142 *J. Chem. Eng. Data* **2003,** *48,* 142−145

Complexation of *N*-Benzoyl-*N*-methyl-*N′*-phenylthiourea by Copper(II) in a Mixed Solvent System

Saeid A. Khorrami,*,† Mehdi Shafai,† and Susan K. Armstrong*

Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, UK

The stability constants for complexation of the Cu^{2+} ion with *N*-benzoyl-*N*-methyl-*N′*-phenylthiourea have been determined at different wavelengths in the range 240 to 265 nm in 0.02 mol dm^{-3} of sodium chloride as a background salt in the mixed solvent system of 75% THF + water (v/v) in the pH ranges 5.90 to 7.30 and 9.42 to 10.12 with high ligand-to-metal ratios, by a combination of spectrophotometric and potentiometric methods at 23.5 ± 0.5 °C. Our studies have shown that the ligand forms mononuclear 1:1 and 1:2 complexes with the Cu^{2+} ion. The protonation constants of the ligand were also determined.

Introduction

Pursuing our systematic study on stability constants,[1−9] we reported earlier some features of absorbance as a function of pH.[10−12] We now report an investigation in a mixed solvent system of the protonation constant of *N*-benzoyl-*N*-methyl-*N′*-phenylthiourea and the complexation of Cu(II) with this ligand by a combination of spectrophotometric and potentiometric methods.

N-Acylthioureas, although known as metal-binding ligands for some years,[13] have recently seen a resurgence of interest from groups around the world, in fields as diverse as water purification,[14] platinum group metal purification,[15] and combinatorial chemistry.[16] A quantitative study of their metal binding is therefore of considerable interest. Such studies have generally been undertaken in single solvents, but in recognition of the fact that the chemistry of these ligands is generally exploited in rather more complex systems, we have investigated copper binding in a mixed (homogeneous) solvent system.

Experimental Section

Reagents. Copper(II) sulfate pentahydrate was obtained from Fisons Scientific Equipment and used without further purification. *N*-Benzoyl-*N*-methyl-*N′*-phenylthiourea was synthesized as described in our previous work[16] and recrystalized from methanol.

Methanol, tetrahydrofuran (THF), potassium hydroxide volumetric standard, and sodium chloride were obtained from Aldrich. Perchloric acid was supplied by Riedel-De Haën. Copper(II) sulfate solutions were standardized titrimetrically against standard EDTA using fast sulfon black F as indicator.[17] Dilute perchloric acid solutions were standardized against $KHCO_3$.[18] Dilute solutions were prepared from distilled water with conductivity 1.3 ± 0.1 $\mu\omega^{-1}$.

Measurement. All measurements were carried out at 23.5 ± 0.5 °C and in 75% THF + water (by volume), because all reactants and complexes are soluble in these conditions. The ionic strength was maintained at 0.02 mol dm^{-3} with sodium chloride. The pH was measured using a Corning pH meter with a sensitivity of 0.01 units. The hydrogen ion concentration was measured with an Hmilt LIQ-glass electrode. To determine hydrogen ion concentration in the mixed solvent system, it was necessary to calibrate the electrode and pH meter.[19] Spectrophotometric measurements were performed on a UV−vis Shimadzu 1601 spectrophotometer at different wavelengths in the range 240 to 265 nm using a cell of path length 10 mm. The absorbance and pH of the solution were measured simultaneously. Absorbance, *A*, and pH were measured at a range of wavelengths for solutions containing Cu^{2+} (1×10^{-5} mol dm^{-3}) with a large excess of ligand (2×10^{-3} mol dm^{-3}) in the mixed solvent system. For each experiment, two solutions of Cu^{2+} and ligand were prepared in the above THF + H_2O mixture with the same concentration, but the ionic strength of the first was maintained with sodium chloride and that of the second with sodium chloride and potassium hydroxide. The first solution was then titrated with the second one. The pH and absorbance were measured after the addition of a few drops of titrant, and this procedure was extended up to the required pH.

Calibration of the Glass Electrode. The term pH has significance only in an aqueous medium. All pH readings taken in the mixed solvent system will hereafter be called *B* values. The *B* values obtained from the calibration solutions were converted to a quantity U_H,[20] which is defined by eq 1, where $[H^+]$ is the known stoichiometric hydrogen ion concentration of the solution, assuming 100% dissociation of the acid not only in aqueous solution but also in partially aqueous solutions, for example $HClO_4$ in water and (THF + water).

$$U_H = \frac{\text{antilog}(-B)}{[H^+]} \tag{1}$$

U_H is then a conversion factor for obtaining the hydrogen ion concentration from the pH meter reading *B* according to eq 2, and it is a function of ionic concentration and solvent composition.[21]

$$-\log[H^+] = B + \log U_H \tag{2}$$

Determination of Stability Constants and Acid Dissociation Constant. Methods based on the relationship $A = f(\text{pH})$ were employed, on account of the high

---

* To whom correspondence should be addressed. E-mail: sakhorrami@hotmail.com (S.A.K.); s.armstrong@chem.gla.ac.uk (S.K.A.).

† M.S. is of, and S.A.K. is formerly of, the Department of Chemistry, Islamic Azad University, North Tehran Branch, Tehran, Iran.

10.1021/je025585m CCC: $25.00

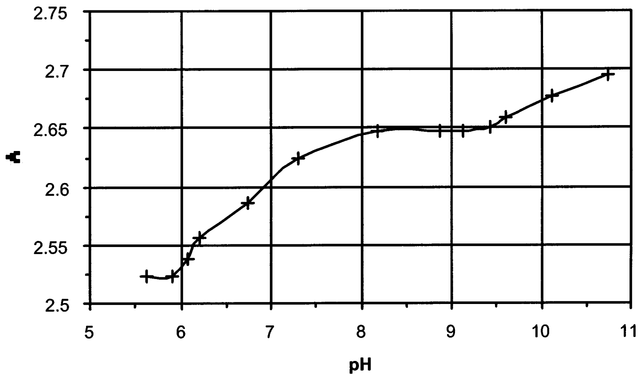
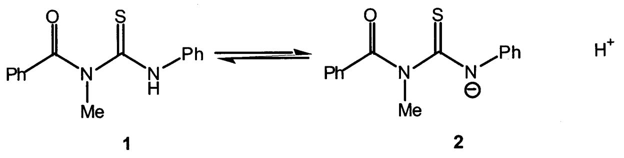


Figure 1. Absorbance A vs pH curve for Cu^{2+} + ligand **1** at 250 nm in 0.02 mol dm^{-3} of sodium chloride in the mixed solvent system.

stability of the complexes studied. Absorbance (A) and pH were measured for solutions containing a large excess of ligand at pH 5.60 to 10.74 at 23.5 ± 0.5 °C and are illustrated in Figure 1, as described below.

Results and Discussion

Protonation Equilibrium of N-Benzoyl-N-methyl-N′-phenylthiourea 1. Prior to studying the metal–ligand complexes, we determined the stability constants of protonation equilibria of the ligand in the mixed solvent system of THF + water. The equilibrium studied is given in eq 3, where L^- represents the fully dissociated ligand anion **2**;



that is

$$HL \rightleftharpoons H^+ + L^- \tag{3}$$

The protonation constant of the ligand, K_a (eq 4), has been determined using spectrophotometric and potentiometric techniques simultaneously.

$$K_a = \frac{[H^+][L^-]}{[HL]} \tag{4}$$

The absorbance at a wavelength of UV range is given by eq 5, where ϵ_0 and ϵ_1 are the molar absorptivities of the ligand **1**, HL, and ligand anion **2**, L^-, respectively.

$$A = \epsilon_0[HL] + \epsilon_1[L^-] \tag{5}$$

Equation 6 allows for the material balance,[22] where C_{HL} is the total concentration of ligand.

$$[HL] = C_{HL} - [L^-] \tag{6}$$

Thus, the protonation constant K_a for eq 3 is given by eq 7 when $n = 1$.

$$\frac{A}{C_{HL}} = \epsilon_1 + \frac{(\epsilon_0 C_{HL} - A)[H^+]^n}{K_a C_{HL}} \tag{7}$$

Considering that A is a function of pH,[10,11] the values of ϵ_0 are shown in Table 1.

Table 1. Values of the Molar Absorptivity ϵ_0 of *N*-Benzoyl-*N*-methyl-*N′*-phenylthiourea 1

λ/nm	240	245	250	255	260	265
$\epsilon_0 \times 10^{-3}$	1.009	1.091	1.221	1.354	1.455	1.513

Table 2. Values of the Molar Absorptivity ϵ_1 of the Ligand Anion 2

λ/nm	240	245	250	255	260	265
$\epsilon_1 \times 10^{-3}$	2.078	2.382	2.131	2.427	2.316	2.065

Table 3. Absorbance, A, of Solutions at Different pH Values and Wavelengths λ in THF + Water

λ /nm	pH	A	λ /nm	pH	A
240	5.9	2.0808	255	5.9	2.4738
240	6.08	2.0901	255	6.08	2.4857
240	6.21	2.1123	255	6.21	2.5151
240	7.3	2.1465	255	7.3	2.5664
245	5.9	2.4738	260	5.9	2.3517
245	6.08	2.4801	260	6.08	2.3599
245	6.21	2.494	260	6.21	2.364
245	7.3	2.5424	260	7.3	2.4242
250	5.9	2.524	265	5.9	2.0842
250	6.08	2.5377	265	6.08	2.0914
250	6.21	2.5565	265	6.21	2.1178
250	7.3	2.6239	265	7.3	2.1868

Table 4. Values of the Molar Absorptivity ϵ_2 of Cu^{2+} in the Mixed Solvent System

λ/nm	240	245	250	255	260	265
$\epsilon_2 \times 10^{-3}$	3.614	4.531	4.567	4.440	3.977	3.023

Table 5. Values of Molar Absorptivities ϵ_3 of CuL^+ in the Mixed Solvent System

λ/nm	240	245	250	255	260	265
$\epsilon_3 \times 10{-}^3$	4.156	5.211	5.252	5.106	4.574	3.476

The number of protons, n, was examined by applying eq 7. The straight line plots of A/C_{HL} against $(\epsilon_0 C_{HL} - A)[H^+]^n/C_{HL}$ with $n = 1$ thereby obtained confirmed the formation of a single anionic species. The values of ϵ_1 were determined from the intercepts of the plots and are listed in Table 2.

Through the rearrangement of eq 7, the pk_a can be calculated directly if eq 8 is considered.

$$pK_a = B + \log U_H - \log\frac{(A - \epsilon_0 C_{HL})}{(\epsilon_1 C_{HL} - A)} \tag{8}$$

The mean value of $-\log K_a$ is thus found to be 13.15 ± 0.14 at different wavelengths in the range 240 to 265 nm.

Complexation of Cu^{2+} Ion with Ligand. The method based on the relationship $A = f(pH)$ was employed,[10,11] on account of the high stability of the complex studied. Absorbance, A, and pH were measured at a range of wavelengths for solutions containing Cu^{2+} (1×10^{-5} mol dm^{-3}) with a large excess of ligand (2×10^{-3} mol dm^{-3}) at pH values in the range 5.90 to 7.30 in the mixed solvent system. The results are listed in Table 3, and representative data (for a wavelength of 250 nm) are illustrated in Figure 1.

From Figure 1, it seems very likely that a complex is formed in solution (pH 5.60 to 8.19), and the general equation for the complexation is given by eq 9, with the formation constant, K^H_{CuL}, given by eq 10.

$$Cu^{2+} + HL \rightleftharpoons H^+ + CuL^+ \tag{9}$$

$$K^H_{CuL} = \frac{[CuL^+][H^+]}{[Cu^{2+}][HL]} \tag{10}$$

Table 6. Average Values of pK^{H}_{CuL} in the Mixed Solvent System

λ/nm	240	245	250	255	260	265
pK^{H}_{CuL}	2.34 ± 0.05	2.53 ± 0.05	2.41 ± 0.04	2.11 ± 0.06	2.11 ± 0.06	1.75 ± 0.05

Table 7. Average Values of $\log K_{CuL}$ in the Mixed Solvent System

λ/nm	240	245	250	255	260	265	mean value
$\log K_{CuL}$	10.81 ± 0.14	10.62 ± 0.14	10.74 ± 0.13	11.04 ± 0.15	11.04 ± 0.15	11.04 ± 0.15	10.88 ± 0.14

Table 8. Absorbance *A* of Solutions at Different Values and Wavelengths in THF + Water

λ/nm	pH	*A*	λ/nm	pH	*A*
240	9.42	2.1926	255	9.42	2.5865
240	9.6	2.2028	255	9.6	2.6074
240	10.12	2.2183	255	10.12	2.6121
245	9.42	2.5767	260	9.42	2.4548
245	9.6	2.5863	260	9.6	2.4623
245	10.12	2.6185	260	10.12	2.4701
250	9.42	2.6499	265	9.42	2.2129
250	9.6	2.6587	265	9.6	2.2275
250	10.12	2.6771	265	10.12	2.2704

Table 9. Values of Molar Absorptivities ϵ_4 of CuL_2 in the Mixed Solvent System

λ/nm	240	245	250	255	260
$\epsilon_4 \times 10^{-3}$	4.571	5.732	5.777	5.616	5.031

Table 10. Average Values of pK^{H}_{CuL2} in the Mixed Solvent System

λ/nm	240	245	250	255	260
pK^{H}_{CuL2}	5.32±0.06	5.55±0.06	5.45±0.05	5.34±0.04	5.09±0.05

The absorbance of Cu^{2+} and ligand at wavelengths in the UV range is given in the pH range 5.90 to 7.30 by eq 11, where ϵ_2 and ϵ_3 are the molar absorptivities of Cu^{2+} and complex, respectively.

$$A = \epsilon_0[HL] + \epsilon_1[L^-] + \epsilon_2[Cu^{2+}] + \epsilon_3[CuL^+] \quad (11)$$

The mass balance is then given by eqs 12 and 13, where C_{Cu} and C_{HL} are the total concentrations of Cu^{2+} and ligand, respectively.

$$[Cu^{2+}] = C_{Cu} - [CuL^+] \quad (12)$$

$$[HL] = C_{HL} - [L^-] - [CuL^+] \quad (13)$$

The molar absorptivity of Cu^{2+}, ϵ_2, can be calculated from these equations individually; the values are given in Table 4.

Thus, the formation constant of eq 10 is given by eq 14, where K_1 and α are defined by eqs 15 and 16, respectively.

$$K^{H}_{CuL} = \frac{(A + k_1(-\epsilon_0 - \epsilon_1\alpha) - \epsilon_3 C_{Cu})[H^+]}{(k_1(\epsilon_0 + \epsilon_1\alpha) + \epsilon_3 C_{Cu} - A)k_1} \quad (14)$$

$$k_1 = \frac{C_{HL}(\epsilon_3 - \epsilon_2) - A + \epsilon_2 C_{Cu}}{(\epsilon_3 - \epsilon_2 - \epsilon_1) - \alpha(\epsilon_3 - \epsilon_2 - \epsilon_1)} \quad (15)$$

$$\alpha = \frac{K_a}{[H^+]} \quad (16)$$

The molar absorptivity of CuL^+, ϵ_3, was calculated from the data in the pH range 5.90 to 7.30 with eqs 14−16, for an excess of the ligand. The method of calculation was described in previous papers.[1−9] The values of ϵ_3 are listed in Table 5.

The method of determination of the average ligand number was previously described.[3−9] Calculation shows that the average ligand number $n = 0.97$. Thus, at this range of pH, the ligand forms a mononuclear 1:1 complex with Cu^{2+}, and the formation constant, K^{H}_{CuL}, can be calculated from eqs 14−16. The average values of pK^{H}_{CuL} at different wavelengths are listed in Table 6.

Considering eq 17, the stability constant of the complex, K_{CuL}, can be calculated from eq 18, and the average values at different wavelengths are shown in Table 7.

$$Cu^{2+} + L^- \rightleftharpoons CuL^+ \quad (17)$$

$$K_{CuL} = K^{H}_{CuL}{K_a}^{-1} \quad (18)$$

Above pH 9.13, a second increase in absorbance was observed (cf Figure 1). Absorbance and pH were measured for solutions containing Cu^{2+} (1×10^{-5} mol dm^{-3}) with a large excess of ligand (2×10^{-3} mol dm^{-3}) in the pH range 9.42 to 10.12 in the mixed solvent system. The results are listed in Table 8.

This second increase is attributed to the formation of another species, which is given by eq 19, with the formation constant, K^{H}_{CuL2}, expressed by eq 20.

$$CuL^+ + HL \rightleftharpoons CuL_2 + H^+ \quad (19)$$

$$K^{H}_{CuL2} = \frac{[CuL_2][H^+]}{[CuL^+][HL]} \quad (20)$$

The formation constant of eq 19 was determined in the usual manner, as shown in eq 21, where k_2 is defined by eq 22.

$$K^{H}_{CuL2} = \frac{(A + k_2(-\epsilon_0 - \epsilon_1\alpha) - \epsilon_3 C_{Cu})[H^+]}{(k_2(\epsilon_o + \epsilon_1\alpha) + \epsilon_4 C_{Cu} - A)k_2} \quad (21)$$

$$k_2 = \frac{C_{HL}(\epsilon_4 - \epsilon_3) - \epsilon_4 C_{Cu} - A + 2\epsilon_3 C_{Cu}}{(\epsilon_4 - \epsilon_3 - \epsilon_0) + \alpha(\epsilon_4 - \epsilon_3 - \epsilon_1)} \quad (22)$$

In eq 22, K^{H}_{CuL2} is the formation constant of eq 20 and ϵ_4 is the molar absorbtivity of CuL_2, calculated with eqs 16, 21, and 22, for an excess of the ligand and in the usual pH range. The values of ϵ_4 are listed in Table 9.

Calculation shows that the average ligand number $n = 1.90$. Thus, the ligand forms a mononuclear 1:2 complex with Cu^{2+} whose formation constant, K^{H}_{CuL2}, can be calculated from eqs 16, 21, and 22 at this range of pH. The average values at different wavelengths are listed in Table 10.

Table 11. Average Values of $\log K_{CuL2}$ in the Mixed Solvent System

λ/nm	240	245	250	255	260	mean value
$\log K_{CuL2}$	18.64 ± 0.14	18.22 ± 0.15	18.44 ± 0.16	18.85 ± 0.15	19.01 ± 0.16	18.63 ± 0.15

Considering eq 23, the stability constant of the 1:2 complex can be calculated from eq 24.

$$CuL^+ + L^- \rightleftharpoons CuL_2 \qquad (23)$$

$$K_{CuL2} = K^{H}_{CuL} K^{H}_{CuL2} \cdot K_a^{-2} \qquad (24)$$

The average values at different wavelengths are listed in Table 11.

Conclusions

In this work, equations for the equilibria between ($Cu^{2+} + L^-$) and (CuL^+), and between ($CuL^+ + L^-$) and (CuL_2), typical of many processes, were defined in the mixed solvent system. The two complexes, CuL^+ and CuL_2, are made in the pH ranges 5.90 to 8.19 and 9.13 to 10.74, respectively, but these two complexes are calculated in the pH ranges 5.90 to 7.30 and 9.42 to 10.12, respectively, because it is assumed that their curves are linear in these ranges. Finally, the average values of log K_{CuL} and log K_{CuL2} are 10.88 ± 0.14 and 18.63 ± 0.15, respectively.

Literature Cited

(1) Khorrami, S. A.; Gharib, F.; Zare, K.; Aghai, H. Determination of the Stability Constant of Vanadium(V) with Alanine. *Iranian J. Chem. Chem. Eng.* **1992**, *11*, 19−24.

(2) Gharib, F.; Zare, K.; Khorrami, S. A. Themodynamic Studies on Complexation of Dioxyvanadium(V) with Serine. *J. Chem. Eng. Data* **1993**, *38*, 602−604.

(3) Khorrami, S. A.; Gharib, F. Determination and Comparison of Stability Constants of Vanadium(V) with Serine And Threonine Complexes. *Russ. J. Inorg. Chem.* **1995**, *40*, 486-491.

(4) Gharib, F.; Zare, K.; Khorrami, S. A. Stability Constants of Vanadium(V) with Glycine and Alanine in Acid Solution. *J. Chem. Eng. Data* **1995**, *40*, 186−189.

(5) Gharib, F.; Zare, K.; Khorrami, S. A.; Behju, A. Complex Formation between Aspartic Acid and Molybdenum(VI). *J. Chem. Eng. Data* **1995**, *40*, 1214−1216.

(6) Khorrami, S. A.; Bayat, H.; Sharifi, S.; Gharib, F. Stability Constant of Vanadium(V) with Glycine at Different Ionic Strengths. *J. Chem. Eng. Data* **1996**, *41*, 1322−1324.

(7) Khorrami, S. A.; Khosrari, M.; Gharib, F.; Shafai, M. Ionic Strength Dependence of Stability Constant. Part 2: Spectrophotometric Study of the Dioxyvanadium + Leucine System in the range 0.1 ≤ I ≤ 1.0. *Ind. Acad. Sci. (Chem. Sci.)* **1997**, *109*, 167−171.

(8) Gharib, F.; Khorrami, S. A.; Sharifi, S. Complex Formation between Glutamic Acid and Molybdenum(VI). *Ind. Acad. Sci. (Chem. Sci.)* **1997**, *109*, 71−77.

(9) Khorrami, S. A.; Motiei, F.; Shafai, M. Ionic Strength Dependence of Stability Constant. Part 3: Spectrophotometric Study of the Uranyl + Alanine in the range 0.1−0.8 mol dm^{-3} from $NaClO_4$. *Iranian J. Chem. Chem. Eng.* in press.

(10) Beck, M. T.; Nagypal, I. *Chemistry of complex equilibria*; Van Nosstrand Reinhold Company Ltd.: London, 1990; p 134.

(11) Itoh, J. I.; Yotsuyanagi T.; Aomura, K. Spectrophotometric Determination of the Stability Constant and Acid Dissociation Constant of the Vanadium(V)-cyclohexanediaminetetraacetate Complex. *Anal. Chim. Acta* **1975**, *76*, 471−476.

(12) Connors, K. A. *Binding Constants, The Measurement of Molecular Complex Stability*; John Wiley & Sons: New York, 1987; p 141.

(13) Siddhanta, S. K.; Banerjee, S. N. Complex Compounds of Substituted Thioureas. Part I. Copper Derivatives of N−Acetylthiourea, S−Acetylthiourea and N−Phenylthiourea. *J. Indian Chem. Soc.* **1961**, *38*, 747−752. Banerjee, S. N.; Sukthankar, A. C. Complex Compounds of Substituted Thioureas. Part V. Silver Derivatives of Mono- and Di-N-acetyl- and -phenylthioureas and Mercury(II) Derivatives of N-Acetyl and Di-N-Phenylthiourea. *J. Indian Chem. Soc.* **1963**, *40*, 573−577. Richter, R.; Beyer, L.; Kaiser, J. Crystal and Molecular Structure of bis(1,1-Diethyl-3-benzoylthioureato)copper(II). *Z. Anorg. Allg. Chem.* **1980**, *461*, 67−73. Braun, U.; Richter, R.; Sieler, J.; Yanovski, A. I.; Struchkov, Y. T. Crystal and Molecular Structure of tris(1,1-Diethyl-3-benzoylthiourea)silver(I) hydrogensulfide. *Z. Anorg. Allg. Chem.* **1985**, *529*, 201−208.

(14) Ringmann, S.; Schuster, M. Removal of Heavy Metals from Aqueous Solutions Containing Complexing Agents by Precipitation with Acylthioureas. *Chem. Technol.* **1997**, *49*, 217−226. Visser, A. E.; Swatloski, R. P.; Reichert, W. M.; Mayton, R.; Sheff, S.; Wierzbicki, A.; Davis, J. H.; Rogers, R. D. Task-specific Ionic Liquids for the Extraction of Metal Ions from Aqueous Solutions. *Chem. Commun.* **2001**, 135−136.

(15) Koch, K. R. New Chemistry with Old Ligands: N−Alkyl- and N, N.-Dialkyl-N′-acyl(aroyl)thioureas in Coordination, Analytical and Process Chemistry of the Platinum Group Metals. *Coord. Chem. Rev.* **2001**, *216*, 473−488. Koch, K. R.; Sacht, C.; Grimmbacher, T.; Bourne, S. New Ligands for the Platinum Group Metals: Deceptively Simple Coordination Chemistry of N-Aceyl-N′-alkyl- and N-Acyl-N′,N′-dialkyl-thioureas. *South Afr. J. Chem.* **1995**, *48*, 71−77.

(16) Armstrong, S. K.; Quéléver, G.; Marr, I. L.; Ritchie, A. L. Cross-Referenced Combinatorial Libraries for the Discovery of Metal-Complexing Ligands: Library Deconvolution by LC-MS. *Analyst* **2000**, *125*, 2206−2215.

(17) Vogel, A. I. *A Text Book of Quantitative Inorganic Analysis*, 3rd ed.; Longman: Harlow, U.K., 1961; p 441.

(18) Lagrange, J.; Aka, K.; Lagrange, P. Kinetic Study of Acid Dechelation of some Vanadium(V)-amino-carboxylate Complexes in Aqueous Solution. *J. Chem. Soc., Dalton* **1984**, 239−243.

(19) Avdeef, A.; Comer, J. E. A.; Thomson, S. pH Metric Log. 3. Glass Electrode Calibration in Methanol Water, Applied to pK_a Determination of Water-Insoluble Substances. J. *Anal. Chem.* **1993**, *65*, 42−49.

(20) Bates, R. G. *Determination of pH*, 2nd ed.; John Wiley & Sons: New York, 1973; p 211.

(21) van Uitert, L. G.; Hass, C. G. Studies on Coordination Compounds. I. A Method for Determination of Thermodynamic Equilibrium Constants in Mixed Solvent. *J. Am. Chem. Soc.* **1953**, *75*, 451−457.

(22) Rossotti, F. J. C.; Rossotti, H. *The Determination of Stability Constants*; McGraw-Hill: New York, 1961; p 38.

Received for review July 15, 2002. Accepted October 28, 2002.

JE025585M