Table II. Characteristic Infrared Absorption Bands (2100–2000, 910–790, 870–830, and 400–200 cm^{-1}) for the Differentiation of *cis*- or *trans*-[Cr(cyclam)X_2] X Complexes

	freq of absorption bands, cm^{-1} [a]							
X	C–N[b]	N–H[c]				C–S[b]	CH_2[c]	Cr–X str
trans Cl		890 s	882 s				804 s	338 s
trans NCS	2090 s, 2070 s, 2050 s	885 s	878 m			865 w	802 m	344 s
cis Cl			872 m	862 m sh	854 m		815 w, 805 m	335 s, 316 s
cis NCS	2085 s, 2080 s, 2040 s		870 m	860 m	850 m sh	840 w	818 m, 810 m	340 m, 330 m, 320 m

[a] Abbreviations: s, strong; m, medium; w, weak; sh, shoulder. [b] Vibrations associated with thiocyanate. [c] Vibrations associated with cyclam.

refluxing time was shortened to 3 h. In acid medium, the isomerization was negligible, and this probably accounts for previous unsuccessful attempts[1] to isomerize the cis complexes. We have not been able to synthesize the trans complexes directly from the free cyclic ligand.

The isomeric purity of the new complexes was confirmed by the observation that the electronic absorption spectra were not affected by repeated recrystallization. Furthermore, when these complexes were absorbed on cation exchanger Dowex 50W-X8 (20-50 mesh) in the H^+ form, only a single band was developed which could be eluted with hydrochloric acid (1 M).

As shown in Table I, the assignment of a geometric configuration to these complexes, based entirely on the comparison of the visible absorption spectra with those of known bis(ethylenediamine) [$(en)_2$] analogues,[1] was not too reliable for the pair of isothiocyanato complexes since their visible absorption spectra are rather similar. The use of infrared spectroscopy for the differentiation of cis and trans isomers of cyclam complexes has been explored extensively.[2,7,8] A consistent variation, being independent of the nature of the central metal ions, other ligands, and counterions present, has been found in the 790–910 cm^{-1} region. Trans complexes invariably showed two groups of bands, a doublet near 890 cm^{-1} arising essentially from the secondary amine vibration and a singlet near 810 cm^{-1} due predominantly to the methylene vibration.[7] The amine vibration of cis complexes showed at least three bands in a lower frequency range (840–890 cm^{-1}) while the methylene vibration split into two bands in the 790–830-cm^{-1} region. As shown in Table II, the infrared spectra of the new complexes are clearly consistent with a trans configuration. The far-infrared spectra (400–200 cm^{-1}) of the four complexes *cis*- and *trans*-[Cr(cyclam)X_2]X (X^- = Cl^- or NCS^-) are remarkably similar except for the strong bands which could be assigned to the ν(Cr–X) vibration. The observation that trans complexes showed only one band whereas cis complexes showed two (for X^- = Cl^-) or three bands (for X^- = NCS^-) strongly supports the previous assignment of the geometric configuration to these complexes. As for the differentiation of the N- and S-bonding modes of the ambidentate thiocyanate ligand in *cis*- and *trans*-[Cr(cyclam)$(NCS)_2$]NCS, infrared spectroscopy in the ν(C–N) and ν(C–S) regions is not very useful.[9] We have not been able to detect any band assignable to the S-bonded ν(C–S) vibration in the 690–720-cm^{-1} region. In the N-bonded ν(C–S) region although absorptions are found at 865 and 840 cm^{-1} for the trans and cis isomer, respectively, they are rather weak. The assignment of a N-bonding mode is supported by the far-infrared spectra of these complexes. It was pointed out by Forster and Goodgame[10] that for analogous complexes with the same symmetry the following order of metal–ligand vibrations was observed: ν(M–*N*CS) > ν(M–Cl) > ν(M–*S*CN) > ν(M–Br). As shown in Table I, the two thiocyanate complexes can be assumed accordingly to be N bonded.

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Registry No. *trans*-[Cr(cyclam)Cl_2]Cl, 27385-72-4; *trans*-[Cr(cyclam)$(NCS)_2$](NCS), 72173-09-2; *trans*-[Cr(cyclam)$(NCS)_2$](ClO_4), 72151-28-1; *cis*-[Cr(cyclam)Cl_2]Cl, 27435-95-6; *cis*-[Cr(cyclam)$(NCS)_2$](NCS), 27436-02-8.

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Correspondence

The Noncorrelation of *Dq* and $E_{1/2}$ in Metal Complexes. The Importance of the Spherical Ligand Field Term

Sir:

Recently there has been a great deal of interest in the effect of ligands on the redox potentials of transition-metal ions. Several studies in which the metal ion is held constant and the ligands are systematically varied have revealed surprisingly large changes in the redox potentials caused by rather subtle variations in the ligands.[1–7] It is not uncommon to observe 1–2 V changes in the redox potential of a given metal ion as a result of seemingly minor variations in the ligands. These observations have practical application in the molecular design of new electron-transfer reagents and of complexes containing metal ions in unusual oxidation states.

Although it has been demonstrated for several redox couples, e.g., Cr(III)/Cr(II),[5] Fe(III)/Fe(II),[2,3] Co(III)/Co(II),[2,3] Ni(III)/Ni(II)/Ni(I),[1–3] Cu(II)/Cu(O),[6,7] Ru(III)/Ru(II),[4] that the potentials can be predictably varied over a wide range, there is no satisfactory explanation for the observed changes

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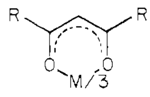
in terms of parameters related to bonding arguments. A logical place to look for an explanation is ligand field theory since the spectral shifts associated with ligand changes are often adequately explained by this theory. A qualitative relationship between ligand field stabilization energy (LFSE) and $E°$ has been postulated for some time,[8,9] but apparently Rock[10] was the first to attempt a quantitative, semitheoretical correlation between $E°$ and Dq.

There are several problems with the treatment put forth by Rock. First, the agreement between the calculated and observed $E°$ values is poor. Some of the disagreement Rock attributed to unreliable potential measurements. However, in a later paper he carefully redetermined the potential for one of the couples, $Co(en)_3^{3+,2+}$, in which the correlation between $E°$ and $10Dq$ was particularly poor and there was no significant improvement after the redetermination ($E°_{exptl} = +0.18$ V, $E°_{calcd} = -0.41$ V).[11] Second, some of the compounds that appear to have a strong correlation between $E°$ and $10Dq$ have been assigned the wrong value of $10Dq$. For example, Rock assigns $10Dq$ in $Fe(phen)_3^{2+}$ as the energy of a spectral transition occurring at 1.96 μm^{-1}.[10] In fact, this transition is a charge-transfer band and the actual value of $10Dq$ is 1.31 μm^{-1}.[12] It is not clear how Rock estimated $10Dq$ for $Fe(phen)_3^{3+}$, but the value used in the calculation, 2.74 μm^{-1}, appears much too large. With the use of Jorgensen's[13] approach that $10Dq = [f(\text{ligand})][g(\text{metal ion})]$, it appears a more reasonable value is about 1.8 μm^{-1}. The $10Dq$ values for $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$, 3.14 and 3.50 μm^{-1}, respectively, are also suspect. They appear much too large since $f(CN^-)$ is generally quoted as being equal to 1.7. It is also not reasonable that the $10Dq$'s would be so similar for the cyanide complexes since $10Dq$ for Fe^{2+} and Fe^{3+} complexes routinely differ by about 40%. Regardless of actual values, the spectra of the $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ complex ions are not well understood[15] and assignments must be considered speculative. The reasonableness of the entire approach is questionable since the $Fe(phen)_3^{3+,2+}$ and $Fe(CN)_6^{3-,4-}$ couples constitute the best fit of experimental and calculated $E°$'s using Rock's theory.

Third, Rock makes a basic, implied assumption that changing ligands on a metal ion results only in changes in Dq. Actually, the ligand field potential is made up of a spherical part, V_s, and a directional part characteristic of the geometry of the complex, e.g., an octahedral potential, V_o. It is the directional potential that is responsible for the splitting, Dq. The spherical part is by far the most important contributor to the total energy and is repulsive in nature.[16] The value of V_s is proportional to q/R for point-charge ligands and q/R^2 for point-dipole ligands where q is charge and R is distance, whereas the directional potential varies as q/R^5 for point charges or q/R^6 for point dipoles. Since the $E°$ is presumably proportional to the energy difference between the electrode with zero applied potential and the acceptor (or donor) levels, ignoring V_s is to ignore the major part of the ligand field potential.

Examination of the data available leads us to conclude that there is no general, simple correlation between $E_{1/2}$ and Dq. As our primary example of the noncorrelation of $E_{1/2}$ and Dq, we use the Cr(III) and Ru(III) complexes of several 1,3-diketonates.[4,5] These systems are unusually strong examples since $E_{1/2}$ varies widely with the nature of the 1- and 3-substituents while Dq is almost invariant. In both cases the reduction processes are completely reversible. The $E_{1/2}$ and $10Dq$ values are given in Table I. The $10Dq$ values for the Cr(III) complexes were measured by Fatta and Lintvedt[17] while the $10Dq$ values for the Ru(III) complexes were estimated by using standard techniques described in Table I. Although the Ru(III) values may not be correct in the absolute sense, within the series they should be internally consistent and the argument against an $E_{1/2}$ vs. $10Dq$ correlation depends more upon internal comparisons than on absolute values. In both the Cr(III) and Ru(III) 1,3-diketonates the $E_{1/2}$ values do correlate very well with the substituent electronic effects as measured by Hammett substituent constants.[4,5]

Table I. Polarographic Reduction Potentials and $10Dq$ Values for Some Cr(III) and Ru(III) 1,3-Diketonates



			M = Cr(III)[5]		M = Ru(III)[4]	
compd	R	R'	$E_{1/2}$,[a] V	$10Dq$,[b] μm^{-1}	$E_{1/2}$,[c] V	~$10Dq$,[d] μm^{-1}
$M(hfac)_3$	CF_3	CF_3	−0.40	1.745	+0.73[e]	2.77
$M(tfbzac)_3$	CF_3	C_6H_5	−0.79	1.754	+0.10	2.79
$M(tfac)_3$	CF_3	CH_3	−1.04	1.764	−0.02	2.80
$M(dbm)_3$	C_6H_5	C_6H_5	−1.26	1.748	−0.50	2.78
$M(pdo)_3$	H	H	−1.32	1.802		
$M(phpdo)_3$	H	C_6H_5	−1.31	1.783		
$M(Bzac)_3$	CH_3	C_6H_5	−1.50	1.776	−0.59	2.82
$M(bdo)_3$	CH_3	H	−1.58	1.786		
$M(t\text{-bupdo})_3$	H	$t\text{-}C_4H_9$	−1.64	1.786		
$M(acac)_3$	CH_3	CH_3	−1.73	1.786	−0.73	2.84
$M(dpm)_3$	$t\text{-}C_4H_9$	$t\text{-}C_4H_9$	(−1.96)[f]	1.770	−1.04	2.81

[a] V vs. SCE in Me_2SO with a dropping mercury electrode. [b] $10Dq$ is assumed equal to the $^4A_{2g} \to {}^4T_{2g}$ transition energy.[17] [c] V vs. SCE in DMF with a rotating platinum electrode. [d] These have not been measured but were calculated from Jorgensen's[13,14] relationship $10Dq = [f(\text{ligand})][g(\text{metal ion})]$ where $g \simeq 27$. The value of g is assumed approximately equal to the value for Rh(III). The value of f is derived from the Cr(III) series $10Dq$ values. [e] Since $Ru(hfac)_3$ is unstable in DMF, this value was obtained in acetonitrile. [f] Calculated from the −0.32 V substituent effect of $t\text{-}C_4H_9$.[5]

Table II. Reduction Potentials and Dq^{xy} Values for *trans*-$Co([13\text{-}16]aneN_4)Cl_2^+$

ligand	$E_{1/2}$,[a] V	Dq^{xy}, cm^{-1}
$[13]aneN_4$	−0.66	2750
$[14]aneN_4$	−0.69	2480
$[15]andN_4$	−0.38	2303
$[16]aneN_4$	−0.15	2249

[a] In acetonitrile with $Ag/AgNO_3$ reference electrode.

Another general area of transition-metal chemistry in which there have been several attempts to correlate ligand field splitting parameters with redox-potential changes is in macrocyclic complexes. This general area, involving the control of redox potentials in macrocyclic complexes, has recently been reviewed by Busch et al.[3] Another example of noncorrelation between $E_{1/2}$ and $10Dq$ comes from these studies. Busch and co-workers have examined a series of Co(III) complexes containing saturated tetraamine macrocyclic ligands of varying

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ring size (13, 14, 15, and 16 membered) as dichlorides. Hence, in each case the metal ion has the same six donor atoms. The reduction potentials vary by about 0.5 V, and there is no obvious correlation between $E_{1/2}$ and the splitting parameter in the *xy* plane, Dq^{xy}. The values reported in ref 3 are given in Table II.

A related study by Endicott and co-workers,[2] in which the macrocyclic ligand was held constant and the axial ligands were varied, does show a nearly linear correlation between $E_{1/2}$ for $\mathrm{Co^{III}/Co^{II}}$ and the axial splitting parameter Dq^z. This system may be unique in that the most probable acceptor orbital, d_{z^2}, is the orbital affected by the ligand changes. In addition, the Co(II) product is low spin[2] so that the electron added most likely remains localized in the d_{z^2} orbital.

In each of the systems we have investigated that exhibit no correlation between $E_{1/2}$ and $10Dq$ (or one observed under only the most closely controlled conditions) there is, however, a strong correlation between appropriate Hammett substituent constants and $E_{1/2}$.[3–5] This is true even though substitutent changes may take place several bonds removed from the electroactive metal center. Interestingly, these correlations often parallel correlations between the Hammett substitutent constants and ligand properties such as $\mathrm{p}K_a$.[18] Thus, although the splitting parameter, Dq, is not a predictor of $E_{1/2}$, one does have the strong indication from these linear free-energy-type relationships that changes in bonding parameters are responsible for $E_{1/2}$ variations within a given series. The following discussion is an attempt to identify these parameters within the scope of existing, useful bonding approaches in transition-metal-complex chemistry.

A general reaction defining $E_{1/2}$ for a $d^n \rightarrow d^{n+1}$ system can be written

$$\mathrm{Ref_{red}} + \mathrm{ML_6}^{3+} \rightleftharpoons \mathrm{Ref_{ox}} + \mathrm{ML_6}^{2+} \qquad (1)$$

The $E_{1/2}$ for the reaction can be expressed as

$$-FE_{1/2} = \Delta G^\circ = G(\text{prod}) - G(\text{react}) = \Delta G(\text{Ref}) + \Delta G(\mathrm{ML_6}^{3+} \rightarrow \mathrm{ML_6}^{2+}) \qquad (2)$$

$\Delta G(\text{Ref})$ for a particular reference electrode is a constant and

$$\Delta G(\mathrm{ML_6}^{3+} \rightarrow \mathrm{ML_6}^{2+}) = \Delta H(\mathrm{ML_6}^{3+} \rightarrow \mathrm{ML_6}^{2+}) - T\Delta S(\mathrm{ML_6}^{3+} \rightarrow \mathrm{ML_6}^{2+}) \qquad (3)$$

The entropic term for the electron transfer can vary widely from compound to compound. However, if the entire range of about 1.5 V observed for the 1,3-diketonates was attributed to changes in ΔS, then the ΔS term for the series would have to vary by 118 eu which would be unreasonably large. There is, in fact, good reason to believe that the ΔS term is small in such complexes and that the variation of ΔS within the series is also small. The ΔS term is often considered to be the sum of a solvent reorganization entropy, ΔS_s, and an internal reorganization entropy, ΔS_i. The ΔS_i term is dependent upon ligand rearrangements, and since the redox couples for the compounds in Table I are reversible, ligand rearrangements must be extremely facile and relatively unimportant in the ΔS term. The ΔS_s term which is often the major contributor can also be expected to be small since these compounds are neutral and the studies carried out in nonaqueous media. Born model calculations[19,20] for a spherical species of 5-Å radius in DMF going from charge 0 to 1− indicate that ΔS_s should be ~4 eu. The general assumption that ΔS_s is small in these bulky, neutral complexes is supported by the conclusions of Hanania et al.[21] and by the recent work of Weaver et al.[22]

Since the large variation in $E_{1/2}$ for the tris(diketonate) systems does not arise from differences in the Dq term nor apparently from ΔS terms, it must arise mainly from the ΔH term. Inasmuch as $P\Delta V$ is negligible, ΔH may be equated to ΔE and is, therefore, equal to the difference in the sum of the energies of the electrons in the oxidized and reduced forms. For the purposes of this discussion it will be assumed that the most significant energy changes occur in the metal–ligand interactive electrons. The most important point to consider in this regard is what factors determine the energy of the acceptor orbital. In complexes of the type discussed herein, the acceptor orbital is considered to be antibonding with a large amount of d character. In ligand field terms, the energies of the antibonding d electrons are determined by the spherical potential term, V_s, and the Dq term. Since Dq variations do not seem to be a major contributor to $E_{1/2}$ variations, one is left, within the context of ligand field theory, with V_s as a major contributor.

Qualitatively, one can predict that the repulsive V_s term should be sensitive to changes in the substituent groups; i.e., an electron-supplying group that increases electron density on the donor atoms will increase V_s, while an electron-withdrawing group will decrease V_s. Thus, one would expect that the partially filled antibonding "d" orbitals are higher in energy in a complex containing electron-supplying substituents than in a complex containing electron-withdrawing substituents. This prediction is in agreement with the often observed linear dependence between the reduction potentials and the Hammett substituent constants in series of closely related complexes. Similar qualitative arguments can be developed for complexes in which donor atoms are changed, macrocyclic ring size is varied, etc.

In summary, there are several studies in which the redox potentials vary significantly (1–2 V) in a series of closely related complexes containing the same metal ion. Within these series Dq may or may not change by an appreciable amount, thereby casting considerable doubt on the concept that changes in Dq are responsible for changes in $E_{1/2}$. Other bonding parameters such as the repulsive spherical ligand field term, V_s, are potentially much more important and are expected to be sensitive to subtle changes in the ligands.

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Oxidative Addition: An Alternative View

Sir:

"Oxidative addition" is a useful general term for reactions of type 1, in which both the formal oxidation state and co-

$$\mathrm{ML}_m + \mathrm{X}_2 \rightarrow \mathrm{ML}_m\mathrm{X}_2 \qquad (1)$$

ordination number of the metal increase by 2 units.[1]

Unfortunately, ambiguities and contradictions attach to the use of the term. These arise from two sources: (i) our inability

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