the final coordinates. This result is in agreement with a force field which includes a relatively large number of nonbonded interactions. At the potential energy minimum of the nonbonded interactions, the relatively fewer valence angles are deformed to strike a net potential energy balance. We interpret the lack of any single dominant strain energy term to indicate that the initial model is reasonably correct.

We have also found that the initial coordinate set may be easily obtained from molecular models, and that this set does not lead to any unusual problems of convergence or false minima. To our knowledge, we have encountered a false minimum only once, and then as a result of an improperly specified interaction set. The false minimum was immediately obvious from an examination of a molecular model—the methyl group appeared as a trigonal plane. We cannot place enough emphasis on the importance of careful and continuous interaction between the computer and the user.

For the present, we doubt that it is possible to specify a force field which will permit exact calculation of the strain energies of a molecule. Moreover, it is highly unlikely that strain energies will ever be determined experimentally.[9] We do believe, however, that comparison of the strain energy within a series of isomers is valid *if* the same potential functions and the same number and kind of interactions are used, and the same degree of convergence is achieved in each calculation. We hope that under these conditions, differences of the order of 10% are meaningful.

Acknowledgments.—The authors gratefully acknowledge a grant of computer time from the graduate school of the Illinois Institute of Technology, helpful discussions with Daryle Busch, Louis De Hayes, and Ken Raymond, and a copy of a listing and writeup for the program MOLBD supplied by R. H. Boyd.

---

[9] Among the few examples of experimentally determined conformational energies the classical equilibrium study of Dwyer and coworkers (*J. Amer. Chem. Soc.*, **85**, 2913 (1963)) remains unique. Most recently, the pmr probe has come into extensive use; a recent paper by Sudmier and Blackmer (*Inorg. Chem.*, **10**, 2010 (1971)) includes a thorough bibliography of recent applications, as well as an elegant example.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
WAYNE STATE UNIVERSITY, DETROIT, MICHIGAN 48202

Outer-Sphere Reductions of Cobalt(III) Complexes Containing Macrocyclic Ligands. A Further Examination of Free Energy Correlations and Anomalous Reorganizational Barriers[1]

BY D. PAUL RILLEMA AND JOHN F. ENDICOTT*

Received January 24, 1972

The outer-sphere reductions of several *trans*-$Co(N_4)(NH_3)_2^{3+}$ complexes have been examined, with Cr^{2+}, V^{2+}, and $Ru(NH_3)_6^{2+}$ as reducing agents and N_4 as a tetradentate macrocyclic ligand. For any reducing agent, the rate constants for the reductions are not very different; however when corrections are made for variations in the reduction potentials of the cobalt(III) complexes, the rate constant increases by about 10^2 when N_4 is changed from a tetraamine to a tetraimine. This variation in reactivity does not agree with current theories of electron-transfer rates and the known variation of Co(III)–Co(II) self-exchange rates. The discrepancy can be attributed to anomalous variations in the Marcus reorganizational parameter (λ). It appears that in reductions of cobalt(III), the reorganizational parameters depend more strongly on the reducing agent and more weakly on cobalt(III) than predicted.

Introduction

Linck[2] has recently articulated the two somewhat antagonistic approaches frequently used in analyses of the reactivity patterns observed in the electron-transfer reactions of transition metal complexes. Thus one frequently encounters attempts to rationalize reactivity patterns in terms of "electronic–structural" relationships, which take no specific account of distinctions between intrinsic ligand reorganizational barriers and the contributions of the free energy of reaction (see ref 2 for a sympathetic representation of this approach and for appropriate documentation). The contrasting approach, which attempts to analyze reactivity patterns in terms of intrinsic reorganizational barriers, taking account of any contributions due only to free energy of reaction, has been most successfully organized in terms of a free energy correlation such as that proposed by Marcus.[3–6]

$$\Delta G_{12}^{\ddagger} = \frac{\lambda_{12}}{4} + \frac{\Delta G_{12}^{\circ}}{2} + \frac{(\Delta G_{12}^{\circ})^2}{4\lambda_{12}} \qquad (1)$$

Until very recently attempts to apply eq 1 to the much studied reactions of cobalt(III) have been frustrated because there have been few reliable estimates of the thermodynamic parameters. This has led to some

---

[1] (a) Partial support of this research by the Public Health Service (Grant AM 14341) is gratefully acknowledged. (b) Presented in part at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1971.

[2] R. G. Linck, *MTP Int. Rev. Sci., Inorg. Chem.*, [1] **9**, 303 (1972).

[3] R. A. Marcus, *Annu. Rev. Phys. Chem.*, **15**, 155 (1964).

[4] W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer," Ronald Press, New York, N. Y., 1966.

[5] (a) R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963); (b) *ibid.*, **72**, 891 (1968).

[6] In eq 1, $\Delta G_{12}^{\ddagger}$ is the overall free energy of activation, λ_{12} is the intrinsic reorganizational parameter, and ΔG_{12}° is the overall free energy of reaction. Subscripts refer to reaction of oxidant 1 with reductant 2. In the specific discussion of cobalt reactions it will be convenient to use λ_{Co} and and λ_{Red} (rather than λ_{11} and λ_{22}, respectively) for the reorganizational parameters observed in self-exchange reactions.

remarkable contradictions. For example, Earley[7] has speculated that changes in electron-transfer rates which occur concomitantly with changes in "nonbridging" ligand arise only from changes in the free energy of reaction. This may be contrasted with our observations[8] that relatively small changes in nitrogen-donor macrocyclic (necessarily nonbridging) ligands can change Co(III)–Co(II) self-exchange rates ($\Delta G^\circ = 0$) by a factor of more than 10^8. In fact relatively recently a sufficiently extensive range of cobalt(III) complexes of the *trans*-$Co(N_4)X_2$ type (N_4 = a nitrogen donor tetracoordinate macrocyclic ligand[9]) have become available,[10-13] together with the reversible[14,15] or quasireversible[15,16] estimates of the cobalt(II)–cobalt(III) electrode potentials to permit the systematic analysis of the applicability of (1) to reactions of cobalt complexes.[15] This previous work has demonstrated that the $\Delta G_{12}^\circ/2$ term of (1) makes the predicted contribution to the rates of reduction of cobalt(III) complexes in all cases where such comparisons are possible. However, these previous studies[15,17] have turned up the unexpected inference that λ_{12} (in cross reactions[6]) does not depend very strongly on the reorganizational parameters (λ_{Co}) inferred from cobalt(III)–cobalt(II) self-exchange rates.

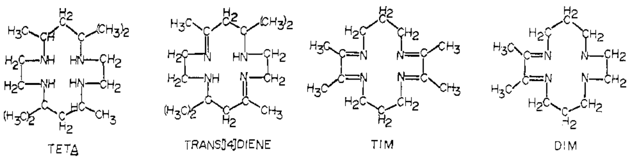

Figure 1.—Macrocyclic ligands (see ref 9).

In the present paper we explore more critically the dependence of $\Delta G_{12}^{\ddagger}$ on λ_{Co}. In this study we employ a series of recently synthesized *trans*-$Co(N_4)(NH_3)_2^{3+}$ oxidants with several common reducing agents. This series of oxidants was chosen for the present study because (1) we had reason to believe that the $Co(N_4)(NH_3)_2^{3+,2+}$ electrode potentials would be very similar[14-16] and (2) the macrocyclic N_4 ligands can be varied from a tetraamine, to a diamine diimine, to a tetraimine (see Figure 1). The replacement of an amine ligand by an imine type ligand has been associated with a relatively large rate enhancement (or "nonbridging ligand effect") in oxidants of the $Co^{III}(en)_2AX$ class,[18,19] and as noted above, this substitution in the $Co(N_4)(OH_2)_2^{3+,2+}$ complexes is accompanied by a very dramatic change in the cobalt(II)–cobalt(III) self-exchange rate.[8,15] A final point of some significance with regard to the class of oxidants employed in the present study is that all reductions must proceed by means of an outer-sphere mechanism.[20] This is a very important mechanistic restriction as some previous studies,[18c,21] employing oxidants of the Co^{III}-$(en)_2AX$ class and labile reducing agents, have yielded peculiar linear free energy correlations.[22] Therefore the present study has the advantage of being uncomplicated by large changes in ΔG_{12}° (for any particular reducing agent), changes in mechanism, or varying stabilities of precursor complexes.

Experimental Section

A. Preparation of Complexes. [*trans*-$Co(N_4)(NH_3)_2](ClO_4)_3 \cdot xH_2O$.—The general procedure which we have employed was to vacuum distil liquid ammonia onto [*trans*-$Co(N_4)X_2](ClO_4) \cdot xH_2O$, where N_4 = teta, *trans*[14]diene, DIM, or TIM and X = Cl or Br. The ammonia was allowed to distil off under a nitrogen stream. The remaining solid was dissolved in 0.1 *M* $HClO_4$. The unreacted $[Co(N_4)X_2](ClO_4)$ was removed by filtration and the product $[Co(N_4)(NH_3)_2](ClO_4)_3$ was precipitated from the filtrate following addition of excess $NaClO_4$. This purification process was repeated as necessary. Elemental analyses are summarized in Table I. The most useful infrared assignments are summarized in Table II and are based on ref 10–12 and 23. The visible–ultraviolet spectra of the complexes are compared in Table III. The preparations of the [*trans*-$Co(N_4)X_2]ClO_4$ complexes have been previously described.[10-12,23] Other reagents were prepared as described elsewhere.[14,15,19]

B. Instrumental Methods.—Visible–ultraviolet and infrared spectra were obtained using Cary 14 and Perkin-Elmer 621 spectrometers, respectively.

Electrochemical techniques employed were similar to those described previously.[16] For purposes of the present study we equipped the Chemtrix Model SSP-2 oscillographic polarograph with an external voltmeter, with a resulting increase in the precision of measured polarographic potentials (±0.01 V). The instrument was calibrated using $Cd(NO_3)_2$.

Solution pH measurements were made using an Instrumentation Laboratories Model 145 pH meter. Solution temperatures were controlled using a Tamsen T-45 constant-temperature water bath with circulating pump and in combination with a glass-jacketed thermostated spectrophotometer cell. Temperature measurements were made with a Digitac digital thermocouple readout thermometer. This apparatus was calibrated against the boiling temperatures of several pure liquids. Temperature measurements were accurate to ±0.1°.

C. Procedure for Kinetic Studies.—Reactant solutions and reaction cells were deaerated using Cr^{2+}-scrubbed nitrogen (argon for $Ru(NH_3)_6^{2+}$). Solutions were mixed using syringe techniques (and platinum needles!) as described previously.[14,15] The reaction of $Co(TIM)X_2$ (X = Cl or Br) with stainless steel needles necessitated the added precaution of transferring all solutions with syringes equipped with platinum needles.

---

[7] J. E. Earley, *Progr. Inorg. Chem.*, **13**, 243 (1970).

[8] D. P. Rillema, J. F. Endicott, and N. A. P. Kane-Maguire, *J. Chem. Soc., Chem. Commun.*, 495 (1972).

[9] The ligands employed in the present study are teta = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, *trans*[14]diene = 5,7,7,12,-14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, DIM = 2,3-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,3-diene, and TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene.

[10] (a) P. O. Whimp and N. F. Curtis, *J. Chem. Soc. A*, 967 (1966); (b) *ibid.*, 1827 (1966).

[11] (a) N. Sadasivan and J. F. Endicott, *J. Amer. Chem. Soc.*, **88**, 5468 (1966); (b) N. Sadasivan, J. A. Kernohan, and J. F. Endicott, *Inorg. Chem.*, **6**, 770 (1967); (c) J. A. Kernohan and J. F. Endicott, *ibid.*, **9**, 1504 (1970).

[12] N. F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968).

[13] D. H. Busch, K. Farmery, V. Goedken, V. Katavic, A. C. Melnyk, C. R. Sperati, and N. Tokel, *Advan. Chem. Ser.*, **No. 100**, 44 (1970).

[14] M. P. Liteplo and J. F. Endicott, *Inorg. Chem.*, **10**, 1420 (1971).

[15] D. P. Rillema, J. F. Endicott, and R. C. Patel, *J. Amer. Chem. Soc.*, **94**, 394 (1972).

[16] D. P. Rillema, J. F. Endicott, and E. Papaconstantinou, *Inorg. Chem.*, **10**, 1739 (1971).

[17] J. F. Endicott, R. F. Schroeder, and D. R. Ferrier, *J. Phys. Chem.*, in press.

[18] (a) C. Bifano and R. G. Linck, *J. Amer. Chem. Soc.*, **89**, 3945 (1967); (b) *Inorg. Chem.*, **7**, 908 (1968); (c) P. R. Guenther and R. G. Linck, *J. Amer. Chem. Soc.*, **91**, 3769 (1969); (d) R. G. Linck, *Inorg. Chem.*, **9**, 2529 (1970); (e) K. W. Hicks, D. L. Toppen, and R. G. Linck, *ibid.*, **11**, 310 (1972).

[19] R. C. Patel and J. F. Endicott, *J. Amer. Chem. Soc.*, **90**, 6364 (1968).

[20] For example see H. Taube, *Can. J. Chem.*, **37**, 129 (1959). In their original discussion,[18a,b] Linck and coworkers argued that for inner-sphere reductions of $Co^{III}(en)_2LX$ the ligands L must be so chosen as to impose no steric constraints on the formation of the bridged intermediate. Linck has on occasion commented (private communication to J. F. E.) that similar steric considerations may be important in outer-sphere reactions. Such a possibility may exist, but, since the interactions between metal centers are necessarily weak in outer-sphere reactions (compared to inner-sphere reactions), it is difficult to see how such variations in stereochemistry as may exist in the oxidants considered here can contribute significantly to the reaction energetics.

[21] R. C. Patel, R. E. Ball, J. F. Endicott, and R. G. Hughes, *Inorg. Chem.*, **9**, 23 (1970).

[22] See also discussion of this point in ref 15 and 21.

[23] D. H. Busch, private communication.

TABLE I

ELEMENTAL ANALYSES

Compd	% C		% H		% N		% Cl	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$[Co(teta)(NH_3)_2](ClO_4)_3 \cdot H_2O$	27.65	27.94	6.38	6.01	12.10	11.88	15.36	15.61
$[Co(trans[14]diene)(NH_3)_2](ClO_4)_3 \cdot 2H_2O$	27.14	27.70	5.99	5.94	11.87	11.90	15.02	15.41
$[Co(TIM)(NH_3)_2](ClO_4)_3 \cdot {}^3/_2H_2O$	25.56	26.84	4.91	4.88	12.78	12.32	16.17	16.40
$[Co(DIM)(NH_3)_2](ClO_4)_3 \cdot H_2O$	22.11	22.55	5.27	4.96	12.90	12.98	16.42	16.42

TABLE II

INFRARED FEATURES (cm^{-1}) OF $Co(N_4)(NH_3)_2^{3+}$ COMPLEXES[a]

Compd	O—H str	N—H[b] str	N—H[c] str	H—N—H bend[d]	C═N	C═N[e] | C═N	ClO₄
$[Co(NH_3)_6](ClO_4)_3$		3220 br		1650 br			1136 br
$[Co(teta)(NH_3)_2](ClO_4)_3 \cdot H_2O$	3530 vw 3590 vw	3240 sh	3145 s	1640 br			1140 vbr
$[Co(trans[14]diene)(NH_3)_2](ClO_4)_3 \cdot 2H_2O$	3430 m	3210 br	3140 s	Masked	1675 s		1140 vbr
$[Co(DIM)(NH_3)_2](ClO_4)_3 \cdot H_2O$	3520 s	3150 s	3060 s	1630 br	1600 w	1210 ms	1080 vbr
$[Co(TIM)(NH_3)_2](ClO_4)_3 \cdot {}^3/_2H_2O$	3480 w	3220 s		1650 w, br			
	3520 w	3120 s			1610 s	1225 s	1080 vbr

[a] Nujol mulls. Key to symbols: vw, very weak; m, medium; s, strong; w, weak; br, broad; sh, shoulder; ms, medium strong; vbr, very broad; unless designated, intensities of broad peaks are strong. [b] For NH_3. [c] For macrocyclic ligand. [d] For NH_3. [e] Characteristic C–C stretch assigned to this stereochemical arrangement.

TABLE III

VISIBLE–ULTRAVIOLET SPECTRAL ASSIGNMENTS OF $Co^{III}N_6$ COMPLEXES IN AQUEOUS SOLUTION[a]

Complex	Dq^{xy}, cm^{-1}	$A_1 \rightarrow T_1$, kK (ϵ)	$A_1 \rightarrow T_2$, kK (ϵ)	CT, kK (ϵ)
$Co(teta)(NH_3)_2^{3+}$	2495[b]	20.6 (75)	28.1 sh	39.5 (2.15×10^4)
$Co(NH_3)_6^{3+}$	2490	21.1 (80)[c]	29.5 (70)[c]	50 (2×10^4)
$Co(trans[14]diene)(NH_3)_2^{3+}$	2675	22.0 (66)	29.6 (80)	42.1 (1.9×10^4), 45.7 (2.1×10^4)
$Co(DIM)(NH_3)_2^{3+}$	2675	22.0 (80)	29.0 (700), 31.6 (760)[d]	
$Co(TIM)(NH_3)_2^{3+}$	2895	23.1 (120)	28.6 sh, 30.8 (1.9×10^3)[d]	

[a] pH 2 in $HClO_4$. [b] R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965). [c] M. Linhard and W. Weigel, *Z. Anorg. Allg. Chem.*, **49**, (1951). [d] May be a ligand-centered transition. The n → π* transition in biacetyl is at 24.2 kK.

Tap distilled water was redistilled over potassium permanganate. The ionic medium was controlled with NaCl, $NaClO_4$, $HClO_4$, and HCl for reduction of the $Co(N_4)(NH_3)_2^{3+}$ complexes. Chloride ion was avoided under all circumstances for V^{2+} and Cr^{2+} reactions lest any ambiguity be introduced regarding the nature of the reductant.[24] The pH of the reaction solution was maintained at 2 or less to avoid base hydrolysis[11c,25] of $Co(N_4)(NH_3)_2^{3+}$. Care was exercised to maintain solutions of $Ru(NH_3)_6^{2+}$ at neutral pH prior to addition to the oxidant solution. This avoids acid catalysis in the formation of ruthenium(II) pentaammines.[26]

Solutions of Cr^{2+} were prepared from $Cr(ClO_4)_3 \cdot xH_2O$ and V^{2+} solutions from $VO(ClO_4)_2$, by reduction over zinc amalgam. $Ru(NH_3)_6^{2+}$ was prepared from recrystallized $Ru(NH_3)_6(ClO_4)_3$ and reduced by Cr^{2+}. The V^{2+} and $Ru(NH_3)_6^{2+}$ solutions were used within 2 hr after preparation. The concentration of reducing agent was determined by adding it to excess $Co(TIM)(OH_2)_2^{3+}$ and determining the absorbance of $Co(TIM)(OH_2)_2^{2+}$ at 345 nm (ϵ 3.45×10^3).[15]

Either the decrease of absorbance of the cobalt(III) reactant or the increase in absorbance of the cobalt(II) product was followed spectrophotometrically as a function of time. The reductions of $Co(TIM)(NH_3)_2^{3+}$ and $Co(DIM)(NH_3)_2^{3+}$ were monitored at the charge transfer to ligand absorption maximum of the cobalt(II) product, 545 nm (ϵ 3.45×10^3) and 515 nm ($\epsilon \simeq 10^3$), respectively. For the Cr^{2+} reductions of $Co(trans[14]diene)(NH_3)_2^{3+}$, the production of $Co(trans[14]diene)(OH_2)_2^{2+}$ was followed at 345 nm, a shoulder of the 325-nm charge transfer to ligand absorbance maximum. In the $Ru(NH_3)_6^{2+}$ and V^{2+} reductions, the disappearance of $Co(trans[14]diene)(NH_3)_2^{3+}$ was monitored at 238 nm (ϵ 1.8×10^4). The disappearance of $Co(teta)(NH_3)_2^{3+}$ was monitored at its 253-nm (ϵ 2.15×10^4) charge transfer to metal absorbance maximum.

D. Treatment of Kinetic Data.—In general the reactions followed the rate law $d[Co^{III}]/dt = k[Co^{III}][Red]$ where [Red] corresponds to any of the three reducing agents $Ru(NH_3)_6^{2+}$, V^{2+}, and Cr^{2+}. The reactions were run under pseudo-first-order conditions with the reducing agent in excess. Plots of log $|A_\infty - A|$ *vs.* time were linear up to 5 half-lives except for the Cr^{2+}–$Co(TIM)(NH_3)_2^{3+}$ reaction.

The Cr^{2+} reductions of *trans*-$Co(TIM)(NH_3)_2^{3+}$ proved to be autocatalytic. This behavior was also observed, but to a lesser degree, in the V^{2+} reductions of this cobalt(III) complex. It is clear from our preliminary observations that the autocatalytic effect depends on a reaction of Cr^{2+} with $Co(TIM)(OH_2)_2^{2+}$, suggesting that cobalt(I) is the catalytic agent. Our detailed investigations of this behavior will be described elsewhere. In order to obtain rate data pertinent to the present study we have estimated the rate constant from the initial reaction rates. We did determine that these initial rates were first order each in $[Cr^{2+}]$ and $[Co(TIM)(NH_3)_2^{3+}]$.

We have generally observed that the $Co(N_4)(OH_2)_2^{2+}$ complexes are well-behaved, relatively stable species in acidic aqueous[8,14,15,27] solution. An exception to this pattern is $Co(DIM)(OH_2)_2^{2+}$. This complex is not stable in solutions which contain perchlorate ion as indicated by the loss in intensity of the $Co(DIM)(OH_2)_2^{2+}$ charge transfer to ligand absorbance at 515 nm. This undesirable reaction is sufficiently fast under most conditions that one can watch the buildup of $Co(DIM)(OH_2)_2^{2+}$ from the reduction of $Co(DIM)(NH_3)_2^{3+}$ followed by the decay of $Co(DIM)(OH_2)_2^{2+}$. We were able to suppress the side reaction in the case of $Ru(NH_3)_6^{2+}$ reduction by using an NaCl medium. In the case of V^{2+} reductions we were able to obtain good reduction rate data by running the reductions rapidly using a very large excess of the reducing agent. The Cr^{2+} reactions were *so* slow that we were unable to obtain satisfactory data, free from complications due to reactions of $Co(DIM)(OH_2)_2^{2+}$.

Results

A. Kinetic Data.—Second-order rate constants, k, for the reductions of the $Co(N_4)(NH_3)_2^{3+}$ complexes are collected in Table IV. For purposes of the com-

---

(24) A. Zwickel and H. Taube, *J. Amer. Chem. Soc.*, **83**, 793 (1961).

(25) D. P. Rillema and J. F. Endicott, in preparation.

(26) P. C. Ford, *Coord. Chem. Rev.*, **5**, 75 (1970).

(27) The axial coordination positions are labile in these macrocyclic cobalt(II) complexes and there is some ambiguity about whether the coordination number should be 4, 5, or 6.[8,14]

TABLE IV

RATE CONSTANTS FOR REDUCTION OF *trans*-$Co(N_4)(NH_3)_2^{3+}$ COMPLEXES WITH $Ru(NH_3)_6^{2+}$, V^{2+}, AND Cr^{2+} [a]

			$Ru(NH_3)_6^{2+}$			V^{2+}			Cr^{2+}		
N_4	$E_{1/2}$,[b] V	$E°_{estd}$,[c] V	k, M^{-1} sec^{-1}	Ionic strength[d]	log k ($\mu = 1$)	10^2k, M^{-1} sec^{-1}	Ionic strength[e]	Log k ($\mu = 1$)	10^3k, M^{-1} sec^{-1}	Ionic strength[e]	Log k ($\mu = 1$)
$(NH_3)_4$		0.10[f,g]	1.1×10^{-2} [f]	0.2	−0.91	0.37[h]	0.4	−1.63	8.9×10^{-2}	0.4	−3.25
tet*a*	0.10	0.34	8.4 ± 0.5	1.0	0.93	17 ± 1[i]	0.14	0.37	4.8 ± 0.2	0.37	−1.47
trans[14]diene	0.07	0.31	2.9 ± 0.1	1.0	0.46	9.8 ± 0.2[i]	0.14	0.13	4.0 ± 0.2	0.65	−1.83
DIM	0.02	0.26	6 ± 1	1.0	0.78	22 ± 3[i]	0.14	0.49			
TIM	−0.14	0.10	3.7 ± 0.3	1.0	0.57	41 ± 2[i]	0.14	0.76	12 ± 2[j]	0.65	1.35

[a] At 25°, pH 2, except as indicated. Rate constants are mean values and error limits are average deviations of two or three determinations except as indicated. [b] *Vs.* sce; pH 2; 0.1 *M* tetraethylammonium perchlorate. [c] Referred to 0.600 V for Cd^{2+}. [d] Chloride medium. [e] Perchlorate medium. [f] J. F. Endicott and H. Taube, *J. Amer. Chem. Soc.*, **86**, 1686 (1964). [g] W. Latimer, "Oxidation Potentials," Prentice-Hall, New York, N. Y., 1952. [h] Reference 24. [i] At 22°. [j] Average and mean deviation of nine determinations.

parisons developed in the Discussion we have also included in Table IV values of log k extrapolated to unit ionic strength.[28] In the case of the $Ru(NH_3)_6^{2+}$ reductions, we found that the rates observed using solutions which were aged 1 hr or more (under argon in the dark and in neutral solution) were generally faster than the rates observed with freshly prepared solutions of $Ru(NH_3)_6^{2+}$. We have also found that $Ru(NH_3)_5OH_2^{2+}$ reacts more rapidly (by a factor of about 2) with $Co(N_4)(NH_3)_2^{3+}$ oxidants than does $Ru(NH_3)_6^{2+}$. All data listed in Table IV were obtained with freshly prepared $Ru(NH_3)_6^{2+}$ solutions. To facilitate direct comparisons, we have included in Table IV data obtained by other workers for the $Co(NH_3)_6^{3+}$ oxidations of $Ru(NH_3)_6^{2+}$,[29] V^{2+},[24] and Cr^{2+}.[24]

We have obtained activation parameters in the 20–60° temperature range from the rate constants obtained for the V^{2+} reductions of $Co(N_4)(NH_3)_2^{3+}$. Values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were obtained from a linear least-squares analysis and are collected in Table V.

TABLE V

ACTIVATION OF PARAMETERS FOR V^{2+} REDUCTIONS OF $CoLN_2^{3+}$

Complex	$\Delta H^{\ddagger}$, kcal mol^{-1} [a]	$\Delta S^{\ddagger}$, eu[a]
$Co(NH_3)_6^{3+}$	9.1[b]	−40[b]
Co(tet*a*)$(NH_3)_2^{3+}$	7.0 ± 0.2	−39 ± 4
Co(*trans*[14]diene)$(NH_3)_2^{3+}$	7.4 ± 0.6	−38 ± 8
Co(TIM)$(NH_3)_2^{3+}$	7.6 ± 0.3	−35 ± 2

[a] Error limits are average standard deviations from the linear least-squares recursion fit of the data points. Points taken approximately every 10° in the 20–60° interval. [b] P. H. Dodel and H. Taube, *Z. Phys. Chem.*, **44**, 92 (1965).

At temperatures greater than 40° the V^{2+}–Co(TIM)$(NH_3)_2^{3+}$ reaction exhibited autocatalytic effects similar to those observed for the Cr^{2+}–Co(TIM)$(NH_3)_2^{3+}$ reaction and initial rate data had to be used. We were unable to obtain activation parameters for reductions of Co(DIM)$(NH_3)_2^{3+}$ owing to the intractibility of the Co(DIM)$(OH_2)_2^{2+}$ product.

For the Cr^{2+}–Co(*trans*[14]diene)$(NH_3)_2^{3+}$ reaction we found $\Delta H^{\ddagger} = 8.8 \pm 0.3$ kcal/mol and $\Delta S^{\ddagger} = -(40 \pm 4)$ eu over the temperature range 20–70°.

We have also observed the $Ru(NH_3)_6^{2+}$ reactions of $Co(N_4)(NH_3)_2^{2+}$ complexes to be about as temperature sensitive as the corresponding reactions of V^{2+}. However, owing to the slowness of the electron-transfer reactions, the temperature-dependent decomposition of $Ru(NH_3)_6^{2+}$, and the necessity of using excess reductant we were unable to obtain reliable estimates of activation parameters for these reactions.

B. Oscillopolarography.—Polarographic half-wave potentials were obtained in water solutions. The complexes, with the exception of Co(*trans*[14]diene)$(NH_3)_2^{3+}$,[16] are unstable in nonaqueous media, decomposing into more than one species. Thus, we were compelled to work with chemically irreversible potentials[30] and to make estimates of $E°$ values from these. The voltammograms were similar in shape for each complex and we believe that with the known quasireversible behavior of Co(*trans*[14]diene)$(NH_3)_2^{3+}$ in DMF,[16,17] we can safely assign potentials for their redox couples. Our measurements of $E_{1/2}$ and estimates of $E°$ are included in Table IV. We have also included in Table IV the literature value of $E°$ for the $Co(NH_3)_6^{3+,2+}$ couple.[31] Our cyclic voltammograms for $Co(NH_3)_6^{3+}$ were not sufficiently well defined to permit a reasonable estimate of $E_{1/2}$. The unusually broad voltammograms obtained for this complex no doubt result from the relatively small[32] (or irreversible) heterogeneous reduction rate constant.

Discussion

In this study we have examined the kinetics of the outer-sphere reductions of each of four cobalt(III) oxidants with three reductants. These oxidants contain ligands of types (amine or imine) thought to give rise to "nonbridging ligand effects."[18,19] However, in the present study, for the first time in such studies of cobalt complexes, we are able to examine reactivity patterns among a closely related series of oxidants and to distinguish differences in thermodynamics from other factors contributing to such patterns. As it turns out the thermodynamic differences between these diammine oxidants is a bit larger than we had anticipated on the basis of their diaquo analogs.[14,15] Comparisons of increasing intricacy are made below.

A. Relative Rate Comparison.—A simple comparison of the data in Table IV shows that the *trans*-$Co(N_4)(NH_3)_2^{3+}$ complexes exhibit a reactivity range of only three- or fourfold for any *given* reductant studied. This contrasts to the ranges of 30 and 80, respectively,

---

(28) The extrapolation is described in ref 15. See also J. W. Gryder, *J. Chem. Phys.*, **37**, 718 (1963).

(29) J. F. Endicott and H. Taube, *J. Amer. Chem. Soc.*, **86**, 1686 (1964).

(30) The observed irreversibility for the $Co(N_4)(NH_3)_2^{3+}$ complexes is to be attributed to the lability of NH_3 in $Co(N_4)(NH_3)_2^{2+}$. Thus we see only the cathodic wave of the cyclic voltammogram. For Co(*trans*[14]diene)$(NH_3)_2^{3+}$, this wave shape is similar to that observed in DMF. It has previously been shown that the rate of electrochemical reduction of these complexes is in the quasireversible range[17] and thus $E_{1/2}$ can be used to estimate $E°$.

(31) W. Latimer, "Oxidation Potentials," Prentice-Hall, New York, N. Y., 1952.

(32) (a) H. Bartlet, *Electrochim. Acta*, **16**, 307 (1971); (b) H. Bartlet and S. Landazury, *J. Electroanal. Chem.*, **22**, 195 (1969).

TABLE VI

COMPARISON OF INTRINSIC ELECTRON-TRANSFER RATE CONSTANTS ($\Delta G_{12}° = 0$) AND APPARENT COBALT SELF-EXCHANGE PARAMETERS FOR REDUCTIONS OF $Co(N_4)(NH_3)_2{}^{3+}$ AND $Co(N_4)(OH_2)_2{}^{3+}$ COMPLEXES

	Hde[a]		$Ru(NH_3)_6{}^{2+}$			V^{2+}			Cr^{2+}		
N_4	k_s, cm sec^{-1}	k_e,[b] M^{-1} sec^{-1}	$(k_{11}k_{22}f_{12})^{1/2}$, M^{-1} sec^{-1}	k_i,[c] M^{-1} sec^{-1}	k_e,[d] M^{-1} sec^{-1}	$(k_{11}k_{22}f_{12})^{1/2}$, M^{-1} sec^{-1}	k_i,[c] M^{-1} sec^{-1}	k_e,[d] M^{-1} sec^{-1}	$(k_{11}k_{22}f_{12})^{1/2}$, M^{-1} sec^{-1}	k_i,[c] M^{-1} sec^{-1}	k_e,[d] M^{-1} sec^{-1}
$(NH_3)_4$[e]	10^{-3} [g]	10^{-2}	0.15	0.15	2.3×10^{-5}	2.3×10^{-5}	3.2×10^{-5}	1.0×10^{-6}	2.8×10^{-8}	5.0×10^{-8}	2.5×10^{-9}
teta[e]			8.0×10^{-2}	8.1×10^{-2}	6.8×10^{-6}	9.2×10^{-5}	2.6×10^{-5}	6.9×10^{-7}	1.6×10^{-8}	5.5×10^{-8}	2.9×10^{-9}
teta[f]			5.4	14	0.20	1.4×10^{-4}	1.1×10^{-3}	1.1×10^{-3}			
trans[14]diene[e]	0.1[h]	10^2	5.0×10^{-2}	5.1×10^{-2}	2.5×10^{-6}	2.8×10^{-5}	6.3×10^{-5}	4.0×10^{-6}	1.2×10^{-8}	3.7×10^{-8}	1.4×10^{-9}
trans[14]diene[f]			2.2	5.0	2.5×10^{-2}	2.6×10^{-5}	1.6×10^{-4}	2.5×10^{-5}			
DIM[e]			0.27	0.27	7.3×10^{-5}	1.4×10^{-4}	3.0×10^{-4}	9.0×10^{-5}			
TIM[e]	0.1[h]	10^2	3.7	3.7	1.4×10^{-2}	5.7×10^{-3}	8.5×10^{-3}	6.2×10^{-2}	2.2×10^{-6}	4.2×10^{-6}	1.7×10^{-5}
TIM[f]			102	2.5×10^2	63	3.1×10^{-3}	2.2×10^{-2}	0.49			

[a] Hanging-drop electrode; 25°. [b] Estimated using $\log k_e = 2.0 \log k_s + 4$ (see ref 17). [c] Estimated using $k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}$ where $k_i = (k_{11}k_{22})^{1/2}$. [d] $k_e = k_i{}^2/k_{22}$ where k_{22} is the self-exchange rate constant for the reducing agent. [e] $Co(N_4)(NH_3)_2{}^{3+}$. [f] $Co(N_4)(OH_2)_2{}^{3+}$, from data in ref 14 and 15. [g] Reference 32. [h] Reference 17; *Frumkin double layer correction applied to k_s values.*

observed in the $Ru(NH_3)_6{}^{2+}$ and V^{2+} reductions of the corresponding *trans*-$Co(N_4)(OH_2)_2{}^{3+}$ complexes.[14,15] This apparent contraction in the range of "nonbridging ligand effect," observed when NH_3 replaces OH_2 in the axial coordination positions, is no doubt a manifestation of the accompanying differences in redox potentials; *i.e.*, the former oxidants differ in potential by 0.24 V and the latter by only 0.05 V. This point will be analyzed in greater detail below. *The reductions of neither the diammine nor the diaquo complexes* provide evidence for the view expounded by Guenther and Linck[18c] that the sensitivity to the nonbridging ligands decreases as more powerful reducing agents are used. *In fact comparison of log k (at $\mu = 1$ in Table IV) within each reductant series could lead to the opposite conclusion (consistent with points developed in detail in section C below). For example for Cr^{2+} the observed reactivity range is 10^4 (or about 10^3 if $Co(NH_3)_6{}^{3+}$ is omitted from the comparison) while there is only a 10^2 (or about fourfold if $Co(NH_3)_6{}^{3+}$ data are not included) range of reactivity exhibited by the "weaker" reducing agent V^{2+} with the same series of oxidants. It is argued below that such variations in the sensitivities which various reducing agents exhibit toward cobalt(III) oxidants appear to be closely related to the free energy independent term of (1).*

B. Comparisons of Activation Parameters.—Such differences in rate constant as we have observed in this study appear to have their source in the $\Delta H^{\ddagger}$ term rather than the $\Delta S^{\ddagger}$ term (*see also comments in ref 18d*). On the whole we find the similarities in rate constants to be paralleled by similarities in activation parameters.

C. Inferences Drawn from Free Energy Correlations.—It has previously been established that the free energy term of (1) is approximately correct for reductions of cobalt(III) complexes.[15] Since varying free energy contributions complicate the comparisons attempted above, we have used the well-known cross relation[3–5] $k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}$ to correct for contributions due only to variations in $\Delta G_{12}°$. Thus in Table VI we have obtained[33–36] "intrinsic" electron-transfer rate constants, $k_i = (k_{11}k_{22})^{1/2}$. As manifested by variations in k_i, it is seen that the intrinsic rate constants for reduction of *trans*-$Co(N_4)L_2$ complexes ($L = NH_3$ or OH_2) vary over about two orders of magnitude (in the case of each reducing agent) as the macrocyclic ligand N_4 is changed from a tetraamine to a tetraimine. Thus it is evident, contrary to Earley's expectation,[37] that "nonbridging ligand effects" *do* lead to appreciable rate variations over and above the contributions due only to changes in $\Delta G_{12}°$.

In terms of the free energy relation (1), the variations of k_i in Table VI must arise from variations in the intrinsic reorganizational parameter λ_{12}. It is usually assumed that $\lambda_{12} = {}^1/_2(\lambda_{11} + \lambda_{22})$ (hence the square root correlation).[3–5] We have previously noted that this assumption may not be valid for reactions involving cobalt.[15,17] In order to examine this assumption more critically we have calculated apparent self-exchange rate constants, $k_e = k_i{}^2/k_{11}$, for the cobalt(III)–cobalt(II) couples (Table VI). It is to be noted that k_e changes markedly with the reducing agent, being smallest with the hanging-drop electrode and decreasing in order for reductions performed with $Ru(NH_3)_6{}^{2+}$, V^{2+}, and Cr^{2+}; thus one may infer that the magnitude of $\lambda_{Co}' \propto -4RT \log k_e$ also increases in this order. Thus, qualitatively, in the expression[6] $\lambda_{12} = {}^1/_2(\lambda_{Co}' + \lambda_{Red})$, the value of λ_{Co}' required by the observations appears to increase as λ_{Red} increases.

In the case of the $Ru(NH_3)_6{}^{2+}$ and V^{2+} reductions, estimated values of k_i are greater for $L = H_2O$ than for $L = NH_3$. Since λ_{12} is generally interpreted as a ligand reorganizational parameter,[3–5] it is instructive to contrast the inference that $\lambda_{12}(H_2O) < \lambda_{12}(NH_3)$ with the *generally observed variation of the stretching frequencies*, $\nu_{M-OH_2} > \nu_{M-NH_3}$.[38] One would have to infer that either the Co^{III}–L stretching modes are not involved in the activation process or that the $\lambda_{12}/4$ term in (1) is not to be interpreted as a reorganizational parameter.

Finally we may contrast k_e values inferred in Table VI to values obtained in reactions of cobalt(II) complexes. The self-exchange rate constants for the $Co(\textit{trans}[14]diene)(OH_2)_2{}^{3+,2+}$ and $Co(TIM)(OH_2)_2{}^{3+,2+}$ couples have been determined to be 2×10^{-7} M^{-1} sec^{-1} (at 70°, 1 M ionic strength) and 1 M^{-1} sec^{-1} (at 25°, 0.1 M ionic strength in D_2O).[8] It is clear that the values inferred in Table VI are not generally related to measured cobalt(III)–cobalt(II) self-exchange rates. The contrast of inferred rates is

---

(33) In this calculation we have used the following values for k_{11} and $E°$, respectively: 10^3 M^{-1} sec^{-1} [34,35] and 0.1 V[34] for $Ru(NH_3)_6{}^{2+}$; 10^{-3} M^{-1} sec^{-1} [36] and −0.26 V[31] for V^{2+}; 10^{-6} M^{-1} sec^{-1} [36] and −0.41 V[31] for Cr^{2+}. The factor $f_{12} = \text{antilog } (\log K_{12})^2/[4 \log (k_{11}k_{22}/Z^2)]$ has been estimated by iteration.

(34) T. J. Meyer and H. Taube, *Inorg. Chem.*, **7**, 2369 (1968).

(35) G. Navon and D. Meyerstein, *J. Phys. Chem.*, **74**, 4067 (1970).

(36) This value is based on the cross reaction rate with $Ru(NH_3)_6{}^{3+}$. See discussion in ref 19.

(37) See ref 7, p 259.

(38) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963.

perhaps most extreme if the $Co(TIM)(NH_3)_2^{3+}$–$Co(TIM)(OH_2)_2^{2+}$ reaction is considered.[15] In this case we would infer for $CoTIM(NH_3)_2^{3+}$, a value of $k_\theta = (6 \pm 4) \times 10^3\ M^{-1}\ sec^{-1}$..

We must therefore conclude that *the free energy correlation (1) does not hold true* for reactions of cobalt(III) even though *it does nearly predict the dependence of the rate constant on the free energy of reaction.*[14] The failure of (1) is clearly in the nature of the λ_{12} term. Since (1) can be obtained from both the adiabatic and nonadiabatic theories,[3,4] the source of difficulty may be in some general assumption common to both approaches. For example when λ_{11} and λ_{22} are very different, the potential surfaces may not couple in such a way that $\lambda_{12} = {}^1/_2(\lambda_{11} + \lambda_{22})$ (*see also ref 3*). It is also possible that the terms represented by $\lambda_{12}/4$ in empirical correlations do not correspond entirely to (ligand, solvent, etc.) reorganizational terms.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF VIRGINIA, CHARLOTTESVILLE, VIRGINIA 22903

The Optical Activity of Dissymmetric Six-Coordinate Cobalt(III) Complexes[1]

BY F. S. RICHARDSON

Received February 14, 1972

The optical activity associated with the d–d transitions in dissymmetric six-coordinate Co(III) complexes is examined on a model which incorporates both ligand-field theory and the one-electron, static-coupling theory of optical activity. This is a perturbation model on which the zeroth-order spectroscopic states are taken as eigenstates of an octahedral CoL_6 cluster (L = ligating atoms). The dissymmetric perturbation of these states orginates with ligand groups outside the ML_6 cluster and with dissymmetric distortions of the ML_6 cluster. The perturbation treatment is carried to second order in both the wave functions and rotatory strengths. Expressions are obtained which relate the sign of the *net* or *total* d–d rotatory strength to specific stereochemical features in the ligand environment. Sector rules based on these expressions are proposed. Applications of these sector rules to chiral Co(III) complexes of several classes are presented, and it is found that these rules are reliable in predicting the signs of the contributions made by various "kinds" of stereochemical features to the *net* d–d rotatory strength.

I. Introduction

The natural optical rotatory properties of chiral transition metal compounds have played an extraordinarily important role in the development of inorganic stereochemistry. The modern structural theories of metal coordination compounds owe their final acceptance to Werner's interpretation of the optical rotatory power of the resolved optically active stereoisomers of six-coordinate metal complexes.[2] The investment of research effort in this field has grown enormously in the past 10 years, due in large part to the availability of improved measurement techniques (*e.g.*, circular dichroism instrumentation) and, perhaps to a lesser extent, due to an improved theoretical understanding of the underlying spectroscopic processes. Considerable progress has been made in correlating the experimental parameters of circular dichroism (CD) and optical rotatory dispersion (ORD) spectra with specific stereochemical features of various classes of transition metal complexes. Furthermore, CD spectra have been used with some success in resolving and characterizing the spectroscopic transitions associated with metal intra-d-shell excitations and with ligand ↔ metal charge-transfer processes. Despite these successes, there remains one important objective of these studies which so far has eluded satisfactory treatment. Simply stated, this objective is to establish a quantitative relationship between the stereochemical variables of a complex (*i.e.*, the relative positional coordinates of the atoms and groups within a coordination compound) and the electronic variables which determine the spectroscopic observables of optical activity.

For isotropic assemblies of dissymmetric molecules, the rotatory strength as defined in eq 1 provides a direct connection between the spectroscopic moments associated with a molecular electronic transition and the contribution which this transition makes to the optical activity observables.

$$R(i \rightarrow j) = \mathrm{Im}[\langle\psi_i|\boldsymbol{\mu}|\psi_j\rangle\langle\psi_j|\mathbf{m}|\psi_i\rangle] \qquad (1)$$

where $\boldsymbol{\mu}$ and $\mathbf{m}$ are the electric and magnetic dipole operators, respectively, and ψ_i and ψ_j are molecular electronic state functions. If ψ_i and ψ_j are obtained as eigenfunctions of the total molecular Hamiltonian, then the stereochemical variables are implicit in the wave functions since, of course, these variables must appear explicitly in the potential energy terms of the total Hamiltonian. Of primary interest, however, is the case where $R(i \rightarrow j)$ is determined from experiment and one then wishes to deduce the stereochemical variables. This requires a knowledge of ψ_i and ψ_j as functions of the dissymmetric parts of the total molecular Hamiltonian.

For many dissymmetric systems the electronic transitions of greatest experimental interest are localized in some subgroup of the system which is nondissymmetric. In these cases, the spectroscopic-state functions can be treated to zeroth-order as eigenfunctions of a local or group Hamiltonian which has the symmetry of the chromophoric subgroup. The influence of the dissymmetric, extrachromophoric parts of the system on the spectroscopic states is then treated by perturbation theory. It is assumed that the local zeroth-order states are well-defined and that the true spectroscopic states

---

(1) This work was supported by a grant from the Petroleum Research Fund (PRF Grant No. 2022-G2) administered by the American Chemical Society.

(2) A. Werner, *Ber. Deut. Chem. Ges.*, **44**, 1887 (1911).