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)

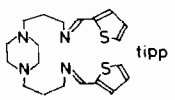
JAMES A. IBERS

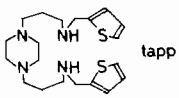
Department of Chemistry, Northwestern University, Evanston, Ill., 60201, U.S.A.

and LUIGI CASELLA

Istituto di Chimica Generale, Via Venezian 21, 20133 Milan, Italy

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.

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	$g_{\|\|}$	$A_{\|\|}.10^4$ (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.

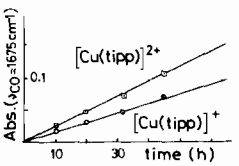


Fig. 1.

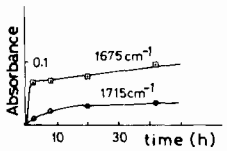


Fig. 2.

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

J. LEGENDZIEWICZ*, E. HUSKOWSKA, H. KOZŁOWSKI and B. JEZOWSKA-TRZEBIATOWSKA

Institute of Chemistry, University of Wrocław, Wrocław, Poland

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

NMR method. These investigations made it possible to determine the coordination mode of aminoacids with lanthanide ions. The results are also of biological interest, since the lanthanides are often used as probes in calcium biochemistry. From our earlier studies on interaction of La(III), Lu(III) and Nd(III) ions with aspartic acid and asparagine it follows that light and heavy lanthanide ions interact in different ways with the carboxylic groups of aminoacids. In order to confirm this suggestion we extended our studies to glutamic acid and γ-carboxyglutamic acid. ^{1}H, ^{13}C NMR and electron spectra were recorded. Correlation of NMR chemical shifts with hypersensitive band intensity changes of lanthanide ions allows the determination of the coordination mode of the discussed aminoacids. Obtained results were confirmed by the Eu(III) luminiscence spectra.

Conformational and Dynamic Aspects of an Ion-Binding Cyclic Peptide Analogue of Valinomycine, Cyclo(LAla-Gly-DPhe-LPro)$_3$

J. P. DEGELAEN, P. PHAM and E. R. BLOUT

Department of Biological Chemistry, Harvard Medical School, Boston, Mass. 02115, U.S.A.

We have investigated the binding of various cations Ba, K, Rb, Cs, Na and Li to a newly synthesized cyclododecapeptide cyclo (LAla-Gly-DPhe-LPro)$_3$ in various solvents by using the Nuclear Magnetic Resonance technique.

It was shown that Na and Li form primarily 1/2 ion peptide complexes with the cyclic peptide while the other cations form mainly 1/1 ion peptide complexes.

Temperature variation and solvent perturbation techniques were used in addition to the coupling constants to deduce the conformations of the 1/1 ion peptide complexes. These were found to be related to the bracelet conformation of the valinomycin-K complex. However, small but significant conformational differences were found in the various cation complexes which could be explained on the basis of the cation characteristics.

Isotope exchange studies also allowed us to propose a mechanism of cation release capture involving the breaking of three of the six intramolecular hydrogen bonds which stabilise the 1/1 ion peptide complex.

NMR Study of Interaction of Nucleic Acid Bases in DMSO

A. L. Al-JIBURY, F. M. ABBAS and SALMAN R. SALMAN

Chemistry Department, College of Science, University of Baghdad, Iraq

The mechanism of the interaction of DNA bases, with DMSO, or with other solutes in DMSO is not clear. It was suggested that this interaction might be through the formation of hydrogen bonding or through charge transfer complex [1].

The aim of this work is to study the interaction of those bases with different acceptors such as nitromethane, nitrobenzene, acetyl acetone, nicotine and acridon, using NMR techniques, in hope of shedding some light on the nature of the above mentioned interaction.

Uracil

At low concentrations (0.06 *M*) N_1H signal did not separate from N_3H, this is a good indication that uracil association is stronger than uracil–DMSO. However when a fixed concentration of uracil is mixed with varying concentration of acetyl acetone, acridon, nicotine and nitromethane, N_1H separates from N_3H and proton 5 splits into a doublet of doublets with $^{4}J_{N_3H,H_5}$ = 1.5 Hz [2]. This indicates that N_3H freezed before N_1H due to the formation of hydrogen bonding between the more acidic proton (N_3H) and the above mentioned acceptors. All these acceptors seem to form similar types of hydrogen bonds with uracil.

Thymine

Dilution of thymine with DMSO will cause N_1H signal to separate from N_3H, this prove that thymine–thymine interaction is weaker than thymine–DMSO interaction. Addition of a small amount of the acceptors to thymine cause N_1H to separate from N_3H, one could conclude that uracil–uracil association is much stronger than thymine–thymine.

Cytosine

This study did not obtain any indication of the formation of tautomer in DMSO as reported before [3]. All acceptors didn't cause any effect on cytosine except for nitromethane, such that when the ratio of nitromethane:cytosine was 5:1, a broad band appears at about 10–11 ppm and protons 5 and 6 split to a doublet of doublets with J = 2.0 Hz. This could be explained, that cytosine exists in the tautomer form [4], which might be stable in nitromethane medium, one could conclude that the coupling observed is between N_3H and protons 5 and 6 [5].