

rivatives to hinder chelation. Again, the analogy may be drawn with the $W(CO)_5(bpy)$ or $W(CO)_5(dab)$ ($bpy = 2,2'$ -bipyridine, $dab = 1,4$ -diazabutadiene) complexes, where the N-donor ligands are π -conjugated and yet undergo chelation much more rapidly than these $M(CO)_5(en)$ compounds.^{8c} Experimental and theoretical studies on the bpy ligand have concluded that it exists in an approximately *s-trans* conformation in the solution phase.²¹ Thus, the π -conjugation of bpy will, in fact, hinder the rotation about the C_2-C_2' bond necessary to achieve the *cis* chelation geometry. Correspondingly, the lack of ring closure in these $M(CO)_5(en)$ complexes cannot be attributed solely to the ease of rotation about the $en C_2-C_2'$ bond. A third factor that has been considered is solvation effects on the uncoordinated nitrogen atom of the en ligand. While previous workers have investigated the solvating influence of aqueous and alcoholic solvents on en ,²² it would be difficult, at best, to believe that the chloroform solvent used in this study could provide the necessary solvating power to prevent coordination of the remaining nitrogen. Moreover, we have determined that the $W(CO)_5(en)$ complex is equally stable in room-temperature cyclohexane and isooctane solutions. A fourth factor to consider is hydrogen bonding between the un-

coordinated amine groups of en , thereby slowing the rate of chelation. However, at the $\sim 10^{-4}$ M concentrations used in this study, it would seem unlikely that this phenomenon would significantly influence the chelation process.

Thus, other interpretations must be invoked to account for the stability of these $M(CO)_5(en)$ complexes. We view it significant that the en ligand, unlike bpy , is able to undergo free rotation about the C-N bonds and, thus, even when it does achieve a *cis* geometry, the overlap of the nitrogen lone pair with the metal center may be poor. Also significant may be the tetrahedral environment surrounding the nitrogen atoms of the en ligand, which results in sp^3 hybridization of these orbitals, whereas the hybridization is sp^2 in most other diimine ligands such as 2,2'-bipyridine or 1,10-phenanthroline. The sp^3 hybridization would result in a substantial decrease in orbital angular overlap for the incoming nitrogen atom as it undergoes bond formation and ring closure. We also note that in previous studies where monodentate en complexes have been observed, the metal center possesses a formal charge of +2 or +3.²⁻⁷ These complexes exist only as reaction intermediates and have not been isolated. In contrast, the stable complexes described here have metal centers that possess a formal neutral charge.

In summary, the unusual stability of these $M(CO)_5(en)$ complexes is attributed to the reduction of ligand orbital overlap that is necessary to bring about chelation and to the diminished affinity of the ligand electrons for the metal center.

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Theoretical Analysis of the Cobalt(III)-Cobalt(II) Tris[(±)-1,2-propanediamine] Electron-Transfer Reaction Using Molecular Mechanics Modeling of the Configurational Isomer Distribution in Both Oxidation States

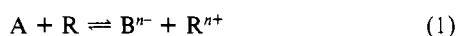
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A theoretical study of the electron-transfer process $[Co(\pm)\text{-pn}]_3^{3+} + e^- \rightleftharpoons [Co(\pm)\text{-pn}]_3^{2+}$ ($pn = 1,2$ -propanediamine) based on molecular mechanics modeling of the relative strain energies of the configurational isomers available in each oxidation state leads to the prediction that four different E° values may be expected between isostructural pairs. The four E° values arising from the *lel*₃, *lel*₂*ob*, *ob*₂*lel*, and *ob*₃ configurations are calculated to lie within a range of 20 mV. That is, the values of the configurational equilibrium constants are different in the cobalt(III) and cobalt(II) oxidation states. Electrochemical reduction at mercury electrodes of the configurational isomers of $[Co(\pm)\text{-pn}]_3^{3+}$ demonstrates that the calculated range of E° values is of the correct order of magnitude. However, more detailed theory and experiment correlations could not be made because of lack of resolution of electrochemical measurements and lack of independent experimental information on the numerous equilibrium and/or rate constants that accompany electron transfer. Electrochemical data are extremely dependent not only on the configurational form but also on the electrolyte, which further highlights the complexity of electron-transfer processes involving configurational change when considered in microscopic detail.

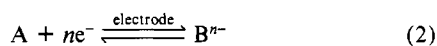
Introduction

Electron-transfer processes of the kind



(chemical redox process, R = reductant)

or the equivalent electrochemical process



are quantified thermodynamically by an E° value (E° = standard

redox potential) and kinetically by a self-exchange homogeneous rate of electron transfer (chemical redox process) or by k_s and α (k_s = standard heterogeneous rate constant for electron transfer at E° ; α = charge-transfer coefficient) for electrochemical reduction. The theoretical relationship between homogeneous and heterogeneous electron-transfer rates can be described by the Marcus-Hush theory or other models of electron transfer.⁴

Spectroscopic, crystallographic, and other forms of examination of species A and B^{n-} (reactants and products of the electron-transfer process, respectively) reveal that configurational (conformational) changes may be associated with electron transfer in many instances; i.e., A and B^{n-} are not necessarily isostructural.

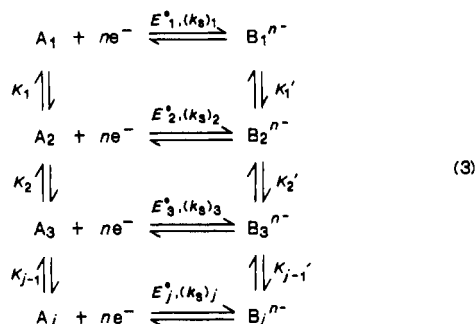
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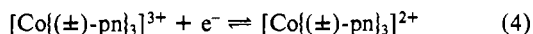
If this possibility exists, then an ambiguity may exist in the theoretical description of the electron-transfer process.⁵ The simplest and commonest approach has been to include the configurational change in the kinetic description and assume that this influences the overall rate of electron transfer.⁴ Effectively, this assumes electron transfer and structural change occur simultaneously and that the two processes are indistinguishable. Recently, Bond and Oldham^{6,7} have argued that while this concept produces a mathematically simple model, important thermodynamic aspects must also be considered when free energy differences exist between different structures. Unfortunately, the Bond and Oldham model, while realistic, is almost mathematically intractable, except for some relatively simple cases.^{6,7} The Bond–Oldham mechanism in its simplest form when applied to electrochemical reduction assumes that if there are j structural forms of A and Bⁿ⁻, then $j E^\circ$ values exist between isostructural pairs and that these $j E^\circ$ values in addition to homogeneous and heterogeneous rate constants (equilibrium constants in limiting cases) define the redox process. In a simplified form, eq 3 is an example of this approach.



If the free energy differences between A₁ and A_j and B₁ⁿ⁻ and B_jⁿ⁻ are equal (or zero), then of course the models presented in eq 2 and 3 are equivalent. However, if free energy differences exist, then eq 1 and 2 are unlikely to be satisfactory representations of redox processes. A model analogous to that in eq 3 also can be applied to homogeneous electron-transfer reactions.

The distinction between the simple model (eq 2) and the Bond–Oldham model (eq 3) lies in the assessment of whether free energy differences exist between different structural forms of a molecule. Calculation methods based on molecular mechanics have recently been used to provide a theoretical explanation of the redox potentials of the different geometric isomers of [Co(dien)₂]³⁺ and [Co(dien)₂]²⁺ (dien = diethylenetriamine), where the free energy differences between E_j^o values are on the order of tens of millivolts. Consideration of configurational or conformational changes that produce smaller changes in free energy than geometric isomerization (cis ⇌ trans, tetrahedral ⇌ planar, facial ⇌ meridional, etc.) have rarely been considered in the thermodynamic sense in electron-transfer studies^{5,9-12} even though they are commonly present. Adsorption properties of different conformers have of course been well recognized in electrochemical studies^{9,10} as being important.

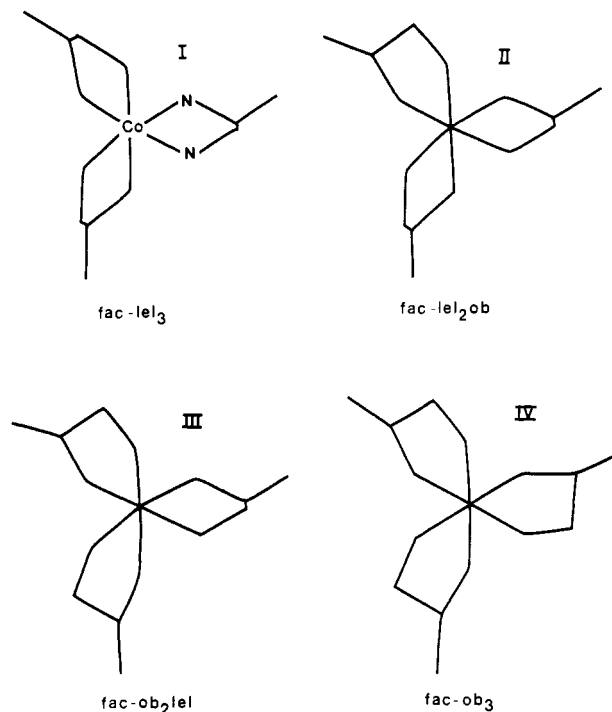
In the present work, a theoretical study of the [Co{(±)-pn}₃]^{3+/2+} (pn = 1,2-propanediamine) electron-transfer process as in eq 4 has been undertaken. This system is regarded as typical of the



many Co(III) reduction processes studied where almost invariably the one-step theoretical model has been used in both chemical and

electrochemical reduction processes without considering the configurations present and determining the free energy relationships that need to be considered.

The [Co{(±)-pn}₃]³⁺ system represents 24 isomers whose properties and stabilities have attracted considerable interest in connection with optical activity problems and configurational analyses.¹³⁻²³ The complex [Co{(±)-pn}₃]³⁺, like [Co(en)₃]³⁺ (en = 1,2-ethanediamine), can exist in the *lel*₃, *lel*_{2ob}, *ob*_{2lel}, and *ob*₃ configurations as presented in structures I–IV (*lel* refers to the



configuration with the C–C vector of the chelate ring approximately parallel to the “C₃” axis of the complex and *ob* to the configuration where this vector is at an angle to this axis). However, the methyl group of the pn ligand destabilizes the configuration with this group axially disposed and so confers a stereospecificity for either *lel* or *ob* geometry that depends on the absolute configuration of both the ligand and the complex. For example, (–)-pn ligands coordinated to a metal atom as part of a complex with Λ helicity will adopt the *ob* configuration. Thus Λ -[Co{(±)-pn}₂{(–)-pn}]³⁺ will adopt the *lel*_{2ob} arrangement. As a consequence of the stereospecificity and kinetic inertness of the cobalt(III) atom, the four different arrangements can be separated. All four isomers have been prepared and separated and the equilibrium proportions determined at 20 °C¹⁵ and at 100 °C.²⁰ Further levels of isomerism are possible within each of these four isomers and arise from the orientation of each methyl group with respect to the axis ($\sim C_3$) of the molecule. For example, the *lel*₃ isomer can have all these methyl groups disposed in one direction (designated facial) or two disposed in one direction and one in another (designated meridional). For *lel*_{2ob} and *ob*_{2lel} there are

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an even greater number (four) of isomers possible and in all there are 12 energetically distinct isomers of $[\text{Co}(\pm)\text{-pn}]_3^{3+}$. However, energy minimization calculations²¹ and experimental determinations of isomer distribution²² indicate the *mer* and *fac* arrangements for a given configurational isomer have almost identical stabilities.

Unfortunately, the reduced-oxidation-state (II) complexes have yet to be synthesized, and direct measurement of their configurational distribution is not possible. However, theoretical calculations using molecular mechanics modeling of the cobalt(II) complexes are possible. Additionally, electrochemical reduction of the cobalt(III) complexes may provide a partial examination of the usefulness of the theory. The possible complexity of configurational changes associated with cobalt electron-transfer reactions is illustrated in the recent work of Saar, Smith, and Cais,²⁴ who examined the electrochemical reduction of some β -diketonate cobalt(III) chelates. Reduction of $[\text{Co}(\pm)\text{-pn}]_3^{3+}$ could be far more difficult to unravel since many more configurations are possible.

In this work, energy minimization calculations on the configurational isomers of both cobalt(III) and cobalt(II) 1,2-propanediamine complexes were performed in order to assess the influence of this kind of isomerization in electron-transfer reactions. Results are compared with electrochemical data for reduction of the *lel*₃-, *lel*₂*ob*-, *ob*₂*lel*-, and *ob*₃- $[\text{Co}(\pm)\text{-pn}]_3^{3+}$ complexes at the dropping mercury electrode.

Experimental Section

Preparation and Separation of the Isomers of $[\text{Co}(\pm)\text{-pn}]_3^{3+}$. An equilibrium mixture of the isomers of $[\text{Co}(\pm)\text{-pn}]_3^{3+}$ was prepared by methods described previously for Co(III)-hexamine complexes.²⁴ Cobalt(II) perchlorate hexahydrate (1.85 g, 5 mmol) was dissolved in deionized water (30 mL), and this solution added to a solution containing (±)-1,2-propanediamine (1.15 g, 1.5 mmol) and perchloric acid (0.5 mL, 11 M) in water (20 mL). Freshly ground activated charcoal was then added, and with the mixture maintained at 100 °C, oxygen was bubbled through for 18 h. The reaction was quenched by addition of perchloric acid (2 mL, 11 M), and the charcoal was filtered off. The resultant orange solution was diluted to 1 L by the addition of water and then sorbed onto a chromatography column (2.5 × 80 cm) packed with C-25 SP-Sephadex cation-exchange resin. The column was washed with water and then eluted with a Na_2HPO_4 (2 M) solution, the pH of which had been adjusted to 7 by addition of H_3PO_4 . Four separate bands were obtained corresponding to the *lel*₃, *lel*₂*ob*, *ob*₂*lel*, and *ob*₃ species and eluted in that order. Each fraction, once eluted, was diluted fivefold by addition of water and resorbed onto a smaller column (1.5 × 30 cm) also packed with C-25 SP-Sephadex resin. The columns were washed successively with water to remove phosphate, 0.1 M hydrochloric acid to remove sorbed sodium, and 1.0 M hydrochloric acid to remove the complex. The resultant solutions were taken to dryness on a rotary evaporator. The remaining solid was redissolved in a small quantity of perchloric acid (11 M) and the solution stirred and warmed at 80 °C for 10 min to remove hydrochloric acid. Evaporation of the solutions under vacuum and in the presence of phosphorus pentoxide yielded crystals of the perchlorate salt of each isomer. These crystals were filtered off, washed with ethanol, and air-dried.

The individual isomers were characterized and their purity was established by ¹³C NMR spectroscopy. For each spectrum a sample of the perchlorate salt (0.25 g) was dissolved in D₂O and proton-decoupled spectra, referenced to an external dioxane standard, were obtained at 20.1 MHz on a Bruker WP-80 spectrometer. Chemical shifts relative to dioxane are listed in Table I. The spectra of the *lel*₃- and *ob*₃- $[\text{Co}(\pm)\text{-pn}]_3^{3+}$ isomers each show three signals, arising from the three different carbon atoms of each ligand, as expected if C₃ symmetry is maintained. This result suggests that different methyl dispositions (giving *mer* and *fac* isomers) scarcely perturb the geometry of the complex molecules away from C₃ symmetry as reported previously.²⁵ The *lel*₂*ob*

Table I. 20.1-MHz ¹³C NMR Chemical Shifts (δ , Relative to Dioxane) of the Isomers^a of $[\text{Co}(\pm)\text{-pn}]_3^{3+}$ at 25 °C

isomer	shifts		
	methyl	methylene	
<i>lel</i> ₃	49.58	16.09	11.96
<i>lel</i> ₂ <i>ob</i>	50.10	17.07, 16.64, 15.79	13.12, 12.09, 11.48
<i>ob</i> ₂ <i>lel</i>	49.44	16.76 (broad)	13.24, 12.88, 11.78
<i>ob</i> ₃	48.64	16.45	13.11

^a These isomers are mixtures of *mer* and *fac* species.

and *ob*₂*lel* spectra each show broadened methyl carbon signals and generally three separate signals for each type of methylene carbon. These separate signals presumably arise one from each chelate ring and reflect the lack of symmetry of these isomers. Again there is no evidence of separate signals arising from the four different *mer* or *fac* arrangements for each isomer.

Preparation of the Solutions for Electrochemistry. The perchlorate salts of each isomer, prepared as described above, were used for electrochemical measurements. The tetraalkylammonium salts, which were used as supporting electrolytes, were first purified by water-induced recrystallization from methanol solution and then dried and stored under vacuum. Analytical reagent grade acetone was used without further purification.

Solutions for electrochemical measurements were prepared just prior to each experiment by dissolving accurately weighed quantities of the electrolyte and complex perchlorate salt in measured volumes of solvent. All solutions were degassed with dry nitrogen for at least 10 min prior to undertaking measurements.

Electrochemical Instrumentation. All polarographic data were recorded at 22 ± 1 °C with Princeton Applied Research (PAR) corp. Model 174 polarographic analyzers equipped with X-Y chart recorders. For dc and differential pulse measurements a mechanically controlled drop time of 0.5 s was used. The reference electrode was Ag/AgCl (saturated LiCl; acetone) separated from the test solution by a salt bridge containing the supporting electrolyte being used for the particular measurement, while the auxiliary electrode was a platinum wire. For cyclic voltammetry, the scan was initiated approximately 0.5 s after the commencement of drop formation.

Calculations. The force field used in all calculations has been fully detailed elsewhere.³⁴ Energy minimization was achieved by the Newton-Raphson method, adapted for the study of metal complexes by Snow.³⁵

Results and Discussion

E^0 values are a measure of the difference in free energy in each oxidation state. In order to obtain an estimate of this change in free energy accompanying reduction of each isomer, energy minimization calculations were undertaken for both Co(III) and Co(II) oxidation states.

An energy minimization study of the *lel*₃, *lel*₂*ob*, *ob*₂*lel*, and *ob*₃ isomers of $[\text{Co}(\pm)\text{-pn}]_3^{3+}$ was first carried out by Crossing³⁶ using the force field described by Snow.³⁵ More recently all 12 isomers were considered with use of a slightly different force field.²¹ Both studies gave similar results with the stability order *lel*₃ > *lel*₂*ob* > *ob*₃ > *ob*₂*lel* and an overall energy difference of approximately 2.3 kJ mol⁻¹. These results are somewhat at variance with the experimentally determined stabilities, which give *lel*₃ > *lel*₂*ob* > *ob*₂*lel* > *ob*₃ with an overall energy difference of 6.7 kJ mol⁻¹.²⁰

The calculations were repeated with use of the force field described elsewhere³⁴ with all 12 isomers being considered. Final minimized strain energies are given in Table IIa and are similar to those reported by Laier and Larsen²¹ except that *ob*₂*lel* and *ob*₃ conformers now have similar strain energies. The relative

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Table II. Minimized Strain Energies of the $[\text{Co}(\pm)\text{-pn}]_3^{3+}$ Isomers (kJ mol^{-1})

isomer	E_b	E_{nb}	E_θ	E_ϕ	U_{TOTAL}
(a) $[\text{Co}(\pm)\text{-pn}]_3^{3+}$					
<i>fac-lel</i> ₃	9.7	26.2	7.8	7.3	51.0
<i>mer-lel</i> ₃	9.7	26.2	7.8	7.3	51.0
<i>fac-lel</i> _{2ob}	10.0	27.2	7.7	7.9	52.8
<i>mer-lel</i> _{2ob}	10.0	27.3	7.7	7.8	52.8
<i>mer-lel</i> _{2ob}	10.0	27.2	7.7	7.9	52.8
<i>mer-lel</i> _{2ob}	10.0	27.2	7.6	7.9	52.7
<i>fac-ob</i> _{2lel}	10.2	28.4	7.7	8.2	54.5
<i>mer-ob</i> _{2lel}	10.2	28.4	7.7	8.2	54.5
<i>mer-ob</i> _{2lel}	10.2	28.4	7.7	8.3	54.6
<i>mer-ob</i> _{2lel}	10.2	28.3	7.7	8.3	54.5
<i>fac-ob</i> ₃	10.2	28.2	7.7	8.4	54.5
<i>mer-ob</i> ₃	10.2	28.1	7.7	8.5	54.5
(b) $[\text{Co}(\pm)\text{-pn}]_3^{2+}$					
<i>fac-lel</i> ₃	2.1	5.9	5.8	5.1	18.9
<i>fac-lel</i> _{2ob}	2.2	6.6	5.7	5.2	19.7
<i>fac-ob</i> _{2lel}	2.3	7.5	5.6	5.2	20.6
<i>fac-ob</i> ₃	2.3	8.8	5.7	5.2	22.0

Table III. Strain Energies and Calculated and Observed Enthalpy Differences (kJ mol^{-1}) for the Isomers^a of $[\text{Co}(\pm)\text{-pn}]_3^{3+}$

isomer	U_{TOTAL}	rel ΔH	$\Delta H_{\text{exptl}}^b$
<i>lel</i> ₃	51.0	0	0
<i>lel</i> _{2ob}	52.7	1.8	2.9
<i>ob</i> _{2lel}	54.5	3.5	5.5
<i>ob</i> ₃	54.5	3.5	6.7

^aThese isomers are mixtures of *mer* and *fac* species. ^bData taken from ref 20.

orientations of the methyl groups (*mer* or *fac*) have little effect on the strain energies or on the geometry of the "Co(en)₃" core, consistent with the high symmetries suggested by the ¹³C NMR spectra. This result also concurs with the observation²² of a 3:1 mixture of *mer*- and *fac-ob*₃- $[\text{Co}(\text{pn})_3]^{3+}$, as expected from the statistical preference for the lower symmetry *mer* isomer.

Energy minimization calculations were also performed on the four *fac* isomers of $[\text{Co}(\pm)\text{-pn}]_3^{2+}$, with use of a force field developed for Co(II) complexes,⁸ and the results are recorded in Table IIb. In the Co(II) system the order of stabilities is *lel*₃ > *lel*_{2ob} > *ob*_{2lel} > *ob*₃.

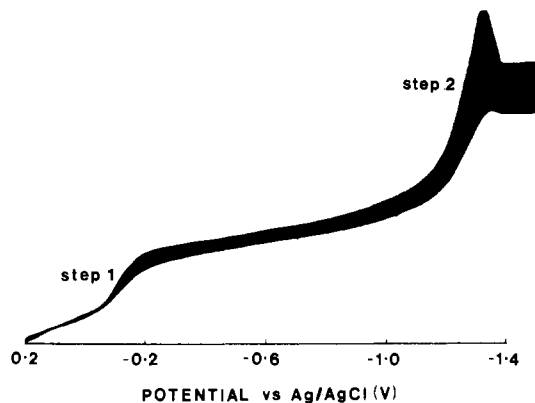
A comparison of the strain energy differences with the experimentally determined enthalpy differences²⁰ is given in Table III. While better agreement is obtained than was observed with previous force fields,^{21,34} there are significant discrepancies between the observed and calculated results. The differences in all cases are understated by the molecular mechanics model. It is noteworthy that the discrepancy approximates 1.0 kJ mol^{-1} for each ligand in the *ob* configuration, corresponding to an apparent destabilization of this configuration in solution. The *lel* ligand configuration associates more strongly with solvents and anions than does the *ob* configuration,³² so these discrepancies may reflect stabilization of the former by such interactions. However, only chloride, water, and charcoal were present when the equilibrium was determined²⁰ and generally "multidentate" species are necessary⁸ to have a significant influence on the isomer distribution. A vibrational entropy preference for the *lel* configuration over the *ob* could also explain the discrepancies between observed and calculated energies. In this context it is interesting that molecular mechanics calculations reported by Laier and Larsen²¹ similarly failed to reproduce the isomer distribution for $[\text{Co}(\pm)\text{-pn}]_3^{3+}$ but successfully reproduced the *lel*₃:*lel*_{2ob}:*ob*_{2lel}:*ob*₃ ratios for $[\text{Co}(\pm)\text{-chxn}]_3^{3+}$ (chxn = 1,2-cyclohexanediamine), where vibrational freedom is restricted by the six-membered ring.

The differences between the strain energies of the Co(III) and Co(II) states for each isomer correspond to the relaxation of steric strain on reduction from Co(III) to Co(II). If electronic factors are constant, which is likely to be the case for the $[\text{Co}(\pm)\text{-pn}]_3^{3+}$ isomers, then the isomer that gives the greatest difference may be expected to have the least negative E° value. These differences

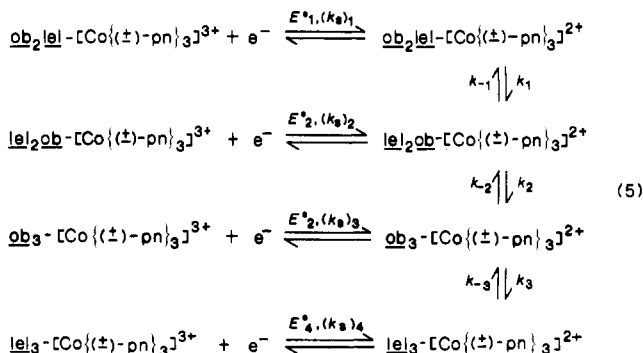
Table IV. Strain Energies of the Isomers^a of $[\text{Co}(\pm)\text{-pn}]_3^{3+}$ and $[\text{Co}(\pm)\text{-pn}]_3^{2+}$ and the Change in Strain Energy on Reduction from Co(III) to Co(II) (kJ mol^{-1})

isomer	$U_{\text{TOTAL}}(\text{Co(III)})$	$U_{\text{TOTAL}}(\text{Co(II)})$	diff
<i>lel</i> ₃	51.0	18.9	32.1
<i>lel</i> _{2ob}	52.7	19.7	33.0
<i>ob</i> _{2lel}	54.5	20.6	33.9
<i>ob</i> ₃	54.5	22.0	32.5

^aThese isomers are mixtures of *mer* and *fac* species.

**Figure 1.** Dc polarogram for reduction of 5×10^{-4} M *lel*_{2ob}- $[\text{Co}(\pm)\text{-pn}]_3(\text{ClO}_4)_3$ in acetone (0.1 M Bu_4NClO_4 ; drop time 0.5 s; temperature 22 °C).

are recorded by Table IV and suggest the order of E° values should be *ob*_{2lel} at the most positive potential, followed by *lel*_{2ob} and *ob*₃, with *lel*₃ having the most negative value. However, the differences are extremely small and E° values for isostructural couples are predicted to be very similar. Applying this result to the Bond-Oldham model would lead to a theoretical description of the reaction in eq 5 being required to explain the electron-transfer process at an electrode (simplified form).



NMR and other data demonstrate that the configurational isomers of $[\text{Co}(\pm)\text{-pn}]_3^{3+}$ are not in dynamic equilibrium, that is, they are kinetically inert, and that interactions in cobalt(III) complexes can be ignored, if second-order cross-redox reactions can be neglected. This has been done in eq 5. Unfortunately, the kinetic situation is unknown in the cobalt(II) state. Cobalt(II) complexes are frequently kinetically labile so that interactions between the different $[\text{Co}(\pm)\text{-pn}]_3^{2+}$ species are likely to be important and are therefore included in eq 5. Calculations indicate that the maximum likely overall relative free energy change from the most easily reduced cobalt(III) isomer to that reduced with the most difficulty is 2 kJ mol^{-1} . That is, $E_{1/2}$ values, which are related to E° values, should lie within a range of about 20 mV, which is close to the resolution available in most voltammetric (polarographic) data and is of the order observed experimentally (see below).

A dc polarogram of *lel*_{2ob}- $[\text{Co}(\pm)\text{-pn}]_3^{3+}$ in acetone (0.1 M Bu_4NClO_4) over a wide potential range is shown in Figure 1 and is typical of those obtained for all isomers. The dc polarogram is similar to that reported for *mer*- $[\text{Co}(\text{dien})_2]^{3+}$ ²⁶ with two re-

Table V. Dc Polarographic, Differential Pulse Polarographic, and Cyclic Voltammogram Data at Mercury Electrodes for the One-Electron Reduction of Isomers^a of $[\text{Co}(\pm)\text{-pn}]_3^{3+}$ in Acetone with Bu_4NClO_4 and Bu_4NPF_6 Electrolytes (0.1 M) at 22 °C

isomer	electrolyte	$10^4(\text{concn}),$ M	dc polarogr ^b				diff pulse polarogr ^c E_p, V	cyclic voltam ^d	
			$i_d, \mu\text{A}$	$E_{1/2}, \text{V}$	slope, V	correln coeff		$E_p^{\text{ox}} - E_p^{\text{red}}, \text{V}$	$E_{1/2}, \text{V}$
<i>lel</i> ₃	Bu_4NClO_4	5.2	0.912	-0.092	0.055	0.9995	-0.075	0.115	-0.096
<i>lel</i> _{2ob}		5.3	0.865	-0.111	0.057	0.9986	-0.095	0.122	-0.111
<i>ob</i> _{2lel}		5.2	0.850	-0.123	0.065	0.9966	-0.095	0.108	-0.123
<i>ob</i> ₃		5.2	1.039	-0.136	0.071	0.9982	-0.114	0.141	-0.136
<i>lel</i> ₃	Bu_4NPF_6	4.5	0.771	-0.101	0.075	0.9957	-0.089	0.439	0.022
<i>lel</i> _{2ob}		4.4	0.711	-0.110	0.069	0.9989	-0.107	0.412	-0.001
<i>ob</i> _{2lel}		1.0	0.166	-0.068	0.062	0.9978	-0.069	0.303	-0.024
<i>ob</i> ₃		4.6	0.751	-0.108	0.077	0.9995	-0.103	0.348	-0.034

^a These isomers are mixtures of *mer* and *fac* species. ^b i_d = limiting current; $E_{1/2}$ = half-wave potential; slope and correlation coefficient refer to a straight-line graphical plot of E vs. $\log [(i_d - i)/i]$; drop time 0.5 s. ^c E_p = differential pulse polarographic peak potential; amplitude -50 mV; drop time 0.5 s. ^d E_p^{red} = reduction peak potential; E_p^{ox} = oxidation peak potential; $E_{1/2}$ = calculated standard redox potential from cyclic voltammetry at the dropping mercury electrode on the assumption that the process is simple electron transfer between complexes obeying the simple theory.

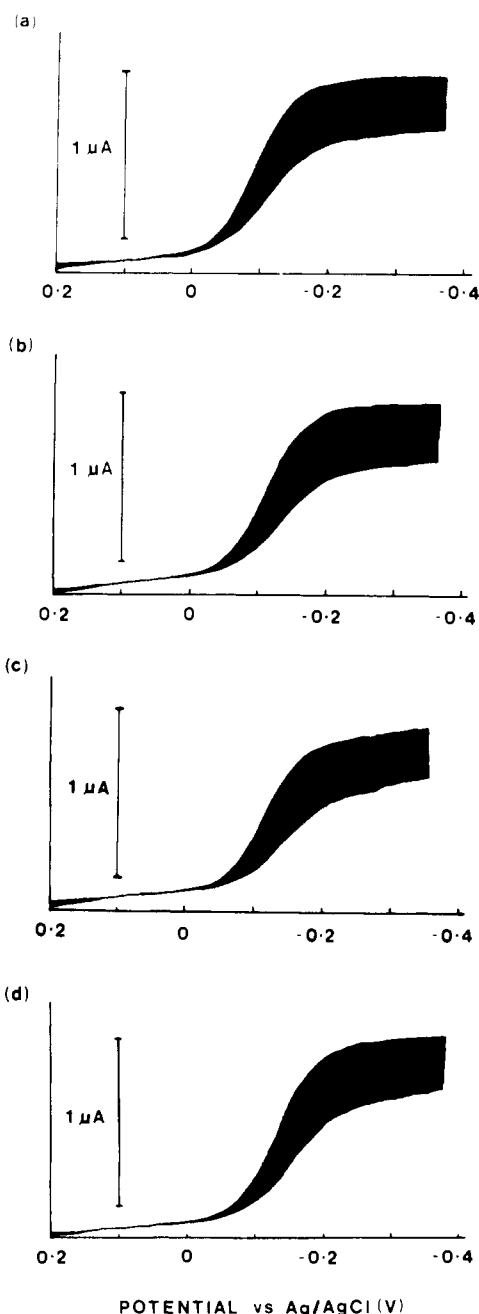


Figure 2. Dc polarograms for the $\text{Co(III)} + e^- \rightleftharpoons \text{Co(II)}$ reduction process for approximately 5×10^{-4} M solutions of (a) *lel*₃-, (b) *lel*_{2ob}-, (c) *ob*_{2lel}-, and (d) *ob*₃- $[\text{Co}(\pm)\text{pn}]_3(\text{ClO}_4)_3$ in acetone (0.1 M Bu_4NClO_4 ; drop time 0.5 s; temperature 22 °C).

duction waves being observed. The first of these (step 1, Figure 1) is due to the one-electron reduction, $\text{Co(III)} + e^- \rightarrow \text{Co(II)}$, while the second (step 2), which has a limiting current twice that of the first, corresponds to the two-electron reduction, $\text{Co(II)} + 2e^- \rightarrow \text{Co(0)}$, to produce metallic cobalt and free ligand. A very pronounced maximum is observed in the second step when Bu_4NPF_6 is used as the supporting electrolyte. However, less of a maximum was observed with Bu_4NClO_4 as the electrolyte. The second process is observed for all isomers but is not discussed further in this paper, since it is not relevant to the topic under consideration.

Dc polarograms of the first $\text{Co(III)}/\text{Co(II)}$ reduction step for all isomers in Bu_4NClO_4 and Bu_4NPF_6 electrolytes are shown in Figures 2 and 3. Measurably different half-wave reduction potentials, $E_{1/2}$ values, are obtained for each isomer, and some difference in the wave shape is also observed. Results of plots of E vs. $\log [(i_d - i)/i]$ (E = potential, i = current, i_d = diffusion-controlled limiting current) for each measurement are summarized in Table V. The results vary with both isomer and electrolyte and suggest that only *lel*₃ and *lel*_{2ob} species in Bu_4NClO_4 give apparently reversible charge-transfer steps on the time scale of dc polarography. However, even the "log plots" for these two isomers are not completely linear despite the fact that the average gradients are close to that expected for a reversible process ($2.303RT/nF = 0.058$ V at 22 °C). In view of these complications, $E_{1/2}$ values cannot be assumed to be exactly equal to the reversible half-wave potentials, $E_{1/2}^r$, nor therefore can these values be used as measure of the standard redox potential E° .

Differential pulse polarograms for the four isomers in Bu_4NClO_4 and Bu_4NPF_6 electrolytes are shown in Figures 4 and 5, respectively. The measured peak potentials (E_p values) from these differential pulse polarograms are also presented in Table V after correction for an instrumental artifact.²⁷

Cyclic voltammograms for each isomer are shown in Figures 6 and 7, while the values of $E_p^{\text{ox}} - E_p^{\text{red}}$ (E_p^{ox} = oxidation peak potential on the reverse scan, E_p^{red} = reduction peak potential on the forward scan) and $E_{1/2}$ from these voltammograms are listed in Table V. The $E_p^{\text{ox}} - E_p^{\text{red}}$ values, which according to the Nicholson and Shain criteria²⁸ should be approximately 0.056 V for a reversible charge-transfer process, are all slightly larger than this value in Bu_4NClO_4 electrolyte (0.108–0.141 V). The cyclic voltammograms obtained in the presence of Bu_4NPF_6 , with the $E_p^{\text{ox}} - E_p^{\text{red}}$ values varying from 0.303 to 0.439 V, all suggest nonreversible charge-transfer processes if simple theoretical concepts are employed. Data were also obtained in a range of other electrolytes and are significantly dependent on this parameter.

For the purposes of comparison with the electrochemical behavior of the $[\text{Co}(\pm)\text{-pn}]_3^{3+}$ isomers, a dc polarogram and a differential pulse polarogram of $[\text{Co}(\text{sep})]^{3+}$ (*sep* = sepuhrate) were obtained in the presence of Bu_4NPF_6 electrolyte. A plot of E vs. $\log [(i_d - i)/i]$ for the dc polarogram was essentially linear within experimental error and gave a slope of 0.058 V as expected

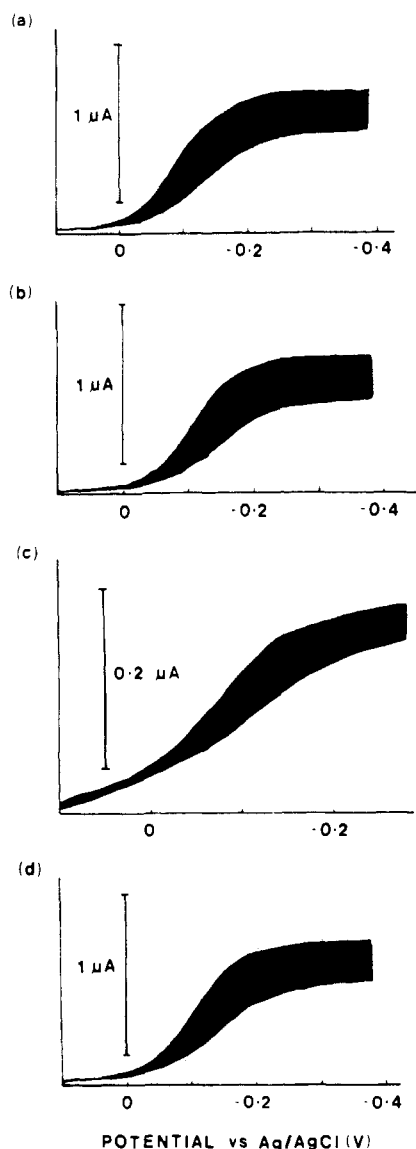
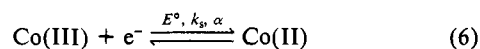


Figure 3. Dc polarograms for the $\text{Co(III)} + e^- \rightleftharpoons \text{Co(II)}$ reduction process for (a) 4.5×10^{-4} M lel_3 , (b) 4.4×10^{-4} M lel_2ob , (c) 1.0×10^{-4} M ob_2lel , and (d) 4.6×10^{-4} M ob_3 -[Co(\pm)-pn] $_3$ (ClO $_4$) $_3$ in acetone (0.1 M Bu $_4$ PF $_6$; drop time 0.5 s; temperature 22 °C).

for a reversible $\text{Co(III)} + e^- \rightleftharpoons \text{Co(II)}$ reduction process. The differential pulse polarogram is also consistent with a chemically and electrochemically reversible one-electron-reduction process. Crystallographic and other data for both cobalt(III) and cobalt(II) sepulchrates imply that no conformational change occurs on reduction.^{29,30} Such systems are of course predicted to obey the simple electrochemical theory, and the reversible behavior may in part reflect the lack of any configurational change accompanying electron transfer. Interestingly, this system behaved reversibly in all electrolytes examined.

The data reported above on the 1,2-propanediamine system confirm that the simple treatment of reduction of cobalt(III) complexes according to the equation



cannot be correct and that a detailed knowledge of the isomeric form in both oxidation states is essential. This feature is highlighted by a series of experiments in which the reductions of an unseparated mixture and the separated (lel_3 and ob_3) [Co(\pm)-pn] $_3$ ³⁺ complexes are compared. Data in acetone are presented in Table VI and in Figure 8 with Et $_4$ NClO $_4$ as the electrolyte. dc polarograms of mixed and separated (lel_3 and ob_3) complexes are superficially similar with slopes marginally greater than expected for a reversible step. $E_{1/2}$ values for the lel_3 and ob_3 species

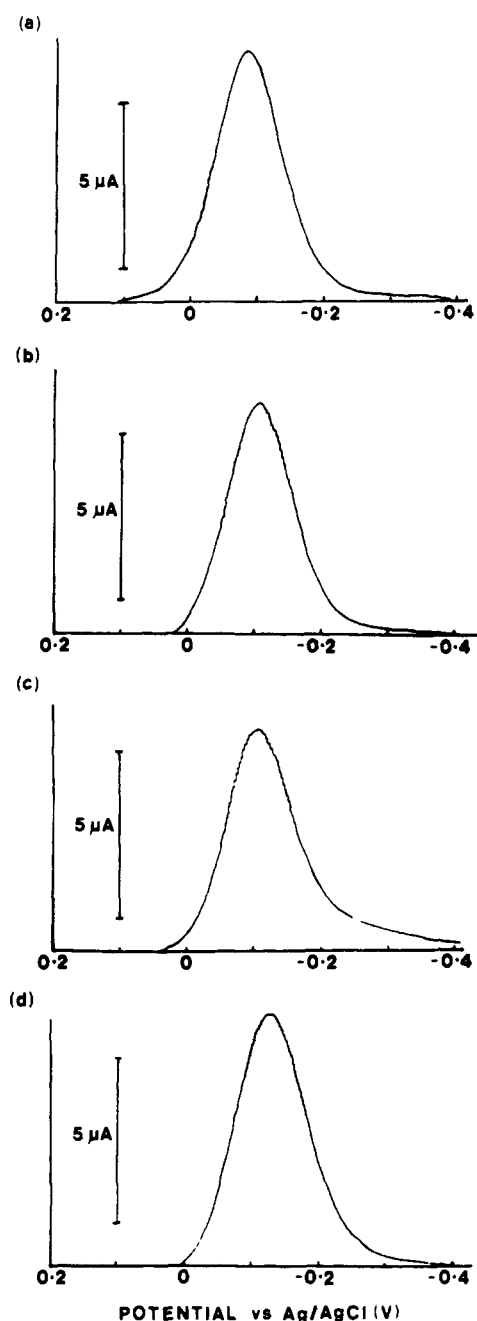


Figure 4. Differential pulse polarograms for the $\text{Co(III)} + e^- \rightleftharpoons \text{Co(II)}$ reduction process for approximately 5×10^{-4} M solutions of (a) lel_3 , (b) lel_2ob , (c) ob_2lel , and (d) ob_3 -[Co(\pm)-pn] $_3$ (ClO $_4$) $_3$ in acetone (0.1 M Bu $_4$ NClO $_4$; pulse amplitude -50 mV; drop time 0.5 s; temperature 22 °C).

differ by 30 mV. Differential pulse polarograms of the separated isomers in 0.1 M Et $_4$ NClO $_4$ are symmetrical and are also close to the shape predicted for a reversible one-electron process (Figure 8a,b). However, differential pulse polarograms of the mixture of isomers (Figure 8c,d) are asymmetric and exhibit a shoulder. Obviously, conventionally prepared solutions of [Co(pn) $_3$]³⁺ contain a mixture of configurations and may give rise to what may be erroneously interpreted as slow electron transfer and/or complex electrochemistry if the standard electrochemical model is employed.

The measured degree of electrochemical reversibility and $E_{1/2}$ value obviously depends on the particular isomer and the supporting electrolyte. The apparently close to electrochemically reversible nature of the $\text{Co(III)} \rightarrow \text{Co(II)}$ reduction process for certain isomers in the perchlorate electrolyte, for all isomers of [Co(dien) $_2$]³⁺ in hexafluorophosphate electrolyte,²⁶ and for [Co(sep)]³⁺⁸ in all electrolytes suggests that the apparent com-

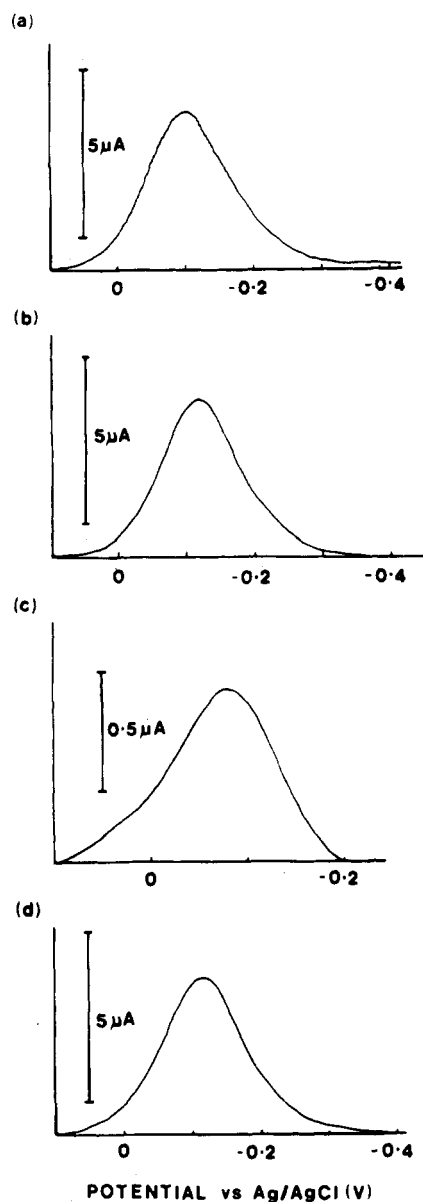
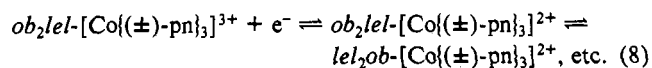
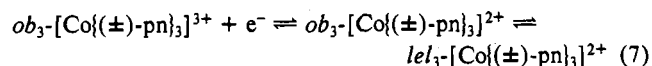


Figure 5. Differential pulse polarograms for the $\text{Co(III)} + e^- = \text{Co(II)}$ reduction process for solutions of (a) lel_3^- , (b) lel_2ob^- , (c) ob_2lel^- , and (d) $ob_3^-[\text{Co}(\pm)\text{-pn}]_3(\text{ClO}_4)_3$ in acetone (0.1 M Bu_4NPF_6 ; concentrations as in Figure 3; pulse amplitude -50 mV; drop time 0.5 s; temperature 22°C).

plexity observed for some isomers arises from sources other than electron transfer. The most probable source is reorganization of the reduced species. In the case of $[\text{Co}(\pm)\text{-pn}]_3^{2+}$, rearrangement from lel_3 to ob_3 and ob_2lel to lel_2ob can occur without complete dissociation of any ligand occurring. Thus, possible reactions are



If in the Co(II) state the lel_3 and lel_2ob isomers are more stable than the ob_3 and ob_2lel isomers, respectively, then such a reorganization might be expected. This could explain why the reduction processes on the time scale of dc polarography for the lel_3 and lel_2ob cobalt(III) isomers are apparently reversible in Bu_4NClO_4 while those for ob_3 and ob_2lel are apparently more complex. The cyclic voltammograms for all four isomers in Bu_4NClO_4 electrolyte indicate a high degree of chemical reversibility. Unfortunately, the configurational distribution of the cobalt(II) complexes is unavailable.

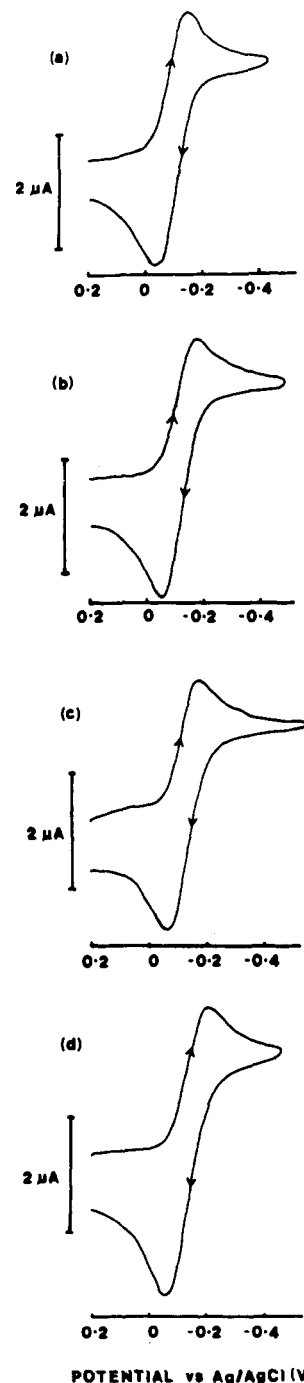
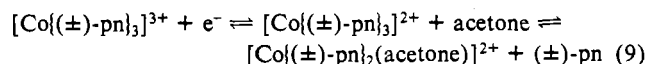


Figure 6. Cyclic voltammograms at a dropping mercury electrode for the $\text{Co(III)} + e^- = \text{Co(II)}$ reduction process for 5×10^{-4} M solutions of (a) lel_3^- , (b) lel_2ob^- , (c) ob_2lel^- , and (d) $ob_3^-[\text{Co}(\pm)\text{-pn}]_3(\text{ClO}_4)_3$ in acetone (0.1 M Bu_4NClO_4 ; scan rate of -500 mV s^{-1} commencing approximately 0.5 s after commencement of drop growth; temperature 22°C).

Structural rearrangement following reduction may not provide a complete explanation for the electrochemically nonreversible and apparently complex nature of the reduction processes observed for all four isomers, particularly in the Bu_4NPF_6 electrolyte. As mentioned above, Co(II) hexamine complexes are labile and therefore also subject to solvation as well as ligand rearrangement. It is possible, therefore, that $[\text{Co}(\pm)\text{-pn}]_3^{3+}$ could dissociate following reduction:



It is worth noting here that the reduction process ($\text{Co(III)} \rightarrow \text{Co(II)}$) for $[\text{Co}(\text{sep})]^{3+}$, also in acetone (0.1 M Bu_4NPF_6), shows a very high degree of chemical and electrochemical reversibility

Table VI. Polarographic Data for Reduction of Isomerically Separated and Unseparated Solutions of $[\text{Co}(\pm)\text{-pn}]_3(\text{ClO}_4)_3$ in Acetone (0.1 M Et_4NClO_4) at 22 °C with a Drop Time of 0.5 s

soln	dc polarogr		diff pulse polarogr		
	$E_{1/2}$, V	$E_{1/4} - E_{3/4}$, mV	amplitude, mV	E_p , V	$W_{1/2}$, ^a mV
3×10^{-4} M $[\text{Co}(\pm)\text{-pn}]_3^{3+}$	-0.115	65	-10	-0.120	95 ^b
			-25	-0.110	110 ^b
			-50	-0.100	120 ^b
			-100	-0.070	175 ^b
6×10^{-4} M $lel_3\text{-}[\text{Co}(\pm)\text{-pn}]_3^{3+}$ (separated)	-0.115	65	-10	-0.120	100
			-25	-0.115	115
			-50	-0.105	120
			-100	-0.080	135
6×10^{-4} M $ob_3\text{-}[\text{Co}(\pm)\text{-pn}]_3^{3+}$ (separated)	-0.085	65	-10	-0.090	105
			-25	-0.080	115
			-50	-0.070	120
			-100	-0.040	135

^a $W_{1/2}$ = width at half peak height; other symbols as for Table II. ^b Shoulder observed on more positive potential side of peak.

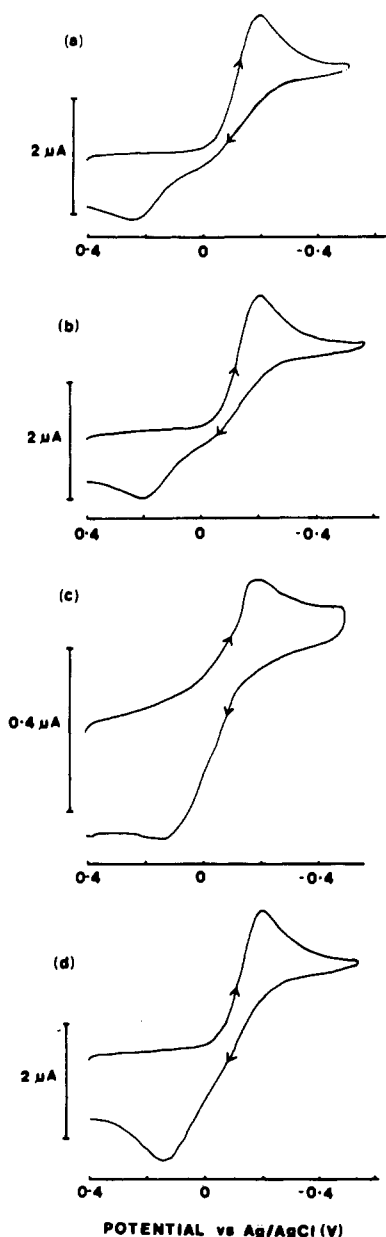


Figure 7. Cyclic voltammograms at a dropping mercury electrode for the $\text{Co(III)} + e^- \rightleftharpoons \text{Co(II)}$ reduction process for solutions (a) $lel_3\text{-}$, (b) $lel_2ob\text{-}$, (c) $ob_2lel\text{-}$, and (d) $ob_3\text{-}[\text{Co}(\pm)\text{-pn}]_3(\text{ClO}_4)_3$ in acetone (0.1 M Bu_4NPF_6 ; other parameters as for Figure 6).

and it has been shown that in the Co(II) state this complex remains totally inert to structural or chemical reorganization. Also, $[\text{Co}(\text{dien})_2]^{3+}$ gives apparently reversible reduction processes,²⁶

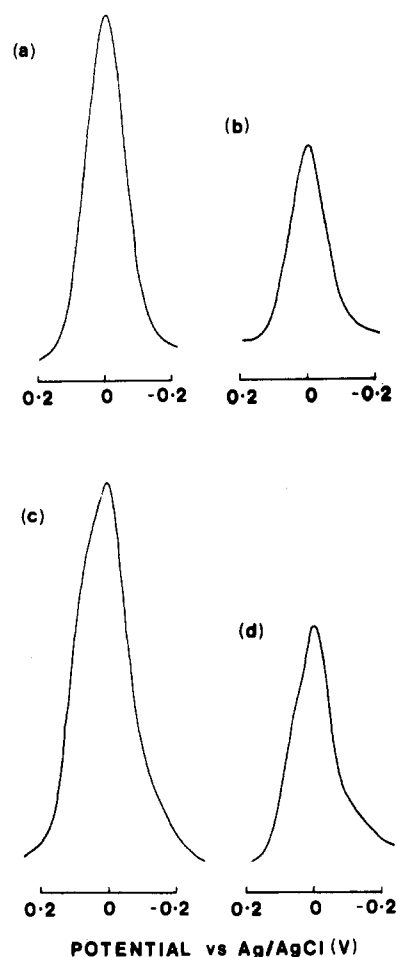


Figure 8. Comparison of differential pulse polarograms for the $\text{Co(III)} + e^- \rightleftharpoons \text{Co(II)}$ reduction process for 3×10^{-4} M $lel_3\text{-}[\text{Co}(\pm)\text{-pn}]_3(\text{ClO}_4)_3$ (a and b) and unseparated complex (c and d) in acetone (0.1 M Et_4NClO_4 ; drop time 0.5 s). Pulse amplitudes are -100 mV (a and c) and -50 mV (c and d).

and consistent with the stronger chelate effect of tridentate dien compared with that of bidentate pn.

Differences with electrolyte can also be considered from another point of view. In solution, perchlorate anions are probably capable of stronger hydrogen bonding than are hexafluorophosphate anions because of their higher basicity and effective charge. Also, perchlorate anions, like other tetrahedral oxyanions,³¹ are able to associate specifically with complexes such as $[\text{Co}(\pm)\text{-pn}]_3^{3+}$. This association is observed in the solid state in $(-)_487\text{-}[\text{Co}(\text{taetacn})](\text{ClO}_4)_3$ (taetacn = 1,4,7-tris(2-aminoethyl)-1,4,7-triazacyclononane)^{31b} and shown in Figure 9. Similar interactions between $[\text{Co}(\pm)\text{-pn}]_3^{3+}$ and ClO_4^- might be expected. This association effectively caps a C_3 face, and if each such face is

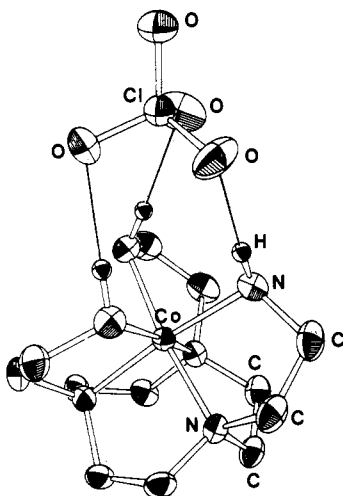
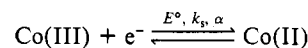


Figure 9. Structural view of $[\text{Co}(\text{taetaen})](\text{ClO}_4)_3$ perpendicular to the C_3 axis, with capping perchlorate anion. Thermal ellipsoids enclose 50% probability. Data were obtained from ref 31b.

capped, then a structure not dissimilar to that of the cage complex $[\text{Co}(\text{sep})]^{3+}$ is produced. The association between cation and anion bridges the three ligands and would serve to stabilize the complex, though to what degree is not known. If this stabilization is significant, then it is possible that the lel_3 and lel_2ob isomers are not subject to solvation or isomerization following reduction. Since the $[\text{Co}(\text{pn})_3]^{3+}$ complexes in the lel configuration have the axially oriented N-H bonds, they are expected and found^{32,33} to associate more strongly with tetrahedral anions than those adopting ob configurations. Consequently, the ob_2lel and ob_3 isomers will be less stabilized by association with perchlorate and therefore more subject to rearrangement or solvation, consistent with the apparently more complex reduction processes observed for these species. Finally, specific adsorption effects are indicated, which can affect the $E_{1/2}$ values. Adsorption effects can be strongly influenced by the configuration. The importance of the concepts described in this paper is also very relevant to enantiomer differentiation effects on the reduction of racemic tris(acetylacetonato)cobalt(III) complexes and related species in the presence of optically active electrolytes.³⁷

Conclusions

The electrochemical reduction of complexes containing configurational isomers cannot be treated as a single electrode process of the kind



Unfortunately, a realistic kinetic treatment of a system containing a wide range of configurations cannot be undertaken without a knowledge of numerous variables in both oxidation states, which must be obtained by independent measurements. In the case of $[\text{Co}(\pm)\text{-pn}]_3^{2+}$, no data are available on the distribution of the configurations except for theoretical information from molecular mechanics, which does not allow for ion pairing and related terms. Even if this information were available, numerous unknown E° values, k_s values, and α values need to be coupled with all the equilibrium constants to provide an essentially intractable problem. The theoretical calculations predict that a range of E° values spanning an approximately 20 mV potential range will be observed for the $[\text{Co}(\pm)\text{-pn}]_3^{3+/2+}$ system. Experimental data are consistent with this prediction. In other systems, crystallographic data are available which confirm that configurational changes accompany electron transfer,^{38,39} although the influence of this phenomenon still has been treated by the simple models depicted by eq 1 and 2. The present work confirms that a complete understanding of electron transfer and structural changes accompanying electron transfer is still not available^{5,40} and that further theoretical studies on conformational⁴¹ (configurational) aspects of redox reactions are still required.

Registry No. *fac*- $[\text{Co}(\pm)\text{-pn}]_3^{3+}$, 46469-36-7; *mer*- $[\text{Co}(\pm)\text{-pn}]_3^{3+}$, 46469-26-5; *fac*- $[\text{Co}(\pm)\text{-pn}]_3^{2+}$, 108509-36-0; *mer*- $[\text{Co}(\pm)\text{-pn}]_3^{2+}$, 108509-37-1; Bu_4NClO_4 , 1923-70-2; Bu_4NPF_6 , 3109-63-5; Hg, 7439-97-6.

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Alkali Metal Ion, Temperature, and Pressure Effects on the Rate of Electron Transfer between Manganate(VI) and Permanganate(VII) Ions in Alkaline Aqueous Solution

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The rate of outer-sphere electron transfer between MnO_4^- and MnO_4^{2-} in aqueous MOH at constant ionic strength (1.1 mol L^{-1}) is given by $(k_0 + k_M[\text{M}^+])[\text{MnO}_4^-][\text{MnO}_4^{2-}]$, where k_0 is defined by the activation parameters $\Delta H_0^\ddagger = 46 \text{ kJ mol}^{-1}$, $\Delta S_0^\ddagger = -35 \text{ J K}^{-1} \text{ mol}^{-1}$, $\Delta V_0^\ddagger(0.1 \text{ MPa}, 318 \text{ K}) = -23 \text{ cm}^3 \text{ mol}^{-1}$, and $\Delta\beta_0^\ddagger \approx -0.06 \text{ cm}^3 \text{ mol}^{-1} \text{ MPa}^{-1}$. For $\text{M} = \text{Li}, \text{Na}, \text{K}$, and Rb , respectively, k_M is given by $\Delta H_M^\ddagger = 33.1, 32.2, 32.9$, and 32.9 kJ mol^{-1} and $\Delta S_M^\ddagger = -67.8, -68.4, -62.9$, and $-59.0 \text{ J K}^{-1} \text{ mol}^{-1}$, while, for $\text{M} = \text{Na}$ and K , $\Delta V_M^\ddagger = +3$ and $-1 \text{ cm}^3 \text{ mol}^{-1}$. The activation parameters for the cation-independent reaction pathway can be accounted for by a modified semiclassical Marcus-Hush theory if, in the transition state for adiabatic or nearly adiabatic electron transfer, the reacting ions are taken to be enclosed within a common cavity in the solvent and the Mn-Mn distance compresses as does the cavity, which is assumed to have the same compressibility as the solvent itself. The lower enthalpies, and markedly more positive volumes, of activation for the M^+ -catalyzed pathway appear to arise at least in part from an easing of these solvational constraints.

Introduction

Wherland¹ has pointed out that the apparent success of Stranks' adaptation² of the classical Hush-Marcus theory³⁻⁶ of outer-sphere

electron-transfer (OSET) reaction rates to cover pressure effects was fortuitous; there was an error in the sign of the term representing the contribution of ionic medium (Debye-Hückel) effects.

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