第 30 卷第 7 期
2014 年 7 月

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CHINESE JOURNAL OF INORGANIC CHEMISTRY

Vol.30 No.7
1733-1740

含吡啶的大环席夫碱锰(Ⅱ)配合物:合成、表征及抗菌性质

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摘要:在 Mn(Ⅱ)模板作用下,2,6-diacetylpyridine (DAP)及合适链状胺化合物通过[1+1]环缩合反应,合成了 3 个大环席夫碱配合物,并进行了红外、元素分析、质谱及电导率等表征及研究。测得了配合物$[MnL^1(CH_3CN)](ClO_4)_2$的晶体结构,中心离子呈现出稍微扭曲的五角锥配位构型。研究了配合物对 *S. aureus* (ATCC 6633),*B. cereus* (ATCC 7064),*C. xerosis* (ATCC 373)(gram-positive bacterial strains),*E. coli* (PTCC 10009),*K. pneuomoniae* (MTCC 109),and *P. vulgaris* (lio)(gram-negative bacterial strains)的抗菌活性。结果显示$[MnL^3](ClO_4)_2$抗菌活性明显优于$[MnL^1(CH_3CN)](ClO_4)_2$ and $[MnL^2](ClO_4)_2$。在 25 ℃条件下 0.1 mol·L^{-1} KCl 溶液中,通过电位计量法测定了化合物的质子化常数。

关键词:大环配体;席夫碱;锰(Ⅱ)配合物;抗菌活性;质子化常数

中图分类号:O614.71+1 **文献标识码**:A **文章编号**:1001-4861(2014)07-1733-08

DOI:10.11862/CJIC.2014.243

Manganese(Ⅱ) Macrocyclic Schiff-Base Complexes Containing Pyridine Moiety: Synthesis and Characterization and Antibacterial Properties

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Abstract: Three new macrocyclic Schiff-base complexes have been prepared via the Mn(Ⅱ) templated [1+1] cyclocondensation of 2,6-diacetylpyridine (DAP) and appropriate linear amines. All complexes were characterized by IR spectra, elemental analysis, EI-Mass and conductivity measurements. The crystal structure of $[MnL^1(CH_3CN)](ClO_4)_2$ is also reported and exhibits a slightly distorted pentagonal-pyramidal geometry. Also the synthesized complexes were screened for their antibacterial activity against *S. aureus* (ATCC 6633), *B. cereus* (ATCC 7064), *C. xerosis* (ATCC 373) (gram-positive bacterial strains), *E. coli* (PTCC 10009), *K. pneuomoniae* (MTCC 109), and *P. vulgaris* (lio) (gram-negative bacterial strains). The results show that the antibacterial activity of $[MnL^3](ClO_4)_2$ is greater than that of $[MnL^1(CH_3CN)](ClO_4)_2$ and $[MnL^2](ClO_4)_2$. The protonation constants of three tetraamines have been determined potentiometrically in 0.1 mol·L^{-1} KCl at 25 ℃. CCDC: 964534.

Key words: macrocyclic ligand; Schiff base; manganese(Ⅱ) complex; antibacterial effect; protonation constant

收稿日期:2013-12-13。收修改稿日期:2014-03-19。

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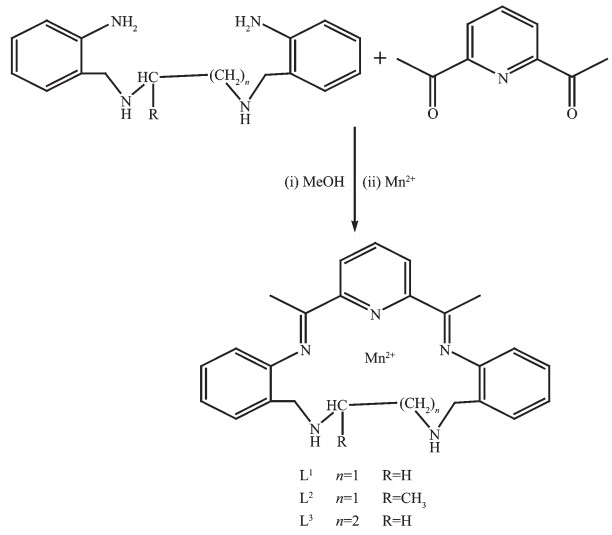
0 Introduction

The synthesis of ligands based on 2,6-disubstituted pyridine has attracted a great deal of attention with a broad array of both acylic and macrocyclic ligands reported[1]. Metal complexes containing synthetic macrocyclic ligands have attracted a great deal of attention because they can be used as models for more intricate biological macrocyclic systems: metalloporphyrins (hemoglobin, myoglobin, cytochromes, chlorophylls), corrins (vitamin B_{12}) and antibiotics (valinomycin, nonactin). These discoveries have created supramolecular chemistry and its enormous diversity[2-6]. The stability of macrocyclic metal complexes depends upon a number of factors, including the number and type of the donor atoms present in the ligand and their relative positions within the macrocyclic skeleton, as well as the number and size of the chelate rings formed on complexation. For transition metal ions, features such as the nature and magnitude of crystal-field effects play also an important role[7]. Among the transition metals that form complexes with polyaza macrocycles, manganese is well known to have an important role in many biological reactions[8], such as water oxidation (photosystem Ⅱ)[9], decomposition of hydrogen peroxide (catalase), and dismutation of the superoxide anion radical (superoxide dismutase). We and others have been interested for some time in the design and synthesis of some new Mn(Ⅱ) macrocyclic Schiff-base complexes[10-13]. As an extension of this idea, in this work, three new macrocyclic Schiff base complexes were prepared from cyclocondensation of three linear aromatic amines and 2,6-diacetylpyridine in the presence of Mn(Ⅱ) metal ion (Scheme 1). The resulting complexes were characterized by IR spectra, EI-Mass, molar conductance and X-ray in case of $[MnL^1(CH_3CN)](ClO_4)_2$. We also explored the antibacterial activities of synthesized complexes against *S. aureus*, *B. cereus*, *C. xerosis*, *E. coli*, *K. pneuomoniae* and *P. vulgaris*. Also the protonation constants of the tetraamines , L^1, L^2 and L^3 at 25 ℃ in 0.1 mol·L^{-1} KCl were reported.



Scheme 1 Template condensation between 2,6-diacetylpyridine and tetradentate amines in the presence of the Mn(Ⅱ) ion

1 Experimental

1.1 Starting materials and Instrumentation

All solvents were of reagent grade quality and purchased commercially. Ethane-1,2-diamine, propane-1,2-diamine, propane-1,3-diamine, 2-nitrobenzaldehyde, 2,6-diacetylpyridine, sodium borohydride, manganese(Ⅱ) perchlorate were obtained from Merck and were used without further purification.

Caution: Perchlorate salts are potentially explosive. While we have not experienced any problems with the compounds described, they should be treated with caution and handled in small quantities.

Elemental analyses were performed in a Carlo-Erba EA microanalyser. IR spectra were measured on a Perkin Elmer FT-IRGX spectrophotometer in the range of 4 000~400 cm^{-1} by KBr pellet technique. Conductivimetry measurements were carried out in 10^{-3} mol·dm^{-3} dimethylsolfoxide solutions at 25 ℃ using a CARISON GLP32 conductivimeter. EI mass spectra were recorded using 5973 Network Mass Selective Detector.

1.2 General synthesis of the Mn(Ⅱ) complexes

The tetradentate amines were prepared according to literature method[14] Briefly, these amines were synthesized by condensation reaction between 2-

nitrobenzaldehyde and ethane-1,2-diamine, propane-1,2-diamine and propane-1,3-diamine followed by the selective reduction of the imine and nitrate groups using $NaBH_4$ and Zn and NH_4Cl in methanol, respectively. A solution of amines (0.5 mmol) in methanol was added dropwise to a refluxing solution of $Mn(ClO_4)_2 \cdot xH_2O$ (0.5 mmol) and 2,6-diacetylpyridine (0.5 mmol) in the same solvent (20 mL). After refluxing for 24 h the solution was then concentrated in a rotary evaporator to *ca.* 5~10 mL. A small volume of diethyl ether was slowly added to the solution, producing a powdery precipitate. The product was filtered off, washed with cold diethyl ether and dried under vacuum. A crystalline compound was obtained by slow diffusion of diethyl ether vapor into a mixed acetonitrile and methanol solution of the above solid.

$[[MnL^1(CH_3CN)](ClO_4)_2$: Yield: 0.21 g (60%). Anal. Calcd. for $C_{27}H_{30}Cl_2MnN_6O_8$ (M_W: 692.41)(%): C, 46.84; H, 4.37; N, 12.14. Found(%): C, 46.75; H, 4.22; N, 11.98. IR (KBr, cm^{-1}) 3 272 ν(N-H), 1 629 $\nu(C=N)_{imi}$. 1 588, 1 447 (ν(C=C) and $\nu(C=N)_{py}$) and 1 094, 623 $\nu(ClO_4^-)$. EI-Mass: (*m/z*, M^+) 551 $[MnL^1]ClO_4^+$. Λ_m / ($S \cdot cm^2 \cdot mol^{-1}$) (in DMSO): 176 (2:1).

$[MnL^2](ClO_4)_2$: Yield: 0.17 g (51%). Anal. Calcd. for $C_{26}H_{29}Cl_2MnN_5O_8$ (M_W: 665.38)(%): C, 46.93; H, 4.39; N, 10.53. Found (%): C,46.86; H, 4.44; N, 10.44 . IR (KBr, cm^{-1}) 3 268 ν(N-H), 1 623 $\nu(C=N)_{imi}$. 1 588, 1 451 (ν(C=C) and $\nu(C=N)_{py}$) and 1 085, 625 $\nu(ClO_4^-)$. EI-Mass: (*m/z*, M^+) 566 $[MnL^2]ClO_4^+$. Λ_m / ($S \cdot cm^2 \cdot mol^{-1}$) (in DMSO): 170 (2:1).

$[MnL^3](ClO_4)_2$: Yield: 0.18 g (54%). Anal. Calcd. for $C_{26}H_{29}Cl_2MnN_5O_8$ (MW: 665.38) (%): C, 46.93; H, 4.39; N, 10.53. Found (%): C,47.18; H, 4.46; N, 11.00 . IR (KBr, cm^{-1}) 3 278 ν(N-H), 1 638 $\nu(C=N)_{imi}$. 1 587, 1 462 (ν(C=C) and $\nu(C=N)_{py}$) and 1 087, 623 $\nu(ClO_4^-)$. EI-MS: (*m/z*, M^+) 566 $[MnL^3]ClO_4^+$. Λ_m / ($S \cdot cm^2 \cdot mol^{-1}$) (in DMSO): 168 (2:1).

1.3 X-ray crystal structure determination

The X-ray data of compound $[MnL^1(CH_3CN)](ClO_4)_2$ were collected at room temperature With STOE IPDS-Ⅱ two circle diffractometer, using graphite monochromated Mo $K\alpha$ X-ray radiation (λ=0.07 107 nm). Crystal data and experimental parameters are reported in Table 1. The data collection was performed at room temperature using the x-scan technique and using the STOE X-AREA software package[15]. The crystal structure were solved by direct methods[16] and refined by using X-STEP32 crystallographic software package[17]. All of the non-hydrogen atoms were refined anisotropically.

CCDC: 964534.

1.4 Antibacterial study

Test organisms for antibacterial assay: Six bacterial strains (three gram positive and three gram negative) were selected on the basis of their clinical importance in causing diseases in humans (Table 3). Some microorganisms were obtained from Persian Type Culture Collection, Tehran, Iran and others locally isolated (Lio). The strains selected for the study are *S. aureus* (ATCC 6633), *B. cereus* (ATCC 7064), *C. xerosis* (ATCC 373) (gram-positive bacterial strains), *E. coli* (PTCC 10009), *K. pneuomoniae* (MTCC 109),

Table 1　Crystal data and structure refinement for $[MnL^1(CH_3CN)](ClO_4)_2$

Empirical formula	$C_{27}H_{30}Cl_2MnN_6O_8$	Crystal size / mm	0.25×0.10×0.05
Formula weight	692.41	Absorption coefficient / mm^{-1}	0.663
Temperature / K	298(2)	Limiting indices	$-28 \leqslant h \leqslant 28, -10 \leqslant k \leqslant 10, -44 \leqslant l \leqslant 41$
Wavelength / nm	0.071 073	Theta range for data collection / (°)	1.86 to 27.00
Crystal system	Monoclinic	Max. and min. transmission	0.980 1 and 0.928 9
Space group	*C*2/*c*	Refinement method	Full-matrix least-squares on F^2
a / nm	2.265 98(14)	Data / restraints / parameters	6 664 / 0 / 417
b / nm	0.846 08(5)	Goodness-of-fit on F^2	0.917
c / nm	3.510 19(17)	Final *R* indices ($I>2\sigma(I)$)	R_1=0.076 5, wR_2=0.116 4
β / (°)	114.359(4)	*R* indices (all data)	R_1=0.085 4, wR_2=0.147 9
F(000)	2 856.6	Largest diff. peak and hole / ($e \cdot nm^{-3}$)	352 and −253

and *P.vulgaris* (lio) (gram-negative bacterial strains). These strains were screened for evaluation of antibacterial activities of the synthesized complexes.

The antibacterial activity of the macrocyclic complexes was evaluated by agar well diffusion method[18]. All the microbial cultures were adjusted to 0.5 McFarland standards, which is visually comparable to a microbial suspension of approximately 1.5×10^8 cfu·mL^{-1}[19]. 20 mL of agar media was poured into each petri plate these plates were then swabbed with a colony from inoculum of the test microorganisms and kept to adsorption for 15 min. Using sterile cork borer of 6 mm diameter, wells were bored into the seeded agar plates and these were loaded with 50 μL volume with concentration of 10 mg·mL^{-1} of each compound reconstituted in dimethylsulphoxide (DMSO). All the plates were incubated at 37 ℃ for 24 h. Antibacterial activity of all the complexes was evaluated by measuring the diameter of zone of inhibition in mm. The medium with dimethylsulphoxide (DMSO) as solvent was used as a negative control whereas media with ciprofloxacin (standard antibiotic for gram positive) and gentamicin (standard antibiotic for gram negative) were used as positive control. The experiments were performed in triplicates.

Determination of minimum inhibitory concentration (MIC): Minimum inhibitory concentration (MIC) is the lowest concentration of an antimicrobial compound that will inhibit the visible growth of microorganisms after overnight incubation. Minimum inhibitory concentrations are important in diagnostic laboratories to confirm resistance of microorganisms to antimicrobial agents and also to monitor the activity of new antimicrobial agents. The MIC of the macrocyclic complexes was tested against bacterial strains through a broth dilution method. In this method, the test concentrations of all the complexes were made from 2.5 to 0.01 mg·mL^{-1} in the sterile wells of the micro-titer plates. In sterile microliter plates (96-u-shaped wells) 50 μL of the sterile nutrient broth was poured in each well in three rows, then from fresh inoculums so formed (10^8 cfu·mL^{-1} diluted with 100 μL Nutrient broth to have 10^6 cfu·mL^{-1}) 50 μL of the suspension was poured in each well in the first and third row, second row was again filled with 50 μL of nutrient broth. Finally the drug sample 50 μL was added in the first row diluting uniformly from 2.5 to 0.01 mg·mL^{-1} till the 8th well. All the microliter plates were incubated at 37 ℃ for 18~24 h. MIC was expressed as the lowest dilution, which inhibited the growth of bacteria observed by lack of turbidity in the well.

1.5 Potentiometric measurements

Each calibration and potentiometric determination was measured in 100 cm^3, jacketed cell thermostated at 25 ℃ by refrigerated circulating water bath. Ionic strength was adjusted to 0.100 mol·L^{-1} by addition of KCl. Purified (pyrogallol) N_2 was used to degas solutions and to purge the cell during titrations. A METROHM pH-meter was used with 6.232.100 glass combination electrode. A 10.0 cm^3 capacity Mettler DV11 piston burette was used which delivered standard potassium hydroxide solution directly in to the sealed cell through a capillary burette tip which was attached to the cell cap. The electrode was calibrated by titration in the absence of the amine. The stability constants were determined using the program BEST[20-21]. The pK_w for H_2O under these conditions was found to be 13.78.

2 Result and discussion

All complexes were synthesized by the template condensation of the amines, L^1, L^2 and L^3 and 2,6-diacetylpyridine in the presence of Mn(Ⅱ) metal ion. These compounds are quite stable in air. The resulting compounds were characterized by IR, elemental analysis, EI-MS and in the case of $MnL^1(CH_3CN)](ClO_4)_2$ by X-ray diffraction .Condensation of all the primary amino group is confirmed by the lack of NH_2 stretching bands in the IR region and the presence of strong C=N stretching bands at 1 629, 1 623 and 1 638 cm^{-1} for L^1, L^2 and L^3, respectively and also bands at ca. 1 590 and 1 460 cm^{-1} associated with ν $(C=N)_{py}$ and ν(C=C) vibrations of the pyridine and phenyl rings[22]. A broad intense band at ca. 1 090 cm^{-1} indicating the absence of coordination of ClO_4 in complexes[23]. The lack of splitting of these bands suggests that the

perchlorate anions are not coordinated[24].

The molar conductivity measurements, recorded for 10^{-3} mol·L^{-1} solutions at 25 ℃ of the Schiff base metal complexes in DMSO. The molar conductivity was applied to help in the investigation of the geometrical structures of the complexes. Metal chelates have molar conductivity of 160~175 S·cm^2·mol^{-1} indicating the 1:2 ionic natures in all cases[25]. These values are indicative of the presence two outer sphere perchlorate anions and are in agreement with the results obtained from the IR and X-ray studies.

2.1 Description of the crystal structure of $[MnL^1(CH_3CN)](ClO_4)_2$

The crystal structure of $[MnL^1(CH_3CN)](ClO_4)_2$ has been determined by X-ray diffraction. The projection view of the molecular structure of the cationic unit present in the complex, with non-hydrogen atoms represented by 30% thermal ellipsoids, is shown in Fig.1, together with selected bond lengths and angles relating to the coordination environment of the metal. The crystals contains the cation $[MnL^1(CH_3CN)]^{2+}$ containing one acetonitrile molecule in inner sphere of complex coordinated to Mn(Ⅱ) ion and two independent perchlorate anions. The $[MnL^1(CH_3CN)](ClO_4)_2$ complex crystallizes in the Monoclinic, *C2/c* space group. The Mn atom is six coordinated arising from coordination by the five nitrogen atoms of the ligand, L^1, and the one nitrogen atoms from acetonitrile molecule and the geometry around the metal can be better described as in a slightly distorted pentagonal-pyramidal geometry. The sum of the five N-Cd-N chelate angles (385.61) in an approximately pentagonal plane is almost 360° for an ideal planar structure. The pentagonal plane is confirmed by the five nitrogen atoms from the ligand and the rms of the equatorial plane is 0.065 4 and the Mn(Ⅱ) ion is 0.022 1 nm out of this plane. The perchlorate ions give typical bond distance and angles. The pyridine group provides the shortest bond to the metal, Mn(1)-N(3) 0.218 8(4) nm while the longest belongs to the nitrogen atoms of acetonitrile , Mn(1)-N(6) 0.237 5(6) nm. selected bond lengths and angles are summarized in Table 2.

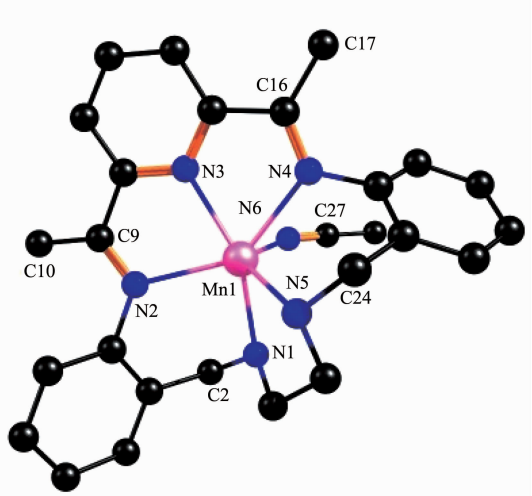


Fig.1　Crystal structure of cation $[MnL^1(CH_3CN)]^{2+}$

2.2 Antibacterial activities

Antibacterial activity of the synthesized complexes was studied against some bacterial strains viz. *S. aureus*, *B. cereus*, *C. xerosis*, *E. coli*, *K. pneuomoniae* and *P. vulgaris*. Preliminary screening for all the complexes was performed at fixed concentration of 10 mg·mL^{-1}. The results obtained were compared with standard antibiotics: ciprofloxacin (for gram-positive) and gentamicin (for gram-negative) bacterial strains. Three complexes were found to be active on both types of bacterial strains. On the basis of the data obtained for diameter of zone of inhibition $[MnL^3](ClO_4)_2$ complex

Table 2　Selected bond lengths (nm) and angles (°)

Mn(1)-N(1)	0.223 9(5)	Mn(1)-N(2)	0.228 8(4)	Mn(1)-N(3)	0.218 8(4)
Mn(1)-N(4)	0.230 0(4)	Mn(1)-N(5)	0.224 9(4)	Mn(1)-N(6)	0.237 5(6)
N(3)-Mn(1)-N(1)	149.65(16)	N(3)-Mn(1)-N(5)	129.83(17)	N(1)-Mn(1)-N(5)	76.85(16)
N(3)-Mn(1)-N(2)	72.21(15)	N(1)-Mn(1)-N(2)	83.22(16)	N(5)-Mn(1)-N(2)	116.05(16)
N(3)-Mn(1)-N(4)	70.12(15)	N(1)-Mn(1)-N(4)	135.08(16)	N(5)-Mn(1)-N(4)	83.21(16)
N(2)-Mn(1)-N(4)	141.47(15)	N(3)-Mn(1)-N(6)	93.24(17)	N(1)-Mn(1)-N(6)	79.84(19)
N(5)-Mn(1)-N(6)	122.04(18)	N(2)-Mn(1)-N(6)	112.76(16)	N(4)-Mn(1)-N(6)	77.44(17)

Table 3 Minimum inhibitory concentration (MIC in mg·mL^{-1}) of the macrocyclic complexes

Bacterial strains	Complexes		
	$[MnL^1](ClO_4)_2$	$[MnL^2](ClO_4)_2$	$[MnL^3](ClO_4)_2$
S. aureus	0.613	0.512	0.502
B. cereus	0.623	0.746	0.732
C. xerosis	0.392	0.348	0.311
E. coli	0.843	0.754	0.711
K. pneuomoniae	0.810	0.712	0.688

Table 4 Inhibition zones (mm) of complexes against bacterial strains

Complex	Bacteria					
	S. aureus	*B. cereus*	*C. xerosis*	*E. coli*	*K. pneuomoniae*	*P. vulgaris*
$[MnL^1](ClO_4)_2$	26	18	22	19	19	21
$[MnL^2](ClO_4)_2$	27	20	25	21	22	23
$[MnL^3](ClO_4)_2$	31	25	28	25	27	25
Ciprofloxacin	30	27	27	—	—	—
Gentamicin	—	—	—	25	25	25

was found to be very effective (Table 4).

The minimum inhibitory concentration of these complexes was determined by broth dilution method in which the effectiveness was observed at lower concentrations. According to Table 3, the MIC values were showed that $[MnL^3](ClO_4)_2$ complex was quite effective against on bacterial strains (Table 4). Comparison of antibacterial activities of Mn (Ⅱ) macrocyclic Schiff base complexes in this work and similar Mn(Ⅱ) macroacyclic Schiff base complexes in previous work show that the Mn(Ⅱ) macrocyclic Schiff base complexes are greater antibacterial effects against than the macroacyclic complexes one[26].

2.3 Protonation constants

The distribution curves for the protonated L^1, L^2 and L^3 species, as a function of pH, are shown in Fig. 2, 3 and 4, respectively. Analysis of the curves yield the successive protonation constants (defined in Equations (**1**) and (**2**)), which are shown in Table 5.

$$H_{n-1}L^{(n-1)+}+H^+ \rightleftharpoons H_nL^{n+} \quad (\mathbf{1})$$

$$K_n=\frac{c_{H_nL^{n+}}}{c_{H_{n-1}L^{(n-1)+}}\cdot c_{H^+}} \quad (\mathbf{2})$$

Protonation constants for these amines show that the value for each stage is less than in the previous stage. This is to be expected on the basis on both statistical factors and electrostatic repulsion between the hydrogen ion and ligand as it becomes progressively more positively charged. Similar trends are seen for all the polyamine ligands[27-28]. The magnitude of the pK_a value clearly indicates that the diprotonated, triprotonated and diprotonated forms of L^1, L^2 and L^3, respectively dominate over a wide central of pH range.

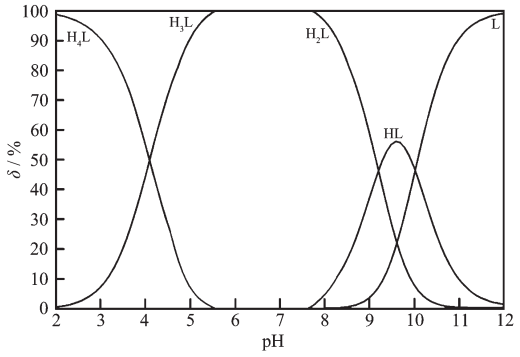


Fig.2 Distribution curves for the protonated (L^1) species as function of pH

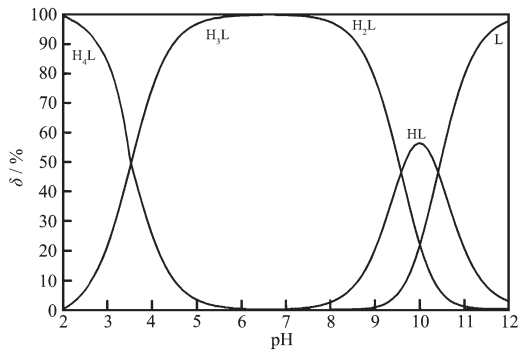


Fig.3 Distribution curves for the protonated (L^2) species as function of pH

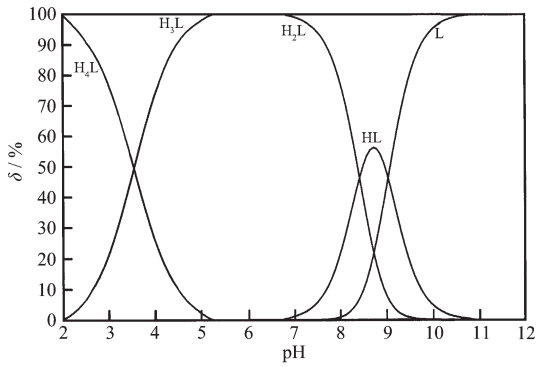


Fig.4　Distribution curves for the protonated (L^3) species as function of pH

Table 5　Protonation constants for L^1, L^2 and L^3 measured at 298.2 K, 0.100 mol·dm^{-3} KCl

	L^1	L^2	L^3
lgK_1	9.53	9.9	9.86
lgK_2	8.95	9.38	9.31
lgK_3	7.64	8.10	8.06
lgK_4	6.43	6.97	6.92

3　Conclusions

We report the successful synthesis of three new Mn(Ⅱ) macrocyclic Schiff base complexes by the metal ion-templated [1+1] cyclocondensation of 2,6-diacetylpyridine and amines. The complexes have been characterized by some spectroscopic methods. In addition, the solid state structure of [Mn L^1(CH_3CN)](ClO_4)$_2$ shows the Mn(Ⅱ) ion to be in a distorted pentagonal pyramidal site with a coordination number of six. Results of this research showed that all complexes to be active on both types of bacterial strains. The magnitude of the pka value clearly indicates that the diprotonated, triprotonated and diprotonated forms of L^1, L^2 and L^3, respectively dominate over a wide central of pH range.

Acknowledgments: We are grateful to the Faculty of Chemistry of Bu-Ali Sina University and Ministry of Science, Research and Technology of Iran, for financial support.

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