

Notes

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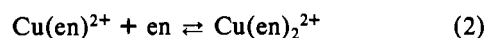
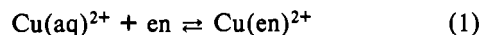
Statistical Factors and the Ratio of Successive Stability Constants

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A general analysis by Chung of statistical factors as they apply to metal complex equilibria has appeared recently.¹ The computational method involves the calculation of statistical factors as the sum of symmetry and isomer effects and is an extension of ideas previously applied² to the type of correlations involved in linear free energy relationships. Such statistical factors can be directly related either to entropy changes³ or, in an entirely equivalent way, to the ratio of successive equilibrium constants.⁴ The importance of statistical factors is not that experimental and calculated values of entropy changes should necessarily be comparable but rather that an understanding of the thermodynamics of complex formation requires that the purely statistical (entropic) contribution must be taken into account when successive equilibria are compared. Although the method presented by Chung¹ is entirely accurate in principle, we differ with the results as presented for complex formation with bidentate ligands. The present note contains a reexamination of that case and a simple alternative way to evaluate statistical factors.

Consider reactions of tetragonal $\text{Cu}(\text{aq})^{2+}$ with ethylenediamine (en). The reactions are



The symmetry numbers and distribution of isomers are

species	symm no.	rel distribn	species	symm no.	rel distribn
$\text{Cu}(\text{aq})^{2+}$	8		$\delta\delta\text{-Cu}(\text{en})_2^{2+}$	4	1
en	2		$\lambda\lambda\text{-Cu}(\text{en})_2^{2+}$	4	1
$\delta\text{-Cu}(\text{en})^{2+}$	2	1	$\delta\lambda\text{-Cu}(\text{en})_2^{2+}$	2	2
$\lambda\text{-Cu}(\text{en})^{2+}$	2	1			

For reaction 1, the symmetry effect⁵ is

$$-\frac{1}{2}R \ln 2 - \frac{1}{2}R \ln 2 + R \ln 2 + R \ln 8 = +4.1 \text{ eu}$$

and the isomer effect is

$$-\frac{1}{2}R \ln \frac{1}{2} - \frac{1}{2}R \ln \frac{1}{2} = +1.4 \text{ eu}$$

Therefore, $\Delta S_1 = +5.5 \text{ eu}$. For reaction 2, the symmetry effect is

$$-\frac{1}{4}R \ln 4 - \frac{1}{4}R \ln 4 - \frac{1}{2}R \ln 2 + \frac{1}{2}R \ln 2 + \frac{1}{2}R \ln 2 + R \ln 2 = +0.7 \text{ eu}$$

and the isomer effect is

- (1) Chung, C.-S. *Inorg. Chem.* 1979, 18, 1318.
- (2) Benson, S. W. *J. Am. Chem. Soc.* 1958, 80, 5151.
- (3) Rosotti, F. J. C. In "Modern Coordination Chemistry"; Lewis, J., Wilkins, R. G., Eds.; Interscience: New York, 1960; pp 34-39.
- (4) For successive complexation processes, $\Delta S_1 - \Delta S_2 = -R \ln (K_2/K_1)$ if $\Delta H_1 = \Delta H_2$.
- (5) The precise method of calculation is presented in ref 1.

$$-\frac{1}{4}R \ln \frac{1}{4} - \frac{1}{4}R \ln \frac{1}{4} - \frac{1}{2}R \ln \frac{1}{2} + \frac{1}{2}R \ln \frac{1}{2} + \frac{1}{2}R \ln \frac{1}{2} = +0.7 \text{ eu}$$

Therefore, $\Delta S_2 = +1.4 \text{ eu}$ and $\Delta S_1 - \Delta S_2 = +4.1 \text{ eu}$.

The difference between this calculation and the previous one¹ lies in the relative distribution taken for the chelate ring conformations. Assuming that δ and λ conformations are equally probable, the statistical ratio⁶ $\delta\delta:\lambda\lambda:\delta\lambda$ is 1:1:2. Chung uses a nonstatistical ratio of 5:5:1 which is based on a calculation of the relative importance of nonbonded interactions in the various conformations.⁷ It is the purely statistical value that should be employed in the calculation, and the effect of nonbonded interactions is one reason for the difference between calculated and experimental entropy changes.

We present another method of evaluation of statistical factors that represents an extension of the method normally applied for complexes involving unidentate ligands.⁸ In that case, the formation of a complex ion is assumed to be proportional to the number of coordination sites available for attachment of the incoming ligand and its dissociation is proportional to the number of bound ligands.⁹ This general idea can be extended to ligands of increasing denticity. In these cases, however, a ligand does not occupy a single coordination site on the metal ion but rather a geometric entity such as an edge or, in the case of terdentate ligands, a facial or meridional position in an octahedron. What is required in working out the statistics is to recognize that complex formation is proportional to the number of such geometric entities available to the incoming ligand and that dissociation, as in the case of unidentate ligands, is proportional to the number of bound ligands.

Considering the previous case (eq 1 and 2) in this way, four edges are available for the first incoming ligand. Dissociation can occur in only one way. Following the addition of the first ligand, only one edge remains that can be occupied by a second ligand. The resulting bis complex can dissociate in two ways. Hence, $K_1/K_2 = (4/1)/(1/2) = 8$. Note that $\Delta S_1 - \Delta S_2 = -R \ln \frac{1}{8} = +4.1 \text{ eu}$, which is exactly the result obtained by the application of symmetry and isomer effects.

Although the previous example involves a symmetrical bidentate ligand, either method can be extended to consider the case of an unsymmetrical bidentate ligand. With the method of Chung, there are six possible isomers of the bis complex. Assigning symmetry numbers and taking a purely statistical relative distribution of isomers give a result identical with that for the symmetrical case. With our method, an unsymmetrical ligand might be considered to occupy an edge in either of two orientations. This is, however, also true of additional ligands, and such multiplicative factors cancel out in computing the statistical ratio.

Our method can obviously be easily extended to consider different symmetries and ligands of increasing denticity. An octahedron has twelve edges, and coordination of a bidentate

- (6) For a similar case, see: Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Interscience: New York, 1980; p 80.
- (7) Corey, E. J.; Bailar, J. C., Jr. *J. Am. Chem. Soc.* 1959, 81, 2620.
- (8) Bjerrum, J. "Metal Ammine Formation in Aqueous Solution"; P. Haase and Son: Copenhagen, 1941.
- (9) Chung presents an objection to this method of calculation for unidentate ligands unless "there is no preference for cis or trans positions". Obviously, in some cases, there is a marked preference of an incoming ligand for a particular coordination site. The fact that experimentally determined ratios may differ considerably from calculated statistical ratios is simply indicative of the importance of nonstatistical effects.

Table I. Statistical Factors for Successive Stability Constants

ligand type and coord symm	K_1/K_2	K_2/K_3
unidentate		
octahedral	2.40	1.88
tetrahedral/square planar	2.67	2.25
bidentate		
octahedral	4.80	9.38
tetrahedral	12	
square planar	8	
terdentate		
octahedral		
facial	16	
meridional	24	
facial or meridional	40	

ligand leaves only five edges available for a second bidentate ligand. Hence, $K_1/K_2 = (12/1)/(5/2) = 4.8$. An additional statistical problem emerges when K_2/K_3 is calculated in that a third ligand cannot add at all if the second ligand is trans to the first. Of the five positions available for addition of the second ligand, four are cis and one is trans. In computing K_2/K_3 , the number of available edges for an incoming ligand must be taken as the average number of edges available in the two possible bis complexes.¹⁰ Hence, $K_2/K_3 = (5/2)/(0.8/3) = 9.38$. The extension of this method to terdentate ligands in octahedral symmetry is straightforward. Results of calculations for a number of common examples are presented in Table I.

The method presented here is extremely simple and leads to results identical with those obtained by the application of symmetry and isomer effects. The importance of taking into account statistical effects in the evaluation of thermodynamic data is clear when one considers that, in relatively simple systems, such factors may be as large as 40.

(10) An earlier analysis (Sen, B. *Anal. Chim. Acta* **1962**, *27*, 515) of bidentate ligands in square-planar symmetry has been criticized by Chung. However, it should be pointed out that that paper also contains a discussion of bidentate ligands in octahedral symmetry, which leads to conclusions identical with those presented here.

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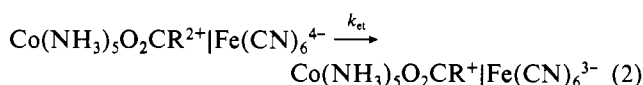
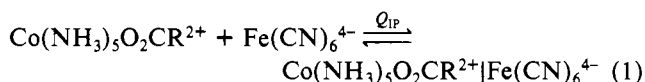
Electron-Transfer Reactions of Ion Pairs: Reduction of Various (Carboxylato)pentaamminecobalt(III) Complexes by Hexacyanoferrate(II)

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The importance of measuring rates of electron-transfer reactions in the intramolecular mode has been emphasized repeatedly.¹ In previous publications we reported both inner-sphere^{2,3} and outer-sphere^{4,5} internal electron-transfer reactions involving positively charged (pyridine)pentaamminecobalt(III) and negatively charged hexacyanoferrate(II) complexes. For the inner-sphere reactions, the relative orientation of the cobalt(III) and iron(II) centers is firmly established³ and the effects of electronic² and geometric³

factors can be ascertained. However, for outer-sphere reactions, because of the lability of the ion pairs, the relative orientation of cation and anion, when at least one of these does not possess octahedral symmetry, is unknown. Under these circumstances, indirect criteria² must be invoked to obtain information about the detailed pathway for the electron transfer and it becomes important to accumulate kinetic data for first-order, outer-sphere reactions. In the present paper we report such data for the reduction of a variety of (carboxylato)pentaamminecobalt(III) complexes by hexacyanoferrate(II). By utilizing relatively high concentrations of the iron reagent, we have been able to measure the ion-pair formation constants (eq 1) and the rate constants for internal electron transfer within the ion pairs (eq 2).



Experimental Section

Materials. The perchlorate salts of the cobalt(III) complexes were synthesized by standard procedures.^{6,7} Each complex was recrystallized several times from water. The purification of the water and of the lithium perchlorate was described previously.⁴ All other chemicals were of reagent grade and were used as received.

Kinetic Measurements. Solutions containing the desired concentrations of the cobalt(III) complex, ascorbic acid, sodium ethylenediaminetetraacetate (Na₂EDTA), Tris buffer, and lithium perchlorate were prepared and brought to the desired temperature. The desired volume of a freshly prepared solution of hexacyanoferrate(II) was added, and the resulting solution was treated by one of two alternative procedures. For the experiments with $\text{Co}(\text{NH}_3)_5\text{O}_2\text{CCH}_3^{2+}$ performed at Stony Brook, the resulting solution was poured into a spectrophotometric cell that was then placed in the modified⁸ water-filled cell compartment of a Cary 17 spectrophotometer. A recording of the absorbance at 500 nm vs. time was obtained. For the experiments with the benzoate and nitrobenzoate complexes performed in Montevideo, the resulting solutions were kept in a constant-temperature bath. At the desired time intervals, aliquots were withdrawn and their absorbances at 500 nm were measured in a Beckman DB spectrophotometer. First-order rate constants, k_{obsd} , were obtained by linear least-squares fitting of $\ln(A_t - A_\infty)$ to t . A_t and A_∞ are the absorbances of the solution at time t and after 10 half-lives, respectively.

Results and Discussion

The kinetic measurements of the $\text{Co}(\text{NH}_3)_5\text{O}_2\text{CR}^{2+}$ - $\text{Fe}(\text{CN})_6^{4-}$ reactions were carried out in the presence of EDTA²⁻ and ascorbic acid. The addition of EDTA²⁻ serves to sequester the free cobalt(II) released upon reduction of the cobalt(II) complexes and thus prevents the precipitation of cobalt(II) hexacyanoferrate(II).⁸ Ascorbic acid reduces hexacyanoferrate(III) very rapidly⁹ and therefore serves to keep the iron complex in the +2 oxidation state and at constant concentration. Under these circumstances, the disappearance of cobalt(III) obeys first-order kinetics even when the $\text{Fe}(\text{CN})_6^{4-}$ is not in excess with respect to the initial concentration of the cobalt(III) complex.⁹ Moreover, the rapid reduction of $\text{Fe}(\text{CN})_6^{3-}$ by the added ascorbic acid prevents the occurrence

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