a THF solution of **3** is treated with 2 equiv of HCl/ether at −78 °C, the product obtained by ether extraction shows a two-line ν(CO) pattern at 1990 and 1895 cm^{-1}. This species may be the dienol analogue of complex **2**, although further characterization is needed. Such a complex would not possess a direct, formal carbon analogue.

The preparation and complexation of the dianion **3** and its derivatives and the synthesis of the neutral, dienol complexes are being pursued actively.

Acknowledgment. We thank the University Research Council of Vanderbilt University and the National Science Foundation (Grant No. CHE-76-14304) for support of this research.

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(3) C. M. Lukehart and J. V. Zeile, *J. Am. Chem. Soc.*, **98**, 2365 (1976).

(4) C. M. Lukehart and J. V. Zeile, *J. Am. Chem. Soc.*, **99**, 4368 (1977).

(5) Infrared and ^1H NMR spectra were recorded on Perkin-Elmer 727 and JOEL MH-100 spectrometers, respectively. Microanalyses were performed by Galbraith Laboratories, Inc. Knoxville, Tenn.

(6) Hafnium could not be analyzed in the presence of rhenium.

(7) $(PPN)BF_4$ was prepared by the metathesis reaction of (PPN)Cl and $AgBF_4$ in acetone solution in 95% yield.

(8) This dianion is very similar to the dianion $[fac\text{-}(PhCH_2CO)_3Mn(CO)_3]^{-2}$ prepared by M. Y. Darensbourg et al.[9] However, this manganese dianion was prepared quantitatively using a 20-fold excess of $PhCH_2MgCl$. Presumably such an excess of the alkylating reagent would inhibit the successful coordination or protonation of this dianion.

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(10) The rapid addition of the methyllithium produces **3** directly. If unreacted acetyl complex is present, the dianion **3** will react with it producing the rhenium monoanion analogous to **1**.

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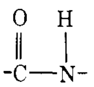
Cobalt(II) Induced Amine Deprotonation in Aqueous Solution in the Near Basic pH Range

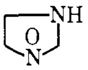
Sir:

There are three major types of N–H bonds generally found in proteins: amide (i), imidazole (ii), and amino ($-NH_2$). Metal ions have been reported to induce both amide[1] and imidazole[2] proton ionizations which are often accompanied by concomitant stereochemical changes about the metal ion; e.g., the nickel(II) complex of the triglycine undergoes a change from octahedral to square-planar geometry upon amide proton ionization[1c] and the bis(histidinato)cobalt(II) chelate is reported to undergo transformation from an octahedral to tetrahedral environment upon imidazole proton ionization. We now wish to report the first case of stereochemical changes induced in cobalt(II) chelates upon amino proton ionization in aqueous solution near the physiological pH range. We chose to study the colbalt(II) complexes of tridentate bis(2,2′-pyridylmethyl)amine (DPA) (I)[3] and bidentate 2-aminomethylpyridine (AMP) (II)[4] because of possible charge stabilization due to dispersal from the ionized amino group through the metal ion into the pyridine rings via "d"–π^* orbital interactions.[5]

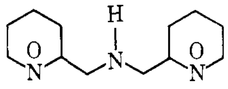


$-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}-$

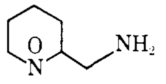
i



ii



I



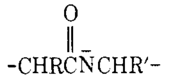
II

Potentiometric formation curves of 1:1, DPA·3HCl to cobalt(II), solutions have an inflection at $a = 3$, moles of base per mole of ligand, indicating the formation of $[Co(DPA)(H_2O)_3{}^{2+}]$.[6] At pH 8.5, a second buffer zone with slow equilibrium times (up to 15 min/titration point) is found, indicating that a reaction other than that of a simple deprotonation (usually quite fast) is occurring. The color of the solution turns from pink to deep blue as the deprotonation reaction occurs, indicating a change in cobalt(II) stereochemistry.[7-10] Computer treatment of the titration data indicate that there are two proton ionizations in the second buffer region.[11] Infrared spectra (KBr disk) of the isolated blue compound,-$[Co(H_{-1}DPA)OH]\cdot 3H_2O$[12] indicated the lack of a N–H band. Upon recrystallization from MeOH, the infrared spectrum (KBr disk) of $[Co(H_{-1}DPA)OH]$ (III) contained no N–H band and a sharp strong band at 3640 cm^{-1}, indicating a nonhydrogen-bonded OH group.[13,14] The conductivity of III (9.7×10^{-4} M) in CH_3NO_2 was measured to be 5.4 $\Omega\ cm^2/mol$,[15] and the molecular weight of III obtained by vapor pressure osmometry in MeOH was determined as 265 ± 5. The above indicate that III is a nonionic monomeric metal complex. This together with infrared and visible spectral data supports the formulation of III as $[Co(H_{-1}DPA)OH]$. DPA was found not to undergo amine proton ionization in the presence of Zn^{2+}, Ni^{2+}, or Cu^{2+}.

Potentiometric formation curves of 1:1 and 2:1, *N*-methylbis(2,2′-pyridylmethyl)amine (MeDPA) to cobalt(II), solutions have an inflection at $a = 3$, indicating the formation of $[Co(MeDPA)(H_2O)_3{}^{2+}]$ and $[Co(MeDPA)_2{}^{2+}]$, respectively.[16] In both systems, the color of the solutions remained pink above pH 10, the equilibria times above pH 8 were fast, and there was no near basic buffer zone as in the Co:DPA formation curves. The above indicates that the replacement of the amino hydrogen in DPA by a methyl group drastically alters the solution chemistry of Co^{2+}; i.e., there is no proton ionization in the near basic pH range and there appears to be no change in the stereochemistry of Co^{2+}. The above further supports the ionization of the amino proton in $[Co(DPA)(H_2O)_3{}^{2+}]$.

Potentiometric formation curves of 2:1, AMP·2HCl to cobalt(II), solutions had an inflection at $a = 2$, indicating the formation of $[Co(AMP)_2(H_2O)_2{}^{2+}]$, followed by a second buffer zone similar in nature (long equilibrium times) to that of the 1:1, $Co^{2+}\cdot$DPA, system.[17] Again two protons were liberated in the second buffer zone as the solution turned deep blue, indicating the formation of $[Co(H_{-1}AMP)_2]$.[18] It is interesting to note that $Co(DPA)^{2+}$ with two pyridyl donors per amine undergoes deprotonation at a lower pH value (0.3 unit) than does $Co(AMP)_2{}^{2+}$ with only one pyridyl residue/amine nitrogen. This suggests that the aromatic ring possibly acts as an electron density sink for the deprotonated amine, where charge is dispersed through the "d" orbitals of the metal into the π^*-antibonding orbitals of the pyridine rings. This would also explain why similar amine deprotonation reactions have not been reported in diethylenetriamine or other polyalkylenepolyamine complexes of Co^{2+}.

The biological consequences of the above are possibly great. Deprotonation reactions observed in the metal ion binding of peptides and proteins, often thought to be due to the ionization of peptide protons, could in some cases be due to amino proton ionization. $[Co(DPA)(H_2O)_3{}^{2+}]$ begins to deprotonate at pH 8.5, a pH value similar to that at which bis(glycylglycinato)cobalt(II) starts to undergo amide proton ionization.[19] The consequences of amino vs. amide proton ionization arise not only in the resultant stereochemistry of the metal ion,[1b,c] but also the conformation of the peptide. X-ray studies[20] have shown that deprotonated peptide groups usually contain planar



$$-\mathrm{CHR}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\bar{\mathrm{N}}\mathrm{CHR'}-$$

iii

iii moieties. Deprotonated amine groups, on the other hand, may not require any great change in peptide conformation. Considering the relatively low pH value at which [$\mathrm{Co(DPA)(H_2O)_3}^{2+}$] undergoes amine deprotonation, care probably should be exercised now in the assignment of metal ion induced deprotonation reaction in metal-peptide and -protein systems to amide proton ionization.

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(4) Potentiometric studies of $\mathrm{Co(AMP)_2}^{2+}$ formation have been reported previously, L. G. Sillén and A. E. Martell, *Chem. Soc. Spec. Publ.*, **No. 17,** 482 (1964); **No. 25,** 415 (1972). None of the papers listed apparently involved studies of these complexes at high pH. Perhaps oxygenation reactions were encountered (see ref 3).

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(6) $[\mathrm{Co}^{2+}] = 1.33 \times 10^{-3}$ M; the titrant was 0.121 M NaOH. All potentiometric measurements were made on a Corning Digital Research Model 112 pH meter equipped with Corning glass and calomel extension electrodes. The ionic strength of all solutions was maintained at 0.10 M ($\mathrm{KNO_3}$).

(7) Titrations of 2:1, DPA•3HCl to cobalt(II), solutions had an inflection at a = 3.0, indicating the formation of [$\mathrm{Co(DPA)_2}^{2+}$]. Above pH 8.8, a second buffer zone similar to that for the 1:1 system was observed. Log $K_{1a} = -10.13 \pm 0.02$ and $K_{2a} = -11.82 \pm 0.06$. The visible spectrum of the 2:1 DPA to cobalt(II) deprotonated species is very similar that of the deprotonated 1:1 metal chelate. We are not at this time prepared to assign both proton ionizations in [$\mathrm{Co(DPA)_2}^{2+}$] to the formation of [$\mathrm{Co(H_{-1}DPA)_2}$].

(8) A. B. Blake and F. A. Cotton, *Inorg. Chem.*, **3,** 5 (1964).

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(10) The visible spectrum (320–650 nm) of deprotonated [$\mathrm{Co(DPA)^{2+}}$] shows a strong absorption at 595 nm, which coupled with the large extinction coefficient (ϵ_{max} 1680 M^{-1} cm^{-1}) is typical of tetrahedral cobalt(II). However, the spectrum is more complex with weaker bands at 474 nm (800 M^{-1} cm^{-1}) and 380 nm (1280 M^{-1} cm^{-1}). These latter bands are shoulders on a very intense charge transfer band which tails into the visible. These latter bands are not yet understood and are probably not due to the presence of small amounts of oxygenated complexes. Molecular models indicate that $\mathrm{Co(H_{-1}DPA)OH}$ must be greatly distorted if indeed the geometry about Co is tetrahedral.

(11) Log $K_{1a} = -9.60 \pm 0.04$, $\mathrm{Co(DPA)^{2+} \rightleftharpoons Co(H_{-1}DPA)^+ + H^+}$; log $k_{2a} = -11.87 \pm 0.08$, $\mathrm{Co(H_{-1}DPA)^+ \rightleftharpoons Co(H_{-1}DPA)OH}$.

(12) Anal. Found: C, 44.06; H, 5.87; N, 12.86. Theoretical: C, 43.90; H, 5.83; N, 12.80. Crystals were obtained by adding 5 equiv of NaOH to a 1:1 DPA•3HCl to $\mathrm{Co(NO_3)\cdot 6H_2O}$ solution (10^{-2} M). The solution was placed in a vacuum dessicator over anhydrous $\mathrm{CaCl_2}$.

(13) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", 2nd ed, Wiley, New York, N.Y. 1970.

(14) R. A. Nyquist and R. O. Kagel, "Infrared Spectra of Inorganic Compounds", Academic Press, New York, N.Y., 1971.

(15) Conductivity was determined at 25 °C on a Serfoss conductivity bridge Model RC M15, Arthur H. Thomas Co.

(16) $[\mathrm{Co}^{2+}] = 1.46 \times 10^{-3}$ M and the titrant was 0.121 M NaOH.

(17) $[\mathrm{Co}^{2+}] = 1.77 \times 10^{-3}$M and the titrant was 0.121 M NaOH.

(18) $\mathrm{Co(AMP)_2}^{2+} \rightleftharpoons \mathrm{Co(H_{-1}AMP)(AMP)^+ + H^+}$, log $K_{1a} = -9.94 \pm 0.10$; $\mathrm{Co(H_{-1}AMP)(AMP)^+ \rightleftharpoons Co(H_{-1}AMP)_2 + H^+}$, log $K_{2a} = -11.03 \pm 0.08$. The conductivity determined on a 2.1×10^{-3} M solution of $\mathrm{Co(H_{-1}AMP)_2\cdot 5.0H_2O}$ was 4.7 Ω cm^2/mol, indicating the presence of a neutral metal complex. Visible spectra of $\mathrm{Co(H_{-1}AMP)_2}$ are quite complex exhibiting λ_{max} values at 594 nm (1600 M^{-1} cm^{-1}), 473 nm (1030 M^{-1} cm^{-1}), and 371 nm (1750 M^{-1} cm^{-1}). The numbers in parentheses are extinction coefficients, and the latter two bands are shoulders on a very intense ultraviolet charge transfer band which tails into the visible. The spectrum is similar to that of [$\mathrm{Co(H_{-1}DPA)OH}$].

(19) M. S. Michaildis and R. B. Martin, *J. Am. Chem. Soc.*, **91,** 4683 (1969): $\mathrm{Co(GG)_2 \rightleftharpoons Co(H_{-1}GG)(GG)^- + H^+}$, log $K_{1a} = -9.85$; $\mathrm{Co(H_{-1}GG)GG^- \rightleftharpoons Co(H_{-1}GG)_2{}^{2-} + H^+}$, log $K_{2a} = -10.15$.

(20) H. C. Freeman, *Adv. Protein Chem.*, **22,** 257 (1967).

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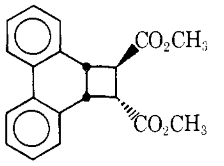
Interception of a Triplet Biradical by Paramagnetic Species. Enhancement of a Photocycloaddition

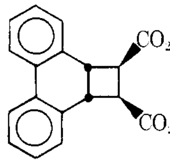
Sir:

The intervention of triplet 1,4 biradicals has long been suggested in Norrish II fragmentations[1] and [2 + 2] photocycloaddition reactions.[2-4] Evidence for their intermediacy in cycloadditions derives largely from the observation of virtually complete stereorandomization in photoproduct under conditions where reactants maintain stereochemical integrity.[3,4] There have been several observations of interception of biradicals.[5-15] Wagner[6] has estimated a lifetime of 300 ns for a 1,4 triplet biradical in the Norrish II reaction from an elegant intramolecular trapping experiment, and Scaiano[12] has directly determined the lifetime of a related biradical as 97 ± 15 ns in methanol[13] and 42 ns in benzene.[14] O'Neal has estimated a longer lifetime in the vapor phase.[7] We here report the interception of a 1,4-biradical intermediate in a [2 + 2] photocycloaddition. Di-*tert*-butyl nitroxide (N) and molecular oxygen interact efficiently with the 1,4 biradical and enhance its collapse to cyclobutanes.

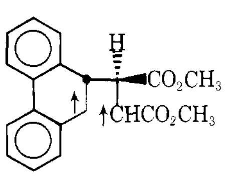
The benzophenone (B) photosensitized reaction of phenanthrene (P) with dimethyl fumarate (F) affords the stereoisomeric cyclobutanes (T) and (C) and dimethyl maleate (M).[16,17] The mechanism is thought to involve a triplet exciplex, ^{3}(P···F), subsequent collapse of which to a biradical (^{3}SS) ultimately affords the photoproducts.[16,17] For both N and oxygen, small *increases* (5–20%) in the quantum yields for C + T occur on addition of small concentrations (10^{-2} M) of "quencher", while ϕ_M decreases. Further increase in [N] quenched both reactions owing to the known[18] quenching of ^{3}B and ^{3}P by N.



T



C



SS

We analyze the reaction in the presence of N as shown in Scheme I. A similar scheme applies for O_2.

For the first two terms, $\phi_{^3P}$ and $\phi_{^3SS}$, all necessary rate constants were either known[18] from competitive quenching of *trans*- to *cis*-stilbene isomerization or measured by the same technique. Concentrations employed minimized the effects of