of N-methylcarbamoil group, is also structurally related to morphine. The methylcarbamate group present in physostigmine differentiates this drug from eseroline and is responsible in determining the well known indirect cholinomimetic activity.

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Synthesis and Chemical Properties of Copper(I) and Copper(II) Complexes of N,N'-Bis(3-(2-Thenylidene)-iminopropyl)piperazine (TIPP) and N,N'-Bis(3-(2-Thenyl)aminopropyl)piperazine (TAPP)

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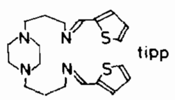
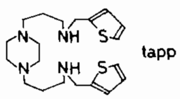
Despite much current interest in the unusual physical properties of a variety of copper containing proteins [1], the chemistry and reactivity of Cu(II) and especially Cu(I) ions in non-classical N_xS_y coordination environments remains rather undeveloped. We have studied the chemical properties of Cu(I) and Cu(II) complexes of the polyfunctional ligands tipp and tapp, which contain four nitrogen and two sulfur atoms as potential donor sites. Preliminary results of the X-ray structural determination of a member of this series of complexes, [Cu(tapp)] $[ClO_4]_2$, indicate a distorted square-planar geometry of the Cu(II) ion, with a CuN_4 coordination. In solution, electronic and EPR spectra of $[Cu(tapp)]^{2+}$ show solvent dependence (Table I). In particular, the intensity of absorption bands (at ~300 and ~600 nm) decreases with time in donor solvents (CH_3CN, CH_3NO_2). We are currently investigating in more detail the nature of these effects.



tipp



tapp

A similar behavior is exhibited by the complex $[Cu(tipp)]^{2+}$. However, in this case the changes observed in the electronic spectra are mainly related to the hydrolysis of the coordinate Schiff base undergone by the complex in the presence of traces of water. This reaction is known to occur in other metal coordinated Schiff bases derived from 2-thiophenecarboxaldehyde [2].

TABLE I. EPR Parameters in Frozen Solutions at 77 K.

Compound	Solvent	$g_\parallel$	$A_\parallel.10^4$ (cm^{-1})
[Cu(tipp)] $[ClO_4]_2$	acetone	2.210	155
	nitromethane	2.235	185
[Cu(tapp)] $[ClO_4]_2$	acetone	2.204	180
	nitromethane	2.243	209

The Cu(I) complexes of tapp and tipp are stable in the solid state. In solution, $[Cu(tapp)]^+$ undergoes rapid aerobic oxidation, while $[Cu(tipp)]^+$ shows a remarkable stability toward oxidation. In Fig. 1 the rate of hydrolysis of $[Cu(tipp)]^{2+}$ and $[Cu(tipp)]^+$ in undried acetonitrile are compared. The faster hydrolysis of the Cu(II) complex is explained in terms of: (*i*) the higher charge of the ion, which produces a higher degree of polarization of the coordinated imine linkage, and (*ii*) a partial displacement of coordinated Schiff base by solvent molecules occurring in the case of $[Cu(tipp)]^+$. An intermediate with intense blue color is formed if $[Cu(tipp)]^{2+}$ is prepared from $Cu(OSO_2CF_3)_2$ in pre-dried CH_2Cl_2. This evolves to the product actually isolated in the standard preparation, but its reaction with traces of water is extremely fast (Fig. 2), and also leads to products formed through a transamination process preceding the hydrolysis step.

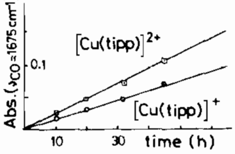


Fig. 1.

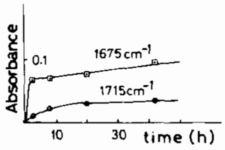


Fig. 2.

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Interaction of Lanthanide Ions with Glutamic Acid and γ-Carboxyglutamic Acid

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Interactions of lanthanide ions with glutamic acid and γ-carboxyglutamic acid has been studied by the