

Mononuclear Complex of Fe(III) with N, N'-tetra(4-antipyryl-methyl)-1,2 diaminoethane. Synthesis and Spectral Properties

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Abstract: The synthesis and spectral properties of a new mononuclear complex of Fe(III) containing the Mannich base N,N'-tetra(4-antipyryl-methyl)-1,2diaminoethane (TAMEN) as ligand, $[\text{Fe}(\text{TAMEN})](\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ are presented. The molar conductivity value of iron(III) complex recorded in DMF solution, shows the 1:3 electrolyte type behavior, proving that the perchlorate anion not coordinate to the central metal ion. The electronic and IR spectra have revealed that the ligand acts as a hexadentate one through the two nitrogen atoms of ethylenediamine bridge and the four oxygen atoms of the antipyryne fragments.

Keywords: mononuclear complex, antipyryne, iron(III), ethylenediamine.

1. Introduction

Antipyryne and its derivatives are well known as antibacterial and anti-inflammatory agents [1-5]. With the hope to obtain new antipyretic agents, Mannich and Kather synthesized two ligands, N,N'-tetra(4-antipyrylmethyl)-1,2 diaminoethane (TAMEN) and N,N'-bis(antipyrylmethyl)-piperazine (BAMP), witch contains four and two, respectively, antipyryne moieties, and in order to explain their biological activity, the complexes they form with oligoelements have been studied [6,7,8,10]. The biological activity *in vitro* for some of them has been demonstrated [11]. The structure of TAMEN has been established and figure 1 present the ORTEP diagram of N,N'-tetra(4-antipyrylmethyl)-1,2diaminoethane (TAMEN). The ligand has six potential coordination sites, namely, four carbonylic oxygen atoms belonging to antipyryne fragments and two nitrogen atoms from ethylenediamine bridge.

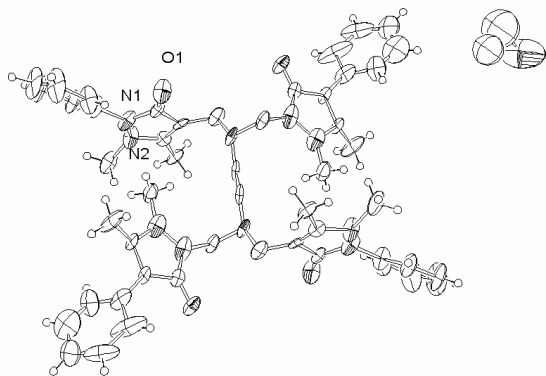


Fig. 1 ORTEP diagram of N,N'-tetra(4-antipyrylmethyl)-1,2 diaminoethane (TAMEN)

Due to ethylenediamine bridge flexibility, the ligand can act as a bis-tridentat ligand through the two O_2N sets or hexadentate through O_4N_2 set. The obtained complex compounds are binuclear in the first case and mononuclear in the second one. Binuclear complexes of TAMEN with 3 d metals, by general type $\text{M}_2(\text{TAMEN})\text{Cl}_4$ have been obtained and reported [9]. In this paper we report the synthesis and some spectral properties of a new mononuclear iron(III)complex of TAMEN.

2. Experimental

Synthesis of the ligand

The ligand TAMEN has been obtained following a Mannich type condensation between antipyryne, 1,2-ethandiamine and formaldehyde, changing the experimental condition from literature, in order to obtain an good yield and a pure ligand [6].

Synthesis of the complex

$[\text{Fe}(\text{TAMEN})](\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ 0,35 g (1 mmol) $\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ dissolved in 5 mL of ethanol was poured drop wise into a solution containing 0,43g (0,5 mmol) TAMEN dissolved in 10 ml ethanol under vigorous stirring at 35°C. The reaction mixture was stirred for 2 hours at the room temperature. After cooling on an ice bath, the dark reed microcrystalline complex was collected by filtration, washed with ether and dried over CaCl_2 in air. Yield: 0,75 g (62 %). Elemental analyses for $\text{C}_{50}\text{H}_{68}\text{Cl}_3\text{N}_{10}\text{FeO}_{22}$ (M = 1323.35): Found: C 49,42; H 4,98; N 10,49; Cl 8,50; Fe 4,48; calc. C 45.38; H 5,18; N 10,58; Cl 8,04; Fe 4,22. IR spectrum (cm^{-1}): 1598 m, 1556 s, 1541 m, 1496 m, 1459 m,

1406 w, 1335 m, 1145 m, 1092 s, 955 m, 929 w, 914 m, 874 w, 769 s, 725 m, 698 s, 666 m, 626 s, 514 m, 469 m, 446 m, 412 m; VIS spectrum : DMF: λ_{\max} : 428 nm. Molar conductivities Λ_m , ($\Omega^{-1}\text{mol}^{-1}\text{cm}^2$); in DMF: 198.

ATTENTION! Perchlorate salts of complexes containing organic ligands are potentially explosive. Although we have experienced no problems with the salt reported, they should be handled with care and in small quantities.

Physical Measurements

All chemicals have been purchased from commercial sources and were used without further purification.

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

Analytical data were obtained by a Perkin-Elmer model 240C elemental analyzer and with GBC SENSAA spectrophotometer.

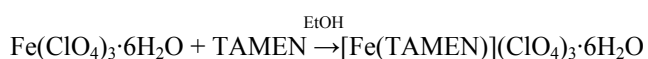
Electric conductivities were measured at room temperature in DMF solution with a WTW conductometer.

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

IR spectra were recorded in KBr pellets with a Jasco FT/IR-430 spectrometer in range 4000 - 400 cm^{-1} .

3. Results and Discussion

The new mononuclear complex compound was obtained as microcrystalline dark red powder by direct metal-ligand synthesis between TAMEN and the corresponding metallic salt in ethanolic solution following the equation:



The nature of the solvent, temperature and the reaction time were varied. Also different ratio metal:ligand were used.

Finally it has been established that only mononuclear species can be obtained when the counter-ion is perchlorate. The mononuclear iron(III) complex is soluble in DMSO and DMF, water and ethanol, sparingly soluble in benzen. The elemental analyses sustains the proposed formula. The value of molar conductivity of the iron(III) complex demonstrates his behaviour as 1:3 electrolyte type [12]. The electronic spectrum of the iron(III) complex, recorded in freshly prepared solution of DMF, exhibit one band in the region 428 nm assignable to the spin allowed electronic ${}^5\text{T}_{2g}(\text{F}) - {}^5\text{E}_g$ transition characteristic to Fe(III) ion in octahedral configuration [13]. The IR spectra of the iron (III) complex was recorded and compared with the IR spectra of free ligand. The disappearance of the strong $\nu(\text{C}=\text{O})$ stretching vibration at 1656 cm^{-1} in the spectrum of free ligand and the appearance of an intense band in the region 1145 cm^{-1} for iron(III) complex is the result of the lowering of the C-O bond order. 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).

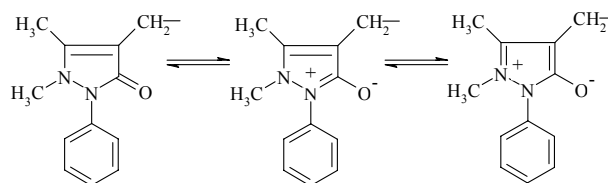


Fig. 2. Mesomeric resonance structure of the antipyrine fragment of the ligand

The band at 1459 cm^{-1} in the IR spectrum of the complex compound can be tentatively assigned to the antipyrine - C = C - group. The new band at 1556 cm^{-1} is assigned to a combination of the $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{N})$ stretching modes.

The Fe-N vibration was identified at 412 cm^{-1} for iron(III) complex. The new band at 514 cm^{-1} is tentatively assigned to Fe-O stretching vibration. Two strong bands in IR spectra of the complex compound in the region 1092 cm^{-1} , belonging to the $\nu_3(\text{ClO}_4)$ mode and that at 626 cm^{-1} , to $\nu_4(\text{ClO}_4)$ are present. Thereby is proved the presence of the uncoordinated perchlorate [14,15]. The IR spectra suggest that iron(III) ion coordinates to carbonyl oxygen atom of the antipyrine moieties and to nitrogen atom of the 1,2-diaminoethane bridge.

4. Conclusions

A new mononuclear complex, $[\text{Fe}(\text{TAMEN})](\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$, has been obtained. The new mononuclear Fe(III) complex containing the Mannich base (N,N'-tetra(4-antipyrilmethyl)-1,2 diaminoethane) TAMEN as ligand, has been obtained by direct metal-ligand synthesis. The structure of iron(III) complex consists of discrete cations of the type $[\text{Fe}(\text{TAMEN})]^{3+}$ and three perchlorate anions. The complex is able to dissociate in solvents as DMF. Electronic spectra reveal that the metal ion is in an octahedral environment described by the O_4N_2 donor set of TAMEN, the ligand acting in this case as a hexadentate one. The IR data are in good agreement with conductivity and electronic spectral data.

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