

MIXED LIGAND COMPLEXES OF IRON(II), IRON(III) AND COBALT(II) WITH PYRAZOLONIC AND PYRIDINE LIGANDS

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The new iron(II, III) and cobalt(II) mixed-ligand complexes with pyridine and one of the Mannich bases N,N'-bis(antipyryl-4-methylene)-piperazine, (BAMP), or N,N'-tetra(antipyryl-4-methylene)-1,2-ethane-diamine, (TAMEN), were synthesized and characterized by elemental analyses, conductometric and magnetic susceptibility measurements, UV-Vis and IR spectroscopy. They belong to the following types $M_2(\text{BAMP})\text{py}_2\text{Cl}_n$, where $M = \text{Co}^{+2}$ (**V**) and Fe^{+2} (**I**) $n=4$; Fe^{+3} $n=6$ (**III**) and $M_2(\text{TAMEN})\text{py}_2\text{Cl}_n$ where $M = \text{Fe}^{+2}$ (**II**) $n=4$; and Fe^{+3} (**IV**) $n=6$. The magnetic susceptibility data in the temperature range 3-300 K show that all the iron complexes reveal antiferromagnetic behaviour, except $\text{Fe}_2(\text{BAMP})\text{py}_2\text{Cl}_4$ which shows ferromagnetic coupling.

INTRODUCTION

The antipyretic and analgesic activity of the pyrazolone compounds is well known, and antitumor, antibacterial or antiviral effects of some metal ions complexes were noticed in the latter half of the 20th century. These results prompted us to study new complexes of some first row metal ions with ligands containing antipyrine fragment like the Mannich bases N,N'-bis(antipyryl-methyl)-piperazine, BAMP, and N,N'-tetra(antipyryl-methyl)-1,2-ethane-diamine, TAMEN. Thus, homo- and heterobinuclear complexes of some first row metal ions have been obtained^{1,2,3} and some of them have shown an important antitumor activity.⁴ Also, mixed ligand complexes containing in addition to these Mannich bases, relevant biological molecules like imidazole,⁵ 2-aminobenzothiazole⁶ or mercaptobenzothiazole⁷ as coligands have been obtained and tested on the marine Hydrozoon *Hydractinia echinata*.⁸ As a continuation of the works in this field, we report here the synthesis, spectral and magnetic properties of some binuclear Fe(II, III) and Co(II) mixed ligand complexes containing the above mentioned Mannich bases and pyridine.

RESULTS AND DISCUSSION

The Fe(II, III) and Co(II) mixed-ligand complexes $M_2(\text{BAMP})\text{py}_2\text{Cl}_n$, where $M = \text{Co}^{+2}$ (**V**) and Fe^{+2} (**I**) $n=4$; $M = \text{Fe}^{+3}$ $n=6$ (**III**) and $M_2(\text{TAMEN})\text{py}_2\text{Cl}_n$ where $M = \text{Fe}^{+2}$ (**II**) $n=4$ and $M = \text{Fe}^{+3}$ (**IV**) $n=6$, have been obtained by the reaction of the metal salts with the corresponding Mannich base and pyridine. As expected, the core of the complexes is provided by the large binucleating ligands BAMP and TAMEN, and

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the elemental analyses data confirm their binuclear nature in the microcrystalline form. Both of these ligands have two groups of donor atoms situated on each side of the piperazine or the 1,2-ethanediamine bridge, respectively, to which metal ions can coordinate (Fig. 1). Despite the bulkiness of these ligands, pyridine was able to penetrate into the coordination sphere of the metal ions. However, the attempt to obtain compounds with an increased amount of pyridine has failed. The solid complexes are stable in dry air atmosphere, insoluble in most of the common solvents, like water, ethyl alcohol, acetone, chloromethane but they are soluble in nitrobenzene, DMSO and DMF. The molar conductivities in nitrobenzene for $\text{Fe}_2(\text{TAMEN})\text{py}_2\text{Cl}_4$ (**II**) and $\text{Fe}_2(\text{TAMEN})\text{py}_2\text{Cl}_6$ (**IV**) correspond to 1:2 electrolytes whereas, the third chloride ion in (**IV**) dissociates in DMSO.^{9,10} A very stable O_2N_2 coordination sphere seems to be present in the Fe^{+3} -TAMEN complex. In fact, all the complexes seem to be completely dissociated in DMSO.

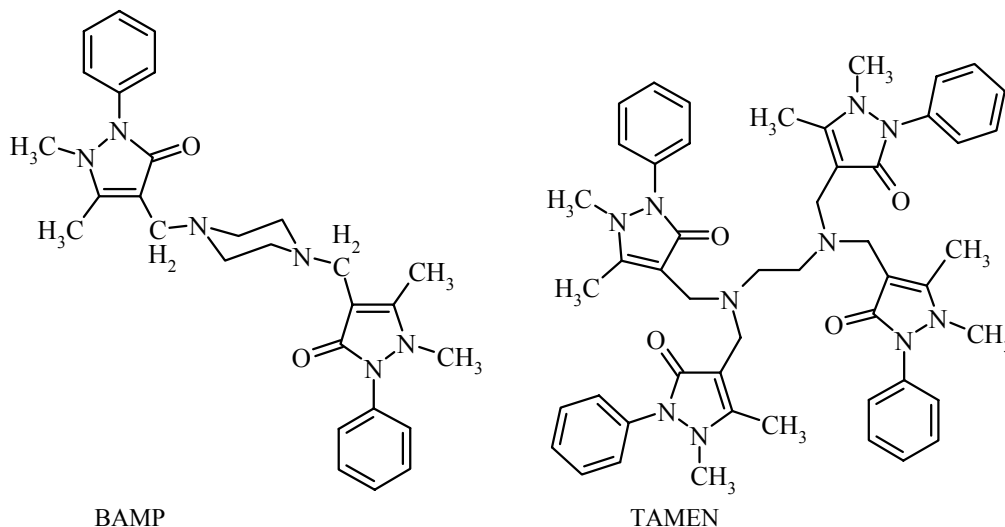


Fig. 1 – The pirazolonic Mannich bases.

In the infrared spectra of the complexes, bands belonging both to the pirazolonic and pyridine ligands can be noticed, some of them being modified as a result of coordination. Thus, the intense band at 1662 cm^{-1} assigned to the $\nu_{\text{C}=\text{O}}$ mode in the free ligand is missing in the spectra of all the complexes and a weak peak in the $1158 - 1185\text{ cm}^{-1}$ region, attributable to $\nu(\text{C}-\text{O})$ appears. These denote the coordination of the antipyrine ring through the carbonylic oxygen. Additionally, the presence of $\nu(\text{C}=\text{C}=\text{N})$ shows the stabilization of antipyrine in the resonance form 2 (Fig. 2) as a consequence of the coordination in this manner. The shift of $\nu(\text{C}-\text{N})$ toward lower frequencies proves the implication of piperazine, respectively, 1,2-diaminoethane nitrogen in the coordination.

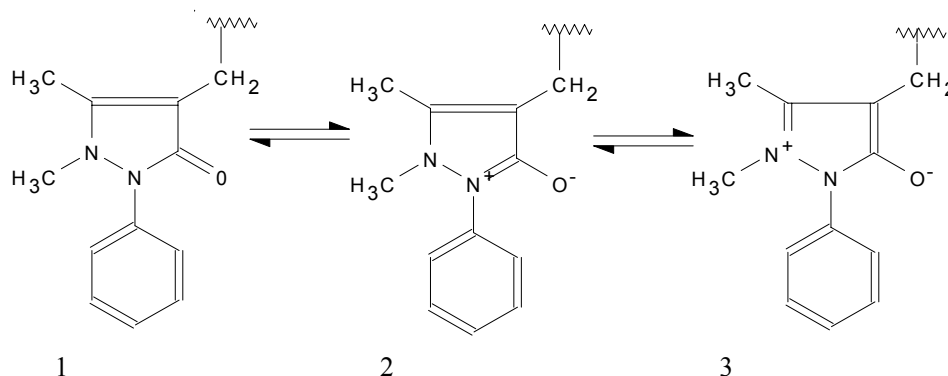


Fig. 2 – Mesomeric forms of the antipyrine fragment.

Small changes in the band position and intensities can be noticed as a result of the pyridine coordination. Two of the lowest ring vibrations in the pyridine spectrum are located at 405 cm^{-1} , which is attributed to an out-of-plane ring deformation, and at 604 cm^{-1} , attributed to an in-plane ring deformation.¹¹ These bands are shifted toward higher frequencies in the spectra of the complexes. Bands assignable to both M-N and M-Cl vibrations are usually observed.

In the far-infrared region of the spectra, the weak bands attributable¹² to the M-N_{pyridine} can be identified between 235 and 260 cm^{-1} and more intense ones in the 300 cm^{-1} region, typical for terminal chlorides.¹³ No other bands in the 200 cm^{-1} region can be observed so that the presence of chloride bridge is ruled out.

The electronic spectrum of **V** on DMSO solution shows a broad band at 680 nm attributable to the $v_3\ ^4T_1(P) \leftarrow ^4A_2$ transition characteristic for cobalt(II) in a distorted tetrahedral surrounding. Their large width may result from a spin-orbit coupling as well as from a Jahn-Teller distortion characteristic for tetrahedral cobalt(II) derivatives.¹⁴ The small differences between the mull and DMSO spectra can be a result of a chloride ion replacement by a solvent molecule in the first coordination sphere of cobalt(II), thereby the molar conductivity value being explained. The magnetic moment of 4.2 B.M. also supports the distorted tetrahedral coordination sphere of the cobalt(II) ions.

The spectra of the iron(II) complexes **I** and **II** show a broad, low-intensity band in the $900\text{-}1100\text{ nm}$ region. Its position as well as its intensity suggest the presence of iron(II) in a distorted tetrahedral surrounding. A very intense ligand to the metal charge transfer band at 380 nm and a low-intensity one at about 615 nm are arguments for the presence of distorted tetrahedral iron(III) in **III**. A single broad and intense band centred at 360 nm appears in the spectrum of **IV**.

The magnetic properties of the compounds **I-IV** are represented in Figs. 3-6 in the form of $\chi_M T$ versus T and μ_{eff} versus T plots. For **I**, the $\chi_M T$ value at room temperature is $7.20\text{ cm}^3\text{ mol}^{-1}\text{ K}$. On cooling, this value slightly increases to $10.94\text{ cm}^3\text{ mol}^{-1}\text{ K}$ at $90\text{-}95\text{ K}$ and further decreases rapidly to $0.66\text{ cm}^3\text{ mol}^{-1}\text{ K}$ at 3 K (Fig. 3). The magnetic moment value at room temperature, calculated by the equation $\mu_{\text{eff}} = 2.828(\chi_M T)^{1/2}$ shows a value of $7.59\ \mu_B$, which is higher than the theoretical value for two uncoupled ions with $S = 4/2$. The value of $8.94\ \mu_B$ is reached at 160 K which corresponds to the theoretical value of two coupled Fe(II) ions with total spin $S = 4$. Further, at 2 K the remanent magnetic moment is $1.88\ \mu_B$. Such a behaviour is characteristic for a ferromagnetic interaction between the two iron(II) ions.

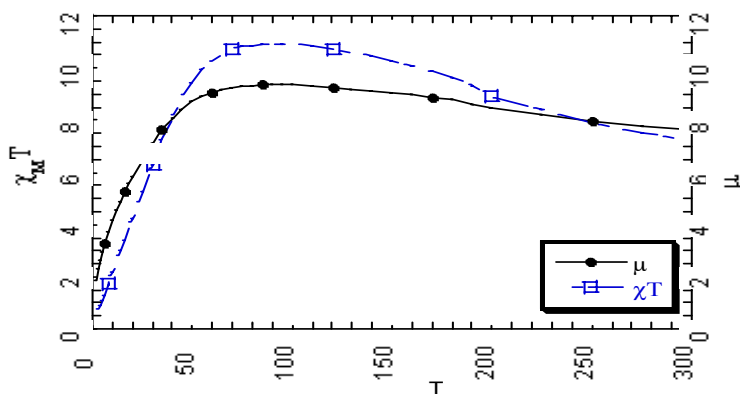
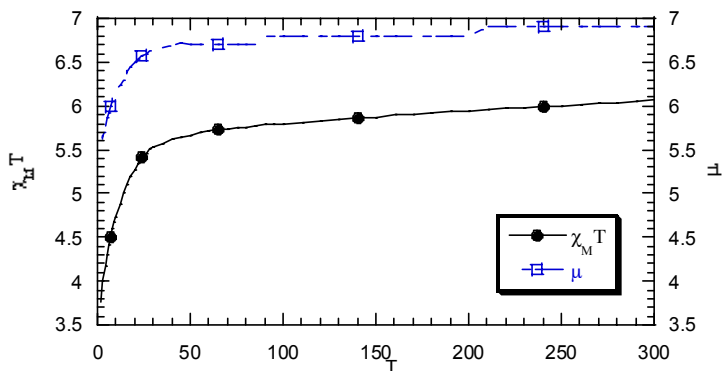
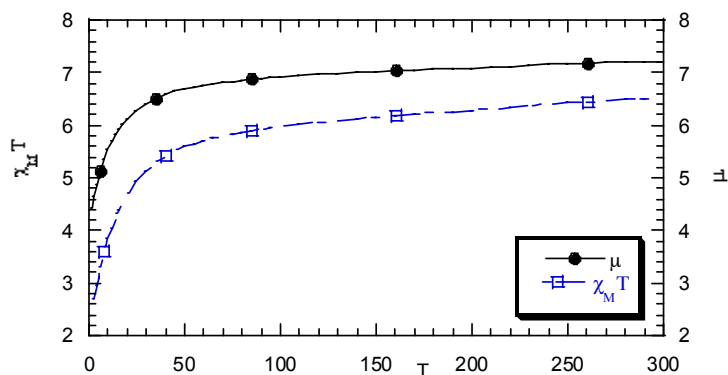
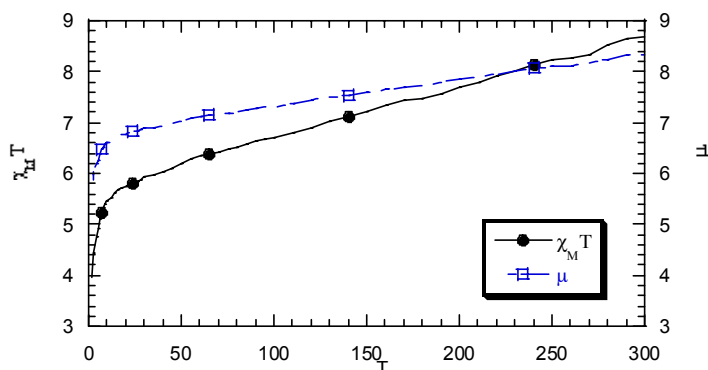


Fig. 3 – Temperature dependence of $\chi_M T$ and μ_{eff} for $\text{Fe}_2\text{BAMP}(\text{py})_2\text{Cl}_4$.

For **II**, the $\chi_M T$ value of $6.09\text{ cm}^3\text{ mol}^{-1}\text{ K}$ at room temperature corresponds to the theoretical value for two isolated iron(II) ions. On cooling, $\chi_M T$ decreases to $5.69\text{ cm}^3\text{ mol}^{-1}\text{ K}$ at 55 K , and further to $3.76\text{ cm}^3\text{ mol}^{-1}\text{ K}$ at 2 K . At room temperature, the effective magnetic moment of $6.90\ \mu_B$ is essentially equal to the theoretical value for two isolated iron(II) ions with $S = 4/2$. As the temperature decreases, μ_{eff} decreases smoothly up to $5.48\ \mu_B$ at 2 K . Such magnetic behaviour can be explained by an antiferromagnetic interaction between the metal centres.

Fig. 4 – Temperature dependence of $\chi_M T$ and μ_{eff} for $\text{Fe}_2\text{TAMEN}(\text{py})_2\text{Cl}_4$.Fig. 5 – Temperature dependence of $\chi_M T$ and μ_{eff} for $\text{Fe}_2\text{BAMP}(\text{py})_2\text{Cl}_6$.

The $\chi_M T$ product has the value of 6.52 for **III** and 8.70 $\text{cm}^3 \text{mol}^{-1} \text{K}$ for **IV** at 300 K. The effective the magnetic moment values for **III** and **IV** were 7.22 μ_B and 8.34 μ_B , respectively, at 300 K. These values are within the expected range for isolated d^5 four-coordinate Fe(III) complexes. Upon lowering the temperature, the effective magnetic moment gradually decreased to 4.41 μ_B for **III** and 5.62 μ_B for **IV**. These results indicate that there are only weak antiferromagnetic interactions between the paramagnetic centres.

Fig. 6 – Temperature dependence of $\chi_M T$ and μ_{eff} for $\text{Fe}_2\text{TAMEN}(\text{py})_2\text{Cl}_6$.

EXPERIMENTAL

All the reagents were used as purchased from Merck. BAMP and TAMEN were obtained by published methods.^{1,15} Analytical data were obtained by a Perkin-Elmer Model 240C elemental analyzer. Electrical conductivities were determined on a WTW LF-340 A conductivity meter. Electronic spectra were obtained on a UV/VIS Perkin Elmer Lambda 12 spectrometer on solutions and on nujol mull. Infrared spectra of the solid complexes (KBr pellet) were recorded on an IR BIO-RAD FTS 135 spectrometer. Magnetic measurements were carried out on polycrystalline samples with a Faraday-type magnetometer equipped with a helium continuous-flow cryostat working in the 4-300 K temperature range. The independence of the susceptibility *versus* the applied field was checked at room temperature. Mercury tetrakis(thiocyanato)cobaltate(II) was used as a susceptibility standard.

Fe₂(BAMP)py₂Cl₄ (I): 1.2 g (6 mmol) FeCl₂·4H₂O dissolved in 20 mL ethanol were treated with 1.458 g (3 mmol) BAMP dissolved in 15 ml ethanol and 0.48 mL (6 mmol) pyridine under vigorous stirring and then with 150 cm³ diethyl ether. The red microcrystalline product was filtered off, washed with ethanol and dried over CaCl₂ in air. Yield: 1.7 g; (68.5%). Elemental analyses: C₃₈H₄₄N₈Fe₂O₂Cl₄ (898.33) Found: C 50.86; H 4.98; N 12.43; Cl 15.12; Fe 12.43; requires: C 50.81; H 4.94; N 12.47; Cl 15.19;

Fe 12.43%; IR spectrum (KBr cm⁻¹): 1620 s (phenyl ring), 1584 s (C=C/C=N), 1531m (py), 1529 m (py), 1158 w (C-O), 1130 w (C=C/C=N), 1126 s (C-N al) cm⁻¹. Far IR: 642 m (py), 609 w (M-O), 598 w (M-N al), 440 m (py), 362 s (M-Cl), 315 s (M-Cl), 245 m (M-N_{py}) cm⁻¹. UV/vis spectrum in DMSO: λ_{max}, nm: 950; UV/vis spectrum in nujol: λ_{max}, nm: 1070; Molar conductivities A_M, Ω⁻¹mol⁻¹cm², in DMSO: 117.

Fe₂(TAMEN)py₂Cl₄ (II): The complex was prepared similarly to **I** except that 1.720 g (2 mmol) TAMEN was used instead of BAMP. Yield: 1.8 g; (70.75%). Elemental analyses: C₆₀H₆₆N₁₂Fe₂O₄Cl₄ (1272.77) Found: C 56.70; H 5.26; N 13.24; Cl 11.20; Fe 8.72; requires: C 56.62; H 5.23; N 13.21; Cl 11.14; Fe 8.70%; IR spectrum (KBr cm⁻¹): 1603 s (phenyl ring), 1580 s (C=C/C=N), 1545 s (py), 1530 m (py), 1182 w (C-O), 1143 w (C=C/C=N), 1118 s (C-N al) cm⁻¹. Far IR: 642 m (py), 600 w (M-O), 595 w (M-N al), 435 m (py), 355 s (M-Cl), 308 s (M-Cl), 254 m (M-N_{py}) cm⁻¹. UV/vis spectrum in DMSO: λ_{max}, nm: 995; UV/vis spectrum in nujol: λ_{max}, nm: 1090; Molar conductivities A_M, Ω⁻¹mol⁻¹cm², in DMSO: 167; A_M, Ω⁻¹mol⁻¹cm², in nitrobenzene: 77.

Fe₂(BAMP)py₂Cl₆ (III): The complex was prepared similarly to **(I)** except that 0.973 g (6 mmol) FeCl₃ was used instead of FeCl₂·4H₂O. Yield: 2.2 g; (81.69%). Elemental analyses: C₃₈H₄₄N₈Fe₂O₂Cl₆ (969.23) Found: C 47.11; H 4.62; N 11.61; Cl 21.89; Fe 11.58; requires: C 47.09; H 4.58; N 11.56; Cl 21.95; Fe 11.52%; IR spectrum (KBr cm⁻¹): 1614 s (phenyl ring), 1584 s (C=C/C=N), 1551 s (py), 1522 m (py), 1180 m (C-O), 1135 w (C=C/C=N), 1120 s (C-N al) cm⁻¹. Far IR: 651 m (py), 614 w (M-O), 587 w (M-N al), 438 m (py), 363 s (M-Cl), 316 s (M-Cl), 250 m (M-N_{py}) cm⁻¹. UV/vis spectrum in DMSO: λ_{max}, nm: 645; UV/vis spectrum in nujol: λ_{max}, nm: 380, 615; Molar conductivities A_M, Ω⁻¹mol⁻¹cm², in DMSO: 126.

Fe₂(TAMEN)py₂Cl₆ (IV): The complex was prepared similarly to **III** except that 1.720 g (2 mmol) TAMEN was used instead of BAMP. Yield: 1.8 g; (67%). Elemental analyses: C₆₀H₆₆N₁₂Fe₂O₄Cl₆ (1343.67) Found: C 53.67; H 4.90; N 12.58; Cl 15.86; Fe 8.27; requires: C 53.63; H 4.95; N 12.51; Cl 15.83; Fe 8.30%; IR spectrum (KBr cm⁻¹): 1598 s (phenyl ring), 1572 s (C=C/C=N), 1536 s (py), 1529 m (py), 1187 w (C-O), 1146 w (C=C/C=N), 1124 s (C-N al) cm⁻¹. Far IR: 642 m (py), 610 w (M-O), 596 w (M-N al), 443 m (py), 364 s (M-Cl), 313 s (M-Cl), 245 m (M-N_{py}) cm⁻¹. UV/vis spectrum in nujol: λ_{max}, nm: 360; Molar conductivities A_M, Ω⁻¹mol⁻¹cm², in DMSO: 261; A_M, Ω⁻¹mol⁻¹cm², in nitrobenzene: 78.

Co₂(BAMP)py₂Cl₄ (V): The complex was prepared similarly to **I** except 1.43 g (6 mmol) CoCl₂·6H₂O was used instead of FeCl₂·4H₂O. Yield: 1.6 g; (64%). Elemental analyses: C₃₈H₄₄N₈Co₂O₂Cl₄ (904.50) Found: C 50.50; H 4.94; N 12.42; Cl 15.62; Co 13.08; requires: C 50.46; H 4.90; N 12.39; Cl 15.68; Co 13.03%; IR spectrum (KBr cm⁻¹): 1598 s (phenyl ring), 1558 s (C=C/C=N), 1553m (py), 1517 m (py), 1185 m (C-O), 1130 w (C=C/C=N), 1119 s (C-N) cm⁻¹. Far IR: 638 m (py), 612 w (M-O), 690 w (M-N al), 452 w (py), 338 s (M-Cl), 305 s (M-Cl), 260 m (M-N_{py}) cm⁻¹. UV/vis spectrum in DMSO: λ_{max}, nm (lgε): 615 sh, 680 (437); UV/vis spectrum in nujol: λ_{max}, nm: 580, 660; Molar conductivities A_M, Ω⁻¹mol⁻¹cm², in DMSO: 138.

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