A Potentiometric Study on Complex Formation of Cadmium(II) and Lead(II) Ions with Ethylenediaminetetraacetic Acid

Noboru OYAMA, Hiroaki MATSUDA, and Hitoshi OHTAKI

Department of Electronic Chemistry, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152

(Received August 23, 1976)

The complex formation of cadmium(II) and lead(II) ions with ethylenediaminetetraacetic acid (EDTA) has been studied potentiometrically in a 1.0 M $NaClO_4$ medium at 25.0 °C by using glass and metal–amalgam electrodes. The results were explained in terms of the formation of the complexes of MH_qL with $q=3$, 2, 1, and 0 for both metals. The corresponding formation constants were determined: for the Cd–EDTA system, log $\beta_{101}=14.25\pm0.02$, log $\beta_{111}=17.41\pm0.02$, log $\beta_{121}=19.71\pm0.02$ and log $\beta_{131}=21.35\pm0.02$; for the Pb–EDTA system, log $\beta_{101}=16.50\pm0.05$, log $\beta_{111}=19.78\pm0.02$, log $\beta_{121}=21.35\pm0.02$ and log $\beta_{131}=22.50\pm0.02$, where $\beta_{pqr}=[M_pH_qL_r^{(2p+q-4r)+}]/[M^{2+}]^p[H^+]^q[L^{4-}]^r$ and L denotes the unprotonated molecule of EDTA. The protonation constants of unprotonated EDTA were found to be log $\beta_{011}=8.63\pm0.02$, log $\beta_{021}=14.99\pm0.02$, log $\beta_{031}=17.63\pm0.02$, log $\beta_{041}=19.87\pm0.02$, log $\beta_{051}=21.54\pm0.02$, and log $\beta_{061}=22.70\pm0.02$.

In a previous work[1] we determined the formation constants of protonated complexes of the type MH_qL with $q=2,1$ and $q=3,2,1$ in the Cd(II)– and Pb(II)–*N*-(2-hydroxyethyl) ethylenediamine-*N*,*N*′,*N*′-triacetate (H_3-hedta) systems, respectively. Since HEDTA is regarded as a monohydroxyethyl derivative of EDTA, the formation of complexes similar to the HEDTA complexes is expected in the Cd(II)– and Pb(II)–EDTA systems. The results of studies on electrode reactions in Cd(II)– and Pb(II)–EDTA solutions suggest that the protonated complexes MH_qL($q=1$, 2, and 3) participate in the charge transfer processes at the electrode surface.[2,3] The formation constants of unprotonated and monoprotonated metal–EDTA (1 : 1) complexes have been determined[4] in the bulk of these solutions, but those of diprotonated and triprotonated complexes have not been reported except by Sudmeier and Reilley,[5] who evaluated the formation constant of the diprotonated complex for the Cd(II)–EDTA system.

The present work, as a continuation of the previous study,[1] has been carried out to study the formation of protonated complexes in these systems.

Symbols

h	Concentration of hydrogen ion at equilibrium
m	Concentration of metal ion at equilibrium
H	Analytical excess of hydrogen ion in a test solution
M	Cd(II) or Pb(II)
c_M	Total concentration of M
L	Ethylenediaminetetraacetate anion ($edta^{4-}$)
c_L	Total concentration of L
l	Concentration of free L
X	Degree of neutralization of H_4L: $\dfrac{-H+[H]-[OH]}{c_L}$
p	Number of metal atoms bound to complexes
q	Number of protons bound to complexes
r	Number of ligands bound to complexes
β_{pqr}	Equilibrium constant for the reaction $pM + qH + rL = M_pH_qL_r$
$\bar{n}$	Formation function of the ligand H_nL
E_g, E_m	Emf of the cells defined by the subscripts and Eqs. 1 and 2 in Ref. 1.
$E_j(h,m)$	Liquid junction potential as a function of h and m
[ ]	Concentration

All charges are omitted for the sake of convenience.

Experimental

Reagents. *Disodium ethylenediaminetetraacetate* (reagent grade, Dojindo Laboratories) was recrystallized twice, dried at *ca.* 85 °C and then stored in a desiccator over silica gel. *Cadmium(II) perchlorate, lead(II) perchlorate, sodium hydroxide,* and *perchloric acid* solutions were prepared by the methods described in the preceding paper.[1]

Sodium perchlorate was prepared according to Biedermann and Ciavatta.[6]

Cadmium– and lead–amalgams were prepared from cadmium(II) perchlorate and lead(II) nitrate solutions, respectively, by electrolysis with a Metrohm E211A coulometer. The metal content of the amalgams was about 3% (weight).

Apparatus. *A potentiometric cell* similar to the one previously employed was used. *A digital pH/mV meter* (Orion Research, Model 801) and a *digital voltmeter* (Takeda Riken, Model TR-6656) were used for potentiometric measurements in combination with glass and amalgam electrodes, an Ag–AgCl electrode being used as a reference.

Emf Measurements. The method of emf measurements was essentially the same as that employed previously.[1]

When $c_{Cd}>0.0025$ M, titration was interrupted in the pH range 1.7—2.3, since white precipitates which might be CdH_2L^0 separated out. In such cases no stable emf's could be recorded. The emf of the amalgam electrode usually required 15 min to attain a constant value and was measured within an accuracy of ±0.02 mV in the pH range 1.0—2.0 and ±0.1 mV in the pH range 2.0—3.5. At pH above 3.5 the emf's became unstable. The emf of the glass electrode cell became constant after about 5 min and was determined within an accuracy of ±0.1 mV over the pH range 1.0—10.0.

Results and Discussion

Evaluation of Protonation Constants of EDTA. Overall protonation constants of the EDTA base, β_{0n1}, were determined from the formation function $\bar{n}$. A generalized least squares method was applied in order to make the error squares sum $U=\Sigma(\bar{n}-\bar{n}_{calcd})^2$ a minimum for the set of overall protonation constants, β_{011}, β_{021}, β_{031}, β_{041}, β_{051}, and β_{061}. This calculation was performed with an electronic computer HITAC 8700. $\bar{n}_{calcd}$ and $\bar{n}$ denote, respectively,

$$\bar{n}_{calcd}=\frac{\sum_{n=1}^{6} n\beta_{0n1}h^n}{1+\sum_{n=1}^{6}\beta_{0n1}h^n} \quad (1)$$

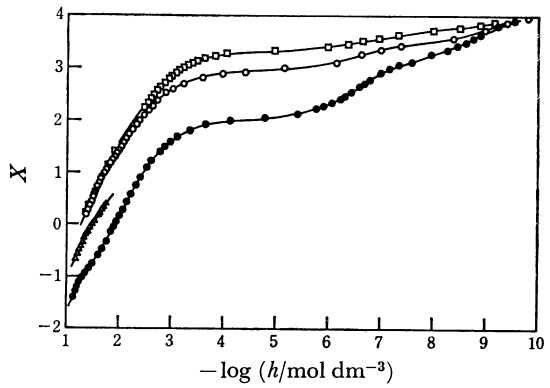

Fig. 1. Degrees of neutralization, X, of ethylenediaminetetraacetic acid (EDTA) solutions for the Cd(II)-EDTA systems.
(●): $c_{Cd}=0.0$ M, $c_L=0.01351$ M,
(○): $c_{Cd}=0.002526$ M, $c_L=0.005002$ M,
(△): $c_{Cd}=0.002408$ M, $c_L=0.009567$ M,
(□): $c_{Cd}=0.008018$ M, $c_L=0.01186$ M.
Solid lines are the values of X calculated by the use of the stability constants in Table 1.

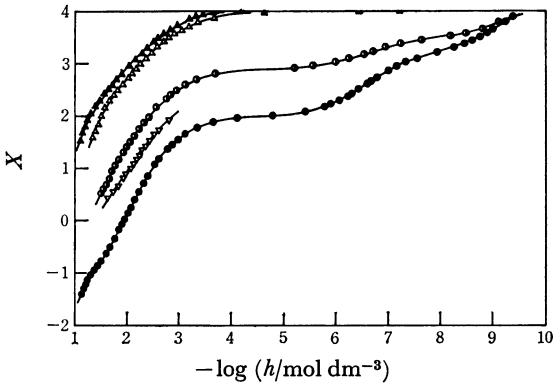

Fig. 2. Degrees of neutralization, X, of EDTA solutions for the Pb(II)-EDTA systems.
(●): $c_{Pb}=0.0$ M, $c_L=0.01351$ M,
(▽): $c_{Pb}=0.001839$ M, $c_L=0.007247$ M,
(◑): $c_{Pb}=0.004601$ M*, $c_L=0.009455$ M*,
(△): $c_{Pb}=0.005067$ M, $c_L=0.005060$ M,
(▲): $c_{Pb}=0.01517$ M*, $c_L=0.007603$ M*.
Solid lines are the values of X calculated by the use of the stability constants in Table 1.
*: c_{Pb} and c_L are the initial concentration of the metal and the ligand, and c_{Pb} and c_L are slightly changed during the course of titration by the addition of the titrants.

and

$$\bar{n}=\frac{4c_L+H-h+(K_w/h)}{c_L} \tag{2}$$

where K_w is the autoprotolysis constant of water in 1.0 M $NaClO_4$ solution, $10^{-13.95}$.[7] The protonation constants thus obtained were $\log \beta_{011}=8.63\pm0.02$, $\log \beta_{021}=14.99\pm0.02$, $\log \beta_{031}=17.63\pm0.02$, $\log \beta_{041}=19.87\pm0.02$, $\log \beta_{051}=21.54\pm0.02$, and $\log \beta_{061}=22.70\pm0.02$. Anderegg reported the values of $\log \beta_{011}=8.85$, $\log \beta_{021}=15.13$, $\log \beta_{031}=17.43$, $\log \beta_{041}=19.63$, $\log \beta_{051}=21.03$, and $\log \beta_{061}=20.19$ in a 1.0 M $NaClO_4$ medium at 20 °C.[7]

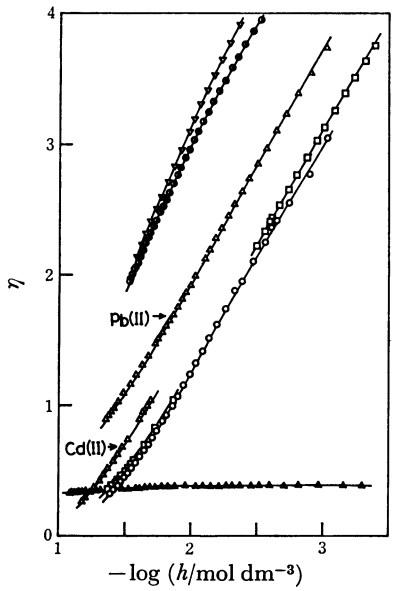

Fig. 3. Relationships between η and $-\log h$ for the Cd(II) and Pb(II) systems.
Symbols are the same as those in Figs. 1 and 2, respectively. Solid lines are curves calculated by the use of the stability constants in Table 1.

Determination of the Composition and the Stability Constants of Complexes. Titration curves of the Cd(II)- and Pb(II)-EDTA solution are shown in Figs. 1 and 2, respectively. In Fig. 3, the quantity $\eta=\log(c_M/m)$, which is a measure of the degree of complexation of the metal ion M, is plotted against $-\log h$. We see that $\eta>0$ at $-\log h=1.2$. This shows that the complex formation reaction takes place between the metal ions and EDTA even in the most acidic solution.

Since EDTA is an analog of HEDTA, the data obtained in the EDTA systems may be treated in the same manner as that used in calculation of the formation constants of the HEDTA complexes. Polynuclear or polyligand complexes may be neglected.[1] As a first approach to analysis of the data, we assume that the complex formation reaction can be written as

$$M^{2+}+qH^{+}+L^{4-}=MH_qL^{(q-2)+} \tag{3}$$

from which we obtain

$$c_M=m+\sum_{q=0}^{Q}[MH_qL] \tag{4}$$

$$c_L=l+\sum_{n=1}^{N}[H_nL]+\sum_{q=0}^{Q}[MH_qL] \tag{5}$$

Insertion of Eq. 4 into Eq. 5 and rearrangement lead to

$$l=(c_L-c_M+m)/(1+\sum_{n=1}^{N}\beta_{0n1}h^n) \tag{6}$$

A function F_0 is defined as follows:

$$F_0=(c_M-m)/ml=\sum_{q=0}^{Q}[MH_qL]/ml=\sum_{q=0}^{Q}\beta_{1q1}h^q \tag{7}$$

The plot of $\log F_0$ against $-\log h$ is shown in Fig. 4 for both systems of Cd(II)- and Pb(II)-EDTA except for the case $c_M \geq c_L$. In each system a single curve was obtained regardless of variations of c_M, c_L and c_M/c_L. This supports the assumption that neither polynuclear nor polyligand species is formed. In the case $c_M \geq c_L$,

Table 1. Stability constants of the Cd(II)- and Pb(II)-EDTA complexes ($\log \beta_{pqr}$)
$\log \beta_{011}=8.63\pm0.02$, $\log \beta_{021}=14.99\pm0.02$, $\log \beta_{031}=17.63\pm0.02$,
$\log \beta_{041}=19.87\pm0.02$, $\log \beta_{051}=21.54\pm0.02$, $\log \beta_{061}=22.70\pm0.02$

Complexes	ML^{2-}	MHL^{-}	MH_2L^{0}	MH_3L^{+}
Cd(II)	14.25±0.02	17.41±0.02	19.71±0.02	21.35±0.02
Pb(II)	16.50±0.05	19.78±0.02	21.35±0.02	22.50±0.02

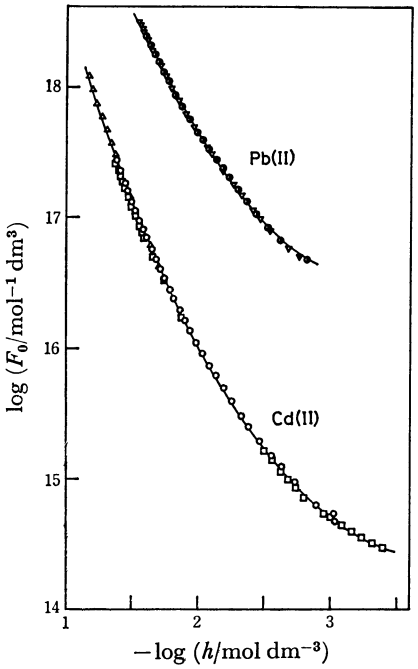

Fig. 4. Plot of $\log F_0$ against $-\log h$ for both systems. Each solid line is the curve calculated with the values of the stability constants in Table 1.

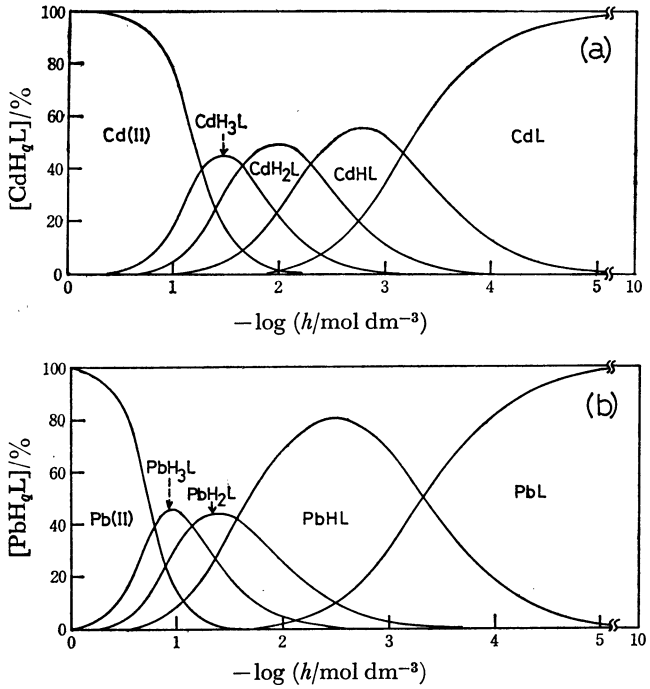

Fig. 5. The distribution of metal-EDTA complexes *vs.* $-\log h$ ($c_M=0.001$ M, $c_L=0.01$ M).
(a): for the Cd(II)-EDTA system.
(b): for the Pb(II)-EDTA system.

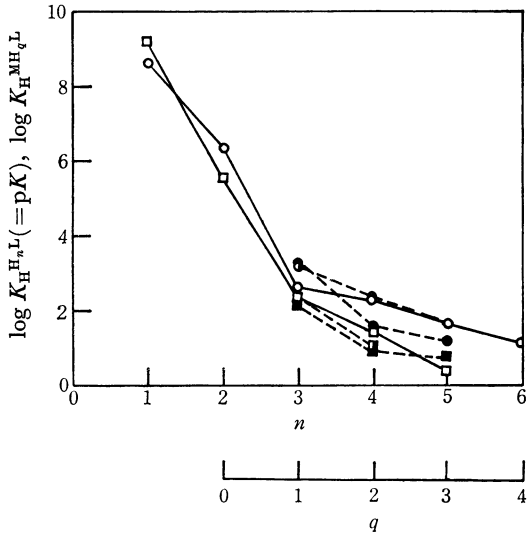

Fig. 6. Plot of $\log K_H^{MH_qL}(=\log\{[MH_qL]/[MH_{q-1}L][H]\})$ and $\log K_H^{H_nL}(=\log\{[H_nL]/[H_{n-1}L][H]\})$ against the number of protons within the complexes q and the ligand n.
○: EDTA, (◑): Cd(II)-EDTA complexes, (●): Pb(II)-EDTA complexes, (□): HEDTA, (◨): Cd(II)-HEDTA complexes, (■): Pb(II)-HEDTA complexes.

the value of the term (c_L-c_M+m) in Eq. 6 becomes too small to use the data for the calculation of F_0.

From the plot of F_0 against h, we obtained the formation constant β_{101}, β_{111}, β_{121}, and β_{131} for both systems according to the procedure reported.[1] By using the values of β_{1q1} thus obtained as the initial values, the formation constants of the complexes were refined by a generalized least squares method. The method was applied to make the error squares sum $U=\Sigma\{\log F_0-\log F_{0,\mathrm{calcd}}\}^2$ minimum for the set of the formation constants over the pH range 1.2—3, where $F_{0,\mathrm{calcd}}$ denotes the value of F_0 calculated for a particular set of the formation constants. The results are given in Table 1.

Since the metal amalgam electrodes did not function well in a high pH range, the data in the high pH range were not analyzed. However, the constants reproduced the experimental results fairly well over the whole pH range (solid lines, Figs. 1 and 2).

The distribution of the Cd(II)- and Pb(II)-EDTA complexes are graphically represented in Fig. 5.

The stepwise protonation constant of the species MH_qL is defined as $K_H^{MH_qL}=[MH_qL]/[MH_{q-1}L][H]$. The values of $\log K_H^{MH_qL}$ are plotted against the number of protons within the complex q, together with the values of $\log K_H^{H_nL}$ $(=\log [H_nL]/[H_{n-1}L][H])$against n(Fig. 6). The values of $\log K_H^{H_nL}$ of the HEDTA and

Table 2. Stability constants of the complexes defined by $\log K_{H_qL}^{MH_qL}=\log\{[MH_qL]/[M][H_qL]\}$

	EDTA				HEDTA			
	$\log K_{L}^{ML}$	$\log K_{HL}^{MHL}$	$\log K_{H_2L}^{MH_2L}$	$\log K_{H_3L}^{MH_3L}$	$\log K_{L'}^{ML'}$	$\log K_{HL'}^{MHL'}$	$\log K_{H_2L'}^{MH_2L'}$	$\log K_{H_3L'}^{MH_3L'}$
Cd(II)	14.25	8.78	4.72	3.72	13.21	6.41	1.96	—
Pb(II)	16.50	11.15	6.36	4.87	14.83	7.77	3.17	1.61

EDTA molecules first steeply decreased with n. According to the NMR and infrared spectrophotometric measurements,[8,9] the first two protons (to form HL and H_2L) are located on the nitrogen atoms of the EDTA and HEDTA molecules. We see that the protonation of the amino groups of the ligands brings about a significant change in the values of the protonation constants. The protonation on the carboxylic groups results in the relatively small change in the $K_{H}^{H_nL}$ values. The stepwise protonation constants $K_{H}^{MH_qL}$ ($q=1$, 2, and 3) of the Cd(II)- and Pb(II)-HEDTA and EDTA complexes are close to the values of $K_{H}^{H_nL}$ with $n=3$, 4, and 5 of the corresponding ligands. Thus we conclude that protonation of the complexes occurs on the acetate groups with the cleavage of the metal–oxygen bonds within the complexes with a decrease in pH, while the strong metal–nitrogen bonds are hardly influenced by the hydrogen-ion concentration over the pH range examined.

Another kind of formation constants of the complexes may be defined as $\log K_{H_qL}^{MH_qL}=\log[MH_qL]/[M][H_qL]$, which is calculated from the values of β_{1q1} and β_{0n1}. The values are given in Table 2. The values of K_{L}^{ML} of the Cd(II)- and Pb(II)–EDTA complexes are larger than those of the HEDTA complexes, as expected from the simple chelate theory, because the former ligand is sexidentate, whereas the latter quinquidentate. Nevertheless, the K_{HL}^{MHL} values of the EDTA complexes are smaller than the $K_{L'}^{ML'}$ ($L'=$ hedta^{3-} anion) values of the HEDTA complexes, the ligand HL (L=edta^{4-} anion) being expected to act as a quinquidentate ligand. The same tendency was found in the complex formation of the MH_2L of EDTA and the MHL′ of HEDTA (Table 2). However, a comparison between the formation constants of the MH_3L complex of EDTA and the MH_2L' complex of HEDTA leads to the opposite result.

The protons within the protonated ligands HL and H_2L are located at the nitrogen atoms of the amino groups of the ligands. On the other hand, the protons of the protonated metal complexes MH_qL are combined with the acetate groups. Thus the free energy change defined by the equation $\Delta G_{MH_qL}=-RT\ln K_{H_qL}^{MH_qL}$ should include the free energy change of the intramolecular rearrangement of protons from the amino groups to the acetate groups. In the MHL complex of EDTA, the free energy change accompanied by the transfer of one proton from a nitrogen atom to an oxygen atom is needed as compared with the corresponding value of the ML′ complex of HEDTA. Since the entropy change for the complex formation of MHL from M and HL (L=edta^{4-}) is nearly equal to that of ML′ from M and L′ (L′=hedta^{3-}) as reported by Brunetti *et al.*,[10] the difference between $K_{L'}^{ML'}$ and K_{HL}^{MHL} is mainly due to the difference in the enthalpy change of the proton transfer reaction from a nitrogen atom to an acetate group in the latter case. In the formation of MH_2L of EDTA, two protons must move from the amino groups to the acetate groups, while the transfer of only one proton is required in the complex formation MHL′ with M and HL′. In contrast to the case considered above, the two proton transfer reaction is always accompanied by the complex formation of MH_qL from M and H_qL ($q\geq 2$) of either HEDTA or EDTA molecule. The free energy change of the intramolecular rearrangement of protons in the complex formation of MH_3L of EDTA may not largely differ from that of the MH_2L' complex of HEDTA. The difference between $K_{H_3L}^{MH_3L}$ and $K_{H_2L'}^{MH_2L'}$ (Table 2) cannot be explained in terms of the enthalpy changes in the chelate formation. The contribution of the hydroxyethyl group to the chelate formation might stabilize the MH_2L' complex, and therefore $K_{H_2L'}^{MH_2L'}$ would be larger than $K_{H_3L}^{MH_3L}$. The difference may be attributed to the entropy difference in the intramolecular rearrangement of the protons of the ligands, but we have no evidence to clarify the phenomenon.

References

1) N. Oyama, T. Shirato, H. Matsuda, and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, **49**, 3047 (1976).

2) N. Oyama and H. Matsuda, *J. Electroanal. Chem.*, in press.

3) N. Oyama, T. Shirato, and H. Matsuda, *J. Electroanal. Chem.*, submitted.

4) L. G. Sillén and A. E. Martell, "Stability Constants," Chemical Society, London (1964), Supplement No. 1 (1971).

5) J. L. Sudmeier and C. N. Reilley, *Inorg. Chem.*, **5**, 1047 (1966).

6) G. Biedermann and L. Ciavatta, *Acta Chem. Scand.*, **15**, 1347 (1961).

7) G. Anderegg, *Helv. Chim. Acta*, **50**, 2333 (1967).

8) J. J. Sudmeier and C. N. Reilley, *Anal. Chem.*, **36**, 1698 (1964).

9) N. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Am. Chem. Soc.*, **85**, 309 (1963).

10) A. P. Brunetti, G. H. Nancollas, and P. N. Smith, *J. Am. Chem. Soc.*, **91**, 4680 (1969).