2. Methyl region in the NMR spectrum of all isomers in the series Co(*p*-Br-bzac)$_n$(acac)$_{3-n}$ (CDCl$_3$ with internal standard Me$_4$Si = 0, sweep width 250 Hz).

starting mixture was 1:1.[21] This is easily understood in view of the fact that in the aromatic β-diketone the keto–enol equilibrium is shifted completely toward the enol tautomer.[22]

There is a particular interest to look at the yield of each stereoisomer in the two groups (*n* = 2, 3) which contain the isomers. For *n* = 3 the statistical yield of the cis isomer is 25%. Unlike results obtained previously[2,23] with some metal benzoylacetonates, indicating a greater stability of the trans isomer, the yield obtained in this case was purely statistical. However, there is consistency between the statistical yield obtained for our series of complexes, when *n* = 2, and the parallel complexes with trifluoroacetylacetone instead of *p*-Br-bzac,[1] getting a ratio 1:1:2 in favor of the cis,cis isomer. None of these results suggest a stability preference of any one isomer in these two groups.

Chromatography and Characterization. With use of preparative thin-layer chromatography, the product mixture was separated into all seven possible stereoisomers of the series Co(*p*-Br-bzac)$_n$(acac)$_{3-n}$. The order of elution is as follows: band 1, *trans*-Co(*p*-Br-bzac)$_3$ (A in Figure 1); band 2, *trans-cis*-Co(*p*-Br-bzac)$_2$acac (B in Figure 1); band 3, *cis*-Co(*p*-Br-bzac)$_3$ (C in Figure 1); band 4, *cis-trans*-Co(*p*-Br-bzac)$_2$acac (D in Figure 1); band 5, *cis-cis*-Co(*p*-Br-bzac)$_2$acac (E in Figure 1); band 6, Co(*p*-Br-bzac)(acac)$_2$ (F in Figure 1); and band 7, Co(acac)$_3$. The elution order depends generally on the number of *p*-bromophenyl groups in the molecule,[1] but there is also significant importance to the relative position of the *p*-bromophenyl groups. Only *trans*-Co(*p*-Br-bzac)$_3$ and *trans-cis*-Co(*p*-Br-bzac)$_2$acac have two *p*-bromophenyl groups in a trans position. It appears from the elution order that the latter effect is more significant than the former one, resulting in the elution order obtained, unlike similar results observed with the trifluoroacetylacetone complexes.[1] In a similar series of Cr³⁺ the same elution order was obtained.[21]

The full characterization of all seven bands was done with NMR spectra and X-ray diffraction patterns. We used the methyl resonances in assigning the spectra for the appropriate compound. There are two types of methyl groups, one from the acac ligand which resonates at −132 ± 3 Hz relative to Me$_4$Si and a second one from the *p*-Br-bzac ligand which resonates at a lower field,

due to the presence of the aromatic ring, at −140 ± 2.5 Hz (Figure 2).

The methyls of Co(acac)$_3$ resonate at −132.0 Hz relative to Me$_4$Si, and the singlet of the symmetric *cis*-Co(*p*-Br-bzac)$_3$ resonates at −140.0 Hz. The trans isomer has three different methyls, two of which are not resolved, and only two resonances appear in its spectrum.

More evidence was obtained in support of the fact that there is no stability preference of the trans isomer, in this series, relative to the cis isomer. We studied the *cis*-Co(*p*-Br-bzac)$_3$ at temperatures up to 90 °C and for as long as 3 h. No resonances appeared in the methyl region of the NMR spectrum, except the singlet of the starting compound, at −140.0 Hz.

The cis-cis isomer of Co(*p*-Br-bzac)$_2$acac, which has no symmetry, gives rise to four methyl resonances, which show clearly in the spectrum. Also Co(*p*-Br-bzac)(acac)$_2$ has no symmetry elements, thus resulting in five resolved resonances. Only the cis-trans and the trans-cis isomers of Co(*p*-Br-bzac)$_2$acac are not distinguishable by their NMR spectra, since both possess a C$_2$ symmetry axis. This identification problem was solved by obtaining the X-ray structure of the cis-trans isomer.

Electrochemical Studies—Heterogeneous Electron-Transfer Rates. Electrochemical studies of Co(acac)$_3$ were performed previously.[7-13,24] The redox process is a one-electron reduction, the reversibility of which is dependent on the medium and the stability of the reduction product in this medium. Generally it is agreed that the reduction is an EC mechanism as shown in Scheme I.

Scheme I

$$Co(acac)_3 + e \underset{}{\overset{k_s}{\rightleftharpoons}} Co(acac)_3^-$$

$$Co(acac)_3^- \rightarrow Co(acac)_2 + acac^-$$
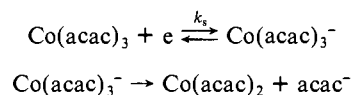
Only in acetonitrile was there evidence for a reversible reduction which included only one step and resulted in the formation of a stable reduction product in this medium.[12] We obtained a more detailed picture for the reduction mechanism of Co(acac)$_3$ in DMF.

Parts A and B of Figure 3 show the AC polarogram and cot φ vs. ω$^{1/2}$ of Co(acac)$_3$, respectively. These studies show that the

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Table II. Data for the Reduction of the $Co(p\text{-}Br\text{-}C_6H_4COCHCOCH_3)_n(CH_3COCHCOCH_3)_{3-n}$ Series in DMF + TEAFB 0.1 M at 298 K

compound	$E_{1/2}$, V	$D \times 10^5$, cm²/s	α	k_s, cm/s
trans-Co(p-Br-bzac)₃ (A)	0.267	1.71	0.686	0.0703 ± 0.0130
cis-Co(p-Br-bzac)₃ (C)	0.296	0.374	0.770	0.0220 ± 0.0058
trans-cis-Co(p-Br-bzac)₂(acac) (B)	0.247	1.67	0.685	0.0647 ± 0.0215
cis-trans-Co(p-Br-bzac)₂(acac) (D)	0.201	0.654	0.718	0.0336 ± 0.0091
cis-cis-Co(p-Br-bzac)₂(acac) (E)	0.183	0,409	0.610	0.0388 ± 0.0011
Co(p-Br-bzac)(acac)₂ (F)	0.107	2.05	0.605	0.113 ± 0.031
Co(acac)₃ (G)	-0.0997	3.44	0.558	0.218 ± 0.036

reduction is irreversible (width of in-phase component at half-height is $>90/n$ mV) and that there is a catalytic process associated with the reduction reaction. Smith and McCord had developed the theory and shown experimental results for an irreversible process with a catalytic step with the mechanism shown below:[25-27]

$$O + ne \underset{}{\overset{k_s}{\rightleftharpoons}} R$$
$$\downarrow \quad \underline{\qquad k_c \qquad}$$
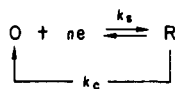
The fundamental harmonic current is given by

$$I(\omega t) = \frac{n^2F^2AC_0(k_cD_0)^{1/2}\Delta E}{4RT \cosh^2 (i/2)} \sin \omega t \qquad (1)$$

where all the notations have their regular electrochemical definition, and this equation holds for $k_c \gg \omega$ which is true at lower frequencies and also the charge transfer kinetics have no effect on the response. The phase angle relation for a catalytic reaction is given as
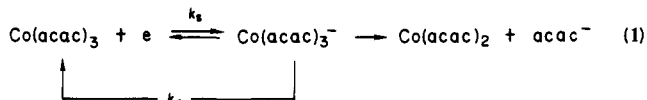
$$\cot \phi = \frac{\dfrac{(2\omega)^{1/2}}{\lambda} + \left[\dfrac{(1 + g^2)^{1/2} + g}{1 + g^2}\right]^{1/2}}{\left[\dfrac{(1 + g^2)^{1/2} - g}{1 + g^2}\right]^{1/2}} \qquad (2)$$

where $g = k_c/\omega$ $\lambda = \dfrac{k_s f}{D^{1/2}}(e^{-\alpha j} + e^{\beta j})$ $f = f_0^\alpha f_R^\beta$

$$\beta = 1 - \alpha$$

The low-frequency limit for eq 2 is

$$\lim_{\substack{g \to \infty \\ \omega \to 0}} \cot \phi = \infty$$

as is seen in the Co(acac)₃ cot ϕ vs. $\omega^{1/2}$ spectrum. On the basis of the mechanism proposed earlier,[13] we assume a similar mechanism here:

$$Co(acac)_3 + e \underset{}{\overset{k_s}{\rightleftharpoons}} Co(acac)_3^- \longrightarrow Co(acac)_2 + acac^- \quad (I)$$
$$\uparrow \quad \underline{\qquad k_c \qquad}$$

Thus we have a disproportionation catalytic mechanism, which involves dissociation of an acac⁻ ligand from the octahedral complex. The overall reaction scheme is

$$Co(acac)_3 + e \rightarrow Co(acac)_2 + acac^- \qquad (II)$$
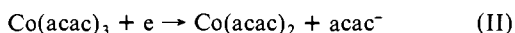
which was proposed previously[13,24] and was supported by potentiostatic coulometry experiments performed by Gross et al.[10] However, these authors had concluded that the Co(acac)₃⁻ formed is stable in acetonitrile and that the reduction is reversible. More supporting evidence for the irreversible reaction mechanism was obtained by Collman[28] and Saar[21] when trying to reduce a nitro
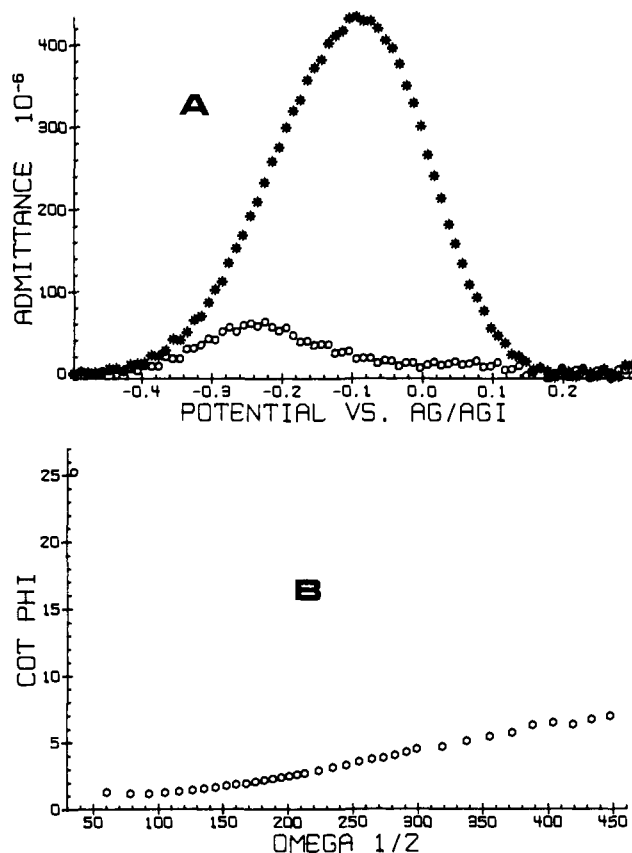

Figure 3. (A) AC polarogram for a 1.6 mM solution of Co(acac)₃ in 0.1 M TEATFB–DMF at 25 °C, 1 s drop time, 10 averages, $f = 196$ Hz: (*) in-phase component of admittance; (O) quadrature component of admittance. (B) Cot ϕ spectrum.

functionalized octahedral Co^{3+} β-diketonate. This leads to decomposition of the octahedral complex to give a rose-red precipitate, indicative of the reduction of Co^{3+} to Co^{2+}.

For the rest of the series $Co(p\text{-}BrC_6H_4COCHCOCH_3)_n\text{-}(CH_3COCHCOCH_3)_{3-n}$ we obtained a similar catalytic mechanism. Unfortunately it is difficult to tell which of the ligands dissociates first in a mixed-ligand complex, without obtaining more data on such a dissociation. We assume that when $n = 1$ or 2, the acac⁻ ligand is the first one to dissociate, based on the fact that the aromatic ring in the other ligand stabilizes the quasi-aromatic character of the β-diketonate.

The individual k_s values for each complex in the series were calculated with eq 3 (ref 29, p 29), which is valid at the potential

$$(\cot \phi)_{max} = 1 + \frac{(2\omega D)^{1/2}}{k_s[(\alpha/\beta)^{-\alpha} + (\alpha/\beta)^\beta]} \qquad (3)$$

corresponding to the maximum in the cot ϕ vs. E_{dc} profile for any given frequency. $(E_{dc})_{max}$ is given in eq 4, which was also used

$$(E_{dc})_{max} = E_{1/2} + \frac{RT}{nF} \ln\left(\frac{\alpha}{\beta}\right) \qquad (4)$$

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to calculate the transfer coefficient α. Since the reduction process proved to be a catalytic one, only high-frequency measurements were used to calculate k_s, a frequency region where $k_c \gg \omega$ does not apply. Looking on the heterogeneous rate constant data (Table II), there are two phenomena to notice. k_s increases with decreasing number of p-Br-bzac ligands, within a single n value, when the complex is less sterically hindered.

Decreasing the number of p-Br-bzac ligands in a complex causes less steric hindrance, when a molecule is reduced at the mercury solution interface. This also reduces the quasiaromatic stabilization of the β-diketonate–metal ring and thus leads to a higher k_s value. However, there is an exception to this general trend, since the trans isomer (A) when $n = 3$ has a larger k_s value than all of the isomers with $n = 2$. As was true for the separation of the compounds, the number of p-Br-bzac ligands is not the only major factor influencing separation but also is important in the relative position of the phenyl rings. The k_s values of the trans isomer (A, $n = 3$) and the trans-cis isomer (B, $n = 2$) are similar, 0.0703 ± 0.0130 and 0.0674 ± 0.0215 cm/s, respectively. They are the only two isomes which have two phenyl rings in trans positions and thus allow the molecule being reduced to come closer to the mercury electrode, resulting in a higher k_s value. Within a single value of n, the variations in k_s are in accordance with the predicted behavior of these complexes, based on steric effects. When $n = 3$, the trans isomer has higher k_s than has the cis, 0.0703 ± 0.0130 and 0.0220 ± 0.0580 cm/s, respectively. From Figure 1 it can be seen that the trans isomer (A) has an open site between the trans phenyl rings, which does not exist in the symmetrical cis isomer (C), and this allows closer access to the electrode surface, resulting in a larger k_s value for isomer A. For $n = 2$ the largest

k_s is for the trans-cis isomer (B) again for the same reason of having two phenyl rings at a trans position. According to these results the isomers which have two phenyl rings in a trans position have a larger k_s value than those who do not. Even though isomer D (cis-trans isomer $n = 2$) appears to be less sterically hindered, it does not have phenyl rings in a trans position and it has a lower k_s value than the trans,cis isomer (B). This strongly implies that the relative trans position has more influence than only the steric hindrance. This phenomenon is under investigation.

Of significant importance is an inductive effect which clearly shows in the $E_{1/2}$ values for the various complexes (Table II). A replacement of one acac ligand by one p-Br-bzac ligand results in a positive shift of $E_{1/2}$ by 72–118 mV on an average. We believe that this positive shift is due to the presence of the bromine in the phenyl ring. This assumption is currently being investigated in a similar series of complexes where the p-Br-bzac ligand is replaced by 1-phenyl-1,3-butanedione (benzoylacetone, bzac). The relative trans position of two phenyl rings has an effect also on the $E_{1/2}$ values. It is clear from the data presented that complex B which has two phenyl groups in a trans position has an $E_{1/2}$ value of 0.247 mV which is much closer to that of complex A [trans-Co(p-Br-bzac)$_3$], 0.267 mV, than to that of the other complexes with $n = 2$, which are reduced at 0.201 and 0.183 mV.

We have shown here a good correlation between the structure of the specific isomers, their behavior in separation, and heterogeneous rate constants for electron transfer. We were able to get a more detailed picture for the reduction mechanism than what was obtained previously.

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On the Concept of Local Hardness in Chemistry

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Abstract: Density functional theory is shown to provide a natural definition for a local atomic or molecular property called the local hardness,

$$\bar{\eta}(r) = \frac{1}{2N} \int \frac{\delta^2 F[\rho]}{\delta\rho(\bar{r})\delta\rho(\bar{r}')}\rho(\bar{r}') \, d\bar{r}'$$

Weighted by the Fukui function $f(\bar{r})$ of Parr and Yang and integrated over all space this gives the global absolute hardness $\eta = \frac{1}{2}(d^2E/dN^2)_v$ of Parr and Pearson

$$\eta = \int f(\bar{r})\bar{\eta}(\bar{r}) \, d\bar{r}$$

The corresponding integral over a portion of a molecule gives a regional or group hardness. Various properties and identities involving local hardness are discussed, and it is shown that local hardness constitutes a generalization of the classical electrostatic potential due to an electron distribution.

By now it is clear that the density functional description[1] of many-electron systems provides a highly useful framework for rigorous quantitative definition of important concepts in chemistry and schemes for their calculation as well. In the present paper

we show how this language includes the idea that different particular places in an atom or molecule can be "hard" or "soft"—the concept of local or site hardness.

Two properties of a molecule as a whole, global rather than local, are its electronegativity χ and hardness η. These may be

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