

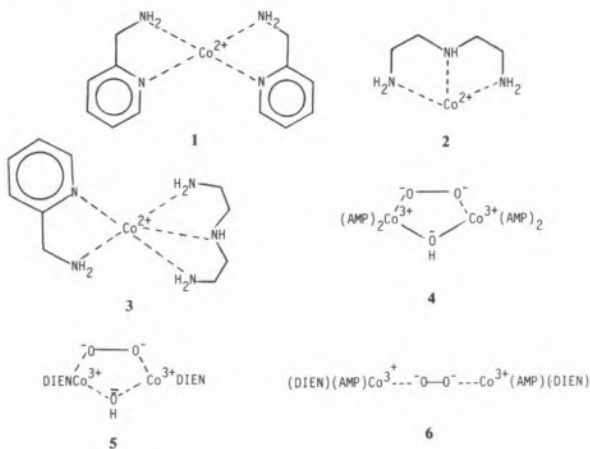


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REACTIONS OF DIOXYGEN COMPLEXES. AUTOXIDATION OF 2-AMINOMETHYL- PYRIDINE THROUGH COBALT DIOXYGEN COMPLEX FORMATION

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.



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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,

conductometric and EPR spectral measurements. Electronic spectral results demonstrate the dependence of such interaction on the nature of the phenolic substituents as well as the solvents. Partial dissociation of the phenolate from the complex was detected in methanol at low concentrations ($\leq 1 \times 10^{-4}$ M). In DMSO the complexes remain intact. The X-band EPR spectral data obtained at ambient temperature and at 77 K are consistent with the results from the electronic spectral and conductometric study.

INTRODUCTION

Metal-phenolate oxygen interaction has been known to exist in Fe(III), Cu(II) and several trivalent metal transferers [1]. An investigation of model compounds of Cu(II) containing a phenolate ligand could be useful in providing an insight into the geometry of the naturally occurring metal enzymes. Several studies [2-4] have reported the binding of phenolate oxygen to Cu(II) in solution. This present study reports some characteristic features of the Cu(II) — phenolate oxygen interaction in several mixed-ligand complexes [Cu(terpy)(RArO)Cl] (terpy = 2,2',2'-terpyridine; RArO = phenolate with substituent R).

RESULTS AND DISCUSSION

The complexes of this study display in both methanol and DMSO, broad d-d absorption bands at 680-720 nm, indicative of tetragonal geometry around Cu(II). An intense band/shoulder is found in the 380-450 nm region ($\epsilon = 400-600 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) (Table I). This is characteristic of the Cu(II) — phenolate oxygen coordination [3,4,6]. Unlike the d-d transitions, this band is solvent dependent, shifting to lower energy in going from methanol to DMSO. Moreover among the complexes contain-

ing the *p*-methoxy-, *p*-chloro-, *p*-bromo-, *p*-fluoro-, *o*-NO₂- and *m*-NO₂-phenolate, the position of this band points to varied phenolate-Cu(II) interaction as one goes from the electron-donating to the increasingly stronger electron-withdrawing phenolic substituents. Among the complexes containing the *p*-NO₂-, 2,4-dinitro- and 2,5-dinitro-phenolate, the absorption in the 380-450 nm region appears as an exceedingly strong and well-defined band ($\epsilon = 1 \times 10^3 - 1 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) in both methanol and DMSO. Although a similar band of lower intensity is found in the corresponding phenol ($\epsilon = 1 \times 10^2 - 1 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), the observed band in the complex is characteristic of the complex as the molar absorptivity remains, in each case, as a constant over a concentration range of $1 \times 10^{-3} - 1 \times 10^{-4}$ M. This contrasts with the decreasing values of the «apparent» ϵ evaluated for the uncoordinated phenol as concentration increases. This would be expected if the strong band in the 380-450 nm is due to the phenolate ion. Thus the strong absorption band in each of the three nitrophenolate complexes is tentatively assigned to a $\pi \rightarrow \pi^*$ transition of the coordinated phenolate which is most probably nonbridging. Values of the molar conductance of all the complexes at concentration $\geq 1 \times 10^{-4}$ M, fall in the range of $90-110 \Omega^{-1} \text{ cm}^{-1} \text{ mol}^{-1}$ in methanol and of $20-40 \Omega^{-1} \text{ cm}^{-1} \text{ mol}^{-1}$ in DMSO, suggesting that these complexes behave as 1:1 electrolytes in both solvents. However as the concentration is lowered further ($< 1 \times 10^{-4}$ M) the molar conductance of the complexes in methanol rises sharply to $400-450 \Omega^{-1} \text{ cm}^{-1} \text{ mol}^{-1}$, accompanied by significant increases in intensities of the phenolate band. These changes indicate partial dissocia-

Table I
EPR Parameters and Electronic Spectra (380-450 nm) for Selected Copper(II) Complexes

Complex (L = ArO)	g_{\perp}	g_{\parallel}	$A_{\parallel} \text{ cm}^{-1}$	$\nu_{\text{max}}, \text{ nm}(\epsilon)$	
				CH ₃ OH	DMSO
[Cu(terpy)(<i>o</i> -NO ₂ L)Cl]	2.09	2.22	0.0162	410(Sh)	450(500)
[Cu(terpy)(<i>m</i> -NO ₂ L)Cl]	2.11	2.23	0.0164	430(Sh)	460(200)
[Cu(terpy)(<i>p</i> -NO ₂ L)Cl]	2.12	2.22	0.0166	390(1×10^4)	434(1.5×10^4)
[Cu(terpy)(<i>p</i> -FL)Cl]	2.11	2.23	0.0163	405(Sh)	460(600)
[Cu(terpy)(<i>p</i> -CIL)Cl]	2.09	2.22	0.0165	405(Sh)	455(200)
[Cu(terpy)(<i>p</i> -BrL)Cl]	2.08	2.21	0.0165	400(Sh)	455(150)
[Cu(terpy)(<i>p</i> -OCH ₃ L)Cl]	2.08	2.23	0.0163	400(Sh)	405(200)
[Cu(terpy)(2,4-di-NO ₂ L)Cl]	2.12	2.22	0.0166	380(Sh)	432(1.2×10^4)
[Cu(terpy)(2,5-di-NO ₂ L)Cl]	2.13	2.23	0.0167	433(3×10^2)	494(3×10^3)

tion of the complexes in methanol, probably yielding Cu(terpy)^{2+} and phenolate at low concentrations. In DMSO, however, both the molar conductance and absorptivity remain nearly constant even at low concentration. For the five complexes containing *p*-methoxy, *p*-Cl, *p*-Br, *p*-F, *o*-NO₂ or *m*-NO₂-phenolate, no distinct phenolate absorption appears in the visible region, rendering it impractical to monitor the behaviour of these complexes at low concentration. However the molar conductivities display sharp increases at low concentrations ($<1 \times 10^{-4}$ M) in methanol, indicative of similar behaviour as for the nitrophenolates.

The solution and frozen-glass EPR spectra of these complexes in 5:1 methanol:water at low concentrations lend further support to the presence of non-bridging phenolate in these complexes as well as to the partial dissociation. Thus at 77 K the spectra are well-resolved, indicating that these complexes are monomeric (Table I). Furthermore the spin-Hamiltonian parameters [g_{\parallel} , g_{\perp} , A_{\parallel} ($^{63/65}\text{Cu}$)] are typical of tetragonal Cu(II) complexes. Substantial covalency of the Cu-N bond is evidenced by the seven well-defined N-14-superhyperfine structure on the g_{\perp} component, demonstrating the equivalence of the three pyridyl N. At ambient temperature, however the spectra are poorly resolved, displaying striking resemblance to that reported recently for $[\text{Cu(terpy)}]^{2+}$ [6]. In the latter the poorly resolved spectrum has been attributed to dynamic Jahn-Teller effect.

REFERENCES

- [1] B.P. GAHER, J. MISKOWSKI, T.G. SPIRO, *J. Am. Chem. Soc.*, **96**, 6868 (1974).
- [2] J.M. PASTOR, A. GARNIER, L. TOSI, *Inorg. Chim. Acta*, **37**, L549 (1979).
- [3] H. KOZLOWSKI, M. BEZER, L.D. PETTIT, *J. Inorg. Biochem.*, **18**, 231 (1983).
- [4] R.J.W. HEFFORD, L.D. PETTIT, *J. Chem. Soc., Dalton Trans.*, 1331 (1981).
- [5] W.L. KWIK, K.P. ANG — Synthesis and Characterisation of these complexes were presented at ICCS XXIII, July 29-August 3, 1984.
- [6] A. GERGELY, T. KISS, *Inorg. Chim. Acta*, **16**, 51 (1976).
- [7] R.B. BONOMO, F. RIGGI, *Transition Met. Chem.*, **9**, 308 (1984).



PS5.25 — TU

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COMPLEX FORMATION IN THE SYSTEM Ni(II) — α -MERCAPTOPHENYLACETIC ACID

INTRODUCTION

The complex chemical significance of biologically active ligands like L-cysteine and D-penicillamine is determined by the mercaptosulphur donor atom, which is quite soft in character. The ability of these ligands to act as chelating agents of metal ions is due to the presence of other electron donor groups in their molecule. A deeper understanding of this type of chelate formation requires extension of research into studies of the effect of different substituents in the chelation properties of a ligand. The aim of the present work is to study the influence of the presence of a phenyl group in the Ni(II) complexing activity of aliphatic α -mercaptoacids.

It has been reported that α -mercaptoacetic acid (I) forms polynuclear — Ni_3L_4 , Ni_4L_6 — and mononuclear — NiL_2 — complexes [1-3]. The same species excluding the Ni_4L_6 have been considered for α -mercaptopropionic acid (II) [4]. In this study formation constants for the Ni(II) complexes of α -mercaptophenylacetic acid (III) have been determined.

