

Mannich Bases as Ligands: N,N'-tetra(antipyryl-4-methyl)-1,2-diaminoethane as hexadentate ligand toward Cu(II)

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Abstract: The new mononuclear complex $[Cu(TAMEN)](ClO_4)_2$ where TAMEN = N,N'-tetra(antipyryl-4-methyl)-1,2-diaminoethane was obtained and characterized by elemental analyses, electric conductivities, electronic and IR spectroscopy. The molar conductivities values of the copper(II) complex in DMF and DMSO solution demonstrate its behavior as 1:2 electrolytes type. Electronic spectra of the complex indicate the octahedral environment of the copper ion, whereas the infrared spectra for the complex support the coordination of TAMEN through the carbonylic oxygen atoms of the pyrazolone moiety and the amine nitrogen atoms of the 1,2-diaminoethane bridge.

Keywords: mononuclear complex, copper(II), antipyryne, Mannich base, ethylenediamine

1. Introduction

Metal complex compounds of antipyryne have been reported to show antitumor and antipyretic properties [1-3]. The Mannich bases obtained from antipyryne and its derivatives have been prepared with the aim to obtain antipyretic and analgesic compounds [4]. Considering that more active fragments would lead to a more efficient antipyretic and analgesic medicine, N,N'-tetra(antipyryl-4-methyl)-1,2-diaminoethane (TAMEN) (Figure 1) has been prepared through a Mannich type condensation. [5] TAMEN has the capacity to function as ligand through

donor atoms from ethylenediamine bridge and oxygen atoms from antipyryne fragment. Thanks to the flexibility of the ethylene bridge, TAMEN can act either as a bistridentate, tetradentate or hexadentate ligand. In the first case, the resulted metal complexes are binuclear whereas in the second one, they are mononuclear.

The coordination particularities of the metal ions as well as the conformation may determine nature of the complex. Here we report the synthesis and some spectral properties of a mononuclear copper(II) complex in which perchlorate ion acts as uncoordinated anion.

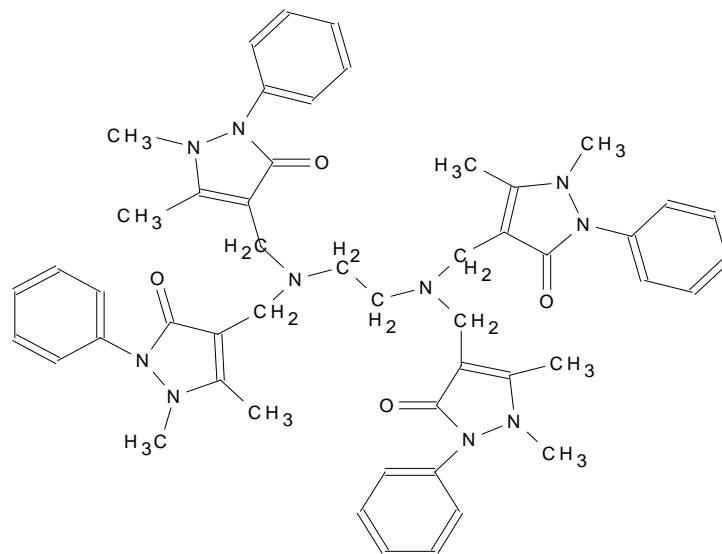


Figure 1. N,N'-tetra(antipyryl-4-methyl)-1,2-ethanediamine (TAMEN)

2. Experimental

Synthesis

TAMEN has been obtained following a Mannich type condensation between antipyrine, 1,2-ethandiamine and formaldehyde following the improved method in the literature. [5]

Synthesis of [Cu(TAMEN)](ClO₄)₂

ATTENTION! Perchlorate salts of complexes containing organic ligands are potentially explosive; they should be handled with care and in small quantities.

0.74 g (2 mmol) of Cu(ClO₄)₂·6H₂O dissolved in 5 ml of ethanol was poured drop wise into a solution containing 0.86 g (1 mmol) TAMEN dissolved in 10 ml ethanol under vigorous stirring at 40 °C. The reaction mixture was stirred for 1 hour at 40 °C and for 1 hour at the room temperature. After cooling in ice, the green microcrystalline complex was collected by filtration, washed with ether and dried over CaCl₂ in air. The product was recrystallised from DMF: trichloroethylene (1:1) as green crystals.

Physical Measurements

The complex characterization was performed by elemental analysis, UV-VIS, IR.

Analytical data were obtained by a Perkin-Elmer model 240 C elemental analyzer.

Electric conductivities were measured at room temperature in DMF and DMSO solutions with a WTW conductivity meter.

Electronic absorption spectra of freshly prepared solution of the complex in DMF and DMSO were measured with a Perkin Elmer Lambda 12 spectrophotometer.

IR spectra were recorded in KBr pellets with a Jasco FT/IR-430 spectrometer (4000-400 cm⁻¹).

3. Results and Discussion

The complex compound was obtained as microcrystalline powder by metal-ligand direct synthesis between TAMEN and Cu(ClO₄)₂·6H₂O in ethanolic solution. The new mononuclear complex was characterized by elemental analysis, IR and electronic absorption spectrum.

TABLE 1. Elemental analysis (calculated values in parentheses)

Compound	Yield (%)	Color	Elemental analysis					Λ_c [$\Omega^{-1}\text{mol}^{-1}\text{cm}^2$]
			H	C	N	Cl	Cu	
[Cu(TAMEN)](ClO ₄) ₂	92,60	green	5.46 (5.02)	53.65 (53.45)	12.50 (12.47)	6.39 (6.31)	5,39 (5.66)	130* 68**

*DMF **DMSO

TABLE 2. Absorption maxima λ_{max} , molar absorption ϵ_{max} of the electron transition spectra and transition identification for complex

Compound	DMF		DMSO	
	λ_{max} [nm]	ϵ_{max} [$\text{mol}^{-1}\text{cm}^{-1}$]	λ_{max} [nm]	ϵ_{max} [$\text{mol}^{-1}\text{cm}^{-1}$]
[Cu(TAMEN)](ClO ₄) ₂	713	81	711	91

The complex is soluble in acetonitrile, DMSO, DMF, partial soluble in benzene, less soluble in acetone.

The electronic spectra of the copper (II) complex recorded with a freshly prepared DMF and DMSO solution are very similar, proving that the structure is preserved in solution.

A broad band appear at 713 nm in DMF and at 711 nm in DMSO, respectively, the position and the intensity of the band indicating that the metal coordination center of complex in solution is in an octahedral environment [6]. The value of molar conductivities of the copper(II) complex demonstrate his behavior as 1:2 electrolytes type [7].

The IR spectra of mononuclear complex was recorded and compared with that of the free ligand and some important differences can be noticed between them.

TABLE 3. IR absorption maxima, in cm⁻¹ and assignments for the free ligand and the complex

TAMEN	[Cu(TAMEN)](ClO ₄) ₂	Assignments
1656 vs	-	$\nu(\text{C=O})$
1591 m	1607 s	Phenyl ring
1535 w	1572 vs	
1495 m	1495 m	
1483 w	1460 m	
1455 w		
1147 m	1438 w	Pyrazolonium fragment
1134 m	1027 m	
1024 w	978 w	
983 w	904 w	
	1145 m	$\nu(\text{C-O})$
	1089 s	$\nu_3(\text{ClO}_4)$
	624 s	$\nu_4(\text{ClO}_4)$
	610 m	$\nu(\text{M-O})$
	417 w	$\nu(\text{M-N})$

Thus, the peak at 1656 cm^{-1} assigned to the $\nu(\text{C}=\text{O})$ mode in free ligand spectrum disappeared and a new band of low intensity appear in region 1145 cm^{-1} for complex attributable to the $\nu(\text{C}-\text{O})$ mode, as a result of the lowering of the C-O bond order. Additionally, changes in the region corresponding to the pyrazolonium fragment can be attributed to the involvement of the carbonyl group into a coordinative bond and can be explained by an important contribution of the mesomeric forms of the antipyrine (Figure 2). The band at 1438 cm^{-1} in the IR spectrum can be tentatively assigned to the antipyrine $-\text{C}=\text{C}-$ group. The new band at 1572 cm^{-1} is assigned to a combination of the $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{N})$ stretching modes.

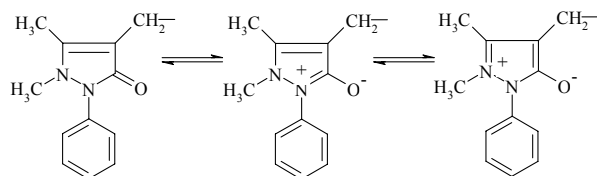


Figure 2. Mesomeric forms of the antipyrine fragment of the ligand.

A new band can be noticed in the spectra of the complexes at 610 cm^{-1} which can be assigned to the Cu-O bond. The band at 417 cm^{-1} in the spectra of complex is attributed to the Cu-N mode. The two bands at 1089 and 624 cm^{-1} are due to the ionic perchlorate [8, 9]. The IR spectra suggest that metal ion of the complex coordinates to carbonyl oxygen from antipyrine and to nitrogen from 1,2-diaminoethane.

4. Conclusions

The new mononuclear Cu (II) complex containing the Mannich base TAMEN was obtained by direct metal – ligand synthesis.

The visible absorption spectra of the complex suggest that the metal ions are in solution in an octahedral environment. TAMEN has the ability to act as a hexadentate ligand through donor's atoms from ethylenediamine bridge and through oxygen atoms from antipyrine fragment to form octahedral mononuclear complexes. Conductivity data shows that complex is able to dissociate in DMF and DMSO solution. The IR spectra show the presence of metal-oxygen and metal-nitrogen bond and the presence of ionic ClO_4 for complex.

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