

The Nature of Amine Deprotonation in Basic Solutions of Bis-(2-aminomethylpyridine)cobalt(II)

DANIEL H. HUCHITAL* and EILEEN DEBESIS

Department of Chemistry, Seton Hall University, South Orange, N.J. 07079, U.S.A.

Received June 6, 1984

Abstract

The report [2] that 2:1, 2-aminomethylpyridine (AMP) to cobalt(II) solutions turn slowly from pink to blue in anaerobic basic media was reinvestigated. Kinetic, spectral, and other features of the reaction are reported. When cobalt(II)–AMP solutions are made basic a peak at 380 nm rapidly appears in the spectrum, followed by a slower appearance of a peak at 595 nm, which gives rise to the blue color observed. The rate of appearance of this peak was studied under different conditions (pH, AMP to cobalt ratios, D₂O, etc.). The results of these studies are reported. Most, but not all of the results can be explained in terms of a tetrahedral complex being formed. Here the kinetic as well as spectral and other evidence is discussed in terms of a dimeric structure for the blue species. This is a triply bridged binuclear complex with one μ -hydroxo and two μ -amido bridges. Each metal center is chelated by two AMP molecules, one of which is bridged to the other metal center. Experiments performed using the N-methyl and N,N-dimethyl derivatives of AMP, the interaction of the blue complex with acid, and other data which lend support to the proposed structure are presented.

Introduction

In aqueous solution cobalt(II) forms several types of complexes with bidentate amine-type ligands such as 2-aminomethylpyridine. This ligand in mildly acidic media forms the expected mono, bis, and tris chelated complexes. In basic solutions, in the presence of oxygen, the bis(2-aminomethylpyridine)-cobalt(II) complex forms a μ -peroxo- μ -hydroxo dimer, a behavior that has been observed for many other similar complexes [1].

In basic solutions, in the absence of oxygen, bis-bidentatecobalt(II) complexes are generally colorless or pale yellow. Anaerobic solutions of bis(2-

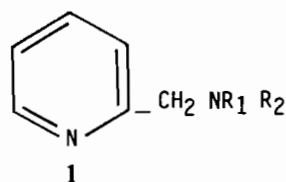
aminomethylpyridine)cobalt(II), however, as reported by Walker and Nakon [2], slowly turn deep blue when made basic. These workers attributed this color change to the deprotonation of the bound amine group and the formation of a tetrahedral complex. Similar color changes undergone by cobalt(II) complexes in basic, anaerobic solutions have been ascribed to changes in geometry about the metal center or to changes in its electronic structure [3–10]. For example, Miller and Wilkins [7] reported that cobalt(II)–triethylenetetramine complexes form 5-coordinate species in basic, oxygen-free solution. Martin and coworkers [5, 6, 8] attributed the blue or violet color produced in cobalt(II)-L-histidine and similar species to an octahedral-tetrahedral conversion, while the pink to green-blue changes for some bis(dipeptide)cobalt(II) complexes were believed to be due to high-spin, low-spin conversions. Appleton and Sarkar [10] suggested that the violet color formed in basic, oxygen-free solutions of cobalt(II) and N-methylimidazole was due to the formation of a μ -hydroxo polymer.

The blue color which forms in anaerobic basic solution of the bis(2-aminomethylpyridine)cobalt(II) complex is similar to, yet different from the above species. It forms at lower pH and does not require a large excess of ligand to insure stability of the final product. The study reported here was undertaken to determine the nature of this blue species and to investigate the details of its formation.

Experimental

Materials

The ligands used in this study have the general structure



*Author to whom correspondence should be addressed.

They were purchased from Aldrich Chemical Company. The purity of these ligands, as determined by area normalization of high performance liquid chromatograms, was 99.7% for 2-aminomethylpyridine ($R_1 = R_2 = H$), 98.6% for 2-picolylmethylamine ($R_1 = H, R_2 = CH_3$), and 99.4% for 2-dimethylaminomethylpyridine ($R_1 = R_2 = CH_3$).

Cobalt(II) chloride hexahydrate, potassium nitrate, and potassium hydroxide were Fisher reagent grade chemicals. Anhydrous cobalt(II) chloride was purchased from Ventron-Alfa Division. D_2O , of 99.8% purity was purchased from Bio-Rad Laboratories. All of these were used without further purification.

Solution Preparation

Stock solutions of cobalt(II) chloride hexahydrate were prepared at 0.010 M and standardized by titration with standard EDTA [11]. Ligand stock solutions were prepared as the amine hydrochloride salts, or as the amine solution to which HCl was added. Solutions for kinetic and spectroscopic runs were prepared at a final ionic strength of 0.10 M.

Kinetic and Spectrophotometric Measurements

All kinetic studies were carried out, and all visible spectra were recorded on a Cary 15 spectrophotometer fitted with a thermostated sample cell. Temperatures in the sample cell were maintained at 25.0 ± 0.1 °C by a Lo-Temptrol Model 154 constant temperature bath. All pH measurements were made on a Fisher Accumet Model 520 pH meter.

For the kinetic studies, appropriate aliquots of solutions of cobalt(II), ligand, and KNO_3 were mixed. The mixture was deoxygenated using argon gas which had been passed through an Oxy-Trap (Alltech Associates). The reaction was initiated by adding deoxygenated KOH to yield the desired pH. The primary wavelength used to monitor the reaction was 595 nm. When noted, 380 nm and 473 nm were also monitored. Pseudo-first-order rate constants were obtained from plots of $\ln(A_\infty - A_t)$ versus time, with values of A_∞ determined by the Mangelsdorf method [12].

Results

Kinetic Experiments

When cobalt(II)–AMP (AMP = 2-aminomethylpyridine) solutions are made basic in oxygen-free solutions, a peak at 380 nm rapidly appears in the spectrum. This is followed by a slower growth in the same peak along with the appearance of a peak at 595 nm which gives rise to the blue color observed. The rate of formation of the blue color (the growth of the 595 nm peak) is the same as

the rate of subsequent growth of the 380 nm peak in the pH range studied. A plot of k_{obs} versus $[OH^-]$ is shown in Fig. 1. The threshold pH for the color change was approximately 8.6, while above pH 12

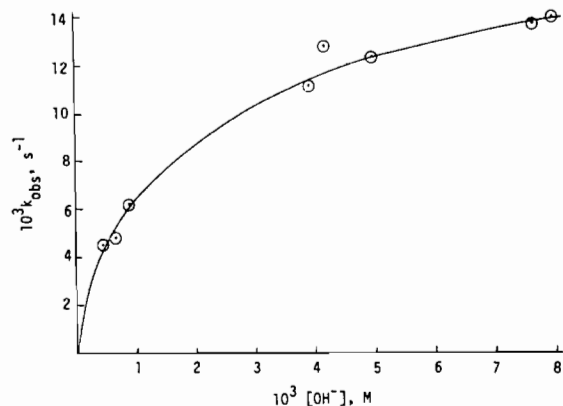


Fig. 1. Dependence of the pseudo-first-order rate constant, measured at 595 and 380 nm, on the hydroxide ion concentration. $[Co(II)] = 8.0 \times 10^{-4}$ M, $[AMP] = 2.8 \times 10^{-3}$ M.

the rate leveled off. Data obtained between pH of 10.6 and 11.9 (ca. 20 fold change in $[OH^-]$) could be fitted to a hydroxide ion dependence of the form $k_{obs} = a[OH^-]/(1 + b[OH^-])$. A plot of k_{obs}^{-1} versus $[OH^-]^{-1}$ was linear and gave values of $a = 12.2$ s $^{-1}$ and $b = 804$ M $^{-1}$. Figure 2 shows the dependence of the pseudo-first-order rate constant upon the concentration of 2-aminomethylpyridine. The results of two series of experiments, performed at pH 10.85 and 11.05, show that the rate reaches a maximum at a ligand to cobalt ratio of approximately 4:1. The slopes of the lines in the lower ligand:cobalt region indicate a first-order dependence on the 2-aminomethylpyridine concentration. In addition, several experiments were performed using equimolar mixtures of cobalt(II), AMP, and a third

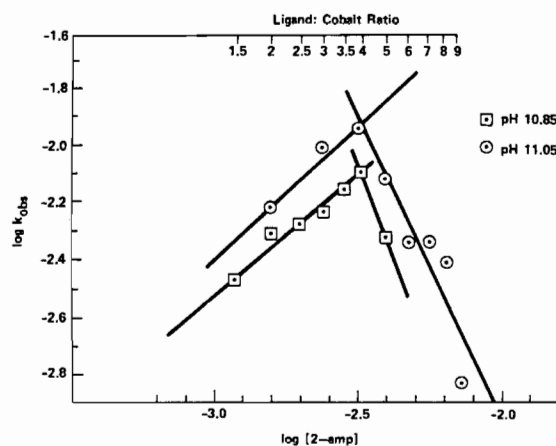


Fig. 2. Dependence of the pseudo-first-order rate constant, measured at 595 nm, on the 2-aminomethylpyridine concentration. $[Co(II)] = 8.0 \times 10^{-4}$ M.

ligand (such as bipyridine or ethylenediamine). Here the blue species also forms but at a slower rate. These results indicate that only one AMP per cobalt(II) is needed for the reaction to occur.

Spectrum of the Blue Complex

The visible spectra of cobalt(II)–AMP solutions in acid and base are shown in Fig. 3. Only a semi-quantitative description of the spectrum in base is possible, as the molar absorptivities of the bands and their relative intensities are dependent upon pH, cobalt(II) concentration, and length of time in solution. Figure 3c, therefore, is a representative spectrum; the major maxima, at 380 nm and 595 nm, may be relatively more or less intense in the spectra of other preparations of the complex. Generally, the peak at 595 nm has a molar absorptivity of approximately 2×10^3 liter mol^{-1} cm^{-1} .

In addition to the peaks at 380 nm and 595 nm, a broad absorbance maximum at 473 nm is also present in aged solutions. This peak formed very slowly over a period of days, and was accompanied by a shift in the 595 nm maximum to 585 nm. A subsequent slower polymerization reaction is proposed as the most likely cause. The nature of these absorbance changes will be described in another paper.

Analytical Data

Attempts to prepare the blue complex as a solid *via* precipitation from aqueous solutions were unsuccessful primarily due to its oxygen sensitivity. A sample was prepared by mixing cobalt(II) chloride hexahydrate with excess AMP, which is a liquid at room temperature. A dark blue solid formed immediately. The excess liquid was removed under vacuum at room temperature; however, attempts to remove all excess liquid were not successful.

The blue solid obtained by this procedure was stable in air. When dissolved in oxygen free water,

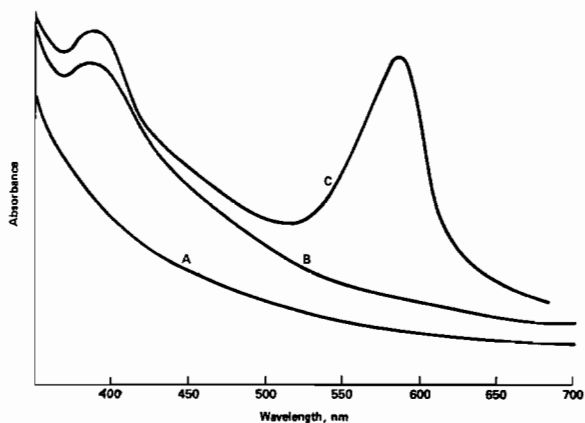


Fig. 3. Spectra of anaerobic solutions of bis-(2-aminomethylpyridine)cobalt(II) A: in acid; B: immediately after addition of base; C: after two hours in base.

it produced a spectrum like that of Fig. 3c. Spectra of the solid dissolved in other polar solvents (*e.g.*, acetonitrile, ethanol and methanol) showed some similarities. The blue solid was analyzed for C, H, N, and Cl. The results were C (44.4%), H (5.3%), N (16.9%), and Cl (14.5%). Calculated values for the proposed (see later) formula are C (47.9%), H (5.35%), N (18.6%), and Cl (5.9%).

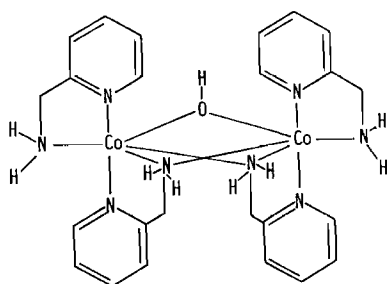
Discussion

The blue complex formed in oxygen-free basic solution of cobalt(II) chloride hexahydrate and 2-aminomethylpyridine shows few of the characteristic features of similar cobalt(II) systems reported in the literature. The structure considered initially, in light of earlier work, was that of the tetrahedral complex proposed by Walker and Nakon [2]. Indeed most of the results can be explained by the formation of tetrahedral $\text{Co}(\text{AMP}-\text{H})_2$ as suggested by these authors. Many early experiments designed to test Walker and Nakon's hypothesis seemed to confirm their conclusions: (a) Several experiments using pure liquid 2-aminomethylpyridine were performed. Mixing anhydrous cobalt(II) chloride with liquid AMP produced no color changes. When solid KOH was added to this mixture, the blue complex formed as above. This showed that hydroxide ion, from the solid KOH, from water of hydration, or from the solvent water is necessary for reaction to occur. Walker and Nakon proposed that this is due to deprotonation of the amine. (b) Supportive evidence for the deprotonation of an amine hydrogen in the formation of the blue complex was obtained by carrying out the reactions with the N-methyl derivatives of AMP (structure 1 with $\text{R}_1 = \text{H}$, $\text{R}_2 = \text{CH}_3$, and with $\text{R}_1 = \text{R}_2 = \text{CH}_3$). The reaction to form the blue complex proceeded with the mono-methyl ligand (2-picolylmethylamine) but there was no reaction with the 2-dimethylaminomethylpyridine ligand, due to the fact that no hydrogens are available for deprotonation. (c) For additional evidence of a deprotonation step, the reaction was run in D_2O under the same conditions which were employed for H_2O . When placed in D_2O the ligand amines readily exchange with solvent deuterium. The results of $\log-\log$ plots of k_{obs} versus $[\text{H}^+]$ or $[\text{D}^+]$ are instructive. The slopes of both lines are equivalent. However, at any given pH the reaction in H_2O is approximately three times faster than in D_2O . This is the magnitude expected for a primary isotope effect [13] and is thus taken to indicate that the deprotonation of the ligand accompanies the formation of the blue complex.

Evidence in opposition to the reaction scheme proposed by Walker and Nakon comes from studies

on the effect of acid on the blue complex followed by the readdition of base. When a solution of freshly prepared blue complex was made acidic, the blue color disappeared, leaving a yellow solution with a nearly featureless visible spectrum. When this solution was immediately made basic again, the blue color returned. Spectral features were identical to the original solution. If, however, the acidified solution was allowed to remain (in an oxygen-free atmosphere) for several hours before the readdition of base, the reaction to form the blue complex was slow, following the kinetics described earlier. These results clearly cannot be explained if the blue complex is a tetrahedral species.

A structure for the blue complex consistent with all the data above is one in which the complex is depicted as a triply-bridged binuclear species, with one μ -hydroxo and two μ -amido bridges, *viz.*



Each metal atom is chelated to two AMP molecules. The structure agrees reasonably well with the analytical data except for percent Cl. This might be explained by noting that the proposed dimer has a net charge of +1 and hence is expected to exist as the mono chloride salt. The excess chloride and lower carbon and nitrogen observed in the analysis might originate in the $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ reactant which is not removed by the gentle vacuum drying process. The analysis does not agree with the $\text{Co}(\text{AMP}-\text{H})_2$ tetrahedral formulation suggested by Walker and Nakon (*e.g.*, %C = 52.8% calculated *versus* 44.4% found). It does, however, agree with a formulation $\text{Co}(\text{AMP})(\text{AMP}-\text{H})^+\text{Cl}^-$ and it is possible that this blue solid, considering its method of preparation and its stability in air, is indeed a tetrahedral species.

In solution, however, the sum of the data supports another structure. The visible absorbance of the blue complex is very intense. The shape of the band at 595 nm resembles that of typical octahedral cobalt bands, but the molar absorptivity of *ca.* $2000 \text{ M}^{-1} \text{ cm}^{-1}$ is far higher than that normally observed in octahedral complexes [14]. The following explanation is presented: in the formation of the proposed dimer, the symmetry about the cobalt atoms is greatly reduced, so that cobalt d-d transitions become symmetry allowed. This removal of a center of symmetry is brought about by the asymmetric orientation of the ligands and bridges

about each metal center. A similar spectrum with relatively high molar absorptivities was proposed by Appleton and Sarkar [10] in their study on cobalt(II) complexes of imidazole and N-methylimidazole. These authors report that, in these systems, cobalt(II) prefers to remain octahedral and they propose the formation of a "discreet polymer system" in these solutions.

The findings of the kinetic studies also support the proposed dimer structure for the blue species in solution. The following reaction sequence is presented as a description of the dimer formation. The addition of base to oxygen free diaquobis-(2-aminomethylpyridine)cobalt(II) solutions produces the dihydroxo species, $\text{Co}(\text{AMP})_2(\text{OH})_2$. This species then rapidly dimerizes to form a bis- μ -hydroxo complex which is yellow and gives rise to the absorbance at 380 nm. Deprotonation of a ligand amine then occurs with the rate determining step being the replacement of a μ -hydroxo bridge by two μ -amido bridges. This is the slow step in the reaction and yields the proposed binuclear complex. The maximum at 595 nm appears when the μ -amido bridges are formed*. The reaction scheme for the formation of the binuclear complex from the bis- μ -hydroxo species is presented in Fig. 4. The observed rate data for hydroxide ion dependence thus takes the form $k_{\text{obs}} = k_2 K [\text{OH}^-] / (1 + K [\text{OH}^-])$ from which values of $K = 804 \text{ M}^{-1}$ and $k_2 = 0.015 \text{ s}^{-1}$ are obtained.

The early experiments which supported the tetrahedral model can be accounted for in the proposed reaction scheme. The inability of anhydrous cobalt(II) chloride to react with liquid AMP, as described above, can be considered evidence for μ -hydroxo bridging. Similarly, the decrease in rate above an optimum ligand to metal ratio can be explained. At approximately a 4:1 ratio, the $\text{Co}(\text{AMP})_2(\text{OH})_2$ complex reaches its maximum concentration. At higher ligand to metal ratios, formation of the tris complex, $\text{Co}(\text{AMP})_3$, is increasingly favored. This complex is unreactive. Lastly, the presence of μ -amido bridges explains the unreactivity of the bis-(2-dimethylaminomethylpyridine)cobalt(II) complex.

The experiments involving acidification followed by readdition of base are readily explained as follows: when acid is added to the blue binuclear complex the μ -hydroxo bridge is immediately broken, while the μ -amido bridges remain intact. Readdition of base results in rapid re-formation of the μ -hydroxo

*In solution, it is possible that another non-bridging amine in 4 may also be deprotonated. This would produce a neutral species and may account for the conductivity data presented by Walker and Nakon. This type of metal induced deprotonation is well documented [1].

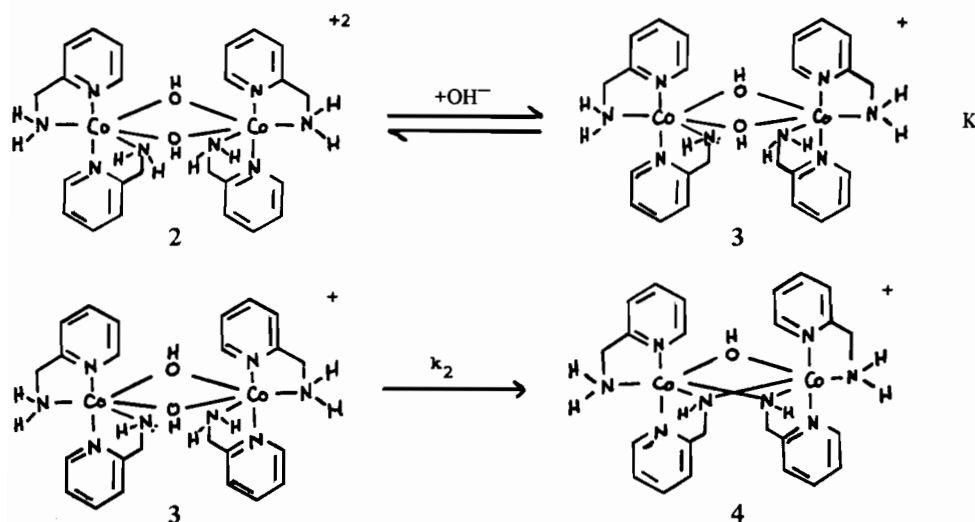


Fig. 4. Reaction scheme for the formation of the proposed binuclear complex.

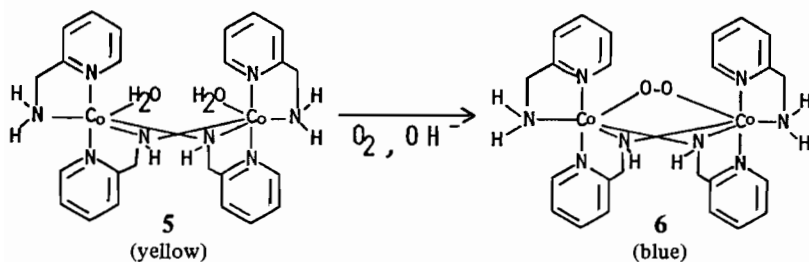
bridge (the μ -amido bridges are already present and the metal centers are in the proper orientation). Hence the rapid return of the blue color. However, if allowed to remain for some time in acid media, the μ -amino bridges are also broken. The result is that the re-formation of the blue complex upon addition of base once again proceeds slowly.

An analogous phenomenon is observed when solutions of the blue complex are acidified and oxygenated. If made basic immediately, the blue color returns immediately. If allowed to stand in acid in the presence of oxygen, the blue color does not return completely after the addition of base. The longer the time in acid, the less intense the blue color. Finally, after several hours in the presence of acid and oxygen, adding base results in the formation of a brown dioxygen adduct. The following reaction is proposed to account for the blue color in acidified solutions of the blue complex which are oxygenated and made basic again immediately.

The addition of acid to the blue complex immediately breaks up the μ -hydroxo bridges, leaving the μ -amido bridged species 5, that was described above. If the solution is quickly oxygenated and made basic, species 6, a μ -amido- μ -peroxocobalt(III)

dimer forms. The known μ -peroxo bridges, such as are found in many dioxygen adducts [1], form even more rapidly than the μ -hydroxo bridges. Thus, with both molecular oxygen and hydroxide ion in solution in competition for one bridging site, the dioxygen bridge will form more readily. Sykes [15] and others have described μ -peroxo- μ -amido bridged cobalt(III) species.

The spectrum of the proposed μ -peroxo- μ -amido complex (6) shows only the 595 nm maximum. The peak at 380 nm has disappeared in favor of a large charge transfer band in the UV characteristic of μ -peroxo bridged species. A species with a spectrum identical to this product was obtained by mixing solid cobalt(II) chloride hexahydrate and an aqueous 30% solution of hydrogen peroxide, and adding 2-aminomethylpyridine. This is presumed to be the same product (the μ -peroxo- μ -amido dimer) formed in the reaction mixture as described above. In contrast, when hydrogen peroxide was added to acidic solutions of cobalt(II) chloride hexahydrate and 2-aminomethylpyridine, there was no color change observed. Adding base produced a brown solution, the color characteristic of a μ -peroxo- μ -hydroxo complex.



Conclusions

There exist many examples in the literature of dimeric cobalt complexes [1, 16–18]. The dimers proposed here for 2-aminomethylpyridine and 2-picolylmethylamine appear to be unique. Other ligands, similar in structure to these, were studied for their ability to form the blue complex in solution. Either the solutions remained colorless or pale yellow (e.g., with picolinamide, 2-picolychloride, bipyridine, or 3-aminomethylpyridine) or a blue precipitate of $\text{Co}(\text{OH})_2$ formed (e.g., with 6-methyl-2-picolylmethylamine or 2-aminoethylpyridine). These latter ligands do not form stable bis complexes with cobalt(II). One ligand, 2-hydrazinopyridine, when present with cobalt(II) in 2:1 to 10:1 ratios, did display a shoulder in the 380 nm region of the spectrum when made basic under anaerobic conditions. The species which formed quickly broke apart however, with the apparent oxidation of the cobalt(II) to cobalt(III).

Results using equimolar mixtures of cobalt(II), AMP, and a second ligand indicate that only one AMP per cobalt(II) is needed for the blue complex to form. This supports the reaction scheme and the proposed structure for the dimer as only one AMP per cobalt(II) is involved in the bridging. More work is in progress on this aspect of the study. In addition, work has been done with the ligand 2-dipicolylamine which Walker and Nakon also report to form a blue complex. These studies show some similarities and some differences from the present systems and will be reported in a subsequent paper.

References

- 1 G. McLendon and A. E. Martell, *Coord. Chem. Rev.*, **19**, 1 (1976) and refs. therein.
- 2 J. K. Walker and R. Nakon, *J. Am. Chem. Soc.*, **99**, 8359 (1977).
- 3 C. C. McDonald and W. D. Phillips, *J. Am. Chem. Soc.*, **85**, 3736 (1963).
- 4 S. Bagger, *Acta Chem. Scand.*, **23**, 975 (1969).
- 5 M. D. Michailidis and R. B. Martin, *J. Am. Chem. Soc.*, **91**, 4683 (1969).
- 6 P. J. Morris and R. B. Martin, *J. Am. Chem. Soc.*, **92**, 1543 (1970).
- 7 F. Miller and R. G. Wilkins, *J. Am. Chem. Soc.*, **92**, 2687 (1970).
- 8 P. J. Morris and R. B. Martin, *Inorg. Chem.*, **10**, 964 (1971).
- 9 K. L. Watters and R. G. Wilkins, *Inorg. Chem.*, **13**, 752 (1974).
- 10 D. W. Appleton and B. Sarkar, *Bioinorg. Chem.*, **7**, 211 (1977).
- 11 A. I. Vogel, 'A Textbook of Quantitative Inorganic Analysis, 3rd. edn.', Wiley, New York, 1961, p. 443.
- 12 D. Margerison, in C. J. Bamford and C. H. Tipper (Eds.), 'Comprehensive Chemical Kinetics, Vol. 1', American Elsevier, New York, 1969, p. 390.
- 13 J. W. Moore and R. G. Pearson, 'Kinetics and Mechanisms, 3rd. edn.', Wiley, New York, 1981, p. 367.
- 14 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry, 4th edn.', Wiley, New York, 1980, pp. 770–772.
- 15 M. R. Hyde and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1550 (1974).
- 16 R. G. Wilkins, 'Adv. Chem. Ser. No. 100', American Chemical Society, 1971, chap. 6.
- 17 A. G. Sykes and J. A. Weil, *Prog. Inorg. Chem.*, **13**, 1 (1970).
- 18 M. Crawford, S. A. Bedell, R. I. Patel, L. W. Young and R. Nakon, *Inorg. Chem.*, **18**, 2075 (1979).