Kinetics of the Formation of the *trans*-Dibromotetracyanoplatinate(IV) Ion

Charles E. Skinner and Mark M. Jones

Contribution from the Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37203. *Received December 23, 1968*

Abstract: The rate of the formation of the *trans*-dibromotetracyanoplatinate(IV) ion from bromine and the tetracyanoplatinate(II) ion in aqueous acid media has been studied with a stopped-flow apparatus. The reaction can proceed by two paths, depending upon the concentration of bromide ion. In the absence of added bromide ion, the data indicate that the bromine oxidation of the tetracyanoplatinate(II) ion occurs in two steps, of which the initial one is a very rapid reaction to form the *trans*-bromotetracyanoaquoplatinate(IV) ion and a bromide ion. The coordinated water is then replaced by the free bromide ion in the rate-determining step. The second step is first order in bromide ion and in *trans*-$Pt(CN)_4Br(OH_2)^-$ with a rate constant of $1.5 \times 10^3\ M^{-1}\ sec^{-1}$ at 25° (μ = 1) and with activation parameters of $\Delta H^{\ddagger} = 15$ kcal/mole and $\Delta S^{\ddagger} = 6$ cal deg^{-1} mole^{-1}. The rate constant for the initial oxidation step must be greater than $10^7\ M^{-1}\ sec^{-1}$. Studies are reported of the effects of pH and bromide ion on the rate of the reaction, and in the presence of large amounts of bromide ion an alternative route is found for the anation reaction. Under such conditions, it appears that the added bromide ion facilitates the anation reaction by association with and partial reduction of the bromotetracyanoaquoplatinate(IV). The consequent labilization of the coordinated water results in a more rapid formation of the *trans*-dibromo product.

In an earlier paper we reported kinetic studies on the base hydrolysis of *trans*-$Pt(CN)_4Br_2^{2-}$.[1] A feature of that work was evidence that added bromide ion accelerated the replacement of the bromide ligand by hydroxide ion through some sort of association with the bromide ligand in the position *trans* to the leaving bromide ligand. The present paper contains the results of kinetic studies of the formation of *trans*-$Pt(CN)_4Br_2^{2-}$ in acid media. These results are of interest for three reasons. First, they give some insights into the detailed mechanism of the oxidation of tetracyanoplatinate(II) by bromine. Second, inner-sphere aquo complexes of platinum(IV) such as the one involved here as an intermediate are generally unstable and their anation has not been previously studied. Third, the unusual acceleration of a replacement reaction by added bromide ion has again appeared as in the hydrolysis reaction.[1] This acceleration does not appear to be consistent with a redox mechanism postulated recently for processes of this type.[2]

Experimental Section

Apparatus. Kinetic measurements were made on the Durrum-Gibson stopped-flow spectrophotometer. A Tektronix oscilloscope camera system was used to record the transmittance *vs.* time trace on Polaroid 3000 Type 107 film. A Beckman Research Model pH meter was used to obtain the pH of the reacted solutions.

Reagents. Commercially available chemicals of analytical reagent grade quality, including NaBr, Na_2CO_3, $HClO_4$, KCN, and Br_2, were used without further purification. Potassium tetracyanoplatinate(II) was prepared and isolated as described previously.[1] Sodium perchlorate, used to control the ionic strength, was prepared from Na_2CO_3 and $HClO_4$. Bromine solutions were prepared by adding approximately 0.2 ml of bromine to a warmed liter flask. Then the flask was stoppered. After vaporization was complete, a liter of water was added through a powder funnel which was resting snugly on the mouth of the flask so that as the water was added the air and bromine vapor in the flask had to bubble through the water to escape. Bromine concentrations of up to $4 \times 10^{-3}\ M$ were obtained in aqueous solution in this manner. The bromine solution was standardized before each use by arsenite titration in $NaHCO_3$ containing 1 M KI using the starch end point.

Kinetic Procedure. For each kinetic run two solutions each adjusted to the proper pH and ionic strength were prepared. One solution was then made twice the desired concentration in $Pt(CN)_4^{2-}$, and the second solution was made twice the concentration desired in bromine and added bromide ion. The solutions were then each added to one of the two drive syringes on the stopped-flow apparatus and after temperature equilibrium was achieved the rate determinations were run. Two different wavelengths were used in the rate studies as the $Pt(CN)_4^{2-}$ ion has a peak at approximately 255 mμ (ϵ $1.09 \times 10^4\ M^{-1}\ cm^{-1}$), and the *trans*-$Pt(CN)_4Br^{2-}$ ion has a peak at 342 mμ (ϵ $1.14 \times 10^3\ M^{-1}\ cm^{-1}$). Aliquots (10 ml) of each solution were combined for pH and final absorption measurements.

Results

A study of the reaction between bromine and tetracyanoplatinate(II) at the tetracyanoplatinate(II) absorbance peak revealed that the reaction was too fast to be measured by the stopped-flow technique. That is, the change in optical transmittance at this wavelength was complete in the period of 2 msec. This indicated that the rate of disappearance of $Pt(CN)_4^{2-}$ is greater than $10^7\ M^{-1}\ sec^{-1}$.

At 342 mμ it was found that a change in absorbance occurred at rates convenient for measurement on the stopped-flow apparatus. It was assumed for reasons presented in the Discussion section that the reaction occurring was the bromide ion replacement of H_2O in *trans*-$Pt(CN)_4Br(OH_2)^-$. The optical transmittance *vs.* time data were treated by assuming that the peak of the trace corresponded to the transmittance of the *trans*-$Pt(CN)_4Br(OH_2)^-$ ion and that the lower trace corresponded to the transmittance of the product, *trans*-$Pt(CN)_4Br_2^{2-}$. The spectrum of *trans*-$Pt(CN)_4Br(OH_2)^-$ is not available due to the instability of this complex, but the kinetic data followed good first-order or second-order plots when the absorbance of this species at 342 mμ was assumed to be the same as that of *trans*-$Pt(CN)_4Br(OH)^{2-}$ (ϵ^{342} 260 $M^{-1}\ cm^{-1}$). That the spectra of these complexes may be approximately the same is not unreasonable since OH^- and OH_2 are not far apart in the spectrochemical series.[3] Furthermore,

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[1] C. E. Skinner and M. M. Jones, *J. Am. Chem. Soc.*, **91**, 1984 (1969).

[2] A. J. Poe and D. H. Vaughan, *Inorg. Chim. Acta*, **2**, 159 (1968).

[3] M. M. Jones, "Elementary Coordination Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1964, p 147.

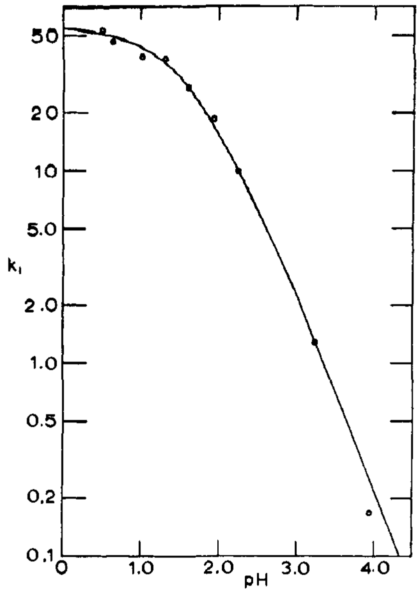

Figure 1. The pH dependence of the anation reaction rate constant (Table III): calculated (———), experimental (○).

although attempts to measure ϵ were thwarted by the rapid rate of the reaction, an approximation of the initial reading on the oscilloscope indicated the ϵ's were close. The output of the oscilloscope is linear in optical transmittance, and thus points on the trace between the extremes can be directly related to the transmittance of the solution at that time. The transmittance readings are then related (for the fixed 1-cm path length) to the concentration of *trans*-$Pt(CN)_4Br_2^{2-}$ by

$$[Pt(CN)_4Br_2^{2-}] = -\left[\frac{\log T + ([Pt(CN)_4^{2-}]_i \times 260)}{880}\right] \quad (1)$$

When equal amounts of bromine and $Pt(CN)_4^{2-}$ were used, the formation of *trans*-$Pt(CN)_4Br_2^{2-}$ was found to be first order in bromide ion and first order in *trans*-$Pt(CN)_4Br(OH_2)^-$. First-order behavior in *trans*-$Pt(CN)_4Br(OH_2)^-$ was found when greater than a 15-fold excess of bromide ion was added to the bromine solution before reaction with $Pt(CN)_4^{2-}$. The data collected displayed pseudo-first-order or second-order behavior.

Studies of the dependence of the reaction rate on the pH of the solution indicated that the reaction rate is directly proportional to $[H^+]$ above pH 2 and almost independent of $[H^+]$ below pH 1 (see Figure 1). This behavior is consistent with a reaction of a protonated species whose pK_a is approximately 1.6 when the reaction rate of the conjugate base is negligible. Table I gives a comparison between the observed and the theoretical reaction rates calculated on the basis of a limiting reaction rate of 5.40×10^1 sec^{-1} and a pK_a of 1.6. The theoretical reaction rate at a given pH was calculated from the fraction of the platinium(IV) reactant present as the aquo complex, *trans*-$Pt(CN)_4Br(OH_2)^-$. This fraction is given by $f = [H^+]/([H^+] + K)_a$.

When the formation of *trans*-$Pt(CN)_4Br_2^{2-}$ is carried out under pseudo-first-order conditions (a large excess of bromide ion), the rate constant increases with increasing bromide ion concentration as shown in Table II and Figure 2. This variation is consistent with the rate law given by eq 2 where $a = 1.25 \times 10^3$ M^{-1} sec^{-1} and $b = 1.00 \times 10^5$ M^{-1} sec^{-1} at pH 1.0 and $a = 6.0 \times 10^2$ M^{-1} sec^{-1} and $b = 3.8 \times 10^4$ M^{-2} sec^{-1} at pH 1.9.

$$d[Pt(CN)_4Br_2^{2-}]/dt = (a + b[Br^-]) \times [Pt(CN)_4Br(OH_2)^-][Br^-] \quad (2)$$

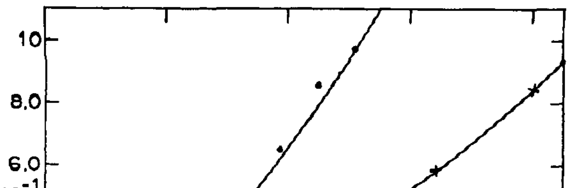

Figure 2. The $[Br^-]$ dependence of the anation reaction rate constant at: pH 1, calculated on the basis of eq 2 where $a = 1.25 \times 10^3$ and $b = 1.00 \times 10^5$ (———), experimentally found (●); pH 2, calculated as above where $a = 6.0 \times 10^2$ and $b = 3.8 \times 10^4$ (———), experimentally found (×) (Table II).

Table I. Observed and Calculated pH Dependence of the Pseudo-First-Order Rate Constants for the Anation Reaction[a]

pH	k_{calcd}, sec^{-1}	k_{obsd}, sec^{-1}
0.566	4.94×10^1	5.4×10^1
0.638	4.87×10^1	4.6×10^1
0.990	4.34×10^1	4.2×10^1
1.016	4.28×10^1	3.8×10^1
1.331	3.51×10^1	3.8×10^1
1.613	2.66×10^1	2.7×10^1
1.924	1.74×10^1	1.8×10^1
2.256	9.78	9.8
3.222	1.26	1.2
3.940	0.246	0.17

[a] $[Pt(CN)_4^{2-}]_i = [Br_2]_i = 4 \times 10^{-4}$ M, $[Br^-] = 1.6 \times 10^{-2}$ M, 25°, $\mu = 1.0$; assume $pK_a = 1.6$ and the limiting value of the rate constant is 5.40×10^1 sec^{-1}.

Table II. Pseudo-First-Order Rate Constants for the Anation Reaction with Added Bromide Ion[a]

$[Br^-]$, M	pH	k_1, sec^{-1}
3.20 ($\times 10^{-2}$)	1.00	13 ($\times 10^1$)
2.56	1.00	9.8
2.24	1.00	8.6
1.92	1.00	6.5
1.60	1.00	4.8
1.28	1.00	3.4
1.12	1.00	2.8
0.96	1.00	1.9
0.80	1.00	1.7
4.00	1.90	8.4
3.20	1.90	5.9
2.40	1.90	3.4
1.60	1.90	1.9
1.28	1.90	1.1
0.96	1.90	0.73
0.80	1.90	0.56
0.64	1.90	0.38

[a] $[Pt(CN_4^{2-}]_i = [Br_2] = 8 \times 10^{-4}$ M, $\mu = 1.0$, 25°.

The temperature variation of "a" in eq 2 was determined at pH 1 over the range 15–35° with the following results (units of M^{-1} sec^{-1}): at 15°, $a = 0.41 \times 10^{-3}$ at 25°, $a = 1.2 \times 10^{-3}$; and at 35°, $a = 2.3 \times 10^{-3}$. The error in this measurement is of the order of 10%. A least-squares fit of the data resulted in $\Delta H^{\ddagger} = 15$ kcal mole^{-1} and $\Delta S^{\ddagger} = 6$ cal deg^{-1} mole^{-1}.

Discussion

In a variety of studies on reduction and replacement reactions by iodide on platinum(IV) complexes, it has been postulated that reduction is preceded by bond formation between the iodide ion and the halide ligand.[2,4,5] It seems probable that oxidation of the

$$[X-\boxed{Pt(IV)}-X]^{n-} + I^- \rightleftharpoons [X-\boxed{Pt(IV)}-X\cdots I]^{(n+1)-}$$
$$\rightleftharpoons X^- + \boxed{Pt(II)}^{n-} + XI$$

tetracyanoplatinate(II) ion by bromine goes through similar steps *in reverse order* in the formation of *trans*-dibromotetracyanoplatinate(IV) ion. On the basis of our results, we propose the following general mechanism for the formation of *trans*-$Pt(CN)_4Br_2^{2-}$ from bromine and tetracyanoplatinate(II) ion.

$$\boxed{Pt(II)}^{2-} + Br_2 \rightleftharpoons \boxed{Pt(II)}-Br_2^{2-} \quad \text{rapid} \quad (3)$$

$$\boxed{Pt(II)}-Br-Br^{2-} \rightleftharpoons H_2O-\boxed{Pt(IV)}-Br^- + Br^- \quad \text{rapid} \quad (4)$$

$$Br^- + H_2O-\boxed{Pt(IV)}-Br^- \longrightarrow Br-\boxed{Pt(IV)}-Br^{2-} + H_2O \quad (5)$$

rate-determining step

There is no evidence in our studies for the formation of a five-coordinate intermediate in the presence of added bromide *ions* which would then be oxidized to give the *trans*-dibromotetracyanoplatinate(IV) ion directly as shown below.

$$\boxed{Pt(II)}^{2-} + Br^- \rightleftharpoons Br-\boxed{Pt(II)}^{3-} \xrightarrow{Br_2} Br-\boxed{Pt(IV)}-Br^{2-} + Br^- \quad (6)$$

This possibility is excluded by the fact that the rate law term describing the acceleration by bromide is second order in bromide. Such five-coordinate adducts between bromide ions and platinum(II) complexes have been reported for positively charged and neutral platinum(II) complexes.[6] In our system, however, the charges would be expected to hinder the formation of such a species.

On the other hand, the formation of a five-coordinate adduct between a bromine *molecule* and the tetracyanoplatinate(II) ion is reasonable in light of the coordinating ability of bromine with bromide ion. Perhaps this intermediate is an adduct in which a lone pair in the d_{z^2} orbital of the platinum is donated to one end of a bromine molecule. The possibility of oxidation by a small equilibrium amount of Br^+ present in the Br_2 solution cannot be ruled out as an alternative to eq 3 and 4, however.

Whichever species is involved in the oxidation, it seems that a complex with a bromide ligand in one of the *trans* positions must result. The other bromide ion from the reduction of the bromine molecule must be free in solution to react further. Otherwise, kinetic data indicating first-order behavior in both complex and bromide ion concentration would not be found under conditions of equal bromine and tetracyanoplatinate(II) ion concentrations. Furthermore, the pH dependence of the reaction is consistent with the presence of H_2O as the ligand in the position *trans* to the bromide ligand in the platinum(IV) reactant. The pH data indicate that a protonated species reacts to form *trans*-$Pt(CN)_4Br_2^{2-}$ at a rate much greater than the corresponding unprotonated species (*trans*-$Pt(CN)_4Br(OH)^{2-}$). The rate of formation of *trans*-$Pt(CN)_4Br_2^{2-}$ from the protonated species as found in this work is $1.40 \times 10^3\ M^{-1}$ sec^{-1}. The rate of the formation of *trans*-$Pt(CN)_4Br_2^{2-}$ from $Pt(CN)_4Br(OH)^{2-}$, calculated from previous equilibrium and kinetic data, is approximately $1.4 \times 10^{-3}\ M^{-1}$ sec^{-1} under similar conditions.[1] Perchlorate ion is the only other species present in solution that could fill this sixth coordination position. It would be difficult to account for the pH dependence of the reaction if perchlorate ion were involved.

Thus, it appears that the behavior of *trans*-$Pt(CN)_4Br_2^{2-}$ in aqueous solution in the pH range of 0–9 can be understood in terms of the following three equations.

$$Pt(CN)_4Br(OH)^{2-} + Br^- \underset{k_{7r}}{\overset{k_{7f}}{\rightleftharpoons}} Pt(CN)_4Br_2^{2-} + OH^- \quad (7)$$

$$Pt(CN)_4Br(OH_2)^- + Br^- \underset{k_{8r}}{\overset{k_8}{\rightleftharpoons}} Pt(CN)_4Br_2^{2-} + H_2O \quad (8)$$

$$Pt(CN)_4Br(OH_2)^- \overset{K_9}{\rightleftharpoons} Pt(CN)_4Br(OH)^{2-} + H^+ \quad (9)$$

A summary of the rate and equilibrium constants for these reactions is given in Table III.

Table III. Summary of the Rate and Equilibrium Constants for the Reactions of *trans*-$Pt(CN)_4Br_2^{2-}$ in Aqueous 1.0 M $NaClO_4$ at 25° in the pH range 0–9

Reaction	k_f, M^- sec^{-1}	k_r, M^{-1} sec^{-1}	K_{eq}
7	1.39×10^{-3} [a]	1.02×10^{2} [b]	1.43×10^{-5} [b]
8	1.40×10^{3}	6.11×10^{-5}	2.29×10^{7} [c]
9			2.51×10^{-2}

[a] Calculated from equilibrium and kinetic data of ref 1. [b] Data from ref 1. [c] Calculated from equilibria 9 and 7, $K_8 = K_7K_9/K_{H_2O}$.

Equation 2 in the Results section presents the experimentally determined rate law for the anation of *trans*-$Pt(CN)_4Br(OH_2)^-$. A dissociative process seems reasonable for the first term. The second term must result from an acceleration of the basic reaction by the association of a bromide ion with the aquo complex. The following equations provide detailed mechanisms for the anation reaction that are consistent with each of the two terms of the experimental rate law.

(a) First term

$$Pt(CN)_4Br(OH_2)^- \rightleftharpoons Pt(CN)_4Br^- + H_2O \quad (10)$$

$$Pt(CN)_4Br^- + Br^- \longrightarrow Pt(CN)_4Br_2^{2-} \quad (11)$$

Assuming (10) is a rapid equilibrium and (11) is the rate-determining step we get the rate equation below.

$$d[Pt(CN)_4Br_2^{2-}]/dt = k_{11}K_{10}[Pt(CN)_4Br(OH_2)^-][Br^-] \quad (12)$$

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[4] A. Peloso, R. Ettore, and G. Dolcetti, *Inorg. Chim. Acta*, **1**, 307 (1967), and references therein.

[5] E. J. Bounsall, D. J. Hewkin, D. Hopgood, and A. J. Pöe, *ibid.*, **1**, 281 (1967).

[6] A. Peloso and R. Ettore, *J. Chem. Soc., A*, 2254 (1968), and references therein.

(b) Second term

$$H_2O{-}\boxed{\text{Pt}}{-}Br^- + Br^- \rightleftharpoons H_2O{-}\boxed{\text{Pt}}{-}Br\cdots Br^{2-} \qquad (13)$$

$$H_2O{-}\boxed{\text{Pt}}{-}Br\cdots Br^{2-} \rightleftharpoons \boxed{\text{Pt}}{-}Br\cdots Br^{2-} + H_2O \qquad (14)$$

$$Br^- + \boxed{\text{Pt}}{-}Br\cdots Br^{2-} \longrightarrow Br{-}\boxed{\text{Pt}}{-}Br\cdots Br^{3-} \qquad (15)$$

$$Br{-}\boxed{\text{Pt}}{-}Br\cdots Br^{3-} \rightleftharpoons Br{-}\boxed{\text{Pt}}{-}Br^{2-} + Br^- \qquad (16)$$

Assuming (13), (14), and (16) are rapid equilibria and (15) is the rate-determining step, we get the rate equation below

$$d[Pt(CN)_4Br_2{}^{2-}]/dt = k_{15}K_{13}K_{14}[Pt(CN)_4Br(OH_2)^-][Br^-]^2 \qquad (17)$$

By combining the rate equations from the two mechanisms, we arrive at the rate law for the formation of *trans*-$Pt(CN)_4Br_2{}^{2-}$ on the basis of the above detailed mechanisms (eq 2′).

$$d[Pt(CN)_4Br_2{}^{2-}]/dt = (k_{11}K_{10} + k_{15}K_{13}K_{14}[Br^-])[Pt(CN)_4Br(OH_2)^-][Br^-] \qquad (2')$$

It appears that the anation of *trans*-$Pt(CN)_4Br(OH_2)^-$ by bromide ion is subject to an acceleration by bromide ion of the same sort that was observed in the base hydrolysis of *trans*-$Pt(CN)_4Br_2{}^{2-}$.[1] A dissociative mechanism is postulated in both cases; and the association of a bromide ion with the reactant apparently shifts the equilibrium of the dissociation probably by increasing the electron density on the central metal ion. As in the case of the hydrolysis, we must consider the possibility that a redox mechanism, described previously,[2] is operative here. In the present system this possibility seems highly unlikely because such a process would only result in the formation of bromine and $Pt(CN)_4{}^{2-}$, the starting material. This should reduce the rate of reaction. The anation reaction appears to fortify our contention that a reduction of this sort does not occur in this system.

It is interesting to compare the results of this study with those of the anation of $Co(CN)_5OH_2{}^{2-}$ by halide ions.[7] In both cases a limiting SN1 mechanism is consistent with the rate law found. The term which is second order in bromide ion complicates this interpretation in the present system. The rate of formation of *trans*-$Pt(CN)_4Br_2{}^{2-}$ is much greater than the rate of formation of $Co(CN)_5Br^{3-}$. The low enthalpy of activation indicates that the difference in rates results from the instability of aquo complexes of platinum(IV).

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[7] R. Grassi, A. Haim, and W. K. Wilmarth, *Inorg. Chem.*, **6**, 237 (1967).

New Multidentate Ligands. VII. Ethylenediamine-N,N′-diacetic-N,N′-di(methylenephosphonic) Acid[1]

K. S. Rajan, I. Murase,[2] and A. E. Martell[2]

Contribution from the Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois, and Texas A&M University, College Station, Texas.

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Abstract: Synthesis, acid–base equilibria, and metal ion chelating tendencies of the new ligand, ethylenediamine-N,N′-diacetic-N,N′-di(methylenephosphonic) acid are reported. On the basis of potentiometric equilibrium measurements of hydrogen ion concentrations at 25° and ionic strength 1.00 (KNO_3), acid dissociation constants of the ligand and the equilibrium constants for the interactions of the ligand with some representative metal ions have been evaluated. Probable structures of the metal chelates formed in solution are suggested on the basis of a comparison of their stabilities with those of analogous ligands.

The synthesis and metal binding tendencies of a new class of chelating ligands containing aminophosphonate groups have been reported by Martell and coworkers.[3,4] By means of potentiometric studies, they determined the acid dissociation constants and metal chelate formation constants for the ligands nitriloaceticdi(methylenephosphonic) acid (NADMP), nitriloacetic-β-propionicmethylenephosphonic acid (NAPMP), and N,N,N′,N′-ethylenediaminetetra(methylenephosphonic)acid (ENTMP). Schwarzenbach and coworkers[5] earlier reported the relatively strong chelating tendency of the phosphonate-containing ligand nitrilodiacetic-methylenephosphonic acid for Ca(II) ion.

In this paper, the synthesis and metal chelating tendencies of the new ligand, ethylenediamine-N,N′-diacetic-N,N′-di(methylenephosphonic) acid (EDAMP), are reported.

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[2] Department of Chemistry, Texas A&M University, College Station, Texas 77843.

[3] S. Westerback and A. E. Martell, *Nature*, **178**, 321 (1956).

[4] S. Westerback, K. S. Rajan, and A. E. Martell, *J. Am. Chem. Soc.*, **87**, 2567 (1965).

[5] G. Schwarzenbach, H. Ackermann, and P. Ruchstuhl, *Helv. Chim. Acta*, **32**, 1175 (1949).