

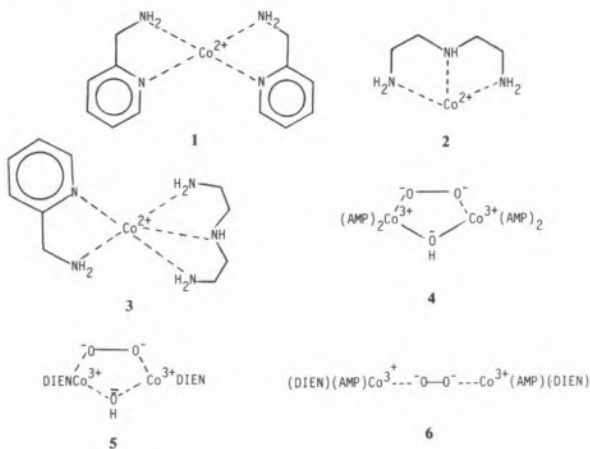


PS5.23 — TH

ARUP K. BASAK
ARTHUR E. MARTELL
Department of Chemistry
Texas A&M University
College Station, Texas 77843
U.S.A.

REACTIONS OF DIOXYGEN COMPLEXES. AUTOXIDATION OF 2-AMINOMETHYL- PYRIDINE THROUGH COBALT DIOXYGEN COMPLEX FORMATION

The metal complex formation constants and the oxygenation constants of the cobalt(II) complexes of diethylenetriamine (DIEN) and 2-aminomethylpyridine (AMP) have been determined by potentiometric measurements under N_2 and O_2 . In the mixed ligand system three cobalt complexes are formed which are capable of combining with dioxygen: the 2:1 AMP complex, **1**, the 1:1 DIEN complex, **2** and the 1:1:1 mixed ligand DIEN, AMP complex, **3**. The corresponding dioxygen complexes are indicated by formulas **4**, **5**, and **6**. The equilibrium constants for the mixed ligand system have been employed to determine the conditions under which the concentration of **3** has its maximum value, and the conditions that favor the formation of the mixed ligand dioxygen complex **6**.



The kinetics of oxidative dehydrogenation of **3** through the formation and degradation of **6** have been measured spectrophotometrically and rate constants are reported. The reaction has been found to be second order, first order in the concentration of the dioxygen complex and first order in the concentration of hydroxide ion. The reaction product in the two-electron oxidation of AMP is the corresponding imine, which under the reaction conditions employed is converted to pyridine-2-carboxaldehyde, determined quantitatively as the 2,4-dinitrophenylhydrazone. The proposed reaction mechanism involves deprotonation of the amino group, through the influence of the Co^{3+} center, as a pre-equilibrium step. This is followed by a concerted process involving homolytic fission of dioxygen, shift of an electron through the metal ion to the coordinated oxygen, and transfer of the α -proton to the oxygen atom. The two-electron oxidation of each AMP ligand is thus balanced by conversion of half of the dioxygen to water, with regeneration of cobalt(II). The proximity of the dioxygen to the α - CH_2 of the ligand is considered an important requirement for this concerted mechanism.



PS5.24 — TH

W.L. KWIK
K.P. ANG
Department of Chemistry
National University of Singapore
Singapore

COORDINATION ABILITIES OF SUBSTITUTED PHENOLATES — A SPECTROPHOTOMETRIC AND CONDUCTOMETRIC STUDY

The copper(II) — phenolate oxygen interaction in several mixed-ligand complexes of copper(II) containing a heterocyclic amine and a phenol has been studied by electronic spectral,