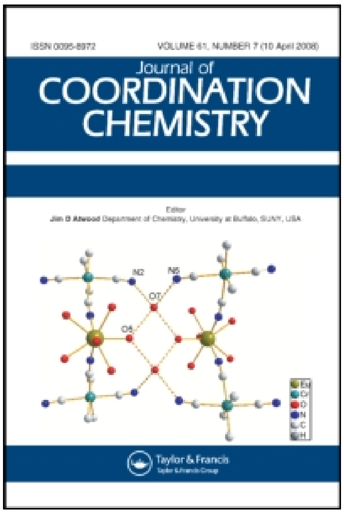

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S. H. Mehdi[a]; B. W. Budesinsky[a]
[a] Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada

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PROTONATED METAL COMPLEXES OF DIETHYLENETRIAMINEPENTAACETIC ACID (DTPA)

S. H. MEHDI† and B. W. BUDESINSKY[1]

Department of Chemistry, University of Waterloo
Waterloo, Ontario, Canada N2L 3P7

Spectrophotometric studies in acidic solutions with pH between 1.10 and 1.80, show the presence of tetraprotonated complexes, MH_4L, of Co(II), Cu(II) and Fe(III) with DTPA. Under identical conditions, Ni(II) forms the complex NiH_2L.

The effective and overall stability constants of these complexes are determined.

INTRODUCTION

The metal complexes of DTPA have been well characterized over the past two decades. A number of metal ions are known to form complexes of high stability with this ligand.[2] In addition to the simple ML and M_2L complexes, protonated species MHL and MH_2L have been reported in solution[3–6]. Solid complexes with one, two and three hydrogens in the stoichiometry have also been isolated from acidic solutions[7,8]. By spectrophotometric methods, we have shown the formation of complexes MH_4L, where M is cobalt(II), copper(II) or iron(III), in solutions with pH between 1.10 and 1.80. The nickel(II) complex seems to resist protonation forming NiH_2L under the same conditions.

EXPERIMENTAL

DTPA (Aldrich Chemical Co., Milwaukee, Wis., U.S.A.) was recrystallized from hot water twice and dried at 80°C for an hour and a half before being used. The recrystallized acid melted at 221°C. Standard solutions of DTPA were made by dissolving the acid in dilute alkali and standardising with lead nitrate and xylenol orange. The solutions of the metal perchlorates of cobalt(II), copper(II), nickel(II) and iron(III) (G. F. Smith & Co., Columbus, Ohio, U.S.A.), were prepared and standardized by accepted procedures. Acidity of solutions in the pH range 1-2, was maintained by hexamine-perchloric acid buffers[9]. The ionic strength of these solutions that were made up using these buffers was 0.1_0.

Absorbance measurements were made on a Cary model 14 recording spectrophotometer with 10.0 mm or 50.0 mm fused quartz cells. The cell compartments were thermostated at 25°C. pH measurements were made on a Cambridge portable pH meter (Cambridge Instruments Co., London, England.) fitted with glass (GHS23 EIL,pH range 0-14, Electronic Instruments, Surrey, England) and calomel electrodes. Absorbance and pH measurements were made after the prepared sample solutions were placed in a thermostated water bath at 25°C for about a half hour. The sequence in the preparation of all sample solutions was: buffer, metal-ion and ligand. Absorbance of the solutions was measured against a buffer blank. Solubility of DTPA in saturated solutions (25°C) at different acidities was determined by titration with standard thorium nitrate using azonol[10] as the indicator. The metal to ligand ration in the complex was determined by the method of continuous variations[11].

THEORETICAL

The effective stability constant for the formation of the complex M_mL_n is given by

$$k_{mn} = c(c_M - mc)^{-m} (c_L - nc)^{-n}$$

where c is the actual concentration of the complex,

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†Author to whom correspondence should be addressed.

TABLE I (a,b)

a) Acidity constants[15, 16], k_n for DTPA. $k_n = \frac{[H_nL]}{[H_{n-1}L][H]}$

b) Values of log $\alpha_{L(H)}$ and $\bar{n}_H$ as a function of pH, calculated from the above acidity constants.

(a)	log k_1	log k_2	log k_3	log k_4
	10.58	8.60	4.27	2.64
	log k_5	log k_6	log k_7	log k_8
	2.2	1.5	0.7	-0.1

	pH	log $\alpha_{L(H)}$	$\bar{n}_H$
(b)	1.00	24.29	6.12
	1.10	23.69	5.99.
	1.20	23.10	5.86
	1.30	22.52	5.73
	1.40	21.95	5.60
	1.50	21.40	5.46
	1.70	20.33	5.18
	1.80	19.82	5.03
	1.90	19.33	4.87
	2.00	18.85	4.72

c_M, c_L are the total concentrations of M, L respectively and m,n denote the stoichiometry of the complex. The absolute values of m,n and the value of k_{mn} were determined by the method of stoichiometric dilution[12,13].

For a complex with the degree of protonation j, *i.e.*, for the complex $M_mH_jL_n$, the overall stability constant β_{mjn} will be given by the relations

$$\beta_{mjn} = c[M]^{-m}[H]^{-j}[L]^{-n} = k_{mn}\,\alpha_{L(H)}^{n}[H]^{-j} \qquad (1)$$

where $\alpha_{L(H)}$ is the side reaction coefficient of the ligand with protons[13,14], the bracketed terms refer to the respective concentrations and c again denotes the concentration of the complex. The side reaction coefficients of the metal need not be considered since under the conditions of our determinations, there is no hydrolysis of metal ions and the buffer-metal ion interactions are negligible. Values of $\alpha_{L(H)}$ as a function of pH have been calculated for DTPA using previously determined[15,16] acidity constants. These values, as well as those of $\bar{n}_H$, the average number of hydrogens bound to the ligand[14], are shown in Table 1.

Linear algebraic transformation of Eq. 1, gives the Budesinsky and Haas relations (Eq. 2) which can be used to determine the degree of protonation j, of the complex[17]

$$\text{Log } k_{mn} + n \log \alpha_{L(H)} = \log \beta_{mjn} - j\,\text{pH} \quad (2)$$

If there is a range of pH in which just one protonated form of the complex is exclusively formed, then it follows from the above relation that a plot of log k_{mn} + n log $\alpha_{L(H)}$ against pH should be linear and that the negative slope of the line should give j. The overall stability constant can then be determined from equation 1 or from the extrapolated intercept on the ordinate axis of the Budesinsky and Haas plot, when pH is zero. Deviations from linearity indicate the presence of more than one protonated species in that region of acidity.

RESULTS AND DISCUSSIONS

The value of $\bar{n}_H$ for DTPA (Table 1) becomes 5.0 between pH 1.80–1.85. This corresponds to the neutral H_5L species. Increasing the acidity leads to further protonation and increases in the value of $\bar{n}_H$. This is experimentally borne out by the solubility of DTPA as a function of pH (Figure 1), which shows a minimum around pH = 1.85 and a sharp rise thereafter as the pH is decreased. Thus in the pH region from 1.10 to 1.80, the region of our studies, hydrogen ions in solution will compete strongly with the metal ions for sites on the ligand. A high degree of protonation of the metal complex must result under these conditions.

Continuous variation curves for all the metal ions studied, indicated the presence of only 1:1 species below pH = 3. Increasing the pH above this value resulted in shifts and irregularities in the extremum values of $x = (c_L/(c_L + c_M))$, indicating the presence

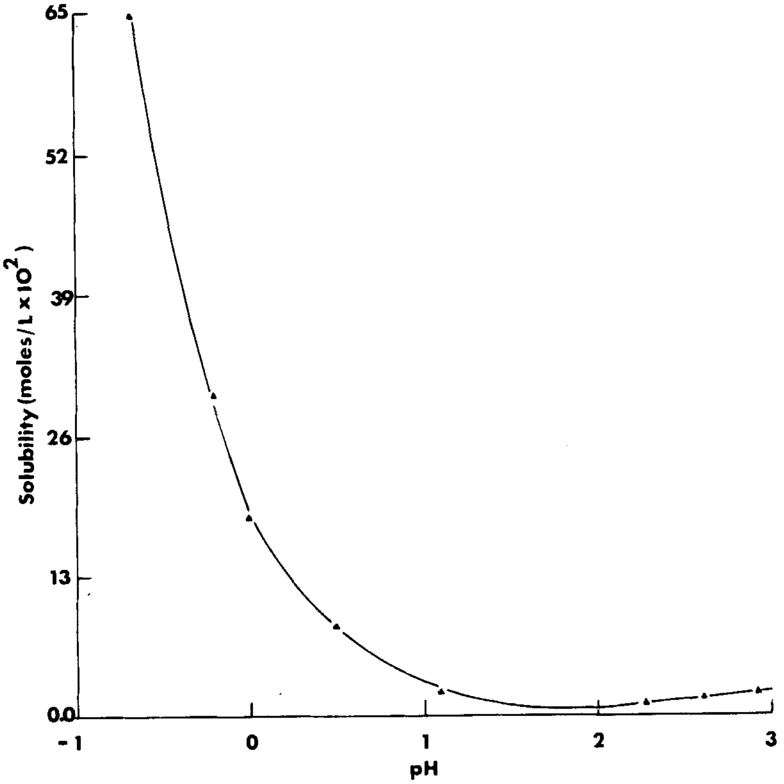

FIGURE 1 The solubility of DTPA as a function of pH. The negative values refer to the Hammett Function H°.

TABLE II
Effective and overall stability constants of protonated metal complexes of DTPA at 25°C and $\mu = 0.1_0$

Metal ion	wave-length (nm.)	pH	m/n	m+n	log k_{mn}	log $\alpha_{L(H)}$	slope[a]	j	log β_{mjn} (average)	complex
Cu(II)	710	1.10	1	2	4.05	23.68	-3.76	4	32.25	CuH_4L
		1.27	1	2	4.49	22.68				
		1.55	1	2	4.93	21.12				
Co(II)	530	1.32	1	2	2.46	22.40	-3.83	4	30.18	CoH_4L
		1.56	1	2	2.81	21.41				
		1.77	1	2	3.16	19.98				
Fe(III)	300	1.10	1	2	6.28	23.68	-4.23	4	34.27	FeH_4L
		1.32	1	2	6.55	22.40				
		1.59	1	2	6.94	20.91				
Ni(II)	600	1.14	1	2	3.13	23.45	-2.01	2	28.85	NiH_2L
		1.30	1	2	3.71	22.52				
		1.56	1	2	4.60	21.07				

[a] slope from the Budesinsky–Haas plot determined by least-squares analysis.

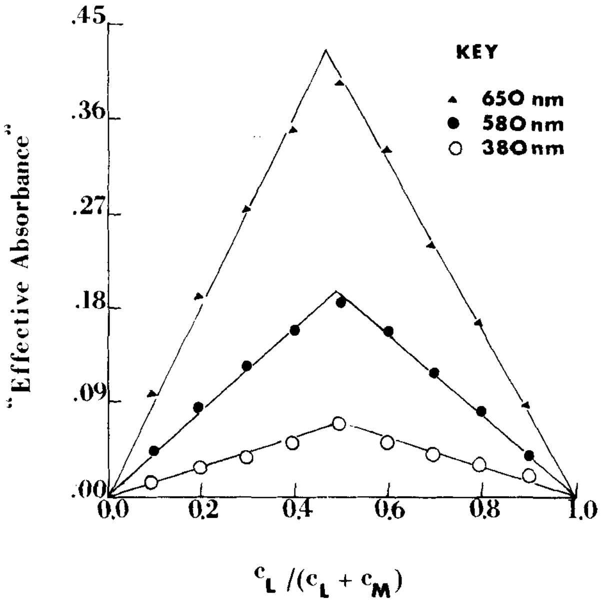

FIGURE 2 Continuous variations for Cu(II)–DTPA at pH = 1.10. $C_L + C_M = 2 \times 10^{-2} M$.

of a mixture of presumably 1:1 and 2:1 complexes. Representative continuous variation curves for the copper(II)-DTPA system are shown in Figure 2.

Results of the determination of k_{mn} by the stoichiometric dilution method and the determination of j and β_{mjn} from the Budesinsky-Haas plot are summarised in Table II. For the divalent ions the order of the effective stability constants follows the Irving-Williams series. The type of complex is seen to be MH_4L when M is cobalt(II), copper(II) or iron(III), while it is MH_2L for nickel(II). It may be noted that the value of log β_{121} determined for the NiH_2L complex is in very good agreement with the value of 28.89 previously determined by Chaberek and coworkers[4a].

In view of the high acidities of the solutions in which our studies were conducted, the tetradentate behaviour of DTPA in the MH_4L complexes is not unexpected. This is especially so in case of the copper(II) complex owing to the high susceptibility of that ion to the Jahn-Teller effect. Since there is no reason to suspect any deviation from the regular hexacoordinate behaviour of these metal ions, it might be surmised that water molecules will occupy the uncoordinated fifth and sixth positions on the metal ion.

There seem to be two major reasons for the hexadentate nature of DTPA in the nickel(II) complex even in strongly acidic solutions. One is the low tendency of the ion to the Jahn–Teller effect and the other is the very weak interaction between nickel(II) and water molecules. This weakness of the nickel(II)-H_2O bond is reflected in the pK_a values of the reaction.

$$M(H_2O)_n^x + \rightleftharpoons [M(H_2O)_{n-1}OH]^{(x-1)^+} + H^+$$

The pK_a's for various metal ions are: Co(II) 8.9; Cu(II) 6.8; Fe(III) 0.7 and Ni(II) 10.6[2]. It is to be expected that this interaction will be even weaker in the presence of DTPA. The hexadentate NiH_2L seems thus to be favoured over the possible $NiH_4L \cdot 2H_2O$.

In view of the high acidity[4a] and high stability of these protonated DTPA chelates, the possibility of sharing of ligand sites between protons and metal ions must be ruled out. Rather, protonation must result in the rupture of the metal-ligand bond. Protonation of metal chelates, as Beck[18] has pointed out, can be a convenient way of increasing the reactivity of the chelate towards substitution or oxidation-reduction reactions.

Protonation of cobalt(II)-DTPA can be effectively utilised, for example, in the oxidation to cobalt(III)-DTPA which forms the basis for one of the proposed methods for the determination of cobalt by DTPA[19].

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