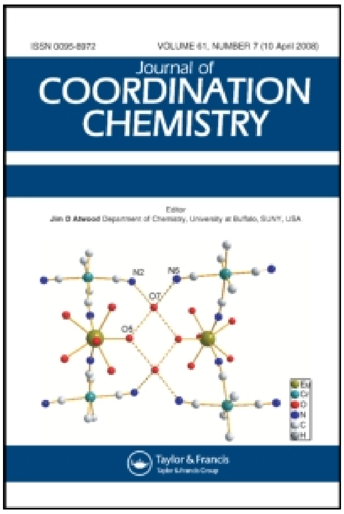

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Mixed-ligand complexes of iron(II), iron(III), copper(II), and cobalt(II) with pyrazolonic and 2,2'-bipyridine ligands

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To cite this Article Tudose, Ramona , Mosoarca, Elena Maria , Simulescu, Vasile , Sasca, Viorel , Linert, Wolfgang and Costişor, Otilia(2010) 'Mixed-ligand complexes of iron(II), iron(III), copper(II), and cobalt(II) with pyrazolonic and 2,2'-bipyridine ligands', Journal of Coordination Chemistry, 63: 24, 4358 — 4366, First published on: 07 December 2010 (iFirst)
To link to this Article: DOI: 10.1080/00958972.2010.539683
URL: http://dx.doi.org/10.1080/00958972.2010.539683

Journal of Coordination Chemistry
Vol. 63, No. 24, 20 December 2010, 4358–4366

Mixed-ligand complexes of iron(II), iron(III), copper(II), and cobalt(II) with pyrazolonic and 2,2′-bipyridine ligands

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(*Received 1 March 2010; in final form 29 October 2010*)

New mixed-ligand complexes, $[M_2(BAMP)(bipy)_2][MCl_4]_2$, M=$Co^{+2}$(**1**), Cu^{+2}(**2**), $[M_2(TAMEN)(bipy)_2][MCl_4]_2$, M=$Fe^{+2}$(**3**), Co^{2+}(**4**), and $[Fe_2(TAMEN)(bipy)_2][FeCl_6]_2$ (**5**), where BAMP and TAMEN stand for the Mannich bases *N*,*N*′-bis(antipyryl-4-methylene)-piperazine and *N*,*N*′-tetra(antipyryl-4-methylene)-1,2-ethane-diamine, respectively, have been obtained and characterized by elemental analyses, conductometric and magnetic susceptibility measurements at room temperature, mass spectrometry, UV-Vis, infrared, and mass spectroscopy, and ^{1}H NMR spectra for the ligands.

Keywords: 2,2′-Bipyridine; Copper(II); Cobalt(II); Iron(II, III); Mannich bases

1. Introduction

Synthesized in 1883, antipyrine – the first drug with fever and pain release effect is considered to be the start of synthetic drug industry. Since then, a variety of antipyrine derivatives have been obtained with applications in medicine, chemical analyses, or catalyses. Interest in coordination chemistry of pyrazolone ligands increased constantly and several reviews are dedicated to this subject [1–3]. During the 1970s–1980s, antipyrine complexes with certain metal ions, including Pt(II) and Co(II) ions, have been shown to act as antitumoral agents [4–8]. Some first row metal complexes including Ni(II)-, Cu(II)- [9–11] containing pyrazolonic ligands have been reported and some screened for their antibacterial activity against Gram-positive and Gram-negative bacteria [12, 13]. Some lanthanide [14–16] or copper [17] complexes have fluorescent properties with relevance in clinical diagnosis. Also, antipyrine-based metal complexes are used in optical layers for optical data recording [18, 19].

In order to extend the pyrazolonic class of pharmaceutics, Mannich bases *N*,*N*′-bis(antipyryl-4-methylene)-piperazine (BAMP) and *N*,*N*′-tetra(antipyryl-4-methylene)-1,2-ethane-diamine (TAMEN) were obtained (figure 1) following the method of

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958972.2010.539683

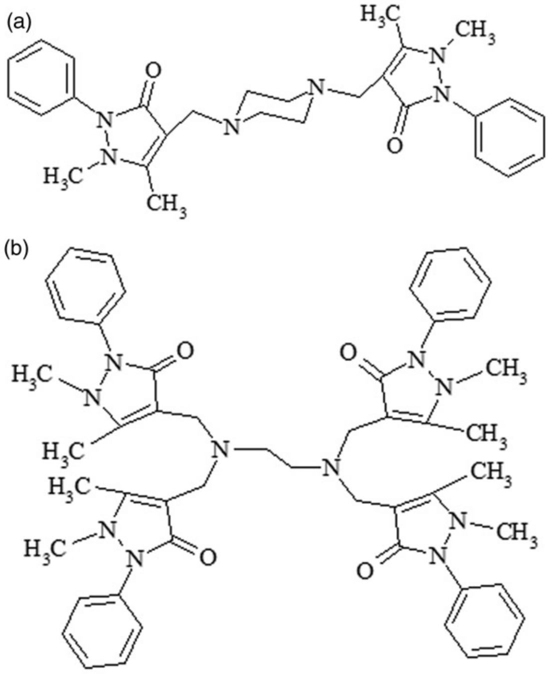

Figure 1. The pyrazolone Mannich bases: (a) BAMP and (b) TAMEN.

Mannich and Kather [20]. In order to increase the yield and to obtain purest compound, BAMP has been obtained by the Mannich synthesis, starting from antipyrine, formaldehyde, and piperazine chlorohydrate, changing the condition indicated in the literature by working at higher concentration, in the dark, and at lower temperature (0–5°C) [21]. Similarly, the experimental conditions for TAMEN were changed to achieve a better quality product with higher yields. TAMEN was obtained by a Mannich reaction from antipyrine with ethylenediamine in an aqueous formaldehyde solution [22].

Presuming that the biological activity may be affected by the number of antipyrine fragments in the ligand molecule, $Co(BAMP)(NCS)_2$ [23], $M_2(L)X_n$ where L=BAMP, TAMEN were obtained [24–30] and for some of them the structure has been resolved [31–36]. Both BAMP and TAMEN contain antipyrine fragments disposed symmetrically on each side of the piperazine or ethylenediamine bridge, respectively. The nature of the complexes depends on the conformation adopted by these bridges. Thus, BAMP behaves as a N_2O_2 tetradentate ligand leading to mononuclear complexes when piperazine adopts the *bath* conformation and, as a bis-binucleating ligand through two NO donor sets when it adopts the *chair* conformation. Due to the flexibility of the ethylene bridge, TAMEN can act either as a tetradentate or a hexadentate ligand. The conformation of the bridge determines the nature of the complexes. When the ethylenediamine bridge adopts an *anti* conformation, dinuclear complexes can be obtained. The donor properties of TAMEN offer the opportunity to prepare mononuclear complexes when this ligand is hexadentate through its N_2O_4 donors. In this case, the ethylenediamine bridge should adopt the *gauche* conformation.

Mixed-ligand complexes containing, in addition to these Mannich bases, relevant biological molecules like imidazole [37], 2-aminobenzothiazole [38], or mercaptobenzothiazole [39] as coligands have been obtained and it has been demonstrated that their structure is designed by the big binucleating ligands BAMP and TAMEN. For some of the previously cited complexes cytotoxic/antiproliferative effects were proved [40–45]. Also, their toxicity was tested on marine Hydrozoon *Hydractinia echinata* [46].

As continuation of the work in this field, we report here the synthesis, spectral properties, and mass spectra of some binuclear Fe(II, III) and Co(II) complexes containing BAMP or TAMEN and 2,2′-bipyridine as ligands.

2. Experimental

2.1. *Materials and physical measurements*

All reagents were used as purchased from Merck. BAMP and TAMEN were obtained by published methods [20–22]. Analytical data were obtained by a Perkin-Elmer Model 240C elemental analyzer. Electrical conductivities were measured on a WTW LF-340 A conductivity meter. Mass spectra were obtained using a mass spectrometer Esquire 6000 ESI (electrospray ionization) from Bruker-Daltonik. All compounds analyzed were diluted before measurements at $10^{-5}\,\mathrm{mol\,L^{-1}}$, in acetonitrile. A small syringe pump is included with the instrument system for the introduction of samples directly to the electrospray. The solution was injected into the spray chamber by a Hamilton syringe, with a constant flow of $250\,\mu\mathrm{L\,h^{-1}}$. The atmospheric pressure interface-electrospray ionization (API-ESI) generates ions, focuses and transports them into the ion trap mass analyzer. All the mass spectra were obtained in the positive and negative modes. For these compounds the positive mode offers better results than the negative mode. Electronic spectra were obtained on a UV/VIS Perkin-Elmer Lambda 12 spectrometer on solutions. Infrared (IR) spectra of the solid complexes (KBr pellet) were recorded on an IR BIO-RAD FTS 135 spectrometer. Magnetic susceptibilities were measured on a conventional Gouy balance using freshly prepared $Hg[Co(NCS)_4]$ as calibrant.

2.2. *^{1}H NMR spectroscopy*

BAMP: **^{1}H NMR** (ppm) ($CDCl_3$, 80 MHz) δ: 2.41 (d, 6H, $\geq$C–$\mathbf{CH_3}$), 2.83 (t, 8H, –N–$\mathbf{CH_2}$–CH_2–), 3.08 (m, 6H, >N–$\mathbf{CH_3}$), 3.46 (s, 4H, >N–$\mathbf{CH_2}$–C$\leq$), 7.35–7.55 (m, 10H, C_{ar}).

TAMEN: **^{1}H NMR** (ppm) (DMF-d_7, 200 MHz) δ: 7.43 (m, 16H, aromatic nuclei protons), 7.27 (m, 4H, aromatic nuclei protons), 3.59 (m, 4H, CH_3–$\mathbf{CH_2}$–OH), 3.26 (s, 8H, –N–$\mathbf{CH_2}$–CH<), 3.05 (s, 12H, –N–$\mathbf{CH_3}$), 2.66 (m, 4H, >N–$\mathbf{CH_2}$–), 2.25 (s, 12H, C–$\mathbf{CH_3}$), 1.11 (t, 6H, $\mathbf{CH_3}$–CH_2–OH).

2.3. *Synthesis of $[Co_2(BAMP)(bipy)_2][CoCl_4]_2$ (1)*

Ten millimoles of cobalt(II) chloride hexahydrate (2.4 g) dissolved in 15 mL ethanol was treated with solid 2,2′-bipyridine (0.78 g, 5 mmol) and BAMP (2.43 g, 5 mmol) dissolved in ethanol (25 mL) at 60°C under vigorous stirring. The reaction was finished after 3 h. The blue microcrystalline product was filtered off, washed with ethanol, and dried over calcium chloride in air. Yield: 1.3 g, 20%. Anal. Calcd for $C_{48}H_{50}N_{10}O_2Cl_8Co_4$ (%) (M = 1318.35): C, 43.73; H, 3.82; N, 10.62; Cl, 21.51; Co, 17.88. Found (%): C, 43.61; H, 3.77; N, 10.13; Cl, 21.22; Co, 17.16. IR (KBr cm^{-1}): 3552 l, 2905w, 2855w, 1599m, 1556s, 1379w, 1277w, 1264w, 1185w, 1147w, 1117m, 1059m, 1023m, 831s, 762s, 739m, 695s, 639s, 612m, 509m, 450m, 421m; UV-Vis in DMF: λ_{max}, nm(ε): 678(480), 615 sh; molar conductivities ($c_M = 1.2 \times 10^{-3}\,mol\,L^{-1}$) Λ_M, $\Omega^{-1}\,mol^{-1}\,cm^2$, in DMF: 125; μ, MB: 4,15; MS: *m*/*z*: 487 (M^+-2Co-2dipy-2$CoCl_4$), 1318 (M^+).

2.4. *Synthesis of [Cu_2(BAMP)(bipy)$_2$][$CuCl_4$]$_2$ (2)*

This product was prepared similar to **1** except that copper(II) chloride hexahydrate, (2.4 g, 10 mmol) was used instead of cobalt(II) chloride hexahydrate. The green microcrystalline product was filtered off, washed with ethanol, and dried over calcium chloride in air. Yield: 2.2 g, 33%. Anal. Calcd for $C_{48}H_{50}N_{10}O_2Cl_8Cu_4$ (%) (M = 1336.80): C, 43.13; H, 3.77; N, 10.48; Cl, 21.22; Cu, 19.01. Found (%): C, 43.05; H, 3.60; N, 10.37; Cl, 21.09; Cu, 18.88. IR (KBr cm^{-1}): 3443l, 3106m, 3055s, 3036m, 1602s, 1575m, 1568m, 1496m, 1473s, 1445s, 1320s, 1317s, 1286w, 1247w, 1219w, 1169s, 1159s, 1162s, 1117m, 1059m, 1025s, 778s, 730s, 660m, 635m, 418s, 305s, 290s, 258m, 182m; UV-Vis in DMF: λ_{max}, nm(ε): 780–920(40); molar conductivities ($c_M = 1.1 \times 10^{-3}\,mol\,L^{-1}$) Λ_M, $\Omega^{-1}\,mol^{-1}\,cm^2$, in DMF: 138; μ, MB: 1,97; MS: *m*/*z*: 1337 (M^+).

2.5. *Synthesis of [Fe_2(TAMEN)(bipy)$_2$][$FeCl_4$]$_2$ (3)*

Five millimoles of ferrous chloride tetrahydrate (1 g) dissolved in ethanol (5 mL) was treated with TAMEN (2.15 g, 2.5 mmol) dissolved in ethanol (5 mL) and 2,2′-bipyridine (0.39 g, 2.5 mmol) under vigorous stirring, then a dark red solution was obtained. The reaction mixture was stirred for 3 h, kept in dark for 24 h; then ethyl ether was added to precipitate a red microcrystalline product, which was filtered off, washed several times with ethanol and dried over calcium chloride. Yield: 3.3 g, 49%. Anal. Calcd for $C_{70}H_{72}N_{14}O_4Cl_8Fe_4$ (%) (M = 1680.45): C, 50.03; H, 4.32; N, 11.67; Cl, 16.88; Fe, 13.29. Found (%): C, 49.92; H, 4.23; N, 11.57; Cl, 16.75; Fe, 13.19. IR (KBr cm^{-1}): 3067w, 1647sh, 1598m, 1555s, 1538s, 1493s, 1460s, 1441s, 1437s, 1325s, 1152m, 1024m, 909m, 847s, 763s, 657m, 609m, 508m, 466m, 431s, 428m, 360s, 315s, 254w, 202w; UV-Vis in DMSO: λ_{max}, nm (ε): 354, 456, 900–1100(55); molar conductivities ($c_M = 1.2 \cdot 10^{-3}\,mol\,L^{-1}$) Λ_M, $\Omega^{-1}\,mol^{-1}\,cm^2$, in DMSO: 118; MS: *m*/*z*: 1680 (M^+).

2.6. *Synthesis of [Co_2(TAMEN)(bipy)$_2$][$CoCl_4$]$_2$ (4)*

The complex was prepared similar to **3** except that cobalt(II) chloride hexahydrate (1.190 g, 5 mmol) was used instead of iron(II) chloride tetrahydrate. The final microcrystalline product is light blue. Yield: 2 g, 47%. Anal. Calcd for $C_{70}H_{72}N_{14}O_4Cl_8Co_4$ (%) (M = 1692.79): C, 49.67; H, 4.29; N, 11.58; Cl, 16.75; Co, 13.93. Found (%): C, 49.41; H, 4.20; N, 11.41; Cl, 16.58; Co, 13.86. IR (KBr cm^{-1}): 3460l, 3063w, 1599sh, 1573s, 1492s, 1452s, 1448s, 1374w, 1315s, 1294w, 1250w, 1175w, 1145m, 1113m, 1046m, 1022sh, 979w, 906s, 765s 697s, 642s, 593s, 504m, 469m, 418m, 379s, 347m, 300s, 287s, 219s, 204s; UV-Vis in DMSO: λ_{max}, nm (ε): 671(455), 609sh; molar conductivities ($c_M = 1.1 \times 10^{-3}$ mol L^{-1}) Λ_M, Ω^{-1} mol^{-1} cm^2, in DMSO: 96; MS: *m*/*z*: 1693 (M^+).

2.7. *Synthesis of [Fe$_2$(TAMEN)(bipy)$_2$][FeCl$_6$]$_2$ (5)*

The complex was prepared similar to **3** except that iron(III) chloride (0.81 g, 5 mmol) was used instead of iron(II) chloride tetrahydrate, then a dark red powder separated. Yield: 1.5 g, 67%. Anal. Calcd for $C_{70}H_{72}N_{14}O_4Cl_{12}Fe_4$ (%) (M = 1822.26): C, 46.14; H, 3.98; N, 10.76; Cl, 23.35; Fe, 12.26. Found (%): C, 46.07; H, 3.84; N, 10.55; Cl, 23.24; Fe, 12.19. IR (KBr cm^{-1}): 3407w, 1597n, 1556s, 1541s, 1517sh, 1495s, 1455m, 1407w, 1334m, 1279w, 1187w, 1148w, 1005w, 1075w, 930w, 911w, 874w, 770s, 727m, 697s, 667m, 615m, 515w, 468m, 446m, 429m, 358m, 254w, 228w; UV-Vis in DMSO: λ_{max}, nm (ε) 475; molar conductivities ($c_M = 1.2 \times 10^{-3}$ mol L^{-1}) Λ_M, Ω^{-1}mol^{-1}cm^2, in DMSO: 92.

3. Results and discussion

The Co(II), Cu(II), Fe(II), and Fe(III) complexes containing BAMP or TAMEN as ligands and 2,2′-bipyridine, as a coligand, of general formulae: [M$_2$(BAMP)(bipy)$_2$][MCl$_4$]$_2$, M=Co^{+2}(**1**), Cu^{+2}(**2**), [M$_2$(TAMEN)(bipy)$_2$][MCl$_4$]$_2$, M=Fe^{+2}(**3**), Co^{2+}(**4**), and [Fe$_2$(TAMEN)(bipy)$_2$][FeCl$_6$]$_2$ (**5**) were obtained as microcrystalline powders by reaction of the metal salts with the corresponding ligands in ethanol. The nature of the products does not seem to depend on the molar ratio of the reactants but, the best yields have been obtained for the molar ratio M : pyrazolonic ligand : 2,2′-bipy=2 : 1 : 1, as described in the experimental part. The complexes are stable in dry air, insoluble in most common solvents like water, acetone, dichloromethane, and ethyl ether, but they are soluble in DMSO and DMF. The complexes have been formulated based on elemental analyses, conductometric measurements, UV-Vis, IR spectroscopy, and mass spectra.

3.1. *Molar conductance studies*

The molar conductivity values in the range 125–138 Ω^{-1} mol^{-1} cm^2 in DMF and 92–118 Ω^{-1} mol^{-1} cm^2 in DMSO denote that all the complexes behave as 1 : 2 electrolytes in these solvents [47].

3.2. *Electronic spectra*

Electronic spectra of **1** and **4** exhibit bands with shoulders at lower wavelength at 678 and 671 nm, respectively, assigned to the (ν_3) $^4A_2 \rightarrow ^4T_1(P)$ transition characteristic for

Co(II) in a C_{2v} pseudotetrahedral surrounding [48a]. Its fine structure is a result of spin–orbit coupling that leads to splitting of the $^4T_1(P)$ term.

The electronic spectrum of **2** shows a very large band with low resolution between 780 and 920 nm which indicate a tetrahedral configuration of the copper(II) ion. The band width is concerned with $^2B_2 \rightarrow ^2B_1$ transition and may be explained by intramolecular vibration related to a dynamic Jahn–Teller effect [49].

The electronic spectrum of **3** shows two bands at 456 and 354 nm, assigned to metal-to-ligand charge-transfer transitions $d\pi(M) \rightarrow \pi^*(L)$ and to the $\pi \rightarrow \pi^*$ transitions of the ligands, respectively. In the area 900–1100 nm, a very broad band can be identified. Its position as well as its intensity (55) indicates the presence of iron(II) in a distorted tetrahedral surrounding [48b].

The electronic spectrum of **5** presents a single band at 475 nm, which is assigned to metal-to-ligand charge-transfer transitions $d\pi(M) \rightarrow \pi^*(L)$. Such a simple spectra is argument for the presence of distorted tetrahedral iron(III) in **5** [48b]. The very low intensity explains that the transition will be spin forbidden, as well as Laporte forbidden.

3.3. *Magnetic measurements studies*

The magnetic moment value measured at room temperature, of 4.15 B.M. for **1** agree well with the presence of cobalt(II) in a tetrahedral environment [50]. The magnetic moment of 1.97 B.M. for **2** is close to the spin-only value of an $S = 1/2$, d^9 system, thus denoting that no Cu(II)–Cu(II) interaction exists.

3.4. *IR spectra*

IR spectra of the new compounds are complex. However, bands belonging to both pyrazolone and 2,2′-bipyridine ligands can be identified. The spectra in the region 1700–1550 cm^{-1} of all the complexes show the characteristic vibrations of ν(C=N) and ν(C=C) of pyrazolonic ring and of 2,2′-bipyridine. The bands in the range 1500–910 cm^{-1} can also arise from the stretching and rocking modes of the single bonds in the above heterocycles [51].

IR data supports the involvement of the antipyrine oxygen of pyrazolone in coordination. The intense band at 1658 cm^{-1} assigned to ν(C=O) in free BAMP or TAMEN is missing in spectra of all the complexes. A new peak at 1145–1187 cm^{-1} is attributable to ν(C–O) as a result of the lower C–O bond order. Bands at 1437–1448 cm^{-1} are tentatively assigned to the antipyrine –C=C– group; new bands at 1568–1598 cm^{-1} in **1–5** are assigned to a combination of ν(C=C) and ν(C=N) of antipyrine.

In the IR spectrum bands characteristic of coordinated 2,2′-bipyridine can be identified. Thus, the strong band at 757 cm^{-1} and a weak satellite at 739 cm^{-1}, assigned to C–H out-of-plane deformations of free bipy [52–54] are shifted and split in spectra of the complexes, appearing as two strong/sharp bands at 762–769 and 728–746 cm^{-1}. Below 500 cm^{-1} chelate ring vibrations can be identified. The metal–oxygen bond [55] is identified in the range 504–509 cm^{-1}, whereas metal–nitrogen(bipy) vibrations [56a, 57, 58] appear from 418 to 446 cm^{-1}. The metal–chloride vibrations were identified in the range 305–360 cm^{-1} [56b].

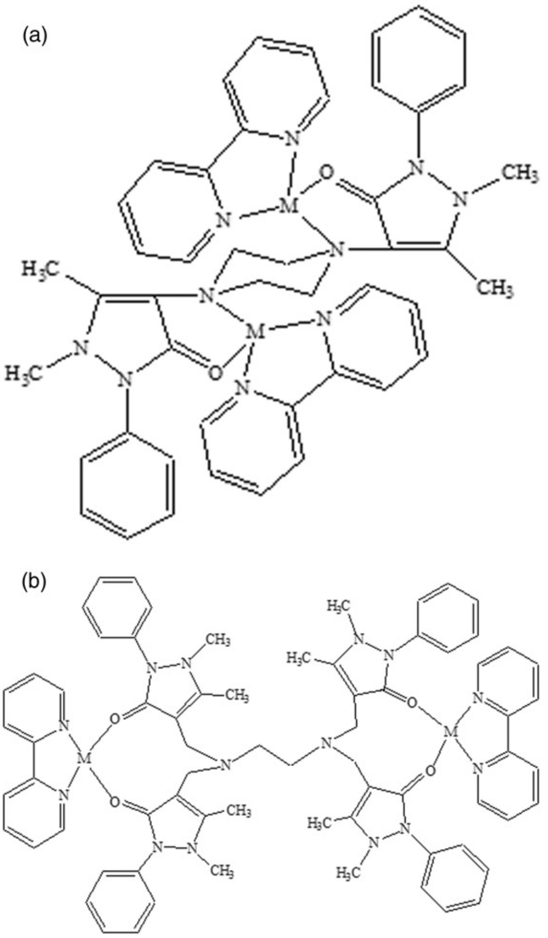

Figure 2. The structure of (a) $[M_2(BAMP)(bipy)_2]^{4+}$ where M=Co^{+2}(**1**), Cu^{+2}(**2**) and (b) $[M_2(TAMEN)(bipy)_2]^{n+}$ where $n=4$ for M=Fe^{+2}(**3**), Co^{2+}(**4**) and $n=6$, M=Fe^{+3}(**5**).

3.5. *Mass spectra*

Mass spectra obtained for the compounds studied here show the molecular peaks for the assumed structures of **1–4**. All compounds showed better mass spectra signals in the positive mode.

The mass spectra of **1** show the molecular peak (1318 m/z) and the isotopic peaks of it at 1317 and 1319 m/z. The signal of the molecular peak in the positive mode was 4×10^3 and the signal for the isotopic peaks was lower. It was found also in the mass spectrum the line at 487 m/z which correspond to BAMP.

Mass spectra of **2** present the highest signal of all compounds used in our study. The molecular peak was at 1336 m/z, together with two isotopic peaks at smaller and bigger m/z values, 1335 and 1337, respectively. In this case the molecular peak shows a higher signal compared with the isotopic peaks, as for **1**. In the mass spectrum were peaks at 255 m/z corresponding to the $Cu(bipy)Cl^+$ (1.5×10^6 intensity).

The mass spectra of **3** proved the assumed structure was correct. The molecular peak was found at 1680 *m*/*z*, together with many isotopic peaks, from 1671 to 1681 *m*/*z*. In this case the highest intensity of the signal was found for 1675. A very interesting thing was to observe in the mass spectra several constant (systematic elimination) differences of 16 *m*/*z* (1435–1451; 1492–1508; 1550–1566; 1608–1624; 1666–1682) attributed to the loss of CH_3 radicals.

According to the mass spectrum of **4**, the molecular peak was found at 1693 *m*/*z*, but the intensity was lower than 10^3. Few isotopic peaks were found as well, at lower *m*/*z* values than the molecular peak (1691 and 1692 *m*/*z*).

4. Conclusions

The mixed-ligand complexes $[M_2(BAMP)(bipy)_2][MCl_4]_2$, M=$Co^{+2}$(**1**), Cu^{+2}(**2**), $[M_2(TAMEN)(bipy)_2][MCl_4]_2$, M=$Fe^{+2}$(**3**), Co^{2+}(**4**), and $[Fe_2(TAMEN)(bipy)_2][FeCl_6]_2$ (**5**) have been obtained by the reaction of metal salts with the corresponding Mannich base and 2,2′-bipyridine. Their formulae have been proposed on the basis of elemental analyses and agree well with the mass spectra. Spectral properties show that their structure is designed by the big binucleating ligands and the metal ions are part of the MON_3 chromophore for BAMP complexes and MO_2N_2 donor set for TAMEN complexes. Based on physico-chemical data, as well as our previous results [59], the structural formulae for the two types of complex cations are proposed in figure 2.

Acknowledgments

The authors would like to thank the Romanian Academy for financial assistance. Thanks for financial support are also due to the ‘‘Fonds zur Förderung der Wissenschaftlichen Forschung in Österreich’’ (Project 19335-N17).

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