Inorganica Chimica Acta, 126 (1987) 167–171

Polynuclear Complexes of Cobalt(II) with 2-Dipicolylamine and 2-Aminomethylpyridine

DANIEL H. HUCHITAL* and EILEEN DEBESIS

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

(Received July 31, 1986)

Abstract

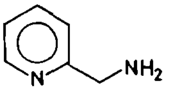
The hypothesis that the blue color of basic anaerobic solutions of cobalt(II) with 2-aminomethylpyridine (AMP) and 2-dipicolylamine (DPA) is due solely to deprotonation of the ligand amine has been modified. Deprotonation does occur, but only as an intermediate step in the reaction. Bis(AMP)cobalt(II) forms stable dimers and polymers in these solutions. The dimerization and polymerization are competitive reactions, the former being directly and the latter inversely dependent on the hydroxide concentration. In the dimer reported earlier, the two metal centers are linked by one μ-hydroxo and two μ-amido bridges. In the polymer reported here, metal atoms are linked by a μ-amido bridge, with μ-hydroxo bridges between alternate metal atoms. Blue complexes of cobalt(II) with DPA contain one mole of ligand per mole of cobalt(II). The dimer is not stable and polymerization readily occurs. The polymer contains one μ-hydroxo and one μ-amido bridge between each pair of metal atoms.

In a previous paper [1] we reported on the nature of amine deprotonation in basic solutions of bis(2-aminomethylpyridine)cobalt(II). The blue color which developed slowly in these solutions was attributed to the formation of a triply-bridged binuclear species in which the two metal centers were linked by one μ-hydroxo and two μ-amido bridges. The results of this work explained the earlier findings of Walker and Nakon [2]. These investigators also reported that bis(2-pyridylmethyl)amine (or 2-dipicolylamine, DPA) solutions with cobalt(II) also turned blue in oxygen-free basic solution. Potentiometric formation data indicated that the reacting species was $[Co(DPA)(H_2O)_3]^{2+}$. As with the 2-aminomethylpyridine (AMP) complex, Walker and Nakon attributed the blue color to a change in cobalt(II) stereochemistry upon deprotonation of the amine hydrogen. They noted, however, that molecular models of a tetrahedral complex indicate severe distortion about the metal center.

Because our initial study on the cobalt(II)–AMP system ruled out a tetrahedral species, we also investigated the cobalt(II)–DPA system. The conditions were similar to those used in our previous study. Some similarities and some differences were noted. The results of this study are reported here. Especially interesting were the similarities between the DPA system and the AMP system at long reaction times for the latter.

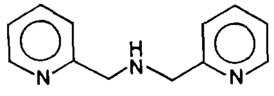
Experimental

The two ligands used in this study have the structures



AMP

and



DPA

The first, 2-aminomethylpyridine (AMP), was purchased from Aldrich Chemical Co. and used without purification. The second, 2-dipicolylamine (DPA), was prepared using a modification of the procedure of Romary *et al.* [3]. Picolylchloride hydrochloride (25 g, 0.15 mol) was dissolved in 50 ml of water and neutralized slowly, in an ice bath, with 15 ml of saturated, aqueous, K_2CO_3. The free base was added to 82.5 g (0.75 mol) of 2-aminomethylpyridine. During addition, the solution was stirred and kept in an ice bath. The mixture was allowed to warm to room temperature, with stirring. KOH pellets were added until the organic oil separated from the aqueous layer. The oil was passed through anhydrous sodium sulfate and distilled at treduced pressure. Two to three milliliters of the desired product distilled at 135 °C (0.35 mm).

HPLC and TLC of this product showed that it contained more than 10% of the starting material, 2-aminomethylpyridine, plus other impurities. The product was purified by semipreparative HPLC, yielding material of greater than 95% purity, as

---

*Author to whom correspondence should be addressed.

0020-1693/87/$3.50

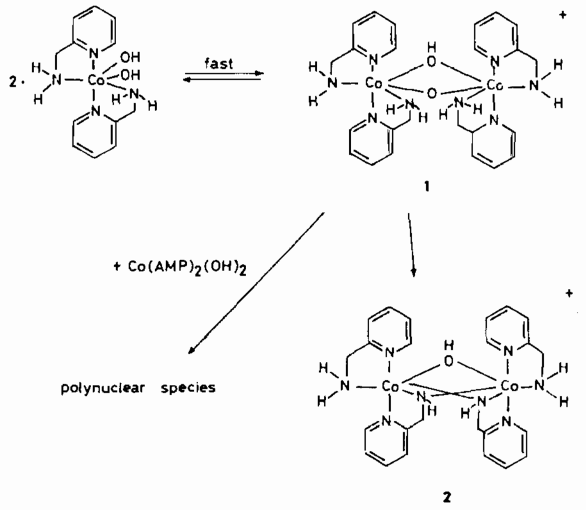
determined by HPLC and NMR, and nearly free of 2-aminomethylpyridine. Mass spectrometry and NMR confirmed the structure as 2-dipicolylamine.

All other chemicals such as cobalt(II) chloride, potassium hydroxide, etc., were purchased from Fisher Chemical Co. These were used without further purification. Solution preparation for kinetic and spectrophotometric runs as well as the measurement procedures were identical to that reported in our previous study.

Results and Discussion

Cobalt(II)–AMP System

The spectrum of an anaerobic solution of bis(2-aminomethylpyridine)cobalt(II) in base has been presented previously [1]. The major maxima are at 380 nm and 595 nm, with the latter peak becoming predominant within 2 h. As the solution ages (within several days) a broad maximum at 473 nm appears, and, as it does, the 595 nm peak shifts to 585 nm. The kinetics of this process was investigated. In the previous work [1], the rate of appearance of the 595 nm peak was found to be approximately half-order in hydroxide ion. For the 473 nm peak, the hydroxide ion dependence (as shown in Fig. 1) is approximately inverse one-half order in hydroxide ion. Thus, kinetically, the two processes are separable under the right conditions. Slow reaction of fractional order, such as this one, are often indicative of polymerization [4]. A proposed structure of a polynuclear complex related to the dimer 2 proposed earlier [1] is shown in Fig. 2. We propose that between pH 9 and 12 there is an equilibrium between the dimeric and polymeric species. Since the polymer forms more readily at lower hydroxide concentrations, and virtually not all above pH 12, a reasonable reaction scheme to explain the spectral changes is



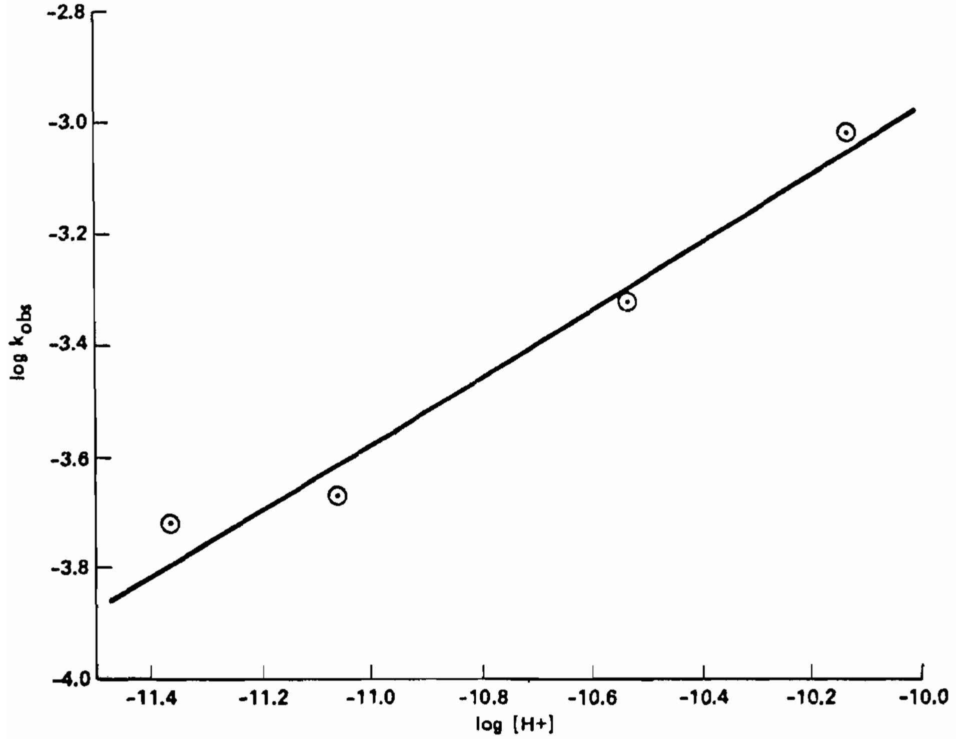


Fig. 1. Dependence of the pseudo-first-order rate constant for appearance of the 473 nm peak on hydrogen ion concentration. [Co(II)] = 1.0×10^{-3} M, [AMP] = 3.5×10^{-3} M.

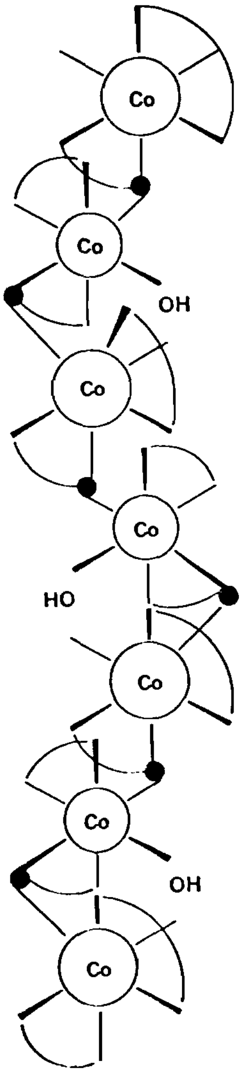


Fig. 2. Proposed structure for the polymer of bis(2-aminomethylpyridine)cobalt(II).

The direct precursor of the dimer **2** is the μ-hydroxo, μ-oxo species **1**. The higher the pH, the more fully formed is this species, and the more likely dimerization is to occur. At or above pH 12, this species is fully formed. Hence, no polymerization reaction is seen to occur. In agreement with this is the fact that the rate constant for formation of the dimer levels off between pH 12 and 13*.

At lower pH values (8.6 to 12), the μ-hydroxo, μ-oxo species is not fully formed. The reaction to form the dimer does occur but, in addition, μ-amido bridges may form to other cobalt centers giving rise to the polymer. The exact nature of this polymerization is not understood at this time. It may involve only mononuclear reactants or the combination of mononuclear dihydroxo-bis(2-aminomethylpyridine)-cobalt(II) with the μ-hydroxo-μ=oxo species, etc.

The scheme presented readily explains the spectral as well as kinetic data. As the peak at 473 nm appears, the intensity of the entire spectrum increases. These slow spectral changes as well as the general increase in absorptivity of the complex are to be expected in a polymerization reaction. The absorbance at 473 nm is increasing as the chain length of the polymer increases. The peak cannot be attributed to the appearance of cobalt(III), which is known to form red complexes with this type of ligand [5]. Oxidation to cobalt(III) has been reported as occurring more rapidly at higher pH [6]; the formation of the 473 nm peak here is inversely related to hydroxide ion concentration. Furthermore, oxygenation of the blue solutions destroys the peak at 473 nm (as well as those at 595 nm and 380 nm). No such similar action of oxygen has been reported for cobalt(III) complexes**.

A measurement of the molecular weight of the polymer by classical techniques was not possible due to its sensitivity to oxygen. The blue solid reported earlier [1], prepared from cobalt(II) chloride and liquid AMP, was stable in air. However, it was not possible to remove all the excess liquid AMP without destruction of the solid. No well-formed single crystals could be obtained for an X-ray analysis. An attempt was made to determine the molecular weight using size separation high performance liquid chromatography or size exclusion chromatography on inert packings. Neither method was successful as the complex either broke apart on contact, under pressure, with acidic silica gel packing, or was not sufficiently soluble in non-polar solvents to obtain meaningful results. Thus, no direct measurement of molecular weight could be made.

The addition of acid to the polymer of cobalt(II) and AMP destroys the violet–red color. As in the case of the dimer, the color returns when the solution is made basic again. However, unlike the dimer, this polymer can remain in acid for several hours without destruction of many of the μ-amido linkages, as the violet–red color still reappears readily upon addition of base.

Cobalt(II)–DPA System

The results with cobalt(II) solutions of 2-dipicolylamine, DPA, mimic (to some extent) the 2-amino-

---

*If the concentration of base is 1 M or greater, there is no reaction. Apparently, hydroxide ion effectively competes for the available coordination sites and bridging does not occur.

**Solutions of the blue complex which are allowed to stand for several weeks with oxygen permitted to leak slowly into the system, turn red. The spectrum of such a solution shows one broad maximum at 540 nm and an intense shoulder at about 370 nm. This spectrum is not affected by oxygen, and is probably that of the oxidized metal monomer complex, dihydroxo-bis-(2-aminomethylpyridine)cobalt(III).

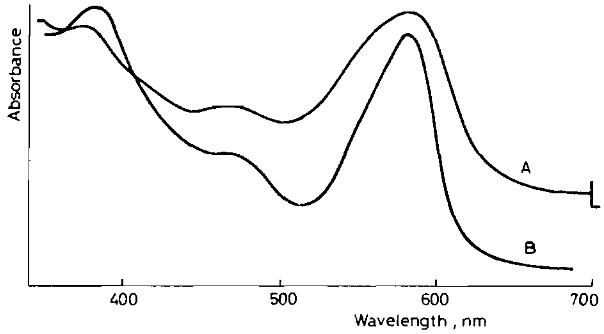


Fig. 3. Spectra of basic anaerobic cobalt(II) solutions. (a) Freshly prepared DPA solution. (b) Aged AMP solution.

methylpyridine system. Both show similar spectral and kinetic features. The spectra of the blue complexes formed in these two systems are shown in Fig. 3. Both have maxima in the same regions and the band shapes are identical. However, the relative absorbance at 473 nm in freshly prepared (<1 h) solutions for the DPA system is quite intense and resembles aged $Co(AMP)_2$ solutions. In the latter system the 473 nm peak forms only slowly, and, as it does, the 595 nm peak shifts to 585 nm. For the DPA system, the 473 peak forms more quickly but the 595 nm peak never develops fully. Rather, the shift to 585 nm occurs together with the appearance of the 473 nm peak.

The kinetics of formation of the blue complex in solutions of cobalt(II) and the DPA ligand was studied and compared to the AMP system. Similar results were obtained, the reaction being first-order with respect to cobalt(II) and DPA. The order with respect to hydroxide ion was difficult to determine. Evidence that this is probably due to a complex dependence of the rate on hydroxide ion concentration is seen on comparing the data with the cobalt(II)–AMP system. The rate of appearance of the 595 nm peak in the AMP system was found to be half-order in hydroxide ion, while that of the 473 nm peak was approximately inverse half-order. In the AMP system the fast (half-order in $[OH^-]$) and slow (inverse half-order in $[OH^-]$) reactions are separable. However, in the DPA system, the rates of the reactions are of the same magnitude; hence, a complex dependence on $[OH^-]$ is not unexpected. For both the AMP and DPA systems the reaction slows down and eventually seems to stop at high ligand to metal ratios. Apparently, when all six coordination sites are occupied by ligand atoms, there is no reaction. In addition, the N-methyl substituted derivative of DPA does not react at all, indicating that deprotonation is a necessary step in the reaction process.

Differences between the DPA and AMP systems rule out a similar structure for their blue or red–blue complexes. First, the initial appearance of the 595 nm peak lasts only a short time for the DPA system as compared to the AMP system. This might be taken as evidence of an initial dimerization followed by polymerization. Second, the spectrum of freshly prepared DPA reaction mixtures (<1 h) resembles aged solutions of AMP reaction mixtures. This also supports a polymeric structure. Third, the color of these freshly prepared DPA mixtures is destroyed by the addition of acid, but, in a manner similar to aged AMP reaction mixtures, there is a longer retention of some bridges in acid, as indicated by the rapid reappearance of color, initially or at long reaction times in acid.

Thus we propose that a polynuclear complex forms in the DPA–cobalt(II) system. The structure is shown in Fig. 4. The polymer is a regular one, with a μ-amido bridge between each pair of metal atoms. A dimer structure for this complex cannot be drawn without leaving one coordination site per cobalt atom unbridged and unchelated. Thus, any dimer which does form can quickly bridge to additional

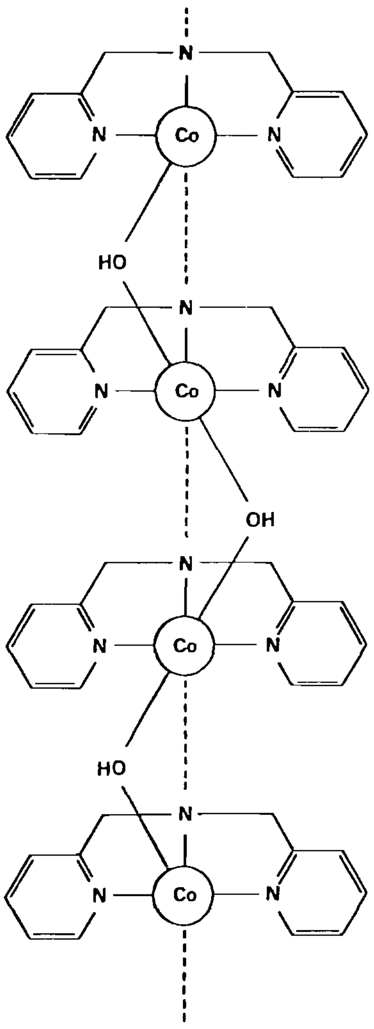


Fig. 4. Proposed structure for the polymer of 2-dipicolylaminecobalt(II).

metal atoms and polymerization rapidly occurs. The kinetic and spectral data reflect such a polymerization, which is indeed rapid in comparison to the analogous AMP system.

Conclusions

The polymers of cobalt(II) with 2-aminomethylpyridine and 2-dipicolylamine appear to be of a new type, an inorganic polymer in which the metal centers are linked by both μ-hydroxo and μ-amido bridges. Appleton and Sarkar [7] observed a violet color formed in basic, oxygen-free solutions of cobalt(II) and N-methylimidazole, and attributed the color to the formation of a polymer in which each cobalt atom was coordinated to three or four ligand molecules and linked via one or two μ-hydroxo bridges. The work described here differs from this in that proton ionization occurs leading to μ-amido bridges in addition to μ-hydroxo bridges. Similarly, proton ionization was postulated by Martin *et al.* [5, 8] for color changes occurring in a series of bis(dipeptide)cobalt(II) complexes in basic oxygen-free solution. These color changes were attributed to a partial conversion from high-spin to low-spin octahedral cobalt(II). The results of the present investigation, however, suggests that a polymer, similar to those described above, cannot be ruled out.

References

1 D. H. Huchital and E. Debesis, *Inorg. Chim. Acta, 98,* 79 (1985).

2 J. K. Walker and R. Nakon, *J. Am. Chem. Soc., 99,* 8359 (1977).

3 J. K. Romary, J. D. Barger and J. E. Bunds, *Inorg. Chem., 7,* 1142 (1968).

4 R. G. Wilkins, 'The Study of Kinetics and Mechanisms of Reactions of Transition Metal Complexes', Allyn and Bacon, Boston, 1974, p. 67.

5 M. D. Michailidis and R. B. Martin, *J. Am. Chem. Soc., 91,* 4683 (1969).

6 F. Miller and R. G. Wilkins, *J. Am. Chem. Soc., 92,* 2687 (1970).

7 D. W. Appleton and B. Sarkar, *Bioinorg. Chem., 7,* 211 (1977).

8 P. J. Morris and R. B. Martin, *Inorg. Chem., 10,* 964 (1971).