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Electron Transfer in Groups of Iron, Cobalt, and Copper Triazene 1-Oxides: Hammett Correlation, Ligand Redistribution, and Crystal Field Effects

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The electron-transfer behavior of groups of pseudooctahedral ML_3 and grossly planar CuL_2 complexes is reported (M = Fe, Co; L = triazene 1-oxide). A quasi-reversible process of type $ML_p + e^- \rightleftharpoons ML_p^-$ (p = 2, 3) is identified with electrochemical techniques. The E°_{298} values (vs. SCE) fall in the following ranges: Fe, −0.76 to −0.14; Co, −0.56 to −0.08; Cu, −1.07 to −0.37. The values become more negative in the order CoL_3, FeL_3, and CuL_2. For a given metal ion, E°_{298} shifts appreciably with ligand substituent, and a linear Hammett relationship is obeyed. The reaction constant is shown to decrease considerably when an extra bond intervenes between the metal and the substituent. Copper(II) complexes of bidentate ligands carrying an ortho substituent as well as those of a tetradentate ligand that enforce cis planar stereochemistry display abnormally negative shifts of E°_{298}. When two iron(III) complexes are mixed, ligand scrambling occurs and the presence of mixed species is neatly established by cyclic voltammetry. The mixed complexes fit smoothly into the Hammett straight lines. The thermodynamic quantities controlling the trends of E°_{298} are considered. An attempt is made to assess the relative importance of spherical and nonspherical parts of the crystal fields. Among complexes of the same metal ion, it is possible to express the shift of E°_{298} in terms of the crystal field splitting parameter with a large proportionality constant. The copper(II) complexes show a ligand field band whose energy linearly correlates with E°_{298}. The shift of E°_{298} between iron and cobalt couples is controlled by metal ionization potential and nearly equally important spherical and nonspherical crystal field contributions.

Introduction

The free energy change of a metal-centered electron-transfer reaction depends on several factors. When the complex and solvent are systematically changed, the contribution of metal ionization potential, metal-ligand complexation energy and solvation energy can be ascertained at least in principle.[1-4] Where a closely related group of organic ligands encompassing a range of substituents is available, it is possible to observe relatively subtle effects of remote polar substituents.[5-8] Such studies help to augment predictive capabilities for the design of reagents with predetermined redox characteristics. Hence the recent interest in this area.[9-18] In this context the transition-metal complexes[19-24] of triazene 1-oxides, RN(O)=NNH(Ar)(HL), provide an excellent opportunity to study the free energy systematics of metal-centered electroactivity by virtue of substitutional flexibility (R, Ar) of the ligands which like their complexes are relatively easily synthesized. In this report the electron-transfer behavior of octahedral iron(III) and cobalt(III) and planar copper(II) complexes of a sizeable group of triazene 1-oxides are investigated with the use of electrochemical techniques.

Table I. Serial Numbers of ML_p Complexes

substituents		serial no.		
X	R or Y	M = Fe	M = Co	M = Cu
OMe	Et			19
Me	Et	1	13	20
H	Et	2	14	21
Br	Et	3	15	22
Cl	Et	4	16	23
CO_2Et	Et	5	17	24
NO_2	Et	6	18	25
OMe	Ph	7		26
Me	Ph	8		27
H	Ph	9a		28a
H	p-MeC_6H_4	9b		28b
H	p-$MeCONHC_6H_4$	9c		28c
H	p-ClC_6H_4	9d		
Cl	Ph	10		29
CO_2Et	Ph	11		30
NO_2	Ph	12a		31
NO_2	p-ClC_6H_4	12b		

Experimental Section

Preparation of Complexes. The triazene 1-oxides are prepared by reacting diazotized aromatic amines with substituted hydroxyl amines. The complexes are synthesized by direct reaction of the ligand with metal acetates in ethanolic or methanolic solution. In the case of cobalt, oxidation by H_2O_2 is required. Iron and copper complexes were recrystallized from acetone and cobalt complexes from a chloroform–hexane mixture. The details of the syntheses are essentially the same as those already described in literature: iron,[19,21] cobalt,[19,20] copper.[19,22,23] Quite a few of the complexes studied here are new as far as the substituents are concerned. However, no special mention of these will be made since the preparative methods are invariant with

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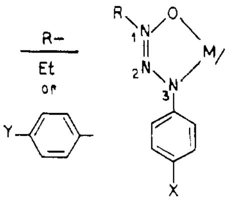
substituent. The purity of every complex was checked by elemental analysis, and the data are collected in a table which is available as supplementary material.

Physical Measurements. Electronic spectra were obtained with a Cary 17 D spectrophotometer. For cyclic voltammetry a Princeton Applied Research (PAR) 174A polarographic analyzer and PAR 175 universal programmer were used in conjunction with a XY recorder (Houston Instruments). Phase-sensitive alternating-current voltammetry was performed with a PAR 124A lock-in amplifier, PAR 174A polarographic analyzer, and PAR 172 AC polarographic interface. Controlled-potential coulometry required the PAR 173 potentiostat, PAR 179 digital coulometer, and a PAR 377 cell system. The three-electrode measurements were carried out with either a Metrohm E 410 hanging-mercury-drop electrode (HMDE) or Beckman model 39273 planar platinum electrode, a platinum wire counterelectrode, and a saturated calomel reference electrode (SCE). The cell was thermostated at 298 K. All measurements were carried out under a dinitrogen atmosphere. The results reported here are uncorrected for junction potential. Tetraethylammonium perchlorate was prepared from tetraethylammonium bromide. Commercial acetonitrile was purified by CaH_2 treatment followed by distillation over P_4O_{10}. Fresh analytical grade dimethylformamide could be used directly without further purification. For voltammetry, the solute concentration was ~2.0 mmol.

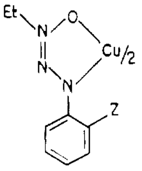
The following σ values[7] for para substituents were used: OMe, −0.27; Me, −0.17; H, 0.00; NHCOMe, 0.00; Br, +0.23; Cl, +0.23; CO_2Et, +0.45; NO_2, +0.78.

Results and Discussion

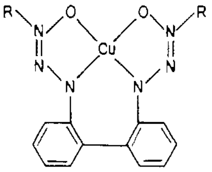
Complexes and Their Structures. The majority of complexes (**1–36**) studied belong to the type ML_p (p = 2 or 3) (Table I). Each such complex is identified by a serial number given in this table. Where ligand identification is required, the symbol L^x is used for the ligand in the complex having the serial number x. While FeL_3 is uniformly high spin[21] ($\mu \approx 5.9\ \mu_B$), CoL_3 is diamagnetic and is known to have trans stereochemistry of the CoN_3O_3 coordination sphere (^1H NMR data[20]). The CuL_2 species are believed to have[22] trans planar MN_2O_2 structure whose presence in a palladium,[25] and a nickel complex[26] of the type ML_2 has been established by diffraction work. The triazene 1-oxide (N(O)=NN<) bonding pattern [as opposed to hydroxytriazene (N(O)N=N<) pattern] of the ligand in metal complexes, first proposed on the basis of IR data,[20] has been fully confirmed by three-dimensional X-ray work.[26] The copper(II) complexes **32–34** are also of type CuL_2 but have ortho substituents (Z) in the Ar ring. Their general properties are closely akin to those of the other bis chelates (**19–31**) considered above, and they are also believed to have the trans planar CuN_2O_2 coordination geometry. In complexes **35** and **36** the ligand is tetradentate and it enforces both planarity and cis geometry for the CuN_2O_2 coordination sphere.[23]



1–31



32, Z = OMe
33, Z = Me
34, Z = Cl



35, R = Et
36, R = Ph

Table II. Electrochemical Data[a] at 298 K

(A) Cyclic Voltammetry:[b] $E°_{298}(\Delta E_p)$

$(a)^{c,d}$ 1, −0.76 (90); 2, −0.71 (90); 3, −0.60 (75); 4, −0.61 (70); 5, −0.46 (75); 6, −0.32 (80); 7, −0.50 (100); 8, −0.49 (68); 9a, −0.46 (65); 9b, −0.53 (75); 9c, −0.51 (75); 9d, −0.43 (85); 10, −0.37 (87); 11, −0.33 (77); 12a, −0.15 (85); 12b, −0.14 (85); 13, −0.56 (80); 14, −0.52 (105); 15, −0.36 (80); 16, −0.40 (75); 17, −0.31 (243); 18, −0.08 (100); 20, −0.80 (70); 21, −0.79 (75); 23, −0.73 (70)

$(b)^{c,e}$ 7, −0.47 (105); 8, −0.46 (73); 9a, −0.42 (70); 19, −0.84 (200); 20, −0.78 (65); 21, −0.75 (65); 22, −0.69 (70); 23, −0.70 (75); 24, −0.61 (70); 25, −0.46 (70); 26, −0.66 (70); 27, −0.63 (65); 28a, −0.60 (60); 28b, −0.60 (65); 28c, −0.61 (65); 29, −0.56 (60); 30, −0.49 (100); 31, −0.37 (70); 32, −0.91 (90); 33, −0.85 (73); 34, −0.81 (80); 35, −1.07 (80); 36, −0.86 (70)

$(c)^{d,f}$ 1, −0.78 (170); 2, −0.73 (93); 4, −0.62 (160); 5, −0.48 (145); 6, −0.32 (115); 9b, −0.54 (97); 9c, −0.51 (75); 9d, −0.45 (247); 11, −0.33 (83); 12b, −0.14 (85)

$(d)^{e,f}$ 20, −0.80 (225); 21, −0.77 (280); 23, −0.73 (360); 27, −0.66 (350); 28a, −0.61 (225); 29, −0.59 (505)

(B) Phase-Sensitive Alternating-Current Voltammetry:[g] E_p (δ)

$(a)^{c,d}$ 1, −0.78 (120); 2, −0.73 (120); 3, −0.61 (102); 4, −0.63 (100); 6, −0.32 (110); 7, −0.52 (120); 8, −0.50 (95); 9a, −0.46 (102); 10, −0.40 (120); 11, −0.34 (100); 12a, −0.15 (100)

$(b)^{c,e}$ 7, −0.49 (120); 8, −0.47 (90); 9a, −0.42 (100)

(C) Constant-Potential Coulometry

10, 16.9 mg electrolyzed at −0.75 V: found, 2.2 Q; calcd, 2.05 Q
11, 15.99 mg electrolyzed at −0.55 V: found, 1.5 Q; calcd, 1.7 Q
18, 10.27 mg electrolyzed at −0.33 V: found, 1.4 Q; calcd, 1.2 Q
31, 7.93 mg electrolyzed at −0.57 V: found, 1.3 Q; calcd, 1.1 Q

[a] The solvent is 0.1 M in tetraethylammonium perchlorate in each case. [b] The dc scan rate was 50 mV s^{-1}. $E°_{298}$ is given in V and ΔE_p in mV. [c] Hanging-mercury-drop electrode. [d] In acetonitrile. [e] In dimethylformamide. [f] Platinum electrode. [g] E_p is the ac peak potential in V, δ is the width at half-height in mV, and ω is the sinusoidal frequency (35 Hz). The ac peak to peak modulation amplitude was 10 mV, and the dc scan rate was 5 mV s^{-1}.

General Electrode Reaction and Formal Potentials. In all cases electroactivity was examined with cyclic voltammetry (CV). FeL_3 and CoL_3 complexes were examined mainly in acetonitrile while the copper complexes were studied primarily in dimethylformamide because of solubility reasons. Voltammograms with well-defined cathodic (E_{pc}) and anodic (E_{pa}) peaks of equal height were observed for all complexes at potentials negative to SCE. Representative examples are in Figure 1. Electrochemical data are summarized in Table II. All potentials are referenced to a saturated calomel electrode (SCE). At a hanging-mercury-drop electrode (HMDE), the peak-to-peak separations (ΔE_p) generally lie in the range 60–80 mV for the majority of complexes, suggesting the presence of a general reversible or quasireversible one-electron process (eq 1) or the equivalent thereof in the case of **32–36**.

$$ML_p + e^- \rightleftharpoons ML_p^- \qquad (1)$$

$$E°_{298} = \tfrac{1}{2}(E_{pc} + E_{pa}) \qquad (2)$$

The near-reversible behavior shows that the stereochemistry of ML_p and ML_p^- are grossly similar. The one-electron involvement was confirmed by constant-potential coulometric reduction studies in several cases (Table II). On the basis of ΔE_p values, the qualitative trend in reversibility and hence the rate of heterogeneous electron transfer is $CuL_2 > FeL_3 > CoL_3$ (for a given ligand). The formal potentials $E°_{298}$ for the couple of (1) were calculated as the average of the cathodic and anodic peak potentials (eq 2) and are collected in Table II. When platinum is used instead of HMDE as the working electrode, deviation from reversibility becomes marked.

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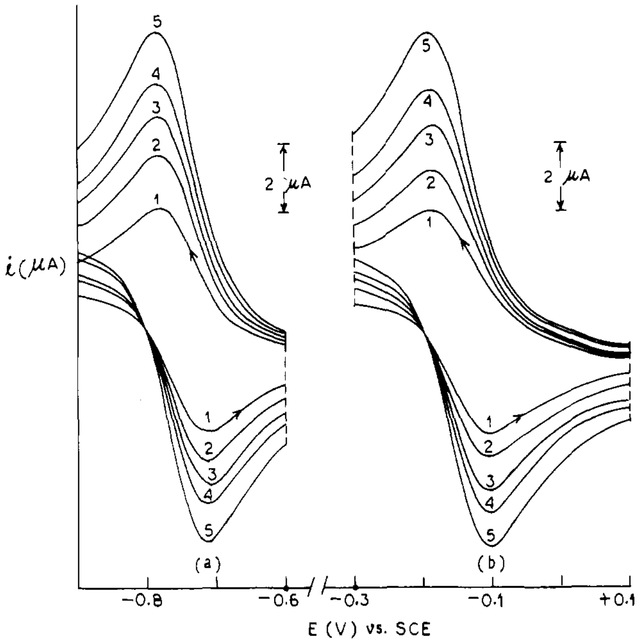

Figure 1. (a) Cyclic voltammograms of complex **21** in dimethylformamide at HMDE. Scan rates (mV s^{-1}): (1) 50, (2) 100, (3) 150, (4) 200, and (5) 300. (b) Cyclic voltammograms of complex **12a** in acetonitrile at HMDE. The scan rates are the same as in (a).

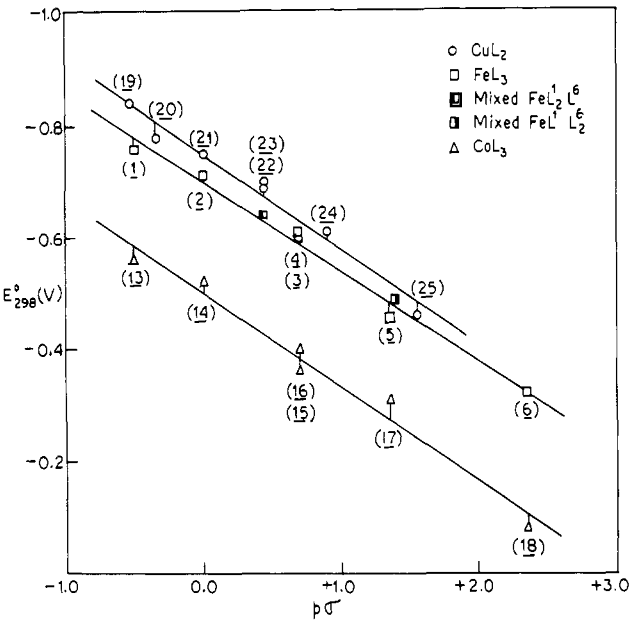

Figure 2. Linear least-squares fit of $E°_{298}$ vs. $p\sigma$ for three groups of complexes.

Table III. Comparative Study of the Values of ρ

complex[a]	bond sequence[b]	couple	ρ, V	ref
FeL_3	X-(C_4)-N-M	Fe(III)/Fe(II)	0.16[c]	this work
FeL_3	X-(C_4)-N-M	Fe(III)/Fe(II)	0.11[d]	this work
CoL_3	X-(C_4)-N-M	Co(III)/Co(II)	0.17[e]	this work
CuL_2	X-(C_4)-N-M	Cu(II)/Cu(I)	0.17[f]	this work
CuL_2	X-(C_4)-N-M	Cu(II)/Cu(I)	0.13[g]	this work
$Cu(pyr)_2$	X-(C_4)-N-M	Cu(II)/Cu(I)	0.08	13
Fe(Cp)(Ar(Cp)	X-(C_4)-C-Fe	Fe(III)/Fe(II)	0.13	10
Fe(tpp)Cl	X-(C_4)-C-C-N-Fe	Fe(III)/Fe(II)	0.05	12
Co(tpp)	X-(C_4)-C-C-N-Co	Co(III)/Co(II)	0.03	11
FeL_3	Y-(C_4)-N-O-Fe	Fe(III)/Fe(II)	0.08[h]	this work

[a] Abbreviations: Cp = $C_5H_5^-$, ArCp = $XC_6H_4C_5H_4^-$, and tpp = tetraarylporphyrin dianion. [b] The -(C_4)-, i.e., -(C-C-C-C)- part, comes from the benzene ring. [c] Complexes 1-6. [d] Complexes 7-9a, 10-12a. [e] Complexes 13-18. [f] Complexes 19-25. [g] Complexes 26-28a, 29-31. [h] Complexes 9a-9d.

In the couple of (1) the 1e⁻ reduction is of the metal rather than of the ligand. In this context the following observations are in order. The free ligands give rise to an irreversible reduction at low potentials; e.g., PhN(O)=NNH(Ar) (Ar = p-$CO_2EtC_6H_4$) has E_{pc} = −1.27 V in acetonitrile (HMDE). Unlike CuL_2, planar NiL_2 does *not* display any metal reduction peak; an irreversible ligand reduction peak is observed at a potential less than −1.0 V (e.g., −1.03 V in the nickel(II) analogue of **31**). This is understandable since the nickel(I) state is not expected[27] to be accessible in combination with a ligand of type HL. On coulometric reduction of CuL_2, the color changes to reddish brown and the characteristic ligand field band[22] near 900 nm disappears as expected. In air the reduced species (CuL_2^-) is rapidly reconverted to CuL_2.

For selected FeL_3 complexes, the electrode reactions were also studied with phase-sensitive alternating-current voltammetry primarily at HMDE (Table II). In general the ac peak potential agreed well with cyclic voltammetric $E°_{298}$ data. The observed width at half-height (90–120 mV) shows that the electrode process is exactly or nearly ac reversible.[28]

Linear Hammett Correlations. The formal potentials are sensitive to R and X (Table II). In general, electron-donating groups are found to make reduction more difficult ($E°_{298}$ more negative) as in the changing of R from Ph to Et for a given X or in changing X from say NO_2 to Me for a given R. When X is systematically varied keeping R fixed, relationship 3 holds.

$$\Delta E°_{298} = p\sigma\rho \qquad (3)$$

Here $\Delta E°_{298}$ is the shift of $E°_{298}$ from the standard complex having X = H and $p\sigma$ is the weighted Hammett substituent constant for p number of ligands and ρ is the reaction constant measuring the susceptibility of the electron-transfer process to polar effects.[6-8] The linear $E°_{298}$ vs. $p\sigma$ plots for ML_p (R = Et) are shown in Figure 2. The iron, cobalt, and copper lines are nearly parallel, implicating the virtual invariance of ρ values (0.16 ± 0.01 V) (Table III). Thus for a given R the weighted change in $E°_{298}$ due to the X substituent is effectively independent of the metal ion in this group of complexes. On changing R, ρ changes but to about the same extent at least for iron and copper as evidenced in the groups of FeL_3 and CuL_2 complexes with R = Ph (Table III).

The phenyl ring carrying the X substituent is unlikely to remain fixed at coplanarity with the triazene 1-oxide frame,[26] thus making resonance contribution to $\Delta E°_{298}$ of minor significance. It might therefore be argued that the Taft constant $\sigma°$ rather than σ should be used in correlation. Our data fits with $p\sigma°$ also, and the ρ parameters thus derived are the same within experimental error (±0.01) with those of Table III. This is not unexpected since in most cases the difference between σ and $\sigma°$ is small.[5]

Attenuation by Intervening Bonds. We now consider certain trends in ρ values based on both the present work and literature data (Table III). In $Cu(pyr)_2$ (Hpyr = pyrrole-2-carboxaldimine), the bond sequence is the same as that in CuL_2 but the redox potential of the copper(II) site in CuL_2 is more susceptible to polar effects. For iron and cobalt, data on tris species comparable to FeL_3 and CoL_3 are not immediately available. However, it is interesting to note that while in arylferrocenes ρ is comparable to that in FeL_3, in substituted tetraarylporphyrin chelates with a longer bond sequence the ρ for the M(III)-M(II) couple is much smaller. Irrespective of the dissimilar nature of these various systems it is clear that the mere number of intervening bonds is crucial for the magnitude of ρ.

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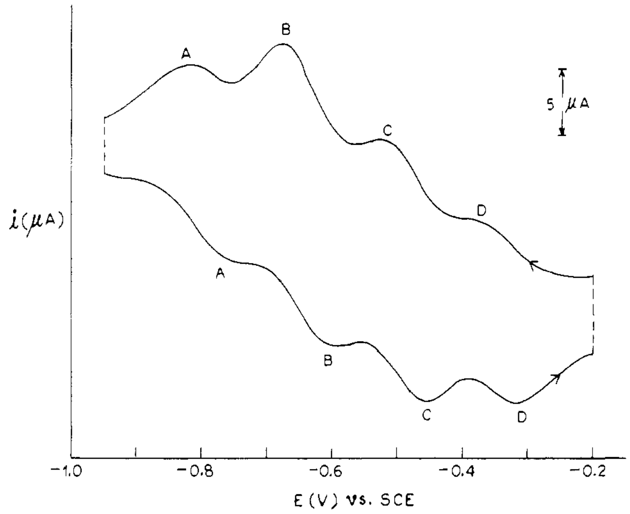

Figure 3. Cyclic voltammogram of an equimolecular mixture of complexes **1** and **6** in acetonitrile at HMDE (scan rate 50 mV s^{-1}): A, **1**; B, $FeL^1_2L^6$; C, $FeL^1L^6_2$; D, **6**.

It is possible to make a more rational study of the effect of intervening bonds on ρ exclusively within the ML_p family by comparing the effects of X and Y substituents on $E°_{298}$. The Y substituent is seven bonds away from the metal as opposed to six bonds for the X substituent. In the FeL_3 group, **9a–9d**, the Y substituent changes. Here $E°_{298}$ varies linearly with 3σ of Y but the slope is considerably smaller than that for the X substituent (Table III). The near equivalence of $E°_{298}$ values of **12a** and **12b** is another manifestation of the mildness of the Y substituent effect at the metal centre. Similarly in CuL_2 series the $E°_{298}$ values of **28a** and **28b** are nearly equal.

Ortho-Substituted and Other Copper Complexes. Each of the complexes **32–34** has an ortho substituent (Z). Their $E°_{298}$ values are systematically more negative (Table II) than those of the corresponding para-substituted compounds (**19–31**). The observed data can be fitted to the CuL_2 line of Figure 2 if it is assumed that the substituent constants for Z are as follows: OMe, −0.46; Me, −0.26; Cl, −0.15. These constants are much more negative than the Taft ortho substituent constants[7] σ_o. The combination of steric with polar factors often vitiates fruitful correlations of the ortho effect.

Among all the copper complexes (R = Et) studied here, **35** has the most negative $E°_{298}$; a similar comment applies to **36** among copper complexes with R = Ph (Table II). The potentials of **35** and **36** are ~300 mV more negaitve than those of **21** and **28a**, respectively. The tetradentate ligands in **35** and **36** enforce[23] both planarity and cis geometry for the CuN_2O_2 coordination sphere. The bis complexes **19–34** are probably trans and grossly planar, but here the ligand pair is sterically less demanding. How these factors bring about the observed electrochemical effect is not clear.

Formation of Mixed Complexes. When two different FeL_3 species are mixed, ligand redistribution occurs spontaneously within the time of mixing of solutions. The equilibrium solution contains the two expected mixed species in addition to the parent pair. The electrochemical response of such solution particularly in cases where the parent $E°_{298}$ values are well separated consists of the four couples. The case of the mixture **1** + **6** is illustrated in Figure 3. The $E°_{298}$ of the mixed-species $FeL^1_2L^6$ and $FeL^1L^6_2$ are respectively −0.64 and −0.49 V. An additivity rule (eq 4) is applicable, and the observed $E°_{298}$

$$E°_{298}[FeL^x_2L^y] = {}^2\!/_3E°_{298}[FeL^x_3] + {}^1\!/_3E°_{298}[FeL^y_3] \qquad (4)$$

values of the mixed complexes fit smoothly into the free energy straight lines of Figure 2. The net Hammett constant for a mixed complex was taken as the weighted sum of the constants for the individual ligands. We wish to stress that few other techniques would have revealed the presence of the mixed species with such ease. The electrochemical method provides a powerful and sensitive tool for the study of such mixed-complex formation. It has been used occasionally for such studies in the past.[29] The triazene 1-oxide complexes of iron, cobalt, and copper quite generally undergo facile ligand scrambling in solution. A full account on the statistics and thermodynamics of such scrambling will be reported separately.

Free Energy Change and Electrode Potential. Further consideration of $E°_{298}$ data in the light of free energy change ($\Delta G°$) of the cell reaction in which the couple of (1) is an electrode can be revealing. This free energy can be written[2] as eq 5 where F is the faraday, I_p is the pth ionization potential

$$-\Delta G° = FE° = I_p - \Delta G_f° - \Delta G_s° + C \qquad (5)$$

of M, $\Delta G_f°$ is the difference between the free energies of formation of $ML_p^-(g)$ and $ML_p(g)$ [in the sense, $(ML_p^-(g) - ML_p(g))$], $\Delta G_s°$ is the difference between the solvational free energies of $ML_p^-(g)$ and $ML_p(g)$, and C is a constant contributed by the reference half-cell. Our interest lies in the variation of $E°$ in going from one couple to another. In the most general case where metal, ligand, and solvent vary, we have eq 6.

$$F\Delta E° = \Delta I_p - \Delta(\Delta G_f°) - \Delta(\Delta G_s°) \qquad (6)$$

Ligand Field Effects. A particularly simple situation arises if the comparison is limited among iron complexes with varying X in a given solvent. Here we have $\Delta I_p = 0$ and

$$\Delta(\Delta G_s°) \approx 0 \qquad (7)$$

and[30]

$$T\Delta(\Delta S_f°) \approx 0 \qquad (8)$$

Equation 6 then becomes eq 9. Here $S_f°$ and $H_f°$ are symbols

$$F\Delta E° = -\Delta(\Delta H_f°) \qquad (9)$$

for entropy and enthalpy, respectively. In eq 9 the variation in each quantity is measured in the sense (X = X) − (X = H). We now write eq 10 where $\Delta(\Delta H_{LF}°)$ is the contribution due

$$\Delta(\Delta H_f°) = \Delta(\Delta H_{LF}°) + \Delta(\Delta H_f°') \qquad (10)$$

to ligand field splitting and $\Delta(\Delta H_f°')$ is attributable to the spherical part of the ligand field.[31] In the couples under consideration both the iron(III) and iron(II) species are high spin and consequently[3]

$$\Delta H_{LF}° = -4Dq^{II} \qquad (11)$$

where Dq^{II} refers to the iron(II) state. From eq 9 and 10 we have eq 12.

$$F\Delta E° = 4\Delta Dq^{II} - \Delta(\Delta H_f°') \qquad (12)$$

In a simple ionic crystal field model, the effect of an electron donating group (X) will be the increase of negative charge on the donor atoms. This is expected to increase both Dq and $\Delta H_f°'$. In this model ΔDq and $\Delta(\Delta H_f°')$ (both positive) should be proportional to each other leading to

$$F\Delta E° = (4 - k)(\Delta Dq) \qquad (13)$$

or equivalently

$$F\Delta E° = [(4 - k)/k][\Delta(\Delta H_f°')] \qquad (14)$$

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Table IV.[a] Comparison of Iron and Cobalt Couples

ligand[b]	solvent	ΔE°_{298}	$\Delta(\Delta H_f^\circ)$	$\Delta(\Delta H_{LF}^\circ)$	$\Delta(\Delta H_f^{\circ\prime})$
H_2O	H_2O	−1.04[c]	−42.0	−22.3	−19.7
$C_2O_4^{2-}$	H_2O	−0.58[c]	−52.6	−20.8	−31.8
$EDTA^{4-}$	H_2O	−0.48[c]	−55.9	−29.9	−26.0
$acac^-$	acetone	−0.33[d]	−58.4	−22.3	−36.1
L^-	acetonitrile	−0.19[e]	−61.6	−22.3	−39.3

[a] Meaning of symbols are as in the text. Units: E°_{298}, V; $\Delta(\Delta H_f^\circ)$, kcal/mol. [b] $EDTA^{4-}$ = ethylenediaminetetraacetate anion, $acac^-$ = acetylacetonate anion, and L^- = 1-ethyl-3-phenyltriazene 1-oxide anion. [c] Value from ref 3. [d] Value from ref 32. [e] This work.

where k is a proportionality constant. Since $(\Delta H_f^{\circ\prime}) >> Dq$, we have $\Delta(\Delta H_f^{\circ\prime}) >> \Delta Dq$. The observed sign of ΔE°_{298} is systematically negative. Hence the spherical contribution is dominant. There has been some recent discussions[3,4] regarding the relative importance of ligand field and spherical contributions to ΔE°. The present analysis, though admittedly oversimplified, brings out an important point at least for high-spin iron couples. For a group of closely related ligands differing only in substituents, Dq and hence the position of ligand field bands need not necessarily vary much, even when E° is found to change significantly (eq 13; small ΔDq but large k). On the other hand, if ΔDq is large enough to be conveniently measurable from ligand field spectra, a correlation between E° and Dq should obtain.

In the case of cobalt, CoL_3 is low spin, and CoL_3^- such as[3] cobalt(II) complexes of acetylacetone and ethylenediaminetetraacetic acid is high spin. Here we write[3] eq 15 and, hence,

$$\Delta H_{LF}^\circ = -7Dq^{II} - (-24Dq^{III} + 2P) \qquad (15)$$

$$\Delta(\Delta H_{LF}^\circ) = 24(\Delta Dq^{III}) - 7(\Delta Dq^{II}) \qquad (16)$$

eq 16 where P is the pairing energy in cobalt(III) (assumed to be remain constant in going from one complex to another). With the assumption that $Dq^{III} \approx 2Dq^{II}$, a treatment similar to the case of iron can follow. The important difference is that here both the spherical and nonspherical terms act together to make ΔE° negative.

Potential Shift between Cobalt and Iron. In order to compare a cobalt couple with an iron couple under conditions of invariant ligand stereochemistry and solvent, we have from eq 6–8

$$F\Delta E^\circ = \Delta I_3 - \Delta(\Delta H_f^\circ) \qquad (17)$$

Here the variation in each quantity corresponds to iron–cobalt. Equation 17 should apply for comparison of one cobalt–iron pair with another even when different pairs are studied in different solvents. The experimental ΔE° values and corresponding $\Delta(\Delta H_f^\circ)$ values calculated with the help of eq 17 for selected couples[3,32] are in Table IV. In each case the cobaltIII complex is low spin while cobalt(II), iron(III), and iron(II) complexes are high spin. All ΔE° values are negative, showing that ΔI_p is controlling. Barring the case of the aquo complex, the variation in ΔE° values and hence $\Delta(\Delta H_f^\circ)$ values are relatively small. For a more closely related group of ligands, one may expect ΔE° to remain virtually constant. This happens for example in the FeL_3–CoL_3 pairs with variable X (Figure 2).

From eq 10, 11, and 15, values of $\Delta(\Delta H_{LF}^\circ)$ can be computed from experimental Dq values (Table IV). The value of $\Delta(\Delta H_f^{\circ\prime})$ were then calculated from eq 10 since $\Delta(\Delta H_f^\circ)$ is known (vide supra). The pairing energy P for cobalt(III) (48.0 kcal) and Dq values of H_2O, $C_2O_4^{2-}$, and $EDTA^{4-}$ are those used by Rock.[3] Acetylacetone[33] and triazene 1-oxide[34] were taken to have the same Dq as that of water. The value of ΔI_3 is −66 kcal.[2] The entries in the last two columns of Table IV are meant to be only rough estimates. The results however clearly bring out the interesting qualitative trend that spherical and nonspherical enthalpy contributions are nearly equally important in deciding ΔE° value in cobalt–iron pairs.

Table V. Band Maximum and Extinction Coefficient in Benzene Solution (λ_{max}, nm (ϵ, M cm^{-1})) for Each Complex

Iron
1, 559 (3260); **2**, 544 (3270); **3**, 548 (3400); **4**, 548 (3650); **7**, 532 (5530); **8**, 562 (4720); **9a**, 548 (4680); **10**, 558 (4840); **11**, 535 (4170); **12a**, 542 (4870)

Cobalt
13, 522 (1620); **14**, 518 (1620); **15**, 520 (1910); **16**, 522 (1810); **17**, 521 (2300)

Copper
20, 915 (81); **21**, 908 (70); **22**, 905 (72); **23**, 908 (79); **24**, 905 (92); **25**, 885 (91); **26**, 900 (95); **28a**, 895 (86); **29**, 890 (97); **30**, 885 (95); **32**, 930 (96); **33**, 910 (94); **34**, 960 (96); **36**, 890 (77)

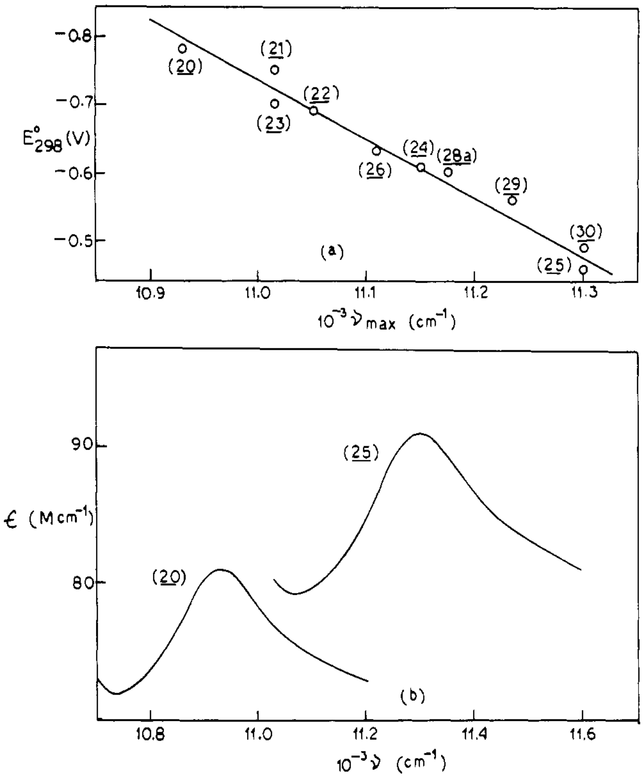

Figure 4. (a) Linear least-squares fit of E°_{298} vs. ν_{max} (band maximum) for CuL_2 species. (b) Ligand field spectra of complexes **20** and **25** in benzene solution.

Spectral Correlations in Copper Complexes. Since the CuL_2 complexes are planar, more than one ligand field integral is needed to describe the splitting.[31] It is however clear that the gross situation will remain qualitatively similar to the iron and cobalt cases. One may expect ΔE° to be roughly proportional to both ligand field splitting and $\Delta(\Delta H_f^{\circ\prime})$. In the case of FeL_3 and CoL_3, no ligand field bands are detectable due to the presence of low-energy allowed charge-transfer transitions (Table V).[20,21] In CuL_2 a ligand field band[22] *is* observed near 900 nm. Representative spectra and data taken in benzene solution are in Figure 4 and Table V. The band energy (ν_{max}) shows significant shifts on changing X. With the approximation in the model and the relative broadness of the band taken into account, the observed E°_{298}–ν_{max} correlation (Figure

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4) can be considered as satisfactorily linear.[35]

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Registry No. **1**, 79971-92-9; **2**, 77188-05-7; **3**, 79971-93-0; **4**, 79971-94-1; **5**, 79971-95-2; **6**, 79971-96-3; **7**, 79971-97-4; **8**, 79971-98-5; **9a**, 28660-76-6; **9b**, 79971-99-6; **9c**, 79972-00-2; **9d**, 79972-01-3; **10**, 79972-02-4; **11**, 79972-03-5; **12a**, 79972-04-6; **12b**, 79972-05-7; **13**, 79972-06-8; **14**, 80008-88-4; **15**, 79972-07-9; **16**, 79972-08-0; **17**, 79972-09-1; **18**, 79972-10-4; **19**, 32425-27-7; **20**, 32425-23-3; **21**, 32425-19-7; **22**, 79972-11-5; **23**, 79972-12-6; **24**, 79972-13-7; **25**, 79972-14-8; **26**, 14647-29-1; **27**, 13986-92-0; **28a**, 14873-21-3; **28b**, 14647-26-8; **28c**, 79972-15-9; **29**, 15006-86-7; **30**, 79972-16-0; **31**, 79972-17-1; **32**, 79972-18-2; **33**, 79972-19-3; **34**, 79972-20-6; **35**, 79972-21-7; **36**, 79972-22-8.

Supplementary Material Available: A table of analytical data (Table I) (2 pages). Ordering information is given on any current masthead page.

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(35) The linearity in Figure 4 is not due to fortuitous choice of two different solvents (benzene (bz) for ν_{max} and dimethylformamide (DMF) for $E°_{298}$) to generate the two axes. In a number of cases ν_{max} was determined in DMF and was found to correlate linearly with $E°_{298}$. A slight shift (~200 cm^{-1}) to lower energy which occurs in going from bz to DMF is probably due to axial coordination as in the case of pyridine solvent.[22] Representative ν_{max} values in DMF are as follows: **20**, 945; **21**, 930; **22**, 925; **23**, 915; **26**, 920; **28a**, 910; **29**, 905 nm.

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Inversion in the Direction of a Chiral Equilibrium Shift Observed in the Pfeiffer Effect of Some Mixed-Chelate Chromium(III) Complexes at the Ligand Field Excited State

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Laser irradiation of an aqueous solution of racemic $[Cr(ox)_2(phen)]^-$ or $[Cr(ox)(phen)_2]^+$ (ox = oxalate dianion and phen = 1,10-phenanthroline) at their ligand field transition regions in the presence of *d*-cinchonine or *l*-cinchonidine hydrochloride led to a relatively rapid shift in a chiral equilibrium between their two enantiomers, which was opposite in direction to that induced by the usual Pfeiffer effect of the corresponding system in the dark. This is in contrast to the observation that the direction of the equilibrium shift induced for homochelate complexes $[Cr(ox)_3]^{3-}$ and $[Cr(phen)_3]^{3+}$ was unaltered whether they were photoirradiated or not. This new finding was interpreted in terms of anisotropic expansion of these mixed-chelate Cr(III) complexes at the ligand field excited state and of the accompanying perturbation in their stereoselective interaction with *d*-cinchoninium or *l*-cinchonidinium ion.

Introduction

Several octahedral Cr(III) complexes have been partially resolved through photoexcitation at their ligand field (LF) transition regions.[1-3] In particular, the use of circularly polarized light has a great advantage in that it affords ORD and CD curves of an optically pure enantiomer. However, the optical yield practically achievable by this technique is governed by the dissymetric factor *g*, and it is low for usual Cr(III) complexes (at most 5%). On the other hand, the optical yield attained by the Pfeiffer effect,[4] an induced shift in a chiral equilibrium between two enantiomers of an initially racemic and labile metal complex under the influence of a chiral compound (called an environment substance) present in solution, depends on the efficiency of chiral discrimination effected in the diastereomeric interaction of the two enantiomers with the environment substance, so that it may amount to almost 20% in a favorable situation.[5] Furthermore, the direction of the equilibrium shift induced, i.e., the absolute configuration of the enantiomer enriched by the Pfeiffer effect, can give some information on the stereoselective interactions involved.[5-7]

In the present study, partial photoresolution of some Cr(III) complexes was attempted by irradiating these complexes with linearly polarized light at their LF transition regions in the presence of hydrochloride salts of some cinchona alkaloids in water. Interestingly enough, we found some mixed-chelate complex systems in which the chiral equilibrium was shifted upon photoirradiation toward the opposite direction to that observed in the usual Pfeiffer effect in the dark.

Experimental Section

Materials. Racemic complexes to be photoirradiated were $[Cr(ox)_3]^{3-}$, $[Cr(ox)_2(phen)]^-$, $[Cr(ox)_2(bpy)]^-$ (bpy = 2,2′-bipyridine), $[Cr(ox)(phen)_2]^+$, and $[Cr(phen)_3]^{3+}$, all of which were prepared by standard methods described in the literature,[8] and their purity was checked by absorption spectra and ion-exchange chromatography. $[Co(phen)_3]^{2+}$, used in place of $[Cr(phen)_3]^{3+}$ in the study of the Pfeiffer effect at the ground state, was prepared by mixing appropriate amounts of $CoCl_2·6H_2O$ and phen·H_2O in water (in 1:3 mole ratio). Chiral environment substances used were commercially available *d*-(8*R*,9*S*)-cinchonine and *l*-(8*S*,9*R*)-cinchonidine hydrochlorides, both of which were recrystallized from hot water. Hydrochloride salts of *d*-(8*R*,9*S*)-quinidine and *l*-(8*S*,9*R*)-quinine, which are 6′-MeO derivtives of *d*-cinchonine and *l*-cinchonidine, respectively.[9] were also used for comparison.

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