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 π-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.

1 F. A. Walker, M.-W. Lo and M. T. Ree, *J. Am. Chem. Soc.*, *98*, 5522 (1976).

M4

'Non-Coordinating' Buffers for Studies Involving Metal Ions

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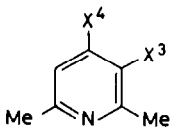
Buffer systems are of outstanding importance for solution chemistry. When it comes to kinetic and thermodynamic studies on metal ions in buffered aqueous solution the extent of complex formation between the buffer applied and the metal ions studied should be negligibly small. In addition, there should 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

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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.