STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, XLV, 2, TOM I, 2010

Dedicated to the memory of Prof. dr. Ioan Silaghi-Dumitrescu marking 60 years from his birth

SYNTHESIS AND THERMAL BEHAVIOR OF COPPER(II) COMPLEXES CONTAINING N,N'-TETRA(4-ANTIPYRILMETHYL)-1,2 DIAMINOETHANE AS LIGAND

ELENA MARIA MOSOARCA[a], IMRE LABADI[b], LUDOVIC SAJTI[a], RAMONA TUDOSE[a], VASILE SIMULESCU[a], WOLFGANG LINERT[c] AND OTILIA COSTISOR[a,*]

ABSTRACT. The synthesis of new complexes $[Cu(TAMEN)][Zn(NCS)_4]$ and $[Cu(TAMEN)ZnCl_4(H_2O)]$, where TAMEN stand for the Mannich base N,N'-tetra(4-antipirylmethyl)-1,2-diaminoethane are reported. The molecular formulas are proposed on the basis of elemental analysis, mass spectra, molar conductivity values, UV-VIS and IR spectra. The thermal behavior of the complexes was also investigated.

Keywords: *antipyrine, copper(II), zinc(II), Mannich base, thermal analysis.*

INTRODUCTION

Antipyrine and its derivatives are reported to exhibit analgesic and anti-inflammatory effects, antiviral, antibacterial and herbicidal activities [1-12]. Formation of complexes with some oligoelements may explain their pharmaceutical activity [13]. Antipyrine complexes with certain metal ions, including Pt(II) and Co(II) ions, have been shown to act as antitumor agents. In order to extend this class of pharmaceutics, Mannich bases containing two or four antipyrine fragments have been obtained [14]. Considering that more antipyrine active fragments would lead to a more efficient antipyretic and analgesic medicine, we synthesized and structurally characterized *3 d* metal complexes of antipyrine Mannich bases, namely, N,N'-bis(4-antipirylmethyl)-piperazine (BAMP) [15-16] and N,N'-tetra(4-antipyrylmethyl)-1,2 diaminoethane (TAMEN) [17]. Some of them have been biologically investigated as antimicrobial and antitumoral agents [18-21].

[a] *Institute of Chemistry Timisoara of Romanian Academy, 24 Mihai Viteazu Bd., 300223, Timisoara, Romania*
[b] *University of Szeged, Department of Inorganic and Analytical Chemistry, H-6701 Szeged, P.O. Box 440, Hungary*
[c] *Institute of Applied Synthetic Chemistry, Vienna University of Technology, Getreidemarkt,9/163-AC, A-1060 Vienna, Austria*
[*] Author for correspondence: ocostisor@acad-icht.tm.edu.ro

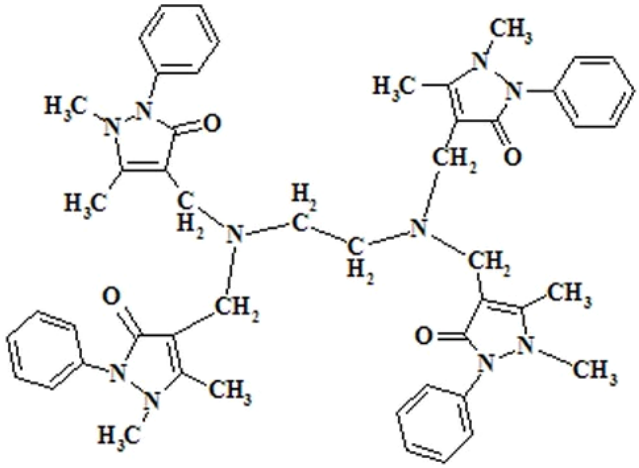

Figure 1. N,N'-tetra-(4-antipyrilmethyl)-1,2-ethanediamine (TAMEN)

The Mannich base, N,N'-tetra-(4-antipirylmethyl)1,2-ethanediamine (TAMEN) has a symmetric molecule with two groups of potential donor atoms separated by the ethylenediamine bridge (Figure 1). Tanks to the flexibility of the ethylenediamine bridge, TAMEN show a great versatility. Thus, when it acts as bis-tridentate ligand, binuclear complexes have been obtained [22]. Mononuclear complexes have been obtained when TAMEN acts as hexa- or tetradentate ligand [23-25]. The thermal behavior of some monometallic complexes containing TAMEN as ligands have been investigated and the decomposition mechanism for the studied complexes has been established [26-30]. As a continuous work in this field, the new bimetallic complexes [Cu(TAMEN)][$Zn(NCS)_4$] and [Cu(TAMEN)$ZnCl_4(H_2O)$] are reported along with their thermal behavior.

RESULTS AND DISCUSSION

The complexes [Cu(TAMEN)][$Zn(NCS)_4$] and [Cu(TAMEN)$ZnCl_4(H_2O)$] were obtained as microcrystalline powders, stable in air, insoluble in most common organic solvents like acetone, chloromethane or benzene, and soluble in DMSO, DMF, acetonitrile. Molar conductivity values of the two complexes in acetonitrile are quite different. Thus, [Cu(TAMEN)][$Zn(NCS)_4$] shows an 1:1 electrolyte type behaviour whereas [Cu(TAMEN)$ZnCl_4(H_2O)$] is a non-electrolyte [31].

The electronic spectrum of the free ligand shows bands at 244 and 280 nm assigned to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively. In the spectra of the complexes, these are shifted to the higher values denoting

the coordination of the ligand to the metal ion. An intense new band appears around 420 nm in the spectra of the complexes which is attributable to a charge transfer process. Further, the spectra show bands of low intensity in the quite similar region, around 700 nm denoting a similar geometry of the metal ion. According to the literature data, these bands can be assigned to the d-d transitions of copper(II) in a distorted octahedral ligand field [32-34].

The FT-IR spectra of the complexes were recorded and compared with that of the free ligand. Some important differences were noticed. First, the strong band at 1656 cm^{-1} due to the ν(C=O) mode in the spectrum of the free ligand is shifted to 1630 and 1631 cm^{-1} for the complexes $[Cu(TAMEN)][Zn(NCS)_4]$ and $[Cu(TAMEN)ZnCl_4(H_2O)]$, respectively, proving coordination through antipyrine carbonyl oxygens, which further affect the pyrazolonic ring. Thus, in the spectrum of the free ligand bands assigned to the pyrazolone ring appear in the region 1347-1494 cm^{-1}. They are shifted to 1374-1493 cm^{-1} in the spectra of the complexes. New bands appear at 1573-1593 cm^{-1} in the IR spectra also and they are assigned to a combination of the ν(C=O) and ν(C=N) stretching modes. These changes can be explained by an important contribution of the mesomeric structures II and III of the antipyrine moiety [35].

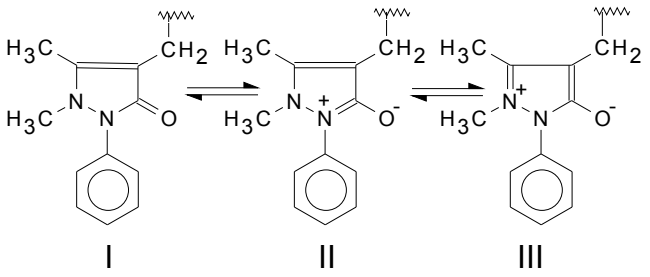

Figure 2. Mesomeric forms of the antipyrine fragment

Bands attributable to ν(Cu-O) and ν(Cu-N) can be identified in the spectra of both complexes. Thus, for $[Cu(TAMEN)][Zn(NCS)_4]$ the weak band at 526 cm^{-1} is assigned to ν(Cu-O) and that at 412 cm^{-1} to ν(Cu-N). For $[Cu(TAMEN)ZnCl_4(H_2O)]$ these modes appear at 439 cm^{-1} for ν(Cu-O) and at 411 cm^{1} for ν(Cu-N), respectively [36, 37]. In the spectrum of this compound a band attributable to ν(Zn-O) at 521 cm^{-1} can be noticed. Infrared spectra demonstrate that TAMEN acts as a hexadentate ligand in the $[Cu(TAMEN)][Zn(NCS)_4]$ complex. The behaviour of TAMEN as a hexadentate ligand through N_2O_4 donor set in the cromophore $[Cu(TAMEN)]^{2+}$ has already been demonstrated [24] on the basis of crystallographic analyses. However, the differences between the positions and intensities of the stretching modes

denote that TAMEN acts in a different mode in $[Cu(TAMEN)ZnCl_4(H_2O)]$. Based on our previous results, we assume that TAMEN acts here as a binucleating ligand with copper(II) coordinated by the NO_2 donor set and zinc(II) by O atoms of two antipyrine moieties. The six coordination number of copper(II) is achieved by coordination of two chloride ions and a water molecule. For Zn(II), the usual coordination number 4 is reached by two chloride ions. Crystallographic studies are in progress for this compound. The complex $[Cu(TAMEN)][Zn(NCS)_4]$ exhibits a ν(CN) vibration at 2074 cm^{-1} and ν(CS) bands at 861 cm^{-1} and 446 cm^{-1} [δ(NCS)], characteristic to the M-NCS bond. Mass spectra showed the molecular peak for both compounds. For $[Cu(TAMEN)][Zn(NCS)_4]$, the molecular peak was found at m/z 1222. Together with this signal, were observed as well other two isotopic signals at m/z 1223 and 1224 in the positive mode. In the same time in the negative mode the molecular peak appear at m/z 1222, together with several isotopic peaks from m/z 1215 to 1221. All of these data proved that the assumed structure of $[Cu(TAMEN)][Zn(NCS)_4]$ is correct. The mass spectra obtained for the compound $[Cu(TAMEN)ZnCl_4(H_2O)]$ showed the molecular peak (m/z 1149) both in the positive and in the negative mode, with a smaller intensity, probably due to the lower ionization process. As in the previous compound, the mass spectra confirmed the proposed structure for $[Cu(TAMEN)ZnCl_4(H_2O)]$.

Thermoanalytical studies of complexes

The decomposition curves in the case of $[Cu(TAMEN)][Zn(NCS)_4]$ shows that below 200ºC there is no definite peak on DTG and endothermic peak on DTA curve, so it could be concluded that there are no coordinated water molecules in the complex compound. In the temperature range 200-340ºC, a mass loss of 32.52% correspond to a partialy loss of ligand, accompanied by an exothermic process. In the temperature range 340-600ºC the mass loss of 45.45% corresponds to the loss of the rest of the ligand and a deposit of $CuO+Zn(SCN)_2$ is formed. On DTA curves the exothermic process is observed. Between 620-1000ºC from the $Zn(SCN)_2$, ZnO is formed. The mass loss is about 7.08 %.

The decomposition curves of complex $[Cu(TAMEN)ZnCl_4(H_2O)]$ shows below the temperature of 150ºC a mass loss of about 1.70% that corresponds to the loss of one water molecule. This process is accompanied by an endothermic process on the DTA curve. The second stage of decomposition takes place between the temperature range 150-250ºC with a loss of two chlorine atoms (the mass loss about 6.25%) and a loss of 0.47 molecule of TAMEN. On DTA curve a large exothermic peak are started in this temperature range with two small maxima. Between 250-450ºC a part of ligand release the solid matter and an exothermic process appears on the DTA curve, corresponding to a 34.96% mass loss. The fourth stage of decomposition

process occurs in the temperature range 450-1000ºC, corresponding to the mass loss of the rest of the ligand, about 45.84%, and to the formation of a deposit of CuO and ZnO. On the DTA curve a continuous exothermic process appears.

EXPERIMENTAL

All chemicals have been purchased from commercial sources and were used without further purification. Analytical data were obtained by a Perkin-Elmer model 240C elemental analyzer. Metal ions analysis was performed by atomic absorption spectroscopy with a GBC SENSAA spectrophotometer. IR spectra were recorded in KBr pellets with a JASCO 430 FT-IR spectrometer (4000–400 cm^{-1}). Electric conductivities were measured at room temperature in acetonitrile solutions with a WTW conductivity meter. Electronic absorption spectra of freshly prepared acetonitrile solutions (10^{-3} M) were measured on a Perkin Elmer Lambda 12 spectrophotometer. The mass spectra were obtained using a mass spectrometer Esquire 6000 ESI (electrospray ionization) from Bruker Daltonics. All the compounds analyzed were diluted before measurements at 10^{-5} M, in acetonitrile. A small syringe pump is included with the instrument system to provide the introduction of samples directly to either the electrospray. The solution was injected into the spray chamber by a Hamilton syringe, with a constant flow of 250 µl/h. The API-ESI (Atmospheric Pressure Interface-ElectroSpray Ionization) generates ions, focuses and transports them into the ion trap mass analyzer. The thermal analysis was performed with a computer-controlled MOM derivatograph. The mass of the investigated samples was 30-60 mg. The measurements were made between room temperature and 1000°C at a heating rate of 5°C/min, in ceramic crucibles under static atmosphere of air, with α-Al_2O_3 as reference substance.

Synthesis of the ligand and the complexes

The ligand TAMEN has been obtained following a Mannich type condensation between antipyrine, 1,2-ethandiamine and formaldehyde [14].

[Cu(TAMEN)][Zn(NCS)$_4$]

$CuCl_2 \cdot 2H_2O$ (0.17 g, 1 mmol) dissolved in 5 ml ethanol was mixed with TAMEN (0.86 g, 1 mmol) dissolved in 10 ml ethanol at 45°C and stirred for 30 min. Further, $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.22 g, 1 mmol) and NH_4SCN (0.37g (4.75 mmol) dissolved in 5 ml EtOH was slowly added to the reaction mixture and stirred for 2 hours. The resulting green product was filtered, washed with ether and dried over $CaCl_2$ in air. Yield: (0.94 g) 77 %; UV-VIS (CH_3CN) spectrum**:** $\lambda_{max}(\varepsilon)$ = 269 (4 940), 295 (3110), 422 (480), 685 (50) nm. IR spectrum (KBr), v /cm^{-1}: 2917 m, 2352 w, 2103 sh, 2074 s, 1630 m,1593 w, 1564 m, 1488 m, 1453 m, 1429 m, 1374 m, 1304 s, 1247 w,

1172 w, 1144 m, 1108 m, 1077 w, 1025 m, 901 m, 861 w, 808 w, 762 s, 695 s, 648 m, 607 m, 526 w, 505 w, 479 w. 446 w, 412 w. Molar conductivity in CH_3CN ($\Omega^{-1}mol^{-1}cm^2$):120. *Anal.* Calcd. mass fractions of elements, *w*/%, for $CuZnC_{54}H_{56}O_4N_{14}S_4$ (MW 1222.30 g/mol) are: C 53.06, H 4.62, N 16.04, O 5.24, S 10.49, Cu 5.20, Zn 5.35; found: C 53.10, H 4.58, N 15.99, O 5.29, S 10.45, Cu 5.19, Zn 5.40. MS+: m/z 1222, 1223, 1224. MS-: m/z.1215, 1216, 1217, 1218, 1219, 1220, 1221, 1222

[Cu(TAMEN)ZnCl$_4$(H$_2$O)]

$CuCl_2{\cdot}2H_2O$ (0.17 g, 1 mmol) dissolved in 2 ml ethanol and $Zn(CH_3COO)_2$ (0.22 g, 1 mmol) was mixed with TAMEN (0.86 g, 1 mmol) dissolved in 20 ml ethanol under vigorous stirring. The green mixture was further stirred for 2 hours and the resulted blue product was filtered, washed with ether and dried over $CaCl_2$ in air. Yield: (0.88 g) 69%; UV-VIS spectrum (CH_3CN): λmax/nm 269, 299, 416 (240), 706, ε/l $mol^{-1}cm^{-1}$ 4940, 3150) (30). IR spectrum (KBr) v/cm^{-1}: 3465m, 2921 m, 2352 w, 1631m, 1573 s, 1493 m, 1457 m, 1431 m, 1379 w, 1299 m, 1249 w, 1145 w,1107 m, 1078 m, 1026 m, 930w, 903 m, 864 w, 762 s, 696 s, 653 m, 607 m, 521w, 507 w, 461 w; 439 w, 411 w. Molar conductivity(CH_3CN) Λ/$\Omega^{-1}mol^{-1}cm^2$: 20. *Anal.* Calcd. mass fractions of elements, *w*/%, for $CuZnC_{50}H_{58}O_5N_{10}Cl_4$ (MW 1149.81 g/mol) are: C 52.23, H 5.08, N 12.18, O 6.96, Cl 12.33, Cu 5.53, Zn 5.69; found: C 51,98, H 5.01, N 12.26, O 6.84, Cl 12.33, Cu 5.58, Zn 6.00. MS+: m/z 1148, 1149, 1150. MS-: m/z 1148, 1149.

CONCLUSION

New Cu(II) and Zn(II) complexes were synthetised and studied. Molar conductivity data shows that the complex [Cu(TAMEN)][Zn(NCS)$_4$] presents a 1:1 electrolyte type in acetonitrile solution and [Cu(TAMEN)ZnCl$_4$(H$_2$O)] a non-electrolyte type behavior. The visible absorption spectra of the complexes suggest that the copper(II) ions are in solution in a distorted octahedral ligand field. IR spectra have revealed that the ligand acts as a hexadentate donor in the case of [Cu(TAMEN)][Zn(NCS)$_4$], through the four oxygen atoms belonging to the antipyrine fragments and two nitrogen atoms of ethylenediamine and as bis-tridentate in the case of [Cu(TAMEN)ZnCl$_4$(H$_2$O)] through the O_2N donor set.

ACKNOWLEDGEMENTS

The authors would like to thank the Romanian and Hungarian Academies of Sciences for financial assistance. Thanks for financial support are also expressed to the "Fonds zur Förderung der Wissenschaftlichen Forschung in Österreich" (Project 19335-N17).

REFERENCES

1. C. H. Sayed, A. A. Hamed, G. A. Meligi, W. E. Boraie, M. Shafic, *Molecules,* **2003**, *8*, 322.
2. Y. Zhang, L. Yzhi, T. Hanbin, Z. Longgen, *Acta Crystallographica,* **2002**, *E58,* 24.
3. G. Turan-Zitouni, M. Sivaci, F. S. Kilic, K. Erol, *European Journal of Medicinal Chemistry,* **2001**, *36,* 685.
4. G. H. Sayed, A. Radwan, S. M. Mohamed, S. A. Shiba, M. Kalil, *Chinese Journal of Chemistry*, **1992**, *10*, 475.
5. M. Daoudi, N. B. Larbi, D. Benjelloun, A. Kerbal, J. P. Launaly, J. Bonvoisin, J. Jaud, M. Mimouni, J. Hadda, *Molecules,* **2003**, *8*, 269.
6. T. N. Sorrel, V. A. Vankai, M. L. Garrity, *Inorganic Chemistry,* **1991**, *30,* 207.
7. A. Togni, L. M. Venanzi, *Angewandte Chemie International Edition Eng.*, **1994**, *33,* 497.
8. A. Kandil, A. Hamid, *Journal of Drug Research,* **1980**, *12*, 27.
9. A. M. Farghlay, A. Hozza, *Pharmazie,* **1980**, *35*, 596.
10. H. Tronnier, *Acta Fac. Med. Univ. Brun*, **1972**, *40*, 211.
11. J. F. Cumming, *Clinical Pharmacology & Therapeutics,* **1976**, *19*, 486.
12. A. Doario, D. Craciunescu, C. Ghirvu, J. Nuno, *An. Quim,* **1977**, *73*, 1120.
13. N. T. Madhu, P. K. Radhakrishnan, M. Grunert, P. Weinberger, W.Linert, *Review in Inorganic Chemistry*, **2003**, *23,* 1 *and references therein*.
14. C. Mannich, W. Krösche*, Archiv der Pharmazie*, **1912**, *250*, 647. C. Mannich, B. Kather, *Archiv der Pharmazie,* **1919**, *18*, 257.
15. O. Costisor, A. Maurer, A. Tomescu, S. Policec, *Buletinul Stiintifico-Tehnic al Institutului Politehnic Timisoara, Seria Chimie,* **1981,** *26*, 93.
16. O. Costisor, A. Maurer, S. Policec, *Buletinul Stiintifico-Tehnic al Institutului Politehnic Timisoara, Seria Chimie,* **1981**, *26*, 87.
17. W. Linert, O. Costisor, R. Tudose, *Oriental Journal of Chemistry*, **1995**, *11*, 107.
18. Al. Stupariu, O. Costisor, E. Bedrosian, L. Radbea, E. Szabo, *Rev. Rom. Med. Veter.,* **1995**, *5*, 81.
19. R. Alexandrova, G. Rashkova, T. Popova, R. Tudose, E. M. Mosoarca, S. Slavov, O. Costisor, *Acta Morphologica and Anthropologica,* **2006**, *11,* 60.
20. R. Alexandrova, G. Rashkova, T. Popova, R. Tudose, E. M. Mosoarca, S. Slavov, O. Costisor, *Experimental Pathology and Parasiology,* **2005**, *8/2,* 93.
21. R. Alexandrova, A.Vacheva, M. Kirilova, G. Miloshev, E. M. Mosoarca, R. Tudose, O. Costisor, *Acta Morphologica and Anthropoogica,* **2007**, *12*, 72.
22. O. Costisor, W. Linert, S. Deusch, C. Stanescu, *Journal of Coordination Chemistry,* **1994**, *33,* 229.
23. R. Tudose, I. Pantenburg, E. M. Mosoarca, G. Meyer, O. Costisor, *Zeitschrift für anorganische und allgemeine Chemie,* **2005**, *632*, 1491.

24. R. Tudose, I. Pantenburg, E. M. Mosoarca, G. Meyer, O. Costisor, *Zeitschrift für anorganische und allgemeine Chemie,* **2005**, *631,* 2423.
25. E. M. Mosoarca, R. Tudose, R. Alexandrova, O. Costisor, *Chemical Bulletin of "Politehnica" University Timişoara,* **2004**, *63*, 49.
26. I. Labadi, R. Tudose, I. Fejer, Z. Jori, O. Costisor, *Journal of Thermal Analysis and Calorimetry,* **1999**, *56,* 553.
27. I. Labadi, Zs. Czibulya, R. Tudose, O. Costisor, *Journal of Thermal Analysis and Calorimetry,* **2004**, *77*, 553.
28. I. Labadi, E. Pal, R. Tudose, O. Costisor, *Journal of Thermal Analysis and Calorimetry,* **2006**, *83*, 681.
29. V. Sasca, E. M. Mosoarca, L. Avram, R. Tudose, O. Costisor, *Journal of Thermal Analysis and Calorimetry*, **2008,** *94(2),* 355.
30. E. M. Mosoarca, V. Sasca, L. Avram, R. Tudose, O. Costisor, *Journal of Thermal Analysis and Calorimetry,* **2008**, *94(2)*, 361.
31. W. Geary, *Journal of Coordination Chemistry Review,* **1971**, *7*, 81.
32. A.B.P. Lever, *Inorganic Electronic Spectroscopy,* Elsevier Publishing Company, Amsterdam, **1968**, 318.
33. N. T. Madhu, P. K. Radhakrishnan, *Transition Metal Chemistry, **2000**, 25, 287.*
34. N. Kalarani, S. Sangeetha, P. Kamalakannan and D. Venkappaya, *Russian Journal of Coordination Cheistry,* **2003**, *29 (12),* 845.
35. M. Hesse, H. Meier, B. Zeeh, *Spektroskopische Methoden in der Organischen Chemie,* G. Thieme Verlag, Stuttgart, **1987**, 255.
36. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds,* John Wiley & Sons, New York, **1986**, 283.
37. J. R. Ferraro, *Low-frequency vibration of inorganic and coordination compounds,* Plenum Press, New York, **1971**, 65.