By an analysis of the binding polynomial [3] on the Bjerrum plane ($\bar{n}$, $-\log L$), it can be shown how the correct equilibrium constant to evaluate the chelate effect is $K_\epsilon = K_{ML}/\beta_{MA_2}^{1/2}$ for bidentate chelating ligands and $K_\epsilon = K_{ML}/\beta_{MA_n}^{1/n}$ for *n*-dentate ligands. These adimensional constants are obtained as the ratio of two operational equilibrium constants, namely $K_{ML}$ and $\beta_{MA_n}^{1/n}$, each of which is expressed in homogeneous reciprocal concentration units (conc.$^{-1}$). If the donor atoms of the chelating ligand are different (heterotropic chelate), then the thermodynamic stability can be evaluated by $K_{\epsilon'} = K_{ML}/\beta_{MAB}^{1/2}$, where MAB is a mixed ligand complex, and similar constants hold for higher complexes. Again the ratio is between two operational constants $K_{ML}$ and $\beta_{MAB}^{1/2}$, each expressed in conc$^{-1}$.

With the same arguments it can be shown that the cooperativity effect, *i.e.* the mutual repulsion or attraction between ligands, can be evaluated by $K_\gamma = \beta_{MA_2}^{1/2}/K_{MA}$ and by $K_{\gamma'} = \beta_{MAB}^{1/2}/(K_{MA} \cdot K_{MB})^{1/2}$ for homotropic and heterotropic cooperativity, respectively.

The chelate effect comprehends in itself the cooperativity effect and this can be taken into account in the constants $K_\eta = K_\epsilon \cdot K_\gamma$ and $K_{\eta'} = K_{\epsilon'} \cdot K_{\gamma'}$. The constants $K_\epsilon$, $K_\gamma$, $K_{\epsilon'}$, and $K_{\gamma'}$ must be corrected for statistical effects. All these constants are expressed in the same units as the activity coefficients. From these constants, the corresponding changes in chemical potentials, $\Delta\mu^\circ = -RT \ln K$ can be calculated. These values expressed in kJ mol$^{-1}$ allow the evaluation on the same scale of chelate and cooperativity effects, together with changes in the activity coefficients.

The correctness of the choice of scale is shown by examining the chelate effect values obtained for copper(II) complexes of dicarboxylic acids at 25 °C [4]. Cu(II)/succinate 1/1 chelate would have been unstable according to $K_{chel.} = 0.32$ mol dm$^{-3}$, whereas it comes out to be stable according to $K_\eta = 11.4$ mol$^{-1}$ dm$^3$ ($\Delta\mu_\eta^\circ = -6.03$ kJ mol$^{-1}$), in agreement with the experimental evidence [5].

The net chelate effect, $\Delta\mu_\eta^\circ$, is linearly related both to the number of donor atoms and to the number of chelate rings.

The enthalpy and entropy contributions to the chelate effect can also be calculated and critically analysed.


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## M3

## Thermodynamics of Axial Ligand Addition and Spectroscopic Trends of a Series of Symmetrical and Unsymmetrical Derivatives of Tetraphenylporphinatozinc(II) and -iron(III)


F. ANN WALKER*, GREGORY A. McDERMOTT and VIRGINIA L. BALKE

*Department of Chemistry, San Francisco State University, San Francisco, Calif. 94132, U.S.A.*


The electronic spectra and equilibrium constants for addition of 3-picoline to a series of symmetrically and unsymmetrically phenyl-substituted ZnTPP derivatives have been measured. It is found that the $\alpha$ band energy varies slightly nonlinearly, yet systematically, with the sum of the Hammett sigma constants of the substituents within the series $(p\text{-Cl})_x(p\text{-NEt}_2)_y$-TPPZn(II) and related complexes, while the smaller variation in the $\beta$ band appears to be linear. The log of the intensity ratio of the $\alpha$ and $\beta$ bands, log $A_\beta/A_\alpha$, however, varies linearly with the band energies of both the $\alpha$ and $\beta$ bands for both 4- and 5-coordinate complexes of unsymmetrical ZnTPP derivatives. Likewise, log $K_{eq}$ for 3-picoline addition to this series of ZnTPPs varies linearly with the sum of the Hammett sigma constants for all complexes investigated, irrespective of the symmetry of placement of phenyl substituents. Thus the electronic effects of unsymmetrically placed substituents are averaged by the metal Zn to yield a Lewis acid strength toward 3-picoline which is dependent only on the sum of the electronic effects and not on the identity of the substituents or the symmetry of their distribution.

In contrast to the results for Zn(II), the same series of TPPFe(III) complexes do not exhibit spectroscopic trends independent of the symmetry of placement of the substituents in either the high-spin chloroiron(III) or low-spin bis-N-methylimidazoleiron(III) forms. Likewise, log $\beta_2$ for N-methylimidazole addition does not vary linearly with the sum of the Hammett sigma constants for unsymmetrically substituted TPPFe(III) derivatives. Rather, unsymmetrically substituted TPPFe(III) derivatives deviate from the linear relationship shown by the symmetrical complexes [1] in either a negative direction (log $\beta_2$ smaller than expected, based on $\Sigma\sigma$), as is found for *p*-Cl, $p\text{-NEt}_2$ mixed substituent complexes, or in a positive direction (log $\beta_2$ larger than expected on the basis of $\Sigma\sigma$), as is found for $p\text{-NO}_2$, *p*-H or $m\text{-NO}_2$, $m\text{-CH}_3$, or *m*- or $p\text{-NHCOCH}_3$, H mixed substituent combinations.

The reason for the difference in thermodynamic and electronic spectral behavior of the unsymmetrically phenyl substituted TPP derivatives of Zn(II) and Fe(III) must be due to the difference in electron configuration of the two metals ($d^{10}$ *vs.* $d^5$), and

the change in spin state of Fe(III) upon bis-N-methylimidazole complex formation. In the case of Fe(III), the unsymmetrical electron configuration of the low-spin Fe(III) product apparently makes the metal sensitive to both the symmetry and the nature of the substituents, probably due to extensive mixing of metal and porphyrin $\pi$-symmetry orbitals (the $d_{xz}$, $d_{yz}$, e-symmetry metal orbitals are unsymmetrically filled). The results imply that the nature and pattern of porphyrin substituents in naturally-occurring heme proteins (*i.e.*, cytochromes b, c, a, hemoglobin, etc.) are carefully chosen to maximize the stability of metal-ligand bonds, in addition to controlling other physical properties.

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## M4

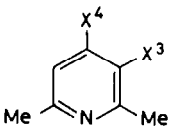
## 'Non-Coordinating' Buffers for Studies Involving Metal Ions

H. ELIAS* and K. J. WANNOWIUS

*Anorganische Chemie III, Eduard-Zintl-Institut, Technische Hochschule Darmstadt, 6100 Darmstadt, Hochschulstr. 4, F.R.G.*

Buffer systems are of outstanding importance for solution chemistry. When it comes to kinetic and thermodynamic studies on metal ions in buffered aqueous solution the extent of complex formation between the buffer applied and the metal ions studied should be negligibly small. In addition, there should be no or at least only a minor catalytic effect of the buffer on systems which are subject to general acid catalysis.

2,6-Lutidine (=2,6-dimethylpyridine) and 2,4,6-collidine (=2,4,6-trimethylpyridine) have often been applied as buffer compounds for the pH range 6.5–8.0 because of their restricted coordination properties due to steric hindrance through the two methyl groups neighbouring the donor nitrogen. A series of lutidines L carrying substituents in the 3- and/or 4-position has been synthesized and characterized with respect to yield upon synthesis, solubility in water, and UV absorption.




L ≙ 3-$X^3$-4-$X^4$-2,6-dimethylpyridine

$pK_a$ values of the free bases L and complex formation constants for the aquo ions $Ag^+$, $Mg^{2+}$, $Ca^{2+}$, $Ba^{2+}$, $Zn^{2+}$, $Cu^{2+}$, $Ni^{2+}$, and $Ce^{3+}$ as determined by potentiometric titration in aqueous solution are presented. A sequence of 2,6-lutidine type buffers is suggested covering the pH range 3–8 in small steps. The formation constants for the 1:1 complexes of divalent and trivalent aquo metal cations are small (mean value: $K = 1.7\ M^{-1}$) and nearly independent of both the nature of the metal and the $pK_a$ of the substituted 2,6-lutidines studied. These results are interpreted as being indicative of weak complex formation sterically restricted to 'outer sphere' interaction.

It is shown that the acids $LH^+$ do not act as catalysts for the dissociation of a nickel(II) triglycine complex which is known to be subject to general acid catalysis.

## M5

## Stability and Structure of Complexes of Transition Metal Ions with Nucleotides and Related Compounds

H. DIEBLER

*Max-Planck-Institut für Biophysikalische Chemie, 34 Göttingen, F.R.G.*

Potentiometric, spectrophotometric and kinetic techniques have been used to determine the stabilities of complexes of transition metal ions with phosphoric acid and ribose-phosphate, purine nucleosides and nucleotides [1–4]. At ionic strength 0.1 *M*, dinegative phosphate groups bind to $Ni^{2+}$ and $Co^{2+}$ with stability constants close to 100 $M^{-1}$ [1, 5]. The neutral purine nucleosides form only weak complexes; the binding constants depend markedly on the base involved, *e.g.* K = 14 for $Ni^{2+}$–inosine, and K = 2 $M^{-1}$ for $Ni^{2+}$–adenosine [3]. The data are consistent with the assumption that the N7 atom of the imidazole ring is the predominant binding site. Similar differences are observed also for the complex stabilities of the nucleotides: K(Ni–IMP) = 920 $M^{-1}$, and K(Ni–AMP) = 300 [3]. The experimental overall stabilities of the nucleotide complexes can be rationalized only by assuming a chelate structure, with the metal ion being bound to the phosphate group *and* to the base. Space-filling models indicate that in the nucleotide complexes only the N7 atom can act as the binding site of the base. The kinetic data, too, can be interpreted only by a stepwise chelate formation process. Moreover, the kinetic data enable also the evaluation of the stepwise equilibria. In the case of NiAMP, about 2/3 of the complexes are present in the chelate form, 1/3 in the monodentate form.

Complex formation of $Ni^{2+}$ with the dinucleoside-monophosphate $ApA^-$ is weaker (K = 2.6 $M^{-1}$) than with $AMPH^-$ (K = 11) [4], despite the availability of an additional adenosine group in $ApA^-$. This observation is attributed to the conformational properties of $ApA^-$ in solution. The ligand prefers a conformation in which the two adenines are in a stacked position.