Inorg. Chem. **1983**, *22*, 1205–1208

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Kinetics of Linkage Isomerization of (5-Methyltetrazolato)pentaamminecobalt(III)

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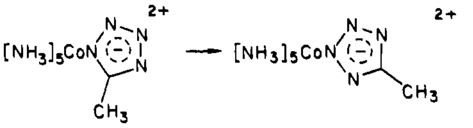
Received July 14, 1982

The kinetics of the linkage isomerization reaction for N_1-bonded (5-methyltetrazolato)pentaamminecobalt(III) rearranging to the N_2-bonded complex has been studied as a function of temperature and pH. Rate constants for isomerization of the protonated (3+) complex and deprotonated (2+) complex were found to differ appreciably, and a base-catalyzed pathway for the 2+ complex was found. At 25 °C and ionic strength 1.0 M, $k_{3+} = (3.1 \pm 2.5) \times 10^{-4}\ s^{-1}$ and $k_{2+} = (1.9 \pm 0.5) \times 10^{-6}\ s^{-1}$. Activation parameters for the two processes are $\Delta H_{3+}^{\ddagger} = 15 \pm 4$ kcal mol^{-1}, $\Delta S_{3+}^{\ddagger} = -24 \pm 13$ cal K^{-1} mol^{-1}, $\Delta H_{2+}^{\ddagger} = 26.0 \pm 1.8$ kcal mol^{-1}, and $\Delta S_{2+}^{\ddagger} = 2.5 \pm 5.6$ cal K^{-1} mol^{-1}. At 41.2 °C in basic media, $k_{obsd} = k_{2+} + k_{OH}[OH^-]$ where $k_{OH} = (3.1 \pm 0.7) \times 10^{-3}\ M^{-1}\ s^{-1}$.

Introduction

Numerous recent literature reports have provided valuable details of the structural, kinetic, and mechanistic aspects of linkage isomers.[1-12] Many of these studies are concerned with the kinetics and mechanism of the nitrito-to-nitro isomerization process[3] where significant new details of the reaction pathway have been delineated from high-pressure kinetic studies,[4] base catalysis of the isomerization reaction,[5] and studies with specifically labeled ligands.[5,6] Linkage isomeric complexes with biologically relevant ligands such as imidazole,[7] glycine,[8] hypoxanthine,[9] histidine,[10] methionine,[11] and uracil[12] are appearing with increasing frequency.

We reported recently synthetic routes to N_1- and N_2-bonded tetrazolato complexes of pentaamminecobalt(III) and the linkage isomerization reaction from the N_1- to the N_2-bonded forms of these complexes.[13] The kinetics of the N_1-to-N_2 isomerization reaction is reported here for the (5-methyltetrazolato)pentaamminecobalt(III) complex (eq 1), and a mechanism consistent with the observed kinetic behavior is proposed.



(1)

Experimental Section

Materials. The N_2- and N_1-bonded isomers of (5-methyltetrazolato)pentaamminecobalt(III) were prepared as described previously[13] with the exception that sodium perchlorate (anhydrous, G. F. Smith Chemical Co.) was utilized to precipitate the complexes in place of sodium iodide. (*Warning*! The perchlorate salt of the complex is potentially explosive and should be handled with caution.) The bonding mode of the complexes was verified by infrared and visible spectroscopy.[13]

Table I. Acid Dissociation Constants of the N_1-Bonded (5-Methyltetrazole)pentaamminecobalt(III) Complex, $\mu = 1.0$ ($NaClO_4$)

temp, °C	exptl K_a[a]	temp, °C	exptl K_a[a]
14.3	0.0222 ± 0.0017	25.0	0.0299 ± 0.0013
	0.0223 ± 0.0020[b]	48.3	0.0270 ± 0.0019
	0.0216 ± 0.0030[c]	63.3	0.0267 ± 0.0026

[a] Determined at 270 nm unless noted otherwise. [b] 280 nm. [c] 290 nm.

Ionic strength of solutions was controlled to 1.0 M with sodium perchlorate and perchloric acid (J. T. Baker Chemical Co.) stock solutions of known concentration. The sodium perchlorate stock was standardized as described previously,[14] and the perchloric acid stock was standardized by titration with sodium hydroxide.

Solutions were prepared from house-supplied distilled water, which was subsequently passed through a mixed-bed ion-exchange resin (Illinois Water Treatment Co.). Complex concentrations in solutions were determined from absorbance measurements in the visible region of the spectrum by using published molar absorptivities.[13]

Instrumentation. Kinetic and spectrophotometric K_a studies were performed on a Cary 17 spectrophotometer equipped with a Forma Scientific Model 2095 refrigerated and heated circulating water bath for temperature control to an estimated ±0.5 °C.

Acid Dissociation Constants. K_a values for the N_1-bonded form of the (5-methyltetrazolato)pentaamminecobalt(III) complex were determined spectrophotometrically at 14.3, 25.0, 48.3, and 63.3 °C in the near-ultraviolet region of the spectrum and are tabulated in Table I. Absorbance measurements (A_{obsd}) were made for six to seven solutions of varying hydrogen ion concentration ($HClO_4$), using $NaClO_4$ for ionic strength control to 1.0 M. Absorbance values for the deprotonated form of the complex (charge 2+) were determined from solutions adjusted to pH 5–8 with acetate or phosphate buffers (0.10 M buffer, $\mu = 1.0$ M). Solutions of cobalt complex were near 2×10^{-3} M for each spectral determination. K_a was evaluated from slopes of $(\epsilon_{obsd,\lambda} - \epsilon_{2+,\lambda})/[H^+]$ vs. ϵ_{obsd} plots ($K_a = -1/\text{slope}$) where $\epsilon_{obsd,\lambda}$ is $A_{obsd,\lambda}/[\text{complex}]$ and $\epsilon_{2+,\lambda}$ is the molar absorptivity of the deprotonated form of the complex at wavelength λ. The wavelengths utilized in these studies were 270, 280, and 290 nm at 14.3 °C and 270 nm exclusively at the other temperatures. Absorbance values at 48.3 and 63.3 °C were extrapolated back to the time of mixing since at these higher temperatures a small but significant amount of isomerization occurred during the measurement process.

Kinetic Measurements. Kinetic studies were performed on solutions of the N_1-bonded linkage isomer in the same perchloric acid and buffer pH range as employed in the K_a experiments. Ionic strength was again adjusted to 1.0 M with sodium perchlorate. Absorbance vs. time traces were obtained at 270 nm where a sizable increase in absorbance occurs as the N_2-bonded linkage isomer forms. Three temperatures were investigated, i.e., 41.2, 50.8, and 65.2 °C. Reaction progress was followed for at least 4 half-lives, and rate constants were obtained

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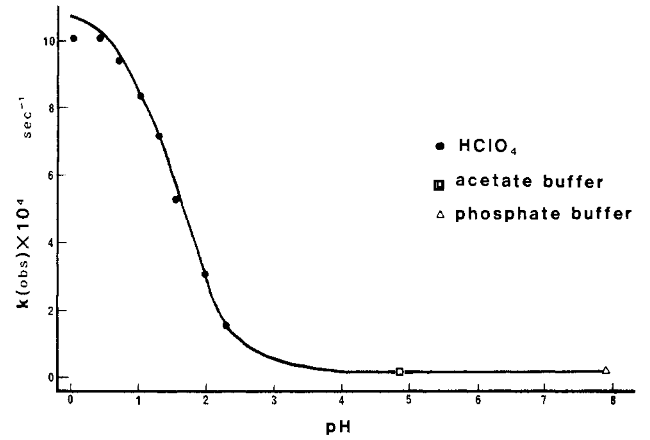


Figure 1. Variation of k_{obsd} for linkage isomerization as a function of pH at 41.2 °C and ionic strength 1.0 M.

from the usual log $(A_\infty - A_t)$ vs. time plots. Eight to eleven different hydrogen ion concentrations were investigated at each temperature although only about half of these runs were repeated for averaging purposes since many reactions were quite slow with half-lives approaching 10 h. Complex concentrations employed in the kinetic studies ranged between 2×10^{-4} and 5×10^{-3} M, and the concentration of complex was always at least 10 times less than the acid concentration to ensure that no significant change in hydrogen ion concentration occurred during the course of the reaction due to protonation of the reactant or product complex. A few kinetic studies were performed at 41.2 °C in basic solution at ionic strength 1.0 M, using sodium hydroxide–sodium perchlorate solutions.

Results

The acid dissociation constants of the N_1-bonded (5-methyltetrazole)pentaamminecobalt(III) complex determined at various temperatures are presented in Table I. From the temperature dependence of the K_a values, ΔH_a and ΔS_a values of 0.8 ± 0.5 kcal mol^{-1} and -4.8 ± 1.6 cal K^{-1} mol^{-1}, respectively, were computed at ionic strength 1.0 M.

The rate of the linkage isomerization reaction (eq 1) was found to vary dramatically with pH, being most rapid at low pH and slowing considerably as neutral solution was approached. The behavior observed at 41.2 °C is shown in Figure 1, and similar behavior was observed at 50.8 and 65.2 °C. For runs near neutral pH, no kinetic difference was observed between solutions buffered by phosphate or acetate.

Moderate rate acceleration of the isomerization reaction was observed in basic solution although, seemingly at random, a few studies were found to produce a small amount of precipitate, which restricted the range of hydroxide concentrations studied. Hence, because of these difficulties, studies in basic solution were not attempted at other temperatures. The 41.2 °C rate data in basic media are presented in Figure 2.

Measurements of the total absorbance changes at 270 nm for solutions containing equivalent concentrations of the N_1-bonded complex but variable initial concentrations of the N_2-bonded complex were performed. With no added N_2 isomer, the change was measured as 0.588 ± 0.026 absorbance unit under the conditions of the experiment, i.e., 6×10^{-3} M complex, ionic strength 1.0 M, and 0.10 M HClO4. Under these same conditions but with 1.07×10^{-2} M N_2-bonded complex added at the start of the isomerization process, this change was 0.571 ± 0.019 absorbance unit.

Discussion

The N_1-coordinated 5-methyltetrazole ligand ligand is considerably more acidic than the free ligand (whose pK_a is 5.63[15]) with a reduction of the pK_a value by 4.1 units at 25 °C. This lowering of the ligand pK_a by coordination is of the same order of magnitude as that observed for isoelectronic imidazole when coordinated to the pentaamminecobalt(III) moiety.[16] Interestingly, the K_a, enthalpy, and entropy changes of the N_2-bonded (5-methyltetrazolato)pentaamminecobalt(III) complex are almost identical with those of the N_1 linkage isomer, 0.0200 ± 0.0006, 0.5 ± 0.3 kcal mol^{-1}, and -6 ± 1 cal K^{-1} mol^{-1} at 25 °C and ionic strength 1.0 M.[17]

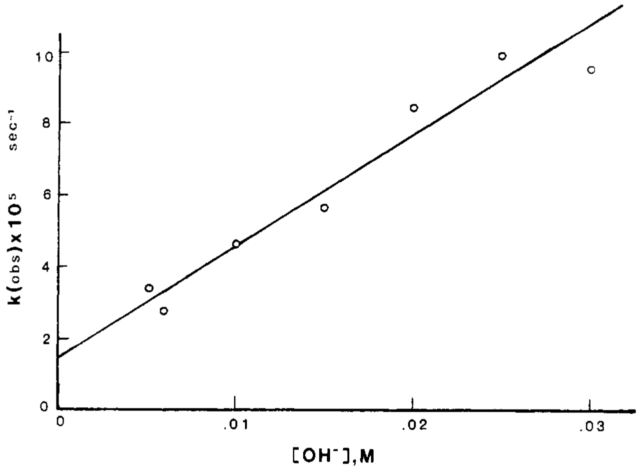
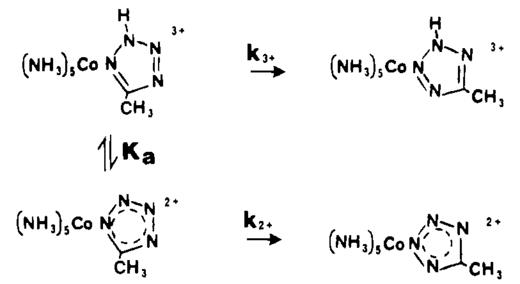


Figure 2. Variation of k_{obsd} for linkage isomerization in basic solution as a function of [OH$^-$] at 41.2 °C and ionic strength 1.0 M.

Scheme I



The N_1-bonded complex exhibits no appreciable isomerization to the N_2 form in the solid state, at least over a period of weeks at room temperature. In solution, however, linkage isomerization occurs at a reasonable rate and isosbestic behavior is observed in ultraviolet–visible spectral scans of such solutions.[13] Cation-exchange chromatography of product solutions shows only the presence of the N_2-bonded isomer; i.e., no aquopentaamminecobalt(III) is detected.[13] Thus, in analogy with the "classical" nitrito-to-nitro linkage isomerization, complete ligand dissociation and long-lived intermediates do not appear to operate in this reaction pathway.[3-6]

The absorbance changes measured with and without added N_2-bonded complex present at the start of N_1 isomerization yield an estimate of the equilibrium constant for isomerization at ionic strength 1.0 M of about 60. Given the error limits for the measured absorbance changes and the conditions employed for these kinetic studies (i.e., no N_2-bonded complex present initially), it is estimated that 98 ± 3% of the N_1-bonded isomer present at the beginning of each kinetic run is converted into its N_2-bonded isomer at the end of each run. Hence, this isomerization reaction is essentially a complete conversion from the N_1- to N_2-bonded complex.

The dramatic pH dependence of the isomerization rate constants shown in Figure 1 is in striking contrast to other reported linkage isomerization reactions. A reasonable

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Table II. Comparison of Spectrophotometric and Kinetic K_a Values

temp, °C	K_a(spectrophotometric)[a]	K_a(kinetic)
41.2	0.026 ± 0.003	0.033 ± 0.002
50.8	0.027 ± 0.003	0.025 ± 0.003
65.2	0.028 ± 0.004	0.016 ± 0.005

[a] Calculated from the ΔH and ΔS values derived from data in Table I.

Table III. Rate Constants for Linkage Isomerization

temp, °C	k_{2+}, s^{-1}	k_{3+}, s^{-1}	k_{OH}, M^{-1} s^{-1}
41.2	$(1.91 \pm 0.03) \times 10^{-5}$,[a] $(2.0 \pm 0.1) \times 10^{-5}$ [b]	$(1.03 \pm 0.03) \times 10^{-3}$	$(3.1 \pm 0.7) \times 10^{-3}$
50.8	$(5.4 \pm 0.1) \times 10^{-5}$ [a]	$(3.37 \pm 0.08) \times 10^{-3}$	
65.2	$(4.2 \pm 0.1) \times 10^{-4}$ [c]	$(6.55 \pm 0.14) \times 10^{-3}$	
25.0	$(1.9 \pm 0.5) \times 10^{-6}$ [d]	$(3.1 \pm 2.5) \times 10^{-4}$ [d]	

[a] pH 4.85 (acetate buffer). [b] pH 7.87 (phosphate buffer). [c] pH 6.58 (phosphate buffer). [d] Calculated from activation parameters in Table IV.

Table IV. Activation Parameters for Linkage Isomerization

pathway	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal K^{-1} mol^{-1}
k_{2+}	26.0 ± 1.8	2.5 ± 5.6
k_{3+}	15 ± 4	−24 ± 13

mechanistic interpretation of such behavior is to attribute different rate constants for isomerization to the protonated and deprotonated (3+ and 2+) complexes. Such a mechanism is presented in Scheme I. It should be noted when Scheme I is considered that the actual site of protontation in the 3+ complexes (both N_1 and N_2) has not been determined and any of the three uncoordinated nitrogens are potential sites for the proton. The mechanism proposed in Scheme I leads to a rate law of the form given in eq 2 and 3.

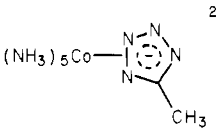
$$\text{rate} = k_{\text{obsd}}[N_1\text{-bonded complex}] \qquad (2)$$

$$k_{\text{obsd}} = \frac{k_{3+} + k_{2+}K_a[H^+]^{-1}}{1 + K_a[H^+]^{-1}} \qquad (3)$$

Analysis of the kinetic data in terms of eq 2 and 3 is facilitated by the nature of the k_{obsd} vs. pH profiles (Figure 1), which permit k_{2+} to be determined independently of K_a and k_{3+} at high pH. This, of course, assumes that no buffer effects exist for the k_{2+} process, a conclusion implied by the excellent agreement between k_{obsd} values in acetate and phosphate buffer systems (see Table III). Hence, any buffer effects are subtle and are not discernible within the accuracy of these measurements. When this is done and eq 3 is analyzed for k_{3+} and K_a, the K_a values obtained agree reasonably well with those extrapolated from the independent spectrophotometric studies as shown in Table II, thus giving credence to the mechanism proposed in Scheme I. However, in order to obtain the most reliable k_{3+} values possible, spectrophotometric K_a values were used in eq 3. Rate constants and their activation parameters are presented in Tables III and IV, respectively. The rate acceleration in basic solution (see Figure 2) can be accommodated by a conjugate base mechanism as recently discovered for the nitrito-to-nitro linkage isomerization reaction[5] with $k_{\text{obsd}} = k_{2+} + k_{OH}[OH^-]$. The value for k_{OH} at 41.2 °C is also presented in Table III.

The rate constants and activation parameters for the tetrazole linkage isomerization (Tables III and IV) compare favorably with those for (nitrito)pentaamminecobalt(III) linkage isomerization.[5] The $\Delta H_{2+}^{\ddagger}$ value is slightly larger than $\Delta H^{\ddagger}$ for the nitrito-to-nitro conversion as would be expected for breaking or stretching a Co–N bond vs. a Co–O bond although the difference (3 kcal mol^{-1}) is not great. An intermolecular process for tetrazole complex isomerization seems unreasonable since k_{obsd} is independent of complex concentration. This, along with the observation of a base-catalyzed pathway for tetrazole and nitrito systems and the product studies discussed above,[13] points to similar mechanisms for linkage isomerization, namely intramolecular isomerization with bond breaking dominant. The observation that $\Delta H^{\ddagger}$ is smaller for the protonated form of the complex (a neutral ligand) vs. the deprotonated form (an anionic ligand) is consistent with this interpretation although we have no systems to which this activation enthalpy may be compared as there have been no reports prior to this study of linkage isomerization kinetic parameters with neutral ligands on pentaamminecobalt(III). The $\Delta H^{\ddagger}$ differences for the k_{3+} and k_{2+} paths could also be explained by stabilization of the N_1-bonded form of the 2+ complex. Such stabilization would obtain if the anionic tetrazolate ligand were hydrogen bonded to a cis ammine. Whether the $\Delta H^{\ddagger}$ difference is normal for neutral vs. anionic ligands, the result of a ground-state stabilization of the 2+ complex, or is due to mechanism differences for the 3+ and 2+ complexes should be revealed as other tetrazolato linkage isomerizations are examined.

The nature of the activated complex for the N_1-to-N_2 isomerization is not defined unambiguously at this time. However, two possible structures seem most likely: the π-bonded complexes I and II. In structure II, the tetrazole ring system is perpendicular to the cobalt–ligand bond. A dissociated ion-pair type of activated complex seems less favorable for reasons discussed in detail for the nitrito-to-nitro isomerization process.[5,6] Conceivably both I and II could operate as transition states here, one for the k_{3+} path and the other for the k_{2+} path. We hope to distinguish between these possibilities in a future report by employing a ^{15}N specifically labeled 5-methyltetrazole complex. On the basis of some reports in the literature, a precedence for type II activated complexes seems to exist. I refer to reports of N_1-to-N_3 isomerization observed for some substituted imidazole complexes that would seem to require a transition state of type II.[10,18] Transition state I would be analogous to that proposed for dinitrogen isomerization in the pentaammineruthenium(II) complex.[19]



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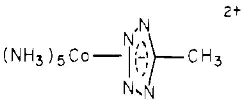

II

The primary driving force for this linkage isomerization seems to be steric relief. MINDO/3 calculations indicate that the N_1 nitrogen of tetrazolate anions is more nucleophilic than the N_2 nitrogen.[20] Thus, electronic consideration favor N_1 coordination. The observed N_1-to-N_2 isomerization, however, does relax the steric congestion existing between the 5-methyl group on the tetrazole ring and the cis ammines of the pentaamminecobalt(III) unit.[13,20] The 5-substituted-tetrazolato complexes offer a unique opportunity to probe some of these more subtle features of linkage isomerization. The relatively straightforward synthetic route to N_1-bonded complexes makes a number of 5-substituted tetrazole complexes with variable electronic and/or steric contributions from the 5-substituents

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feasible. We are currently examining a series of 5-substituted phenyltetrazolato complexes in an effort to separate electronic contributions should they exist.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. N_1-bonded (5-methyltetrazole)pentaamminecobalt(III), 84943-93-1; N_2-bonded (5-methyltetrazole)pentaamminecobalt(III), 84927-27-5; N_1-bonded (5-methyltetrazolato)pentaamminecobalt(III), 84927-29-7; N_2-bonded (5-methyltetrazolato)pentaamminecobalt(III), 84927-31-1.

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Electrochemical and ESR Studies of the Redox Reactions of Nickel(II), Palladium(II), and Platinum(II) Complexes of 1,2-Diphenyl-1,2-ethenedithiolate(2−)-*S*,*S*′

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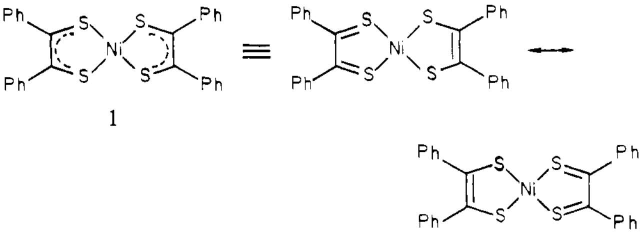
Received July 2, 1982

The electron spin resonance (ESR) spectra of the one-electron-reduction products of the 1,2-diphenyl-1,2-ethenedithiolate complexes $M(Ph_2C_2S_2)_2$ (M = Ni, Pd, Pt) support the view that these reductions are mainly ligand based. Dc cyclic voltammetric studies of the above complexes also show an apparently quasi-reversible oxidation process in each case. ESR studies indicate that several species with slightly differing *g* values are formed in this process under the longer time scale of controlled-potential electrolysis. The 1,2-diphenyl-1,2-ethenedithiolate(2−)-*S*,*S*′ complexes $M(dpe)(Ph_2C_2S_2)$ (M = Ni(II), Pd(II), Pt(II); dpe = 1,2-bis(diphenylphosphino)ethane) and $M(PPh_3)_2(Ph_2C_2S_2)$ (M = Pd(II)) were prepared, as described by previous workers, by ligand substitution reactions between the metal dithiolene complexes and the appropriate phosphine ligand. $Ni(dpe)(Ph_2C_2S_2)$ undergoes a reversible one-electron reduction to the corresponding nickel(I) complex and a reversible one-electron oxidation to give a long-lived species that is characterized by ESR spectroscopy as a complex of the previously unknown dithioketyl $(Ph_2C_2S_2)^{-}\cdot$. The palladium and platinum 1,2-diphenyl-1,2-ethenedithiolate(2−)-*S*,*S*′ complexes do not undergo reversible reduction but like the above nickel complex undergo reversible oxidation to give dithioketyl complexes.

Introduction

The compound bis[1,2-diphenyl-1,2-ethenedithiolato(1−)-*S*,*S*′]nickel, $Ni(Ph_2C_2S_2)_2$ (**1**), first discovered by Schrauzer and Mayweg,[1-3] was one of the first of a large class of transition-metal complexes, known as dithiolene complexes, which have attracted considerable interest over the last 20 years because of their unusual chemical properties.[4-8] One of these properties is the ability of the complexes to undergo a sequence of reversible electron-transfer reactions, and these have been the subject of many chemical, electrochemical, structural, and spectroscopic studies.[4-8] As a result of these studies, it has been concluded that the accessibility of a range of oxidation states of the complex is the result of the accessibility of a number of formal oxidation states for the ligand and that the electron density in the metal orbitals does not change significantly as the oxidation state is changed.[4-8] Thus the redox processes for the Ni-group dithiolenes $M(R_2C_2S_2)_2$ (M = Ni, Pd, Pt; R = CN, CF_3, Ph, etc.)[5,8-10] can be represented in the following way: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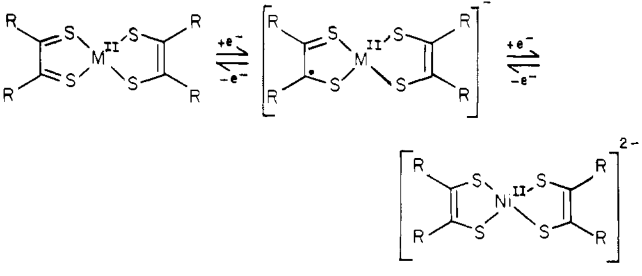

The most highly reduced member of the series involves coordinated dithiolate ligands. The others formally contain in addition coordinated dithioketones, $R_2C_2S_2$, or dithioketyls, $R_2C_2S_2^{-}\cdot$, neither of which are stable as isolated molecules. The true electronic structures of these complexes are of course resonance hybrids involving several different valence-bond structures, as shown for **1** above.[4,7,8] Only one such structure is shown for each of the members of the electron-transfer series in eq 1. In principle, further redox processes for these complexes could exist that involve more highly oxidized states of the ligands.

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