Journal of Thermal Analysis and Calorimetry, Vol. 86 (2006) 2, 379–384

METAL COMPLEXES WITH GIRARD REAGENTS-BASED LIGANDS Part II. Copper(II) and zinc(II) complexes with pyridoxilidene and salicylidene Girard-T hydrazone

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Complex formation reactions of copper(II) and zinc(II) halides with pyridoxilidene Girard-T hydrazone dihydrate $[H_3PLGT]Cl_2\cdot 2H_2O$ and salicylidene Girard-T hydrazone $[H_2SalGT]Cl$ ligands are described. The composition of the complexes, determined by customary methods, can be presented by the formulas $Cu(HPLGT)X_2$ (X=Cl^- and Br^-), $Zn(HPLGT)Cl_2$, $Cu(HSalGT)Cl_2\cdot H_2O$ and $Zn(SalGT)Cl\cdot 2H_2O$. The structures of the compounds were compared by powder X-ray diffraction. Thermal stability of the compounds has been examined by TG and DSC. The ligands and the complexes were tested against some gram-positive and gram-negative bacteria and yeast.

Keywords: *antibacterial activity, copper(II) and zinc(II) halide complexes, pyridoxilidene and salicylidene Girard-T hydrazone, thermal decomposition*

Introduction

Due to their theoretical importance and very diverse applications, including chemotherapy, analytical procedures, catalysis and industrial processes [1–6], Schiff bases and their complexes are often in the focus of chemical research projects. Girard-T (trimethylammonium-acethydrazide) and -P (pyridinium-acethydrazide) reagents form water-soluble hydrazones, enabling by thus the separation of carbonyl compounds from other classes of organic substances [7]. As the applicability of compounds, especially in pharmacology, depends also on their water-solubility, these reagents and their Schiff bases represent an interesting research subject [8]. Besides, with ligating atoms of Schiff bases, these compounds take readily part in complex formation reactions. As the biological activity of complexes is often enhanced, Schiff bases have also been studied as ligands in coordination chemistry [9–15]. The practical applicability of compounds depends on their physico-chemical properties including their thermal behavior. As a consequence, some papers describe in detail thermal decomposition of Schiff bases of Girard-T reagents and their complexes [16–18]. In references [9, 10, 15] transition metal complexes with recently synthesized pyridoxilidene Girard-T hydrazone ($[H_3PLGT]Cl_2\cdot 2H_2O$) and with already known salicylidene Girard-T hydrazone ($[H_2SalGT]Cl$) are described.

In this study we present the preparation, chemical and thermal characterization of new copper(II) and zinc(II) complexes with above Schiff bases (Fig. 1).

Experimental

Synthesis of complexes

All chemicals for syntheses were analytical reagent grade and used without any purification.

The synthesis of the pyridoxilidene Girard-T hydrazone, $[H_3PLGT]Cl_2\cdot 2H_2O$, and salicylidene Girard-T hydrazone, $[H_2SalGT]Cl$, has been described elsewhere [9, 15].

Complexes with $[H_3PLGT]Cl_2\cdot 2H_2O$ of the type $Cu(HPLGT)X_2$ (X=Cl, Br) were obtained from warm methanolic solutions of metal salts and ligand with an M to ligand ratio of 1:1 (0.5 mmol each, total volume: 12 cm^3). The precipitates were filtered off after staying for 24 h at room temperature, washed with MeOH and Et_2O and dried in the air.

$Cu(HPLGT)Cl_2$ was synthesized using either $CuCl_2\cdot 2H_2O$, or $Cu(OAc)_2\cdot H_2O$. Yield: 85 and 70%, respectively. Elemental analysis data for the green crystals, found% (calcd.%): C, 37.10 (37.64); H, 4.75

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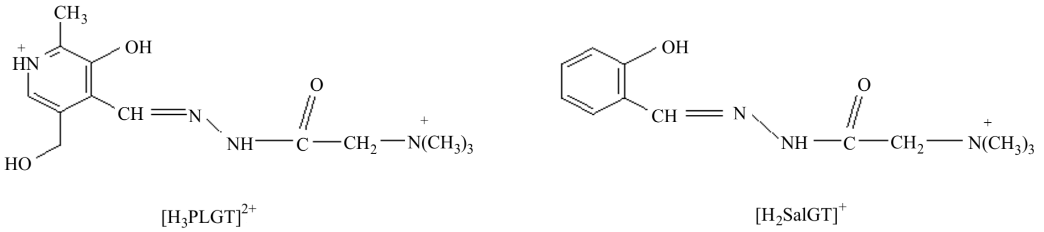


Fig. 1 Structure of the ligand cations

(4.86); N, 13.17 (13.51), Cu, 14.52 (15.32). $\lambda_M(H_2O/DMF)$=217/7.61 S cm^2 mol^{-1}, respectively. μ_{eff}=1.63 μ_B.

$Cu(HPLGT)Br_2$ was prepared using $CuBr_2$. It precipitated in the form of green microcrystals. Yield: 75%. Elemental analysis data, found% (calcd.%): C, 31.60 (31.00); H, 4.11 (4.00); N, 11.24 (11.12), Cu, 13.19 (12.62). $\lambda_M(H_2O/DMF)$=208/11 S cm^2 mol^{-1}, respectively. μ_{eff}=1.63 μ_B.

$Zn(HPLGT)Cl_2$ was obtained by adding solid $Zn(OAc)_2{\cdot}2H_2O$ (0.5 mmol) to 5 cm^3 of warm solution of the ligand (0.5 mmol). The complex formation resulted in a yellow precipitate. Yield: 80%. Elemental analysis data, found% (calcd.%): C, 37.31 (37.47); H, 4.96 (4.84); N, 13.05 (13.44), Zn, 15.48 (15.70). $\lambda_M(H_2O)$=208 S cm^2 mol^{-1}.

$Cu(HSalGT)Cl_2{\cdot}H_2O$ was obtained in the reaction of $CuCl_2{\cdot}2H_2O$ and $CuBr_2$ with the ligand $[H_2SalGT]Cl$. The mixture (0.5 mmol each, total volume: 6 cm^3) was heated mildly for several minutes and left at room temperature for 24 h. The green single crystals were filtered off, washed with MeOH and Et_2O and dried in the air. Yield: 75 and 80%, respectively. Elemental analysis data, found% (calcd.%): C, 37.29 (37.17); H, 5.01 (4.94); N, 18.77 (18.84), Cu, 16.05 (16.39). $\lambda_M(H_2O/DMF)$= 410/33.1 S cm^2 mol^{-1}, respectively. μ_{eff}=1.52 μ_B.

The yellow $Zn(SalGT)Cl{\cdot}2H_2O$ precipitate was filtered off from the ethanolic solution of $Zn(OAc)_2{\cdot}2H_2O$ and ligand (0.5 mmol each, total volume 5 cm^3) after staying for 24 h at room temperature, washed with EtOH and Et_2O. Yield: 29%. Elemental analysis data, found% (calcd.%): C, 37.99 (38.83); H, 4.82 (5.38); N, 10.70 (11.32), Zn, 17.79 (17.61). $\lambda_M(H_2O/DMF)$= 121/6.2 S cm^2 mol^{-1}, respectively.

Methods

Elemental analysis (C,H,N) was performed by standard methods. The metal content of the complexes was determined by chelatometric titration with EDTA, upon their destruction with cc. H_2SO_4 and cc. HNO_3.

IR spectra were recorded at room temperature using KBr pellets, in the range of 4000–400 cm^{-1} on a ThermoNicolett NEXUS 670 FT-IR spectrometer. The spectra were obtained with a resolution of 4 cm^{-1} and with a co-addition of 32 scans.

Powder X-ray patterns were obtained using a Guinier–Hägg focusing camera with $CuK_{\alpha 1}$ radiation (λ=1.5405 Å) and photographic recording. Silicon (a=5.430 880 Å) was added as an internal standard and used for the refinement of the unit cell dimensions. The film strips were measured with an automatic optical reader [19] yielding relative line intensities and geometrical positions. The powder diffraction characteristics were further evaluated with TREOR 90, a trial and error indexing program [20, 21]. The indexed powder diffraction peaks with observed and calculated 2θ values, *d*-values and relative intensities can be obtained upon request from T.W.

Magnetic susceptibility (μ_{eff}) measurements were conducted at room temperature on an MSB-MKI magnetic susceptibility balance Sherwood Scientific Ltd., Cambridge.

Molar conductivity (λ_M) of freshly prepared 10^{-3} mol dm^{-3} DMF and aqueous solutions was measured at room temperature using a digital conductivity meter Jenway 4010.

Thermal analysis was performed in flowing argon and air atmospheres with a heating rate of 10 K min^{-1} using a DuPont 1090 TA system. Sample masses were about 5 mg. In thermogravimetric measurements platinum crucible was employed, while the DSC curves were recorded up to 600 K using an open aluminum pan sample holder and with an empty aluminum pan as reference.

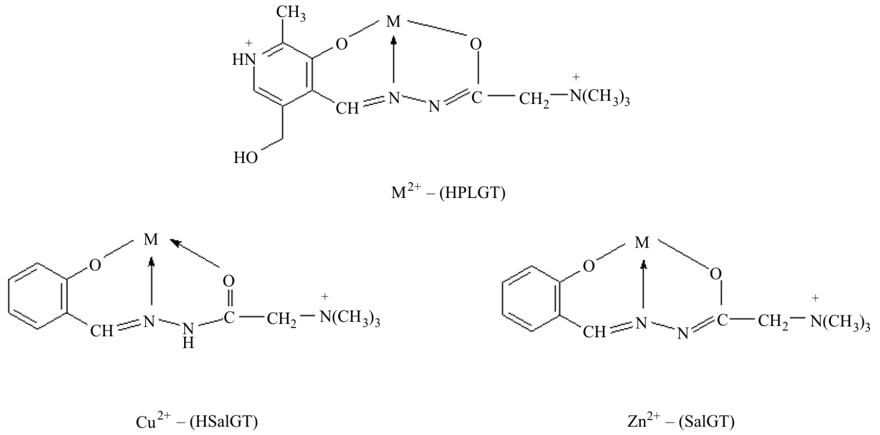
Antimicrobial activities were tested against two strains of bacteria (*Staphylococcus aureus*, gram-postive and *Pseudomonas aeruginosa*, gram-negative) and yeast Saccharomyces cerevisiae. The investigations were carried out by agar diffusion method [22]. Each of the investigated microorganisms was seeded for the slants in the tubes with physiological saline (PS). The PS (1 mL) was homogenized in the tubes with 9 mL of melted (45°C) Mueller Hinton agar (for bacteria) or Malt extract agar (for yeast). The homogenous suspension was poured into Petri dishes. After cooling 20 mL of the investigated sample were placed with micropipette on the formed solid medium. Plates were incubated for 24 (bacteria) or 72 h (yeast), and inhibition zone evaluated. Each test was repeated three times.

Results and discussion

The dicationic $[H_3PLGT]^{2+}$ ligand (Fig. 1) with three acidic protons may be subsequently deprotonated beginning with the removal of the most acidic phenol-proton. The neutral form of the ligand may be obtained by deprotonation of the enolic carbonyl group. The deprotonation of the protonated pyridine nitrogen occurs only in the presence of bases. The complex formation with $CuCl_2$, $CuBr_2$, $Cu(OAc)_2$ and $Zn(OAc)_2$ is taking place with the neutral form of the ligand, in spite of the fact that the acetate ion may induce the extraction of pyridine nitrogen proton. In the reaction of $Zn(OAc)_2$ with the ligand, instead of the expected acetate complex, $Zn(HPLGT)Cl_2$ is formed. IR spectra of the compounds refer to a tridentate ONO coordination, as presented in Fig. 2. The strong $\nu_{C=O}$ vibration, appearing at 1701 cm^{-1} in the spectrum of the ligand, due to the deprotonation of its enol form, in the spectra of the complexes is missing. In the complexes a red shift of the azomethine $\nu_{C=N}$ vibration at 1629 cm^{-1} for 7–21 cm^{-1} is observed. The absorption band in $[H_3PLGT]^{2+}$ at 1305 cm^{-1} is assigned to $\nu_{C_{Ar}-O}$ vibration. The position of this band suffers blue shift in complexes to 1330, 1322 and 1318 cm^{-1} for $CuBr_2$, $CuCl_2$ and $ZnCl_2$ compounds, respectively. These changes support the proposition of ONO coordination as was found in its complex with cobalt(III) [15]. The broad, strong band around 2720 cm^{-1} is characteristic for protonated pyridine nitrogen ν_{NH^+} vibration [23].

The complexes are well soluble in water and DMF. The somewhat lower magnetic susceptibility (1.63 μ_B) of copper(II) complexes compared to the usually observed μ_{eff}=1.8–2.1 μ_B values suggests a possible antiferromagnetic copper–copper interaction in the crystal. The low molar conductivity of the Cu(II) halide complexes measured in DMF [24] refers to their pentacoordinated structure. The molar conductivity value measured in aqueous solution is higher than is expected for a 1:2 type electrolyte, suggesting the complex instability in water. As the lowest coordination number for zinc(II) complexes is 4, the coordination of at least one chloride ion is supposed. However, the high molar conductivity of its aqueous solution is due to the absence of the chloride coordination in solution.

In the complexes with salicylidene Girard-T hydrazone ligand, $[H_2SalGT]Cl$, the same ONO type of coordination is supposed as with the pyridoxilidene Girard-T hydrazone (Fig. 2). In $Cu(HSalGT)Cl_2 \cdot H_2O$, obtained in the reaction of $CuCl_2$ with $[H_2SalGT]Cl$, the ligand is coordinated in its neutral form, which means the deprotonation of the phenol group during complex formation. It is interesting to note that the reaction of $CuBr_2$ with the same ligand gave also a chloride compound, in contrast to the reaction with $[H_3PLGT]Cl_2$ where the corresponding bromide complex was formed. The structure of the chloride complex was solved from single crystal [25]. It showed that Cu(II) is sited in a square-pyramidal surrounding of ONO ligand atoms and one chloride ion forming the basis of the pyramid and with the second chloride in its apex. The same type of coordination was found in other complexes with the same ligand [9, 10]. The IR spectra of the considered complexes are in accordance with this type of coordination. Thus, the very intensive $\nu_{C=O}$ band observed in the ligand spectrum at 1704 cm^{-1}, as a consequence of the oxygen coordination, is in the spectrum of complex shifted to 1608 cm^{-1}. As this band appears to be complex it can be supposed that it is overlapped with the shifted $\nu_{C=N}$ vibration, which is in the ligand spectrum observed at 1622 cm^{-1} [10]. In contrast to the negative shifts of the $\nu_{C=O}$ and $\nu_{C=N}$ bands, the $\nu_{C_{Ar}-O}$ band shows a blue shift from 1272 cm^{-1} in the ligand to 1309 cm^{-1} in the complex, as observed in other complexes with the same ligand [10]. In the spectrum of $Zn(SalGT)Cl \cdot 2H_2O$ the absence of the $\nu_{C=O}$ band refers to its coordination in a deprotonated enolic form, generated by the action of acetate base. As in the case of the copper(II) complex [9,



M^{2+} – (HPLGT)

Cu^{2+} – (HSalGT)

Zn^{2+} – (SalGT)

Fig. 2 Coordination mode of the ligands

10], the $\nu_{C=N}$ and $\nu_{C_{Ar}-O}$ bands in zinc complex are shifted to lower (1617 cm^{-1}) and higher (1281 cm^{-1}) frequency, respectively.

The somewhat lower magnetic susceptibility of the copper(II) compound compared with the spin-only value may be a consequence of antiferromagnetic interactions in the crystal. Both compounds are well soluble in DMF and water, and less soluble in MeOH and EtOH.

The molar conductivity of the salicylidene compounds, similarly to the complexes with pyridoxal derivatives, is lower in DMF than in water. The low value of the molar conductivity of $Zn(SalGT)Cl{\cdot}2H_2O$ suggests its stability in this solvent. On the contrary, the higher value of molar conductivity of $Cu(HSalGT)Cl_2{\cdot}H_2O$ points to the partial ionization of the molecule in DMF. As the thermal decomposition of $Zn(SalGT)Cl{\cdot}2H_2O$ shows that the second water molecule evaporates in the 380–500 K temperature range (vide infra) it may be supposed that, in addition to the chelate ligand and chloride ion, one water molecule belongs to the inner coordination sphere. In water, the molar conductivities of $Cu(HSalGT)Cl_2{\cdot}H_2O$ and $Zn(SalGT)Cl{\cdot}2H_2O$ correspond to 1:2 and 1:1 electrolyte type, respectively, which suggests a complete replacement of coordinated chloride ions with water molecules.

Crystal data for $Cu(HPLGT)X_2$ (X=Cl^- and Br^-), $Zn(HPLGT)Cl_2$ and $Cu(HSalGT)Cl_2{\cdot}H_2O$ ($Zn(SalGT)Cl{\cdot}2H_2O$ being amorphous) are presented in Table 1. According to the findings of the X-ray powder data, the three compounds with the triclinic symmetry have the same kind of molecular packing. The packing of the orthorhombic $Cu(HSalGT)Cl_2{\cdot}H_2O$ complex is not so different, either.

Thermal decomposition

The thermal curves were recorded in air and argon atmospheres. The thermogravimetric decomposition in air is presented in Figs 3 and 4, while the DSC curves in argon are shown in Fig. 5.

The decomposition temperature of copper(II) halide complexes with $[H_3PLGT]Cl_2{\cdot}2H_2O$ is about the same (485 K), while the thermal stability of the zinc(II) chloride is somewhat higher (525 K). The thermal stability of the compounds does not depend on the gas carrier. The first decomposition step consists of several superposed processes that are for the copper(II) compounds faster in argon, for the zinc(II) complex being independent on atmosphere up to 700 K. In view of the structure of the compounds the mass loss to the first decomposition step may correspond to several departing fragments. The probable leaving groups are $–CH_2N(CH_3)_3$, –CNO, hydrogen halides or the substituents of pyridoxal. As the decomposition pattern of the compounds is very similar, on the basis of the mass loss to the first DTG minimum, the most probable leaving groups are $–CH_2N(CH_3)_3$ and one molecule of HCl ($Cu(HPLGT)Cl_2$: 24%, calcd: 26.42%, $Zn(HPLGT)Cl_2$: 24%, calcd: 26.31%) or in the case of the bromide compound, HBr, 30%, calcd: 30.58%. Above 600 K (700 K for $ZnCl_2$) in argon the decomposition slows down and does not complete up to 1000 K. In air, about 970 K some residue of copper(II) complexes (~4–8%) is left. The white residue at 940 K in the case of zinc(II) compound is ZnO, its amount (13.5%) being lower than expected (19.54%), which is not surprising in view of the volatility of halides.

In view of the fact that the complexes $Cu(HSalGT)Cl_2{\cdot}H_2O$ and $Zn(SalGT)Cl{\cdot}2H_2O$, are hydrates, their decomposition temperature is lower than that of the corresponding anhydrous complexes with pyridoxilidene Girard-T hydrazone. The first water molecule of $Zn(SalGT)Cl{\cdot}2H_2O$ evaporates almost at room temperature, followed with the next molecule in the temperature range of 380–500 K. The anhydrous compound is not stable, and it decomposes before the dehydration is completed. The decomposition does not depend on atmosphere up to 750 K. The possible departing fragments in these complexes are most probable the same as in the case of the HPLGT compounds. The decomposition steps are better separated in zinc(II) complex. The calculation suggests that the first decomposition products are fragments of the $–CH_2N(CH_3)_3$ group (21%, calcd: 19.71%). The next mass loss of 10%, like to the decomposition of the

Table 1 Crystal data for $M(HPLGT)X_2$ (M=Cu(II) and Zn(II), X=Cl^- and Br^-) complexes

	$Cu(HPLGT)Cl_2$	$Cu(HPLGT)Br_2$	$Zn(HPLGT)Cl_2$	$Cu(HSalGT)Cl_2{\cdot}H_2O$
crystal system	triclinic	triclinic	triclinic	orthorhombic
a/Å	7.55	7.70	9.51	16.6
b/Å	9.03	9.10	13.4	13.9
c/Å	14.15	13.11	14.9	6.87
α/degree	64.6	77.4	68.8	90.0
β/degree	73.8	99.9	75.7	90.0
γ/degree	78.0	77.5	85.5	90.0
V/Å^3	830.9	853.4	1724.6	1587.7
D/g cm^{-3}	1.66	1.96	1.61	1.55

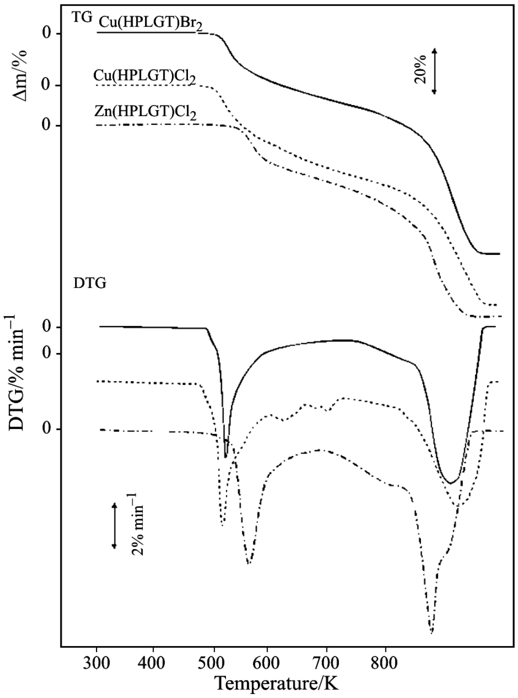


Fig. 3 TG-DTG curves for HPGT complexes

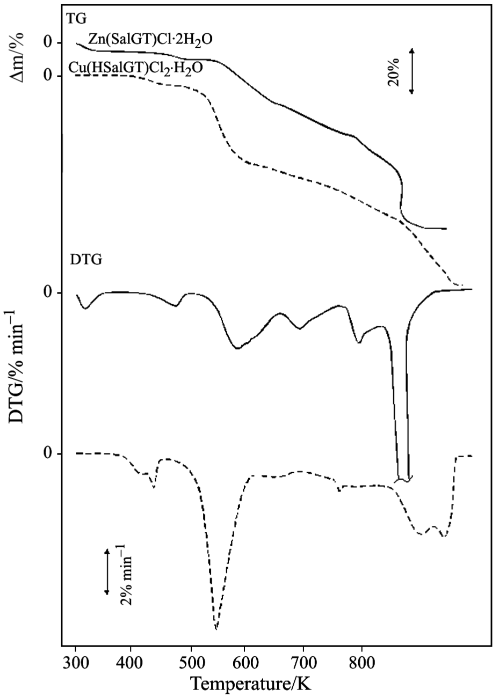


Fig. 4 TG-DTG curves for HSal complexes

complexes with [H_3PLGT]Cl_2, probably corresponds to the departure of HCl (calcd: 9.82%). Above 750 K the decomposition in argon slows down, while in air the residue is the white powder of ZnO (20.15%, calcd: 21.93%).

The mass loss of the Cu(HSalGT)Cl_2·H_2O dehydration in a temperature range of 390–450 K corresponds to the evaporation of one water molecule (4.3%, calcd: 4.65%). The dehydration is followed immediately by further fragmentation with a minimum at around 610 K. At higher temperature the decomposition slows down in argon, while in air, similarly to decomposition of Cu(II) complexes with pyridoxal derivative, copper containing fragments are also departing. The burning of the sample is not observed. Around 950 K some residue (~8%) is left.

Although the DSC curves do not indicate melting of the compounds, inspection of the heated samples of all copper(II) complexes shows that their decomposition is accompanied by melting. No melting of zinc(II) complexes is observed. In Cu(II) complexes with HPLGT the sharp exothermic peaks at around 510 and at 545 K for Zn(II) complex refer to a structural rearrangement during the decomposition, i.e. the square-pyramidal structure with evaporation of HX changes probably to a distorted tetrahedron. This kind of structural change was observed with some other Schiff-base complexes [13]. The corresponding peak at 530 K for Cu(HSalGT)Cl_2·H_2O is boarder, while the decomposition of Zn(SalGT)Cl·2H_2O is endothermic in the whole observed temperature range.

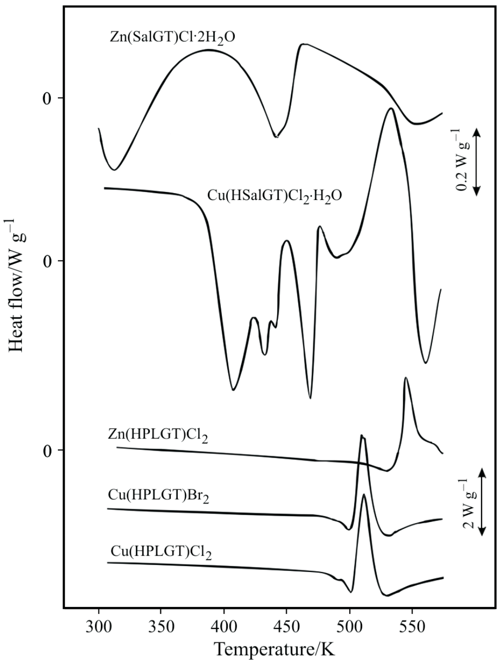


Fig. 5 DSC curves of complexes

Biological activity

Biological activity of the ligands and the complexes was tested against *Staphylococcus aureus* (gram-positive) and *Pseudomonas aeruginosa* (gram-negative) bacteria and *Saccharomyces cerevisiae*.

No biological activity was observed for pyridoxilidene Girard-T hydrazone and its complexes.

The salicylidene Girard-T hydrazone and its complexes, $Cu(HSalGT)Cl_2{\cdot}H_2O$ and $Zn(SalGT)Cl{\cdot}2H_2O$, were active against gram-negative *Pseudomonas aeruginosa* bacteria. The inhibitory effect with concentration of 1 mg cm^{-3} was explicit in the case of $[H_2SalGT]Cl$ and $Cu(HSalGT)Cl_2{\cdot}H_2O$, while $CuCl_2$ showed no bacteriostatic effect. $Zn(SalGT)Cl{\cdot}2H_2O$ exhibited moderate inhibitory effect. The simple $ZnCl_2$ also possesses inhibitory effect, but it is considerably less than that of the complex. The minimal inhibitory effect (MIC) for $[H_2SalGT]Cl$ and its complex with Cu(II), $Cu(HSalGT)Cl_2{\cdot}H_2O$, was 0.5 mg cm^{-3}, while for $Zn(SalGT)Cl{\cdot}2H_2O$ it was 0.75 mg cm^{-3}.

Conclusions

Isostructural, most probably square-pyramidal complexes of $Cu(HPLGT)Cl_2$, $Cu(HPLGT)Br_2$ and $Zn(HPLGT)Cl_2$, were obtained in the reactions of $CuCl_2$, $CuBr_2$, $ZnCl_2$ and $Zn(OAc)_2$ with $[H_3PLGT]Cl_2{\cdot}2H_2O$. In the reaction of $CuCl_2$ and $CuBr_2$ with $(H_2SalGT)Cl$ a square-pyramidal $Cu(HSalGT)Cl_2{\cdot}H_2O$ complex was formed, while with $Zn(OAc)_2$ the same ligand gave $Zn(SalGT)Cl{\cdot}2H_2O$.

The decomposition of the compounds is continuous in the full temperature range. The decomposition pattern of the complexes with $[H_3PLGT]Cl_2{\cdot}2H_2O$ is very similar and the first decomposition step most probably corresponds to the departure of $–CH_2N(CH_3)_3$ and one molecule of HX. The decomposition does not depend on atmosphere to about 600 K. Above this temperature the decomposition in argon is not completed up to 1000 K, while in air at around 950 K; after burning, the residue in the case of zinc(II) compound is ZnO.

The stepwise dehydration of $Zn(SalGT)Cl{\cdot}2H_2O$ begins almost at room temperature and before it is complete (~500 K), the decomposition is followed probably by the same decomposition pattern as is assumed for the HPLGT complexes. The dehydration of the corresponding copper(II) compound begins at higher temperature (390 K) and around 450 K it is accompanied by fragmentation of the complex.

An exothermic structural rearrangement is observed during the decomposition of all of the compounds except for $Zn(SalGT)Cl{\cdot}2H_2O$. The decomposition of copper(II) complexes is accompanied by their melting. On the contrary, no melting was observed in the case of zinc(II) complexes.

The salicylidene Girard-T hydrazone and its complexes exhibited moderate activity against gram-negative *Pseudomonas aeruginosa* bacteria, while neither the pyridoxilidene Girard-T hydrazone nor its complexes showed biological activity.

Acknowledgements

This work was supported by the Ministry of Science and Environmental Protection of the Republic of Serbia and the Provincial Secretariat for Science and Technological Development of Vojvodina.

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Received: October 17, 2005
Accepted: November 18, 2005
OnlineFirst: June 27, 2006

DOI: 10.1007/s10973-005-7402-4