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Synthesis and characterization of poly(N-acryloyl N′-methyl piperazinium(+1)) tetrachlorometallate (II) compounds

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Summary

The interactions of metal ions with poly(N-acryloyl N'-methyl piperazine) in the solid state were studied. The Cu(II) and Zn(II) compounds were prepared and characterized by means of elemental analysis, FT-IR, electronic spectroscopies, and thermogravimetric analysis. PM3 semiempirical calculations on the polymer conformations and the Zn(II) complex have been performed. The piperazine group in the polymer shows the conformations, namely, the chair and a distorted chair conformation. Both structures differ by just ca. 10 kcal/mol. In the compounds $MCl_4(PAPH)_2$, the MCl_4^{2-} complex ion presents a distorted tetrahedral geometry. The electronic spectrum of the yellow Cu(II) coordination compound shows a band at 894 nm. In the IR spectra, an absorption band at 3020 cm^{-1} has been assigned to the ν(N-H) stretching mode of the NH^+ group. The protonated nitrogen atom is the one bonded to the methyl group due to the larger basicity according to the calculated electronic charge density and to the lower steric hindrance. The interaction of the MCl_4^{2-} anion and the polymer is achieved by hydrogen bonding at the NH^+ group and the chloride with N-H···Cl distances lying betwen 1.7 to 3.3 A°.

INTRODUCTION

The polymers containing ligand groups can bind metal ions forming polymer-metal complexes [1-6].
The metal-complexes, which have a free coordination site or a weak ligand, can also coordinate with the polymers. The ionic complexes can also form ionic compounds with the polymer acting as counterion.
According to that, poly(N-acryloyl N'-methyl piperazine) PAP is a very interesting polymer due to its piperazine ring containing a tertiary amino group. The interaction of the piperazine ring and its derivatives with metal ions have been extensively studied in solid state [7-12]. Ionic salts of type $(LH_2^{2-})[MCl_4^{2-}]$ and compounds where the metal ion coordinates with a nitrogen from the piperazine have been reported. In these compounds the piperazine group takes the chair conformation which is the most stable. The hexaatomic piperazine ring may exhibit a chair or a boat conformation, the former one is 17.2 kJ $mole^{-1}$ more stable [13].
The tetrachlorocuprate (II) ions can crystallize in two different structures with the piperazinium dication ($pipzH_2$). Both structures contain discrete $CuCl_4^{2-}$ species. A yellow compound, monoclinic contains the $CuCl_4^{2-}$ ion as a distorted tetrahedron. A green compound, triclinic contains the $CuCl_4^{2-}$ ion with a square planar geometry. This compound shows thermo/photochromism, changing from green to yellow upon heating or laser irradiation [11].
The $CuCl_4^{2-}$ ion does not have a regular tetrahedral geometry due to the Jahn Teller theorem. The predominant geometry is that of compressed tetrahedron. However, it is also possible for $CuCl_4^{2-}$ adopt a square planar geometry with D_{4h} symmetry [14]. To date have been few compounds reported with the square planar geometry compared with the huge number of distorted tetrahedral complexes [15-17]. In these few cases, the counterion is a large organic monocation that is thought to stabilize the square planar geometry by a hydrogen-bonding network.
We have previously reported the interaction of PAP with metal ions in aqueous solution [18].
The aim of this paper is to report the synthesis of compounds of PAP with Cu(II) and Zn(II) chlorides and its characterization in solid state as well as the study of the effect of counterion on the geometry of the anionic complex.

EXPERIMENTAL

Reagents

The metal salts were analytical grade (Merck) $CuCl_2 \bullet 2H_2O$ and $ZnCl_2$.

Synthesis of compounds

Both poly[N-acryloyl N′-methyl piperazinium(+1)] tetrachlorometallate(II) compounds were obtained by reacting methanol solutions of the polymer with the metal(II) chlorides considering an equimolar ratio. The mixture was stirred at 50°C. The pH was adjusted at 4 with 0.2 N NaOH. Subsequently, the solution was precipitated in diethylether. The precipitate was filtered and dried under vacuum at 50°C. At this pH the piperazine group is protonated avoiding the formation of mixture compounds. At basic pH is favored the metal - nitrogen coordination, but this polymer does not coordinate through nitrogen atom, due the probably steric hindrance.

Measurements

Elemental analyses were obtained using a Series II CHNS 10 analyser 2400 Perkin Elmer. The FT IR spectra of the samples were recorded on a Magna Nicolet 550 spectrophotometer and a Nicolet Nexsus spectrophotometer. The diffuse reflectance spectra were measured on a Perkin Elmer Lambda 20 spectrophotometer coupled to Labsphere reflectance diffuse attachment and Spectralon as reference. The thermogravimetric analysis of the polychelates was carried out with a Polymer Laboratories STA 625 analyzer.

The electrical conductivity was determined at room temperature (ca 20°C) with a Wiss-Techn-Werkstaten conductimeter with a Pt electrode.

Quantum Chemical Calculations

PM3 semi-empirical calculations were carried out using a MOPAC 6.0 program that is included in ALCHEMY 2000. The compound was created graphically with support of the ALCHEMY Pprogram. It was optimized by molecular mechanic and subsequently by PM3 calculation method.

RESULTS AND DISCUSSION

Spectroscopy and analyses

The compounds of poly(N-acryloyl N′-methyl piperazine) (L) with Cu(II) and Zn (II), have anionic $[MCl_4]^{2-}$ and cationic $[LH]^{+}$ units linked by bridge bonds [19,20].

The analytical data and thermal stability are summarized in table1.

Table 1. Analytical data and thermal stability of the compounds of poly(N-acryloyl N′-methylpiperazine) (L) with Cu(II) and Zn (II).

Compound	Stoichiometric Ratio M:L	Λ_M [a)]	Color	Weight loss (%) at different temperatures (°C) 100	200	300	400	500
$[CuCl_4]^{2-}(LH_2)^{2+}$	1:2	218	yellow	1.3	2.6	5.8	41.2	56.2
$[ZnCl_4]^{2+}(LH_2)^{2+}$	1:2	193	white	2.3	6.8	21.5	49.8	61.4

a) molar conductivities ($ohm^{-1} \cdot cm^2 \cdot mol^{-1}$) in aqueous solution at 20°C.

The molar conductivity values in aqueous solution are within the corresponding range to the electrolyte type 1:2.

FT-IR spectroscopy

FT-IR spectrum of the polymer shows characteristic absorption bands at 2860 cm^{-1}, ($N\text{-}CH_3$), at 1630 cm^{-1} (C=0), and at 1368 cm^{-1} (C-N, tertiary amine).

The FT-IR (far) of $ZnCl_4^{2-}$ shows two active modes at 285 and 127 cm^{-1} which can be attributed to ν_3 and ν_4 of a system with a T_d symmetry, but $CuCl_4^{2-}$ shows a higher number of bands, at 293, 225, 212, 162 ,147, and 128 cm^{-1}, therefore, it is possible to suggest a C_{3v} symmetry.

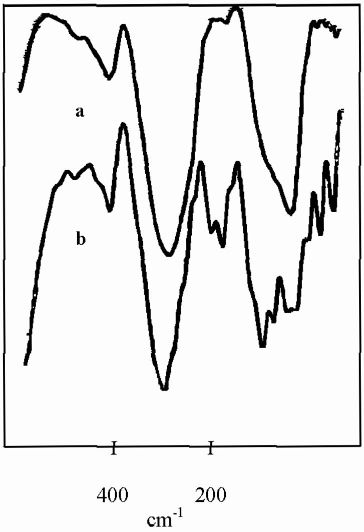

Figure 1. FT-IR-(far) of the compounds of poly(N-acryloyl N′-methyl piperazine) (L) with a) Zn (II) and b) Cu(II).

Electronic spectrum

The compound with Cu(II) is yellow, which is characteristic of a tetrahedral geometry. The reflectance diffuse electronic spectrum shows an absorption band at 894 nm attributed to a pseudo tetrahedral geometry.

Conformational analysis

The piperazine group can present two conformations: a) chair or b) distorted chair with a difference of 10 Kcal/mol (see figure 2).

The PM3 calculations are shown in table 2. The distortion is in agreement with the angle $\omega(1,2,4,5)$ calculated for the two conformations. For the conformations a) and b) the values are -0.8° and -52.3° respectively.

In both conformations, the charge density in N(3), which is the nitrogen atom linked to methyl group, is higher than that of the charge density of N(6). Therefore, the protonated nitrogen must be the nitrogen linked to the methyl group due to its higher basicity.

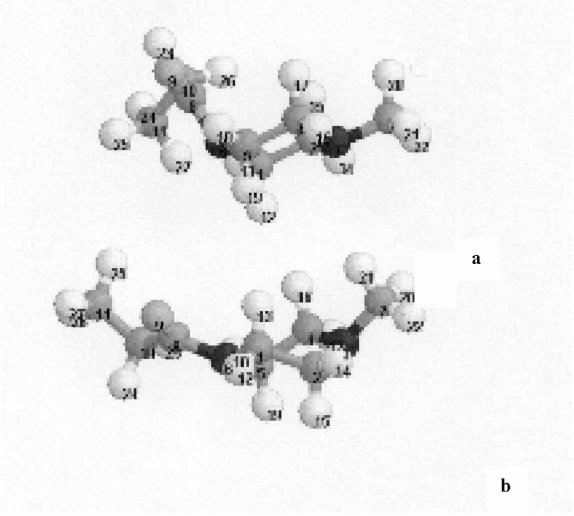

Figure 2. Chair conformation (a) and distorted chair conformation (b) of poly(N-acryloyl N′-methylpiperazine)

Table 2 . Selected structure parameters PM3 of poly(N-acryloyl N′-methyl piperazine).

Parameter	Conformation[a]		Atom No	Net charge conformation[a]	
	a	b		a	b
Length of bond (A°)			N(3)	-0.0735	-0.0800
N(3)-C(2)	1.492	1.490	C(7)	-0.0856	-0.0862
N(3)-C(4)	1.492	1.492	N(6)	-0.0587	-0.0767
N(3)-C(7)	1.478	1.478	C(8)	0.2502	0.2515
N(6)-C(1)	1.487	1.492	O(9)	-0.3644	-0.3677
N(6)-C(5)	1.490	1.488			
N(6)-C(8)	1.439	1.437			
C(4)-C(5)	1.529	1.526			
Angle of bond (°)					
C(2)-N(3)-C(4)	112.5	113.0			
C(1)-N(6)-C(5)	110.4	114.0			
C(5)-N(6)-C(8)	118.5	119.9			
Dihedral angle(°)					
C(1)-C(2)-C(4)-C(5)	-0.8	-52.3			

a) chair and b) distorted chair conformation.

The PM3 calculations of poly(N-acryloyl N′-methyl piperazine) and their compounds with Zn(II) are shown in figure 3 and table 3.

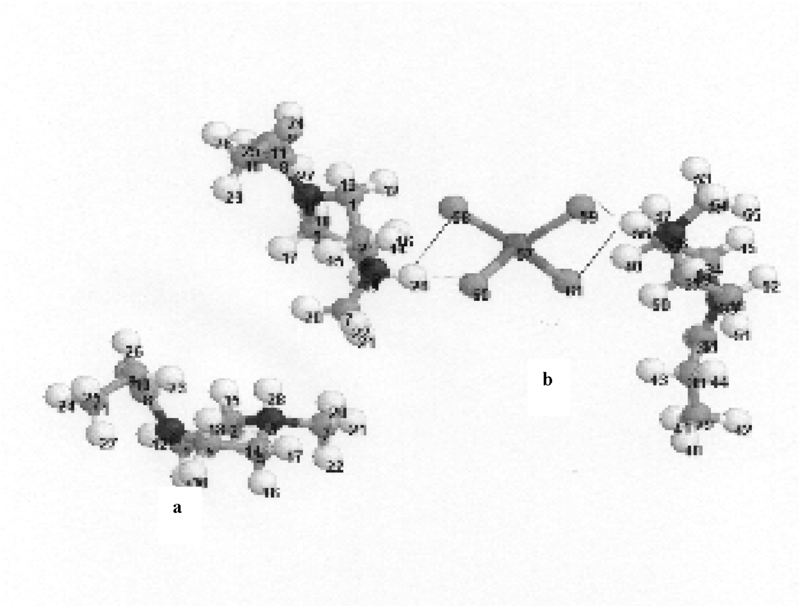

Figure 3. PM3 structures of a) poly(N-acryloyl N′-methyl piperazine), and b) compound of Zn(II).

The interaction of MCl_4^{2-} and the polymer is produced through bridge bonds with the chloride anions with N-H···Cl distances varying between 1.7 and 3.3 A°. This may be attributed to three centre hydrogen bonds. The average distance Cl·····H is 2.42 A° and that reported by Dadon and Bernstein [21] for a series of compounds is 2. 66 A°.
The anionic complex $ZnCl_4^{2-}$ shows a slight distorted geometry which is in agreement with the angle Cl-Zn-Cl varying between 94.8 and 117.4° and the distances Zn-Cl range between 2.258 and 2.293 A°. The distances Zn-Cl(59) and Zn-Cl(60) 2.292 A° and 2.293 respectively are larger indicating a strong bridge bond interaction.
The charge density of N(3) for the protonated polymer and their compounds are low due to the protonation effect, and the charge density of the proton H(28) decreases by the interaction with anion complex $[ZnCl_4]^{2-}$.
The compounds of poly(N-acryloyl N'-methyl piperazine) with the metal ions Cu(II) and Zn(II) are ionic which behave as 1:2 electrolyte in aqueous solution. In solid state, the anionic complex shows a hydrogen bridge through the chloride and the proton linked to the neighbor nitrogen of the methyl group. It should be expected that the high size of the counterion would stabilize a square geometry for $CuCl_4^{2-}$ but in both compounds the anion complex shows a distorted tetrahedral geometry.
The semiempirical calculations were carried out only for the compound of Zn(II) as the program is not parametrized for Cu(II) ions.

Table 3. Selected structural parameters of poly(N-acryloyl N′-methyl piperazine), L, and their compounds of Zn(II).

Parameter	LH^-	$(LH^-)_2$ [Zn Cl_4]	atom	net charge	
			No	L H^-	$(LH^-)_2$ [Zn Cl_4]
Length of bond(A°)					
N(3)-C(2)	1.564	1.526	N(3)	0.2597	0.4411
N(3)-C(4)	1.576	1.510	C(7)	-0.2040	-0.2108
N(3)-C(7)	1.534	1.507	N(6)	-0.0812	-0.0875
N(3)-H(28)	1.012	1.113	C(8)	-0.2487	0.2655
N(36)-H(56)		1.122	O(9)	-0.3705	-0.3500
H(28)-Cl(58)		3.222	H(28)	0.0281	0.1928
H(28)-Cl(60)		1.706	H(56)		0.1974
H(56)-Cl(59)		1.700	Zn(57)		0.2608
H(56)-Cl(61)		3.062	Cl(58)		-0.4193
Zn(57)-Cl(58)		2.258	Cl(60)		-0.4351
Zn(57)-Cl(59)		2.292			
Zn(57)-Cl(60)		2.293			
Zn(57)-Cl(61)		2.264			
Angle of bond(°)					
C(2)-N(3)-C(4)	111.9	111.9			
C(1)-N(6)-C(5)	113.5	113.5			
C(5)-N(6)-C(8)	118.3	118.3			
Cl(61)-Zn(57)-Cl(59)		94.8			
Cl(60)-Zn(57)-Cl(58)		96.7			
Cl(60)-Zn(57)-Cl(61)		115.1			
Cl(58)-Zn(57)-Cl(59)		117.4			

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