18.7 kK) to a separation of *xz*, *yz* orbitals, our epr results are very hard to reconcile with this hypothesis. In an axial system, the shift in the *g* values from the free electron value, 2.0023, is related to the energy levels by

$$\Delta g_{\parallel} = \frac{8\alpha^2\beta^2\lambda}{E_{x^2-y^2}} \text{ and } \Delta g_{\perp} = \frac{2\alpha^2\gamma^2\lambda}{E_{xz,yz}}$$

where α, β, and γ are modified molecular orbital coefficients of the xy, $x^2 - y^2$, and xz, yz orbitals, respectively, λ is the spin-orbit coupling constant, and E_j is the energy of orbital j measured from the ground-state orbital, xy. For the benzilate complex, if we choose $E_{x^2-y^2} = 11.8$ kK and $E_{xz,yz} = (16.7 + 18.5)/2 = 17.6$ kK to fit the above energy level scheme, and reasonably assume $\beta^2/\gamma^2 = 0.8$, we calculate $\Delta g_{\parallel}/\Delta g_{\perp} = 4.8$ in contrast to the experimental value 2.8 ± 0.6. Each of the two other proposed assignments [$xy \rightarrow yz$, $x^2 - y^2$, xz, z^2 (for bands 1–4, respectively)[2] or $xy \rightarrow xz \sim yz$ (first band), $x^2 - y^2$ (second), z^2 (third), and charge transfer (fourth)[6]] produces a calculated $\Delta g_{\parallel}/\Delta g_{\perp}$ within the observed range, 2.8 ± 0.6. At present, particularly as we lack information on the in-plane anistropy, we cannot choose between these two possibilities.[24]

---

(24) NOTE ADDED IN PROOF. Another vanadium compound is reported[25] to exhibit a 15-line epr spectrum in solution, and similarly an 11-line spectrum probably characteristic of triplet-state dimers has been observed[26] in solutions of molybdenum(V) glutathione enriched in ^{95}Mo. We have also found $Na_4[Cu_2$(*d*-tartrate)(*l*-tartrate)$]\cdot10H_2O$ to be binuclear and to exhibit epr evidence of a triplet state similiar to that reported here[27]

(25) C. H. Wirguin and J. Selbin, *J. Inorg. Nucl. Chem.*, 30, 3181 (1968).

(26) T. Huang and G. P. Haight, private communication.

(27) N. D. Chasteen and R. L. Belford, to be submitted for publication.

Thermodynamics of Ion Association. XIX. Complexes of Divalent Metal Ions with Monoprotonated Ethylenediaminetetraacetate[1a]

A. P. Brunetti, G. H. Nancollas,[1b] and P. N. Smith[1c]

Contribution from the Chemistry Department, State University of New York at Buffalo, Buffalo, New York 14214. *Received February 10, 1969*

Abstract: Free energy and enthalpy changes accompanying the protonation of divalent metal–ethylenediaminetetraacetate complexes in the reaction $MY^{2-} + H^+ \rightleftharpoons MHY^-$, where H_4Y represents EDTA, have been measured potentiometrically and calorimetrically at 25° and at an ionic strength maintained at 0.10 *M* with potassium nitrate. The metal ions investigated were Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+}. The data are discussed in terms of the extent of coordination of the multidentate ligand with the metal ions, and comparisons are made with the corresponding thermodynamic functions for the formation of related metal complexes.

There is considerable interest in the structures of aqueous metal complexes involving the EDTA anion. In the absence of any unequivocal method for their determination, they have generally been inferred from free energy, kinetic, and spectral measurements. In the solid state, Hoard and his coworkers[2–6] have used X-ray methods to determine the structures of a number of metal–EDTA complexes. Invariably the ligand was bound in a sexadentate structure, and no evidence was found for the presence of an uncomplexed acetate residue. Additional water molecules were bound in the manganous[2] and ferric[3,4] species in seven-coordinate structures. X-Ray studies of the crystalline protonated complexes $Co(OH_2)YH_2$ and $Ni(OH_2)YH_2$ revealed the presence of one unchelated acetate residue with the ligand bound in a quinquedendate manner.[5,6]

In solution, the structures of the EDTA complexes are uncertain. The similarity of the acid dissociation constants[7] of the protonated complexes, $M(OH_2)YH^-$, of a large number of metal ions led Higginson[8] to conclude that this corresponded to the protonation of a free acetate arm and to propose quinquedentate coordination in $M(OH_2)Y^{2-}$ in every case except, perhaps, for manganese(II). On the other hand, the marked changes in the visible spectrum accompanying the protonation of CuY^{2-} and CoY^{2-}[9] indicated that these complexes contain at least a proportion of six-coordinated species. The results of a recent kinetic study,[10] in which cobaltous EDTA solutions at various acidities were allowed to react with rapid outer-sphere oxidants to form the cobatic complex, also indicated the presence

---

(1) (a) Presented in part at the 23rd Calorimetry Conference, Midland, Mich., Aug 13–15 1968. Supported by National Science Foundation Grants No. GP-6042 and -9231. (b) To whom all correspondence regarding this paper should be addressed. (c) Presently Postdoctoral Fellow at the Argonne National Laboratory, Chemical Engineering Division, Argonne, Ill.

(2) S. Richards, B. Pedersen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, 3, 27 (1964).

(3) J. L. Hoard, G. S. Smith, and M. D. Lind in "Advances in the Chemistry of Coordination Compounds," The Macmillan Co., New York, N. Y., 1961.

(4) M. J. Jamor, T. A. Hamor, M. D. Lind, and J. L. Hoard, *Inorg. Chem.*, 3, 34 (1964).

(5) G. S. Smith and J. L. Hoard, *J. Am. Chem. Soc.*, **81**, 556 (1959).

(6) J. L. Hoard, Proceedings of the 8th International Conference on Coordination Chemistry, V. Gutman, Ed., Springer-Verlag, Vienna, 1964, p 135.

(7) G. Schwarzenbach, R. Gut, and G. Anderegg, *Helv. Chim. Acta*, 37, 937 (1954).

(8) W. C. E. Higginson, *J. Chem. Soc.*, 2761 (1962).

(9) T. R. Bhat and M. Krishnamurthy, *J. Inorg. Nucl. Chem.*, 25, 1147 (1963).

(10) R. G. Wilkins and R. E. Yellin, *J. Am. Chem. Soc.*, **89**, 5946 (1967).

of a six-coordinate $Co^{II}Y^{2-}$ to a greater extent than $Co^{II}Y(H_2O)^{2-}$ in the cobaltous solutions. At pH $\geqslant 4.5$ the former species was estimated to be present in an 80% excess as compared with the latter. More recently, Yasuda[11] has reported the results of a viscosity study of aqueous solutions of a number of metal complexes. The markedly smaller *B* coefficient for the cobaltic complex $Co^{III}EDTA^-$ (0.41) as compared with $Co^{II}EDTA^{2-}$ (0.85) was interpreted as indicating the presence of a substantial amount of pentacoordinated species in the latter. There are, however, other factors to be considered; a relatively greater degree of solvent orientation by the higher charged $Co^{II}EDTA^{2-}$ would also contribute to the observed difference in *B* coefficients.

The free energy changes accompanying the formation of MY^{2-} and MHY^- are well established,[7] and the enthalpy changes for the formation of MY^{2-} have also been determined.[12-14] In the present work, calorimetric studies have been made of the protonation of MY^{2-} in order to gain more information about the structures of the species in solution.

Experimental Section

Materials. Grade A glassware and reagent grade chemicals were used, and solutions were prepared with doubly distilled water; carbon dioxide was excluded by bubbling with nitrogen gas. Ethylenediaminetetraacetic acid was purified by twice dissolving in potassium hydroxide and precipitating with nitric acid; the solid was washed with water and dried. The metal nitrate solutions were analyzed by titration with standard EDTA and also by exchanging the cations for hydrogen ions on a Dowex 50 ion-exchange resin column and titrating the liberated nitric acid with standard potassium hydroxide solution.

Potentiometric Measurements. Emf measurements were made at 25° with the cell

glass electrode|solution under study|saturated $KCl|Hg_2Cl_2Hg$

using small-diameter Beckman glass electrodes (Type 39167) and a Beckman Research pH meter (Model 11019). The cells were standardized before and after each experiment with NBS standard buffer solutions prepared according to Bates:[15] 0.05 *M* potassium hydrogen phthalate, pH 4.008, and 0.09 *M* potassium chloride + 0.01 *M* hydrochloric acid, pH 2.07. pH ($= -\log a_{H^+}$) values were converted to hydrogen ion concentration by using an f_{H^+} activity coefficient value, 0.7815, calculated from the Davies[16] modification of the Debye-Hückel equation.

Calorimetric Measurements. The differential calorimeters have been described in some detail.[17-19] Modified calibration heater coils were wound from No. 30 Evanohm resistance wire (Wilbur B. Driver Co., Newark, N. J.) and protected from the calorimetric solutions with silver thimbles whose outer surfaces were gold plated. Temperatures were read directly to 10^{-4}° using quartz differential thermometers (Hewlett-Packard, Model 2801A) with output fed through a digital-analog converter (Hewlett-Packard, Model 580 A) to a chart recorder (Varian, Model G 4000).

In typical experiments, 1:1 mixtures of metal nitrate and EDTA solutions (5-10 × 10^{-3} *M* with sufficient potassium nitrate to give an ionic strength of 0.10 *M*) were placed in the calorimeters, allowed to equilibrate overnight at 25 ± 0.002°, and titrated with small volumes of nitric acid (0.15 *M*) at the same temperature. Each addition produced temperature changes of about 2 × 10^{-3}°. Parallel experiments were made of the heat of mixing of the nitric acid solution with 0.10 *M* potassium nitrate; the corrections were found to be negligible.

Results and Discussion

In the solutions containing metal ions, the following equilibria are of importance.

$$H_2Y^{2-} \rightleftharpoons HY^{3-} + H^+ \tag{1}$$

$$HY^{3-} \rightleftharpoons Y^{4-} + H^+ \tag{2}$$

$$M^{2+} + Y^{4-} \rightleftharpoons MY^{2-} \tag{3}$$

$$MY^{2-} + H^+ \rightleftharpoons MHY^- \tag{4}$$

Thermodynamic data for reactions 2, 3, and 4 can also be expressed in terms of ion association of the metal cation and protonated EDTA anion.

$$M^{2+} + HY^{3-} \rightleftharpoons MHY^- \tag{5}$$

The pH ranges and concentrations studied were such that further protonation of EDTA and subsequent association of the anions with the metal ions were negligible. Concentrations of ionic species in the potentiometric and calorimetric titrations were calculated from mass-balance and electroneutrality expressions in the usual way,[17,18] and the thermodynamic functions for reaction 4 at a constant ionic strength of 0.10 ± 0.001 *M* and 25° are given in Table I. Equilibrium constants for reaction 4, calculated from the measured pH values, were within 0.10 p*K* unit of those reported by Schwarzenbach, *et al.*,[7] and corrected to 25°; the uncertainty in ΔG, although not given by these authors, was taken as ±0.1 kcal $mole^{-1}$.

Table I. Thermodynamic Functions for the Protonation of $M(EDTA)^{2-}$ Complexes[a]

Metal ion	ΔG, kcal $mole^{-1}$	ΔH, kcal $mole^{-1}$	ΔS, cal deg^{-1} $mole^{-1}$
Mn^{2+}	−4.2 ± 0.1	−1.2 ± 0.3	10 ± 2
Co^{2+}	−4.1 ± 0.1	−1.9 ± 0.3	7 ± 2
Ni^{2+}	−4.4 ± 0.1	−1.8 ± 0.3	9 ± 3
Cu^{2+}	−4.1 ± 0.1	−2.0 ± 0.3	7 ± 3
Zn^{2+}	−4.1 ± 0.1	−2.2 ± 0.3	6 ± 3
Cd^{2+}	−4.0 ± 0.1	−0.4 ± 0.3	12 ± 3
Hg^{2+}	−4.2 ± 0.1	−0.7 ± 0.3	12 ± 3

[a] Reaction 4; *I* = 0.1 *M*, 25°.

Limits of error in the enthalpy and entropy changes are expressed as standard deviations from the mean and include estimated uncertainties associated with the experimentally measured heats, concentrations, and emf's. In Table II thermodynamic data are given for reaction 3 in which Y represents EDTA[12] and HEDTA (hydroxyethylethylenediaminetriacetic acid).[13] Limits of error were not given in these original publications but have been estimated as at least ±0.2 kcal $mole^{-1}$ for $\Delta H(MY^{2-})$ and ±0.4 for $\Delta H(M\text{-}HEDTA^-)$. The data for reaction 5 were calculated from the value ΔH = 5.7 kcal $mole^{-1}$ for reaction 2 reported by Tillotson and Staveley[20] (estimated uncertainty ±0.2 kcal $mole^{-1}$) and the enthalpy changes for reactions 3 and 4.

---

(11) M. Yasuda, *Bull. Chem. Soc. Japan*, **41**, 139 (1968).

(12) G. Anderegg, *Helv. Chim. Acta*, **47**, 1801 (1964).

(13) D. L. Wright, J. H. Holloway, and C. N. Reilley, *Anal. Chem.*, **37**, 884 (1965).

(14) R. A. Care and L. A. K. Staveley, *J. Chem. Soc.*, 4571 (1956).

(15) R. G. Bates, "Determination of pH," John Wiley & Sons, Inc., New York, N. Y., 1963.

(16) C. W. Davies, "Ion Association," Butterworth & Co., Ltd., London, 1962.

(17) S. Boyd, A. Bryson, G. H. Nancollas, and K. Torrance, *J. Chem. Soc.*, 7353 (1965).

(18) G. H. Nancollas "Interactions in Electrolyte Solutions," Elsevier Publishing Co., Amsterdam, 1966.

(19) A. P. Brunetti, M. C. Lim, and G. H. Nancollas, *J. Am. Chem. Soc.*, **90**, 5120 (1968).

(20) M. J. L. Tillotson and L. A. K. Staveley, *J. Chem. Soc.*, 3613 (1958).

Table II. Thermodynamic Functions for Ion Association Reactions[a]

Metal ion	$M^{2+} + Y^{4-}$ (reaction 3)			M^{2+} + HEDTA^{3-}			$M^{2+} + HY^{3-}$ (reaction 5)		
	ΔG, kcal mole^{-1}	ΔH, kcal mole^{-1}	ΔS, cal deg^{-1} mole^{-1}	ΔG, kcal mole^{-1}	ΔH, kcal mole^{-1}	ΔS, cal deg^{-1} mole^{-1}	ΔG, kcal mole^{-1}	ΔH, kcal mole^{-1}	ΔS, cal deg^{-1} mole^{-1}
Mn^{2+}	−19.2	−4.6	49	−14.7	−5.2	32	−9.4	−0.1	31
Fe^{2+}	−19.4	−4.0	52	−15.9	−6.0	33	−9.4	. . .	. . .
Co^{2+}	−22.3	−4.2	61	−19.7	−6.5	44	−12.5	−0.4	40
Ni^{2+}	−25.5	−7.6	60	−23.3	−10.3	45	−15.8	−3.7	40
Cu^{2+}	−25.8	−8.2	59	−23.8	−9.4	48	−15.7	−4.5	37
Zn^{2+}	−22.2	−4.9	58	−19.7	−8.4	38	−12.3	−1.4	36
Cd^{2+}	−22.6	−9.1	45	−17.8	−10.3	25	−12.4	−3.8	29
Hg^{2+}	−30.1	−18.9	38	−27.3	−20.0	25	−19.9	−14.2	29
Limits of error	±0.1	±0.2	±2	±0.1	±0.4	±3	±0.1	±0.4	±3

[a] $I = 0.1\ M$, 25°.

In Table I it can be seen that the enthalpy changes for protonation of the EDTA complexes of Co, Ni, Cu, and Zn are all similar and appreciably more exothermic than would be anticipated if the process was simply one of association with a free carboxyl group. In the protonation of the EDTA molecule itself, both nmr and infrared spectroscopic evidence indicates that the two protons in H_2Y^{2-} are associated with the two nitrogen atoms.[21,22] In the reaction

$$H_2Y^{2-} + H^+ \rightleftharpoons H_3Y^- \qquad (6)$$

therefore, the corresponding thermodynamic functions, $\Delta H = +1.4$ kcal mole^{-1} and $\Delta S = +17.1$ cal deg^{-1} mole^{-1},[20] relate to the association of a proton with an EDTA acetate group.

In the protonation of an MEDTA^{2-} complex in which the ligand molecule is bound sexadentately, a metal–oxygen bond is broken prior to the protonation, and there is a release of much of the strain originally associated with the molecule. Since the actual protonation of the carboxyl group makes only a small endothermic contribution to ΔH, the observed exothermic values probably reflect the more important strain release within the molecule. The existence of such strain in the MY^{2-} complexes in which octahedral coordination has been completed has been shown from the results of X-ray measurements.[23]

It is seen in Table I that the protonation of the mono-EDTA complexes of Co, Ni, Cu, and Zn is accompanied by considerably smaller entropy changes than that for reaction 6 ($\Delta S = +17.1$ cal deg^{-1} mole^{-1}). This may be explained by the fact that reaction 4 represents not only the protonation, but also the subsequent substitution of a coordinated water molecule at the vacated site on the metal ion. In the protonation of H_2Y^{2-}, in which there is considerable hydrogen-bonded structure,[21] its release upon further protonation to H_3Y^- is consistent with the larger entropy change for reaction 6. For Cd and Hg, the larger ΔH and ΔS in Table I may reflect a coordination number less than six in the MY^{2-} complex and a lower degree of hydration of the metal ion in MHY^- as compared with the transition metals.

The ΔH values for the formation of MHY^- (reaction 5, Table II) with all the metal ions studied are less exothermic by 5–7 kcal mole^{-1} than those for the formation of the M–HEDTA$^-$ complexes. This is consistent with a model in which the proton in HY^{3-}, originally located mainly on the nitrogen atoms,[21,22] is removed to an acetate group with the expenditure of most of the $\Delta H = 5.7$ kcal mole^{-1} for reaction 2.[20] It is seen that this effect accounts for a major part of the increased stabilities of M–HEDTA$^-$ as compared with MHY^-; only in the case of Cu(II) is the difference in the ΔS value also considerable.

Additional evidence for the existence of strain in the MY^{2-} complexes can be found in a comparison of their thermodynamic functions with those for the formation of M–HEDTA$^-$ (Table II). The ΔH values for the latter complexes with Fe, Co, Ni, Cu, and Zn are all more exothermic by 2–4 kcal mole^{-1} than those for reaction 3 in spite of the fact that the $-CH_2CH_2OH$ in HEDTA is unlikely to take part in the bonding to the metal ions.[24] For the larger metal ions Mn, Cd, and Hg, the corresponding ΔH differences are smaller. The lower ΔS values for the formation of M–HEDTA as compared with MY^{2-} can be explained in terms of the greater degree of hydration of the higher charged free ligand EDTA^{4-} anion as compared with HEDTA^{3-}.

In an nmr study of EDTA complexes with paramagnetic ions, Rossotti and Sunshine[25] have proposed a method for the determination of the number of water molecules coordinated by aqueous Cu^{2+} ions. Assuming an over-all coordination number of six, one equatorial water molecule was indicated in the CuY^{2-} complex and two were indicated in the $CuHY^-$ complex. This would suggest pentacoordination of the ligand in the former and tetracoordination in the latter complex. As corroborative evidence it was pointed out that the stability constant of $CuHY^-$ is slightly less than that of CuNTA$^-$ (nitrilotriacetic acid) in which the ligand is at most tetradentate. The disadvantages of comparing only the ΔG values have often been enumerated,[18] and with the thermodynamic data presented in this paper, a more detailed comparison can be made with the reaction

$$Cu^{2+} + NTA^{3-} \rightleftharpoons CuNTA^-$$

for which[26] $\Delta G = -17.39$ kcal mole^{-1}, $\Delta H = -1.84$ kcal mole^{-1}, and $\Delta S = 53.0$ cal deg^{-1} mole^{-1}. It is

---

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

(22) J. L. Sudmeier and C. N. Reilley, *J. Ind. Eng. Chem.*, **36**, 1707, 1968 (1964).

(23) H. A. Weaklein and J. L. Hoard, *J. Am. Chem. Soc.*, **81**, 549 (1959).

(24) S. Chaberek and A. E. Martell, *ibid.*, 77, 1477 (1955).

(25) F. J. C. Rossotti and H. Sunshine, *Chem. Commun.*, 447 (1968).

(26) J. A. Hull, R. H. Davies, and L. A. K. Staveley, *J. Chem. Soc.*, 5422 (1964).

seen that the higher stability of $CuNTA^-$ is entirely an entropy and not an enthalpy effect. The more exothermic ΔH for $CuHY^-$ is the result of the coordination of an additional N atom to the metal ion enabling the special structural requirements to be met for the formation of relatively strain-free chelate rings.[27] In the NTA^{3-} ion, the charged carboxyl groups are more restricted than those in HY^{3-}, and the resulting localization of charge will lead to a more effective orientation of water molecules. Upon complex formation, the release of these water molecules will account for some of the observed $\Delta S(CuNTA^-) - \Delta S(CuHY^-)$ difference. Another factor contributing to this entropy difference of 16 cal deg^{-1} mole^{-1} will be the greater loss of librational entropy of the larger HY^{3-} ion as compared with NTA^{3-} when they coordinate with the Cu^{2+} ion.

---

[27] G. Schwarzenbach, *Advan. Inorg. Chem. Radiochem.*, **3**, 257 (1961).

Oxygenation and Oxidation of Cobalt(II) Chelates of Amines, Amino Acids, and Dipeptides[1]

Michel S. Michailidis and R. Bruce Martin

Contribution from the Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901.
Received January 31, 1969

Abstract: In the absence of oxygen, glycylglycine undergoes a cobalt(II) ion promoted amide hydrogen ionization near pH 10. For the 2:1 complex the two amide hydrogen ionizations occur in a cooperative manner, yielding a light blue solution with a magnetic susceptibility of 4.1 BM. These results and the absorption spectrum of the light blue solution suggest an equilibrium between high and low spin states in an octahedral complex. Admission of oxygen to pink or blue solutions of octahedral cobalt(II) complexes rapidly yields yellow or, at higher concentrations, brown solutions of binuclear oxygenated complexes. Depending upon the ligands these complexes decompose at a variety of rates to yield red mononuclear cobalt(III) chelates. Proton balance studies conducted for the oxygenation and oxidation reactions indicate that the binuclear oxygenated complexes of ethylenediamine, histamine, and glycinamide contain hydroxo as well as oxygen bridges. With sufficient ligand, no hydroxo bridges appear with the other ligands studied including diaminopropionic acid, histidine, histidinamide, and histidylglycine. A minimum of three nitrogen donors seems necessary for formation of oxygenated complexes which are obligatory intermediates in the oxidation of cobalt(II) complexes by molecular oxygen. The product cobalt(III) chelates appear to be derived from the binuclear oxygenated complexes by filling the coordination position vacated by the departing peroxo group with an additional chelating group if available, otherwise by a hydroxo group. Absorption spectra and circular dichroism results are reported for all three kinds of complexes studied.

Since the discovery of reversible oxygenation of high-spin, octahedral bis(histidinato)cobalt(II) to yield a brown diamagnetic, binuclear oxygenated complex,[2] subsequent extensions to other ligands have been confusing owing to misidentification of the red complexes of monomeric cobalt(III), obtained from the over-all oxidation reactions, as oxygenated intermediates. Especially in the cases of amino acids other than histidine, and dipeptides where concentrations of oxygenated intermediates do not build up except at high pH, reported results require reinterpretation. Elemental analysis,[3] structures,[4] magnetic susceptibilities,[5] absorption spectra,[3,4,6,7] slow rates of appearance,[4,7] charge on complex,[8] and pmr spectra,[8] all attributed to the oxygenated complexes of dipeptides, should be reassigned to red cobalt(III) chelates. Oxygenation of the bis(histidine) complex of cobalt(II) to give the brown, binuclear, oxygenated complex is so rapid that a stopped-flow method was employed to measure the rates.[9] The formation of H_2O_2 was indicated polarographically in oxidation of the glycylglycine chelate.[10]

This research attempted to define more precisely for a variety of ligands the requirements and conditions for oxygenation and oxidation of cobalt(II) chelates. Since these reactions are often studied at high pH, it is necessary to investigate first the structures of cobalt(II) chelates, especially dipeptides, in alkaline solutions in the absence of oxygen in order to learn the characteristics of complexes undergoing oxygenation. Thus the first parts of the Results and Discussion sections are taken up with a study of cobalt(II) chelates. Extensive spectrophotometric and proton balance studies are then reported and discussed for the oxygenation and oxidation reactions.

---

[1] This paper is abstracted from the Ph.D. thesis (1968) of M. S. Michailidis; the research was supported by the National Science Foundation.

[2] D. Burk, J. Z. Hearon, L. Caroline, and A. L. Schade, *J. Biol. Chem.*, **165**, 723 (1946); J. Z. Hearon, *J. Natl. Cancer Inst.*, **9**, 1 (1948); J. Z. Hearon, D. Burk, and A. L. Schade, *ibid.*, **9**, 337 (1949). A. Earnshaw and L. F. Larkworthy, *Nature*, **192**, 1068 (1961).

[3] J. B. Gilbert, N. C. Otey, and V. E. Price, *J. Biol. Chem.*, **190**, 377 (1951).

[4] C. Tanford, D. C. Kirk, Jr., and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, **76**, 5325 (1954).

[5] J. M. White, T. J. Weisman, and N. C. Li, *J. Phys. Chem.*, **61**, 126 (1957).

[6] E. M. Crook and B. R. Rabin, *Biochem. J.*, **68**, 177 (1958).

[7] G. W. Miller, B. T. Gillis, and N. C. Li, *J. Biol. Chem.*, 235, 2840 (1960).

[8] P. Tang and N. C. Li, *J. Am. Chem. Soc.*, **86**, 1293 (1964).

[9] J. Simplicio and R. G. Wilkins, *ibid.*, **89**, 6092 (1967).

[10] V. Caglioti, P. Silvestroni, and C. Furlani, *J. Inorg. Nucl. Chem.* **13**, 95 (1960).