SYNTHESIS, CHARACTERISATION AND BIOLOGICAL ACTIVITY OF SOME Cr(III), Fe(III), Cu(II), Mn(II)-COMPLEXES OF N,O-AMINOETHANOL TETRACHLOROCYCLOTRIPHOSPHAZENE

Denisa MÂNZU[1], Ticuța NEGREANU-PÎRJOL[2], Florina DUMITRU[3], Mihaela ALEXIE[4], Cornelia GURAN[5]

Complecşii metalici ai N,O-aminoetanol tetraclorociclotrifosfazenei ce contin drept cationi metale tranzitionale Cr(III), Fe(III), Cu(II) si Mn(II), au fost izolați şi caracterizați prin metode fizico – chimice standard: analiză chimică elementală, spectroscopie IR, specroscopie electronică UV-Vis şi spectre RPE. Noii compuşi sintetizați au activitate antibacteriană si antifungică asupra Staphylococcus aureus (bacterie gram pozitivă), Pseudomonas aeruginosa ser. VI, Escherichia coli si Proteus mirabilis (bacterie gram negativă) si Candida albicans (fungi), compusul ($[FeL_2(OH_2)_4](ClO_4)_3$) prezentând efecte comparabile cu ale antibioticelor Amikacină, Ciprofloxacină, si Gentamicină.

Metal complexes of N,O-aminoethanol tetrachlorocyclotriphosphazene containing transition metal cations such as Cr(III), Fe(III), Cu(II) and Mn(II) have been prepared and characterised by standard physico-chemical procedures (elemental chemical analysis, IR, UV-VIS and EPR spectra, conductometric measurement). The new synthesised compounds possess antibacterial and antifungal activity against Staphylococcus aureus (as gram positive bacteria), Pseudomonas aeruginosa ser. VI, Escherichia coli and Proteus mirabilis (as gram negative bacteria) and Candida albicans as fungi species, one of them ($[FeL_2(OH_2)_4](ClO_4)_3$) showing effects comparable to Amikacin, Ciprofloxacine, and Gentamicin.

Keywords: N,O-aminoethanol tetrachlorocyclotriphosphazene, Fe(III), Mn(II), Cr(III), Cu(II) complexes, biological activity

[1] Assistant, Department of Inorganic Chemistry, University POLITEHNICA of Bucharest Romania, manzu_denisa76@yahoo.com
[2] Assistant, Faculty of Dentistry and Pharmacy, "OVIDIUS" University, Romania, 7 Ilarie Voronca St., Constanta, Romania
[3] Assistant, Department of Inorganic Chemistry, University POLITEHNICA of Bucharest, Romania
[4] PhD student, Department of Inorganic Chemistry, University POLITEHNICA of Bucharest Romania,
[5] Prof., Department of Inorganic Chemistry, University POLITEHNICA of Bucharest, Romania, cornelia_guran@yahoo.com

1. Introduction

Although the unsubstituted cyclophosphazene behaves as a poor ligand towards transition metal cations, the presence of moieties containing different heteroatoms attached on the cyclophosphazene ring highly increases their affinity for metal ions [1-5]. The introduction of exocyclic groups on the phosphazene ring is a versatile method to design a large variety of ligands and to isolate coordinative compounds with unusual structures.

The coordination chemistry of the inorganic heterocyclic cyclotriphosphazenes has developed mainly on the use as ligands of cyclophosphazenes derivatives obtained by nucleophilic substitution reactions – *i.e.* aminolysis – at ring phosphorus.

Our group previously reported the synthesis of 1,3,5-tris(8-hydroxyquinolino)-trichlorocyclophosphazatriene, $Cl_2P_3N_3(Ox\text{-}H)_3$, and of some of its complexes of the general formula $[M(Cl_2P_3N_3(Ox\text{-}H)_3)C1_2]$, $[M(Cl_2P_3N_3(Ox\text{-}H)_3)_2]Cl_2$, (M = Cu(II), Co(II), Ni(II)); $[Ni(Cl_2P_3N_3(Ox\text{-}H)_3)Ac]$, $[Ni(Cl_2P_3N_3(Ox\text{-}H)_3)_2Ac]Ac$, $[M(Cl_2P_3N_3(Ox\text{-}H)_3)_3]X_3$ (M = Ni(II), Co(II), X = C1, AcO) [6-8]. By using dichloro-tetramorpholino-cyclophosphazatriene as ligand, a series of Cu(II) new complexes were also synthesised [7]. Some of these complexes [6, 8] inhibited the growth of several fungi species, such as *Aspergillus* and *Candida spp.*

This paper presents the synthesis of an organo-substituted derivative N,O-aminoethanol tetrachlorocyclotriphosphazene, **L,** (from hexachlorocyclotriphosphazene as starting material) which, by coordination to transition ions like Cr(III), Fe(III), Cu(II), Mn(II), led to the complexes with biological activity.

2. Experimental

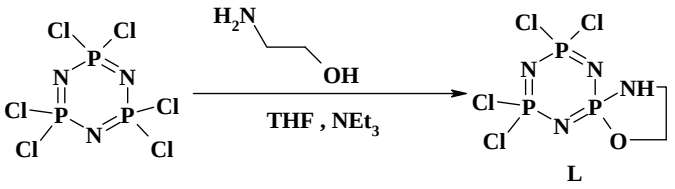
Materials and Methods

All reagents (hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, N,O-aminoethanol, (C_2H_7NO) and the metal salts: $Cr(ClO_4)_3\cdot 6H_2O$, $Fe(ClO_4)_3\cdot xH_2O$, $Mn(ClO_4)_2\cdot 6H_2O$, $Cu(ClO_4)_2\cdot 6H_2O$ were analytical grade and used as received. Commercially available solvents: tetrahydrofurane (THF) and methylene chloride were used without further purification.

Nitrogen was analyzed by microcombustion Dumas. Chloride content was determined by gravimetric method. The electronic spectra were recorded at the room temperature on a Jasco V560 in diffuse reflectance technique. EPR spectra were registered on polycrystalline powders, by using a JEOL JES-FA spectrophotometer (ICF Bucharest). Vibration spectra were recorded with a Bruker Equinox55 spectrophotometer in the wavenumbers range of 400-4000cm^{-1}. Molar

electrical conductivities were determined in MeOH solutions at 25°C with OK 102/1 Radelkis Conductometer.

The ligand N, O-aminoethanol tetrachlorocyclotriphosphazene (**L)** was prepared following the procedure developed in literature [9] according to Scheme 1.



Scheme 1

1.05 g (17.2 mmol) of 2-amino-1-ethanol in 20 ml of THF were added dropwise over 1h to a mixture of 1g (2.8 mmol) $N_3P_3Cl_6$ and 1.741 g (17.2 mmol) of Et_3N in 20 ml THF. The reaction mixture is stirred over 6h. Triethylamine hydrochloride ($Et_3N{\cdot}HCl$) was then filtered off and the solvent removed in vacuum. The residue was recrystallised from dry CH_2Cl_2, yielding **L** as a white, crystalline solid (70% yield). Its characteristics are the following:
Elemental analysis: Calculated for $C_2H_5Cl_4N_4OP_3$ (%): Cl 42.26, N 16.68, found Cl 42.58, N 16.74.
IR (cm^{-1}): $\nu_{N\text{-}H}$ = 3100 (br), $\nu_{CH2sym/asym}$ = 2878.2 (s-br), $\delta_{N\text{-}H}$=1604.64 (m), 1504.03 (m-s), $\delta_{CH2,\ NH2}$ = 1463 (s), $\nu_{P\text{-}N=P(ring)}$=1181.35 (s), 1225.51 (s), $\nu_{P\text{-}O}$ = 1286.24 (m), $\nu_{C\text{-}O}$ = 1076.06 (m), $\nu_{P\text{-}N}$ = 892.41 (m-s), $\nu_{P\text{-}Cl}$ = 650 (m-w).
^{1}H-NMR (400 MHz, D_2O, ppm): δ = 4.362-4.284 (t, 2H, C**H**$_2$-O-), 3.455-3.424 (t, 2H, C**H**$_2$-N-).
^{13}C-NMR (400 MHz, D_2O, ppm): 67.491 (**C**H_2-O-), 42.119 (**C**H_2-N-).
^{31}P-NMR (400 MHz, $CHCl_3$, ppm): 23-24 (t, PCl_2 units), 21-22 (d, PClNH unit).

All complexes have been synthesised according to the following general procedure [6-8]: methanol solutions containing the metal salts $Cr(ClO_4)_3{\cdot}6H_2O$, $Fe(ClO_4)_3{\cdot}xH_2O$, $Mn(ClO_4)_2{\cdot}6H_2O$, $Cu(ClO_4)_2{\cdot}6H_2O$ and the ligand **L,** were mixed with stirring in M: L = 1:2 molar ratio. The complexes were evaporated in air and washed with diethylether and dried in dessicator on P_2O_5.

3. Results and discussion

Organo-substituted cyclotriphosphazene **L** has been synthesized by aminolysis of hexaclorocyclotriphosphazene ($N_3P_3Cl_6$), with N,O-aminoethanol (C_2H_7NO). The results of elemental analysis confirmed the presence of 4 chlorine atoms in the molecule suggesting that the phosphazene derivative is either ansa or

spiro isomer, $N_3P_3Cl_4[HN\text{-}(CH_2)_2\text{-}O]$. However, according to Sournies et al. [10], the aminolysis with N,O-aminoethanol is regiospecific because only the spiro-cyclic isomer is formed. The ^{31}P–NMR spectrum of the ligand synthesized by us also proved the formation of spiro isomer..

Starting from ligand **L** and Cr(III), Fe(III), Cu(II), Mn(II) salts, four complexes have been prepared, (η = 72-75%). The general formulae of these compounds - $[Cr\mathbf{L}_2(OH_2)_3(ClO_4)](ClO_4)_2$ **1**, $[Fe\mathbf{L}_2(OH_2)_4](ClO_4)_3$ **2**, $[Cu\mathbf{L}_2(OH_2)_2](ClO_4)_2$ **3**, $[Mn\mathbf{L}_2(OH_2)_2](ClO_4)_2$ **4**, - are supported by elemental analysis data, IR spectra, and UV/VIS and EPR data, as follows:

1. $[CrL_2(OH_2)_3(ClO_4)](ClO_4)_2$, M = 1076.5 g/mol

Elemental analysis: calculated for $C_4H_{10}O_{17}N_8P_6Cl_{11}Cr$ (%): Cl 23.08, N 10.40 , Found: Cl 23.84, N 10.58.

Molar electrical conductivity: 229 $\mu S\cdot cm^{-1}\cdot mol^{-1}$ (10^{-3}M methanol solution).

IR (cm^{-1}): $\nu_{N\text{-}H,\ OH}$ = 3500-3100 (br), ν_{CH2} = 2907.47 (s), $\delta_{N\text{-}H}$ =1606.55 (m), $\delta_{CH2sym/asym,\ NH2,\ OH}$ = 1464.02 (m), $\nu_{P\text{-}N=P(ring)}$ = 1184.97 (m), 1212.42 (m), 1321.42 (w), $\nu_{P\text{-}O}$ = 1286.13 (m), ν_{ClO4^-} = 1062.88 (s), 621.35 (m), $\nu_{P\text{-}Nring}$ = 955.32 (s), $\nu_{P\text{-}Cl}$ = 594.18 (m).

UV/VIS (nm): 756.77, 573.54, 454.54.

2. $[FeL_2(OH_2)_4](ClO_4)_3$, M = 1080.5 g/mol

Elemental analysis: calculated for $C_4\ H_{10}O_{18}N_8P_6Cl_{11}Fe$ (%) Cl 23, N 10.36, found Cl 22.73, N 10.54.

Molar electrical conductivity: 339 $\mu S\cdot cm^{-1}\cdot mol^{-1}$ (10^{-3}M methanol solution).

IR (cm^{-1}): $\nu_{N\text{-}H,OH}$ = 3300-3100 (br), ν_{CH2} = 2950 (s), $\delta_{N\text{-}H}$ =1612.01 (m), $\delta_{CH2sym/asym,\ NH2,\ OH}$ = 1451.71 (m), $\nu_{P\text{-}N=P(ring)}$ = 1185 (m), 1222.06 (m), 1310 (w), $\nu_{P\text{-}O}$ = 1286.13 (s), ν_{ClO4^-} = 1047.94 (s), 622.87 (m), $\nu_{P\text{-}Nring}$ = 962.30 (s).

UV/VIS (nm): 600, 360.

3. $[CuL_2(OH_2)_2](ClO_4)_2$, M = 1006.5 g/mol

Elemental analysis: calculated for $C_4\ H_{10}O_{12}N_8P_6Cl_{10}Cu$ (%) Cl 21.16, N 11.27, found Cl 20.73, N 11.64.

Molar electrical conductivity: 246 $\mu S\cdot cm^{-1}\cdot mol^{-1}$ (10^{-3}M methanol solution).

IR (cm^{-1}): $\nu_{N\text{-}H,OH}$ = 3300-3100 (br), ν_{CH2} = 2959.86 (s), $\delta_{N\text{-}H}$ =1615.01 (m), $\delta_{CH2sym/asym,\ NH2,\ OH}$ = 1451.03 (m), $\nu_{P\text{-}N=P(ring)}$ = 1211.93 (m), 1328.33 (m), ν_{ClO4^-} = 1048.36 (s), 622.54 (m), $\nu_{P\text{-}Nring}$ = 962.71 (s).

UV/VIS (nm): 941, 749, 572, 380

4. $[MnL_2(OH_2)_2](ClO_4)_2$, M = 998 g/mol

Elemental analysis: calculated for $C_4\ H_{10}O_{12}N_8P_6Cl_{10}Mn$ (%) Cl 21.34, N 11.22, found Cl 21.52, N 11.64.

Molar electrical conductivity: 256 $\mu S\cdot cm^{-1}\cdot mol^{-1}$ (10^{-3}M methanol solution).

IR (cm^{-1}): $\nu_{N-H,OH}$ = 3300-3100 (br), ν_{CH2} = 2952 (s), δ_{N-H} =1613.5 (m), $\delta_{CH2sym/asym, NH2, OH}$ = 1453.41 (m), $\nu_{P-N=P(ring)}$ = 1213.17 (m-s), 1328.09 (m), ν_{P-O} = 1286.13 (s), ν_{ClO4^-} = 1064.37 (s), 623.5 (m), $\nu_{P-Nring}$ = 965.88 (s).
UV/VIS (nm): 563, 460, 380.

Molar electrical conductivity

The values of the molar electrical conductivity for the synthesised complexes correspond to the normal limit for 1:2 or 1:3 electrolyte type [10]. Electroneutrality of the complexes is achieved by uncoordinated perchlorate anions (ClO_4^- was classified as a non-coordinating anion and its very weak basicity is correlated to the very strong acidity of $HClO_4$ (pK =−18) [11]).

IR spectra

The most important changes evidenced in the IR spectrum of **L**, as compared to those of the raw materials (hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ and N,O-aminoethanol, C_2H_7NO) used in synthesis, were: (i) the presence of the weak P-Cl vibration at 650 cm^{-1} (indication of the partially substitution), in contrast to the same band in the spectrum of $N_3P_3Cl_6$, where it is very intense, (ii) the appearance of ν_{P-O}, ν_{P-N} bands at 1286.84 cm^{-1} (iii) characteristic vibrational bands of the organic moiety (-CH_2-, NH-, -CH_2-O-) in 2800-2900 cm^{-1}, 1600-1500 cm^{-1} and 1100-1070 cm^{-1} ranges.

IR spectra of all synthesised complexes display a broad and intense band located around 3400-2900 cm^{-1}. This observation points out the presence of strong hydrogen bonds. These bonds may be assigned to the OH group of the coordination or lattice water molecules. Also, in the IR spectra of complexes **1-4** appear infrared spectral bands, characteristic to ClO_4^- ion (1065-1040 cm^{-1}, respectively 620-625 cm^{-1}).

Characteristic vibrations of the ligand (P-Cl, P-O, P-N=$P_{(ring)}$) are also present in the spectra of complexes **1-4**, but shifted towards higher wavenumbers as compared to the spectrum of free ligand **L**.

UV-Vis spectra

In order to obtain the wavelengths specific to the transition energy, the electronic spectra of the complexes have been analysed by deconvolution procedure, using a program (PeakFit v3.15) with Gauss cumulative function.
The general aspect of the electronic spectra of the isolated complexes is in good agreement with literature data [13].

The electronic spectrum of **1** (Fig. 1a) shows three absorption bands at 13.21kK (756.77 nm) ($^4A_{2g}\rightarrow{}^2T_{2g}$, ^2E_g), 17.44 (573.55 nm) ($^4A_{2g}\rightarrow{}^4T_{2g}$) şi 22.05 kK (453.55 nm) ($^4A_{2g}\rightarrow{}^4T_{1g}$) which are assigned to the spin allowed transition specific for Cr^{3+} in octahedral distorted symmetry.

The absorption bands identified in the electronic spectrum of **2** (Fig. 2a) between 16.67–27.77 kK ($^6A_{1g}\rightarrow{}^4T_{1g,}$ $^6A_{1g}\rightarrow{}^4T_{2g}$) are specific to Fe^{3+} in an octahedral distorted symmetry. As found for $FeCl_3$ and other Fe(III) high-spin complexes [11], the UV-Visible spectrum of the complex **2** exhibits an intense ligand-metal charge transfer band around 360 nm, which can obscure completely the very weak, spin-forbidden *d-d* bands.

The electronic spectrum of **3** (Fig. 3a) presents a large band in the 13.3-17.47 kK range that can be assigned to the superposed *d-d* transitions for Cu^{2+} in tetrahedral distorted geometry.

The absorption bands (26.31, 21.74, 18.86, 17.73, 15.44, 13.88 kK) in the electronic spectrum of **4** (Fig. 4a) were assigned to the spin-forbidden transitions $^6A_{1g}\rightarrow{}^4A_{1g}(G)$ and $^6A_{1g}\rightarrow{}^4E_g(G)$ specific for Mn^{2+} in octahedral distorted geometry.

EPR spectra

The polycrystalline EPR spectra at room temperature show that all complexes are isotropic, with broad, symmetrical signals. The EPR spectra and g_{iso} values for all complexes show that the complexes are monomers, single species, with mononuclear structure.

For **1**, g_{iso}= 1.95. The spectrum of **1** has also the shape characteristic to a paramagnetic species, Cr(III) in distorted octahedral geometry (Fig. 1b).

As expected, the paramagnetic complex **2**, exhibits the typical EPR signal of Fe(III) complexes (Fig. 2b). The Fe(III) ion is a ground state ^6S ($^6A_{1g}$ in the complexes) and is not split within an octahedral or even a lower symmetry ligand field [12]. In addition, there can been no splitting by spin-orbital interaction. Then a single isotropic resonance line at $g \cong 2$ should be always observed. On the other hands, the g value ≅ 1.96 for complex corresponds to high spin Fe(III) complexes because low spin Fe(III) complexes exhibit higher g values.

The complex **3,** presents a strong EPR signal with izotropic parameter g_{iso}=2.11, specific for four-coordinated Cu^{2+} ion with tetrahedral distorted square-planar geometry.

The strong EPR signal of **4**, is specific for a distorted octahedral geometry (g_{iso} = 1.97).

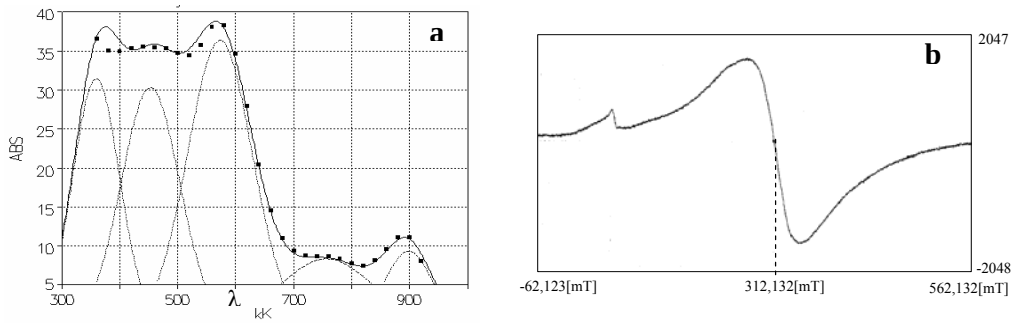


Fig. 1 a) Electronic and b) EPR spectra of **$[CrL_2(OH_2)_3(ClO_4)](ClO_4)_2$**

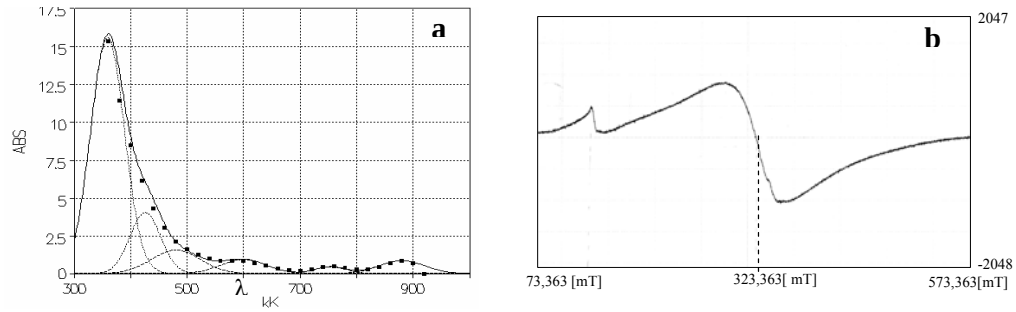


Fig. 2 a) Electronic and b) EPR spectra of **$[FeL_2(H_2O)_4](ClO_4)_3$**

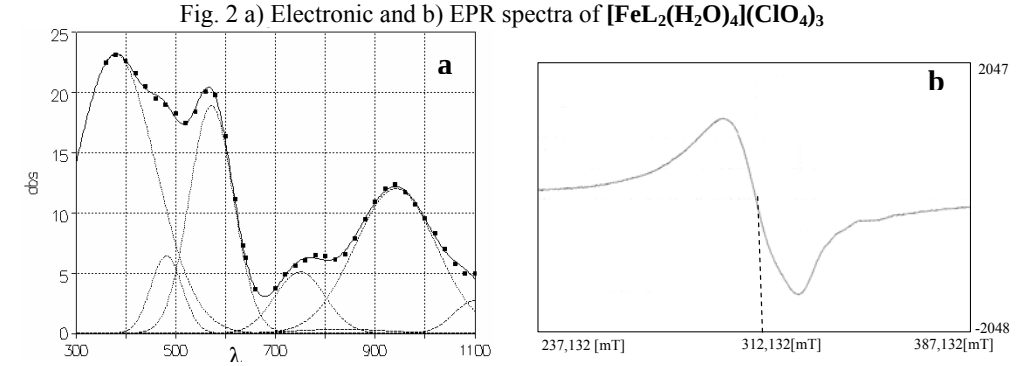


Fig. 3 a) Electronic and b) EPR spectra of **$[CuL_2(H_2O)_2](ClO_4)_2$**

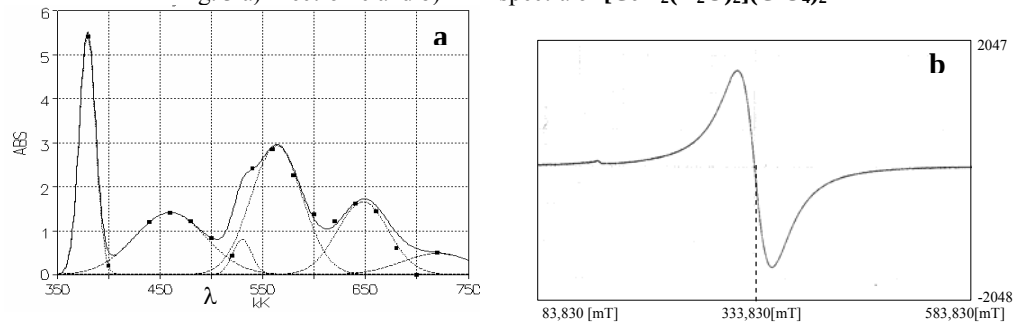


Fig 4 a) Electronic and b) EPR spectra of **$[MnL_2(OH_2)_2](ClO_4)_2$**

Antibacterial activity assay

The diffusion agar technique was used to evaluate the antibacterial activity of the synthesized complexes. The organisms used in the present investigations included *Staphylococcus aureus* (as gram positive bacteria), *Pseudomonas aeruginosa ser. VI, Escherichia coli* and *Proteus mirabilis* (as gram negative bacteria) and *Candida albicans* as fungi species. The complexes **1-4** (0.01 g) were laid on the agar-agar solid medium surface pre-inseminated with the above-mentioned bacteria. When the testing substance has antibacterial action, in a concentration higher than minimum inhibitory concentration (MIC), the inseminated bacteria are inhibited. Thus, we have determined the width (mm) of inhibition area for the synthesised complexes toward the selected bacteria (Table 1).

Table 1

Results of antibacterial activity assay*

Compound	Gram pozitive		Gram negative		Fungi
	Staphylococcus aureus	*Proteus mirabilis*	*Pseudomonas aeruginosa VI*	*Escherichia coli*	*Candida albicans*
L	5	R	9	7	R
$[CrL_2(H_2O)_3(ClO_4)](ClO_4)_2$	6	R	6	R	11
$[FeL_2(H_2O)_4](ClO_4)_3$	5	R	17	R	R
$[CuL_2(H_2O)_2](ClO_4)_2$	10	R	8	9	10
$[MnL_2(H_2O)_2](ClO_4)_2$	R	R	R	R	R
Tetracycline	R	R	Nd	R	Nd
Nitrofurantoin	Nd	R	Nd	21	Nd
Ceftazidine	Nd	24	Nd	21	Nd
Ofloxacin	Nd	Nd	Nd	22	Nd
Amikacin	17	17	21	15	Nd
Metilmicine	Nd	14	14	16	Nd
Amoxicillin	Nd	Nd	Nd	R	Nd
Cephalothin	Nd	20	Nd	17	Nd
Ciprofloxacine	Nd	35	25	21	Nd
Cefuroxime	Nd	Nd	Nd	Nd	Nd
Ceftriaxone	25	Nd	Nd	Nd	Nd
Amoxicillin+clavulanic acid	18	R	Nd	17	Nd
Unasyn	R	Nd	Nd	Nd	Nd
Oxaciline	R	Nd	Nd	Nd	Nd
Imipenem	Nd	26	28	Nd	Nd
Penicillin	R	Nd	Nd	Nd	Nd
Chloramphenicol (standard)	Nd	Nd	R	Nd	Nd
Gentamicin	17	Nd	14	Nd	Nd
Piperacillin	Nd	Nd	20	Nd	Nd
Biseptol	20	Nd	R	Nd	Nd
Kanamycin	Nd	R	Nd	Nd	Nd
Nalidixic acid	Nd	15	Nd	Nd	Nd
Erythromycin	22	Nd	Nd	Nd	Nd
Rifampicin	23	Nd	Nd	Nd	Nd
Vancomycin	18	Nd	Nd	Nd	Nd
Amphotericin B	Nd	Nd	Nd	Nd	15

Itraconazole	Nd	Nd	Nd	Nd	R
Econazole	Nd	Nd	Nd	Nd	18
Ketoconazole	Nd	Nd	Nd	Nd	25
Nystatin	Nd	Nd	Nd	Nd	20
Miconazole	Nd	Nd	Nd	Nd	24

* Nd = non detected, R = resistant. Inhibition values = 1-5 mm = (less active); inhibition values = 6-10 mm = (moderate active); inhibition values = 11 -15 mm = (highly active);
The values represent the width (mm) of inhibition area identified on different samples containing 0.01g of **1-4** complexes.

The obtained data for biological activity reflect the following findings:
1. The ligand **L** has moderate activity in comparison with *Pseudomonas aeruginosa* and *Escherichia coli* and is less active in comparison with *Staphylococcus aureus*. For *Proteus mirabilis* no activity has been detected.
2. None of the four complexes showed biological activity toward Proteus mirabilis.
3. **$[MnL_2(H_2O)_2](ClO_4)_2$** has no activity toward the organisms used to evaluate the biological activity: *Staphylococcus aureus*, *Pseudomonas aeruginosa ser. VI, Escherichia coli, Proteus mirabilis* and *Candida albicans*.
4. **$[FeL_2(H_2O)_4](ClO_4)_3$** presented a remarkable activity toward *Pseudomonas aeruginosa ser. VI* comparable to some known antibiotics such as Amikacin, Ciprofloxacine, and Gentamicin.
5. **$[CrL_2(H_2O)_3(ClO_4)](ClO_4)_2$** and **$[CuL_2(H_2O)_2](ClO_4)_2$** are the only complexes with antifungal activity, having values slightly inferiors to the ones presented toward *Candida albicans* by Amphotericin B and Econazole.
6. The data collected in Table 1 show that Unasyn, Oxaciline and Penicillin have resistance effect toward *Staphylococcus aureus*, in contrast to the synthesised Cr(III), Fe(III), Cu(II)-complexes. The same behaviour was observed in the case of *Pseudomonas aeruginosa ser. VI*: Cefuroxime, Amoxicillin and clavulanic acid, Unasyn, Chloramphenicol, and Biseptol are resistant toward this bacteria while the synthesised Cr(III), Fe(III), Cu(II)-complexes are moderate (Cr and Cu) or highly active (Fe).

4. Conclusions

This paper presents the synthesis and characterization of the Cr(III), Fe(III), Cu(II), Mn(II) complexes with N, O-aminoethanol tetrachlorocyclotriphosphazene, **L**. Elemental analysis, molar conductivity data, IR and electronic spectra support the general formulae of obtained complexes: $[Cr\mathbf{L}_2(OH_2)_3(ClO_4)](ClO_4)_2$, $[Fe\mathbf{L}_2(OH_2)_4](ClO_4)_3$, $[Cu\mathbf{L}_2(OH_2)_2](ClO_4)_2$, $[Mn\mathbf{L}_2(OH_2)_2](ClO_4)_2$

The biological activity of these compounds was studied toward the following organisms: *Staphylococcus aureus* (as gram positive bacteria), *Pseudomonas*

aeruginosa ser. VI, Escherichia coli and *Proteus mirabilis* (as gram negative bacteria) and *Candida albicans* as fungi species.

$[FeL_2(H_2O)_4](ClO_4)_3$ complex shows a remarkable activity toward *Pseudomonas aeruginosa ser. VI* comparable to some known antibiotics such as Amikacin, Ciprofloxacine, and Gentamicin.

Acknowledgements

The work was supported by the Romanian National University Research Council by the TD-Research Grant No. 119/2007 and MD-Research Grant No **3/2007.** The authors would like to acknowledge Dr. Agneta Caragheorgheopol (ICF-Bucharest) for EPR measurements.

R E F E R E N C E S

[1] *G.A. Carriedo*, *L. Fernandez-Catuxo, F.G.J. Alonso, P. Gomez-Elipe*, J. Organomet. Chem., **503**, 1995, 59-68.
[2] *R. Hasselbring, H.W. Roesky, A. Heine, D. Stalke, G.M. Sheldrick*, Z. Naturforsch. B, **49**, 1994, 43-49.
[3] *A. Chandrasekaran, S.S. Krishnamurthy, M. Nethaji*, J. Chem. Soc. Dalton Trans., **1**, 1994, 63-68.
[4] *P. Wisian-Neilson, K.T. Nguyen, T. Wang, S. Rippstein, C. Claypool, F. J. Garcia-Alonso*, Phosphorus, Sulfur Silicon Relat. Elem., **87**, 1994, 277-286.
[5] *M. Veith, M. Kross, J.F. Labarre*, J. Mol. Struct., **243**, 1991, 189-209.
[6] *M. Barboiu, C. Guran, I. Jitaru, M. Cimpoesu, C.T. Supuran*, Metal Based Drugs, **3(5)**, 1996, 233-240.
[7] *C. Guran, M. Barboiu, A. Meghea, I. Jitaru, M. Cimpoesu, D. Berger, P. Diaconescu, M. Bojin, V. Iluc, I. Bita*, Rev. Roum. Chim**., 42(7)**, 1997, 609-614.
[8] *C. Guran, M. Barboiu, P. Diaconescu, V. Iluc, M. Bojin, A. Scozzafava, C. T. Supuran*, Metal Based Drugs, **5(5)**, 1998, 287-294.
[9] *F. Sournies, K. Zai, K. Vercruysse, M.-C. Labarre, J.-F. Labarre,* J. Mol. Str., **412**, 1997, 19-26.
[10] *R. J. Angelici,* Synthesis and Technique in Inorganic Chemistry*,* 2nd ed, Saunders: Philadelphia, 1977
[11] *J.-L. Pascal, F. Favier*, Coord. Chem. Rev., **178–180**, 1998, 865–902.
[12] *A.B.P. Lever*, Inorganic electronic spectroscopy, 2 ed., Elsevier, Amsterdam 1984.