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ORIGINAL ARTICLE

Synthesis and biological activity of Magnesium(II) complexes of heptaaza Schiff base macrocyclic ligands; ^{1}H and ^{13}C chemical shifts computed by the GIAO-DFT and CSGT-DFT methodologies

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Abstract Two new pendant armed Schiff base macrocyclic complexes, $[MgL^1](ClO_4)_2$ (**1**), and $[MgL^2](ClO_4)_2$ (**2**), have been prepared via cyclocondensation of 2,6-diformylpyridine and 2,6-diacetylpyridine with two hexadentate hexaamines, ten and tmen, in the presence of Mg(II) ion. The ligands are 15-membered pentaaza macrocycles having two 2-aminoethyl pendant arms. The newly prepared complexes are investigated by IR, ^{1}H NMR, $^{13}C\{^{1}H\}$ NMR, DEPT(135), COSY(H, H) and HMQC spectroscopic methods. The antimicrobial screening of newly prepared complexes, **1** and **2**, as well as previously prepared similar complexes, $[MgL^3](ClO_4)_2$ (**3**) and $[MgL^4](ClO_4)_2$ (**4**), against *Escherichia coli*, *Staphylococcus aureus* and *candidia albicans* showed that the macrocyclic complexes of Mg(II) containing 15-membered pentaaza ring (**1**, **2** and **3**) have no activity. Where as the compound **4,** which contain 16-membered pentaaza ring, had remarkable inhibition zone on the culture of *S. aureus* and *E. coli* as compared with standard drugs. The ^{1}H and ^{13}C chemical shieldings of gas phase complexes were also studied by the gauge independent atomic orbital (GIAO) and continuous set of gauge transformations (CSGT) methods at the level of density functional theory (DFT). The computed ^{13}C chemical shifts are in reasonably good agreement with the experimental data.

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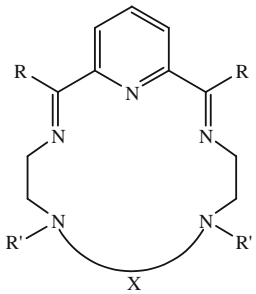
Introduction

The preparation of polyaza macrocyclic ligands bearing functional pendant donor groups and their subsequent ligation to various metal ions has been an active area of research in recent years [1–5]. Although the coordination chemistry of polyaza macrocyclic ligands has been studied extensively during the last decades, the complexes of alkaline earth cations have tended to receive less attention than those of other metal ion groups [6–8]. Alkaline earth macrocyclic complexes are interesting, since they may serve as useful synthetic reagents. In metal template work, for example, the combined templating ability of alkaline earth metal ions and their kinetic lability create a favourable situation for generation of the corresponding transition metal complexes which are difficult to obtain directly [9–11].

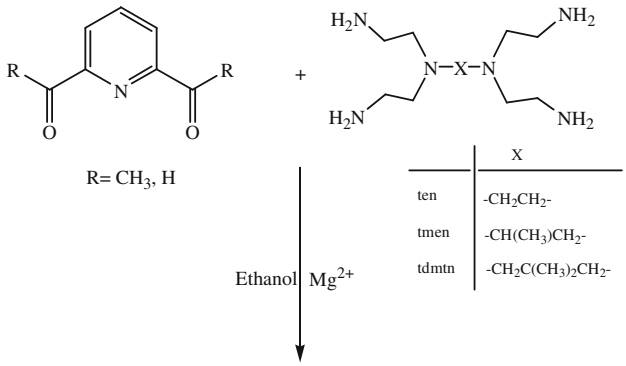
Most efforts to date have focused on the design and synthesis of polyaza Schiff base macrocyclic complexes by using 2,6-diacetylpyridine (DAP) and/or 2,6-diformylpyridine (DFP), as dicarbonyl head units of macrocyclic rings [1, 12, 13]. In contrast, little work has been reported on the use of prepared complexes to evaluate their biological activities [14, 15]. Recently, we reported the design, synthesis and structural studies of Magnesium(II) complexes of two heptaaza Schiff base macrocycles, L^3 and L^4 (Scheme 1(a)), derived from template condensation reaction of ten and tdmtn with DAP [16, 17].

The aim of this investigation was to prepare new Magnesium(II) heptaaza Schiff base macrocyclic complexes apart from those already reported, and to compare the biological activity of these compounds against

(a)

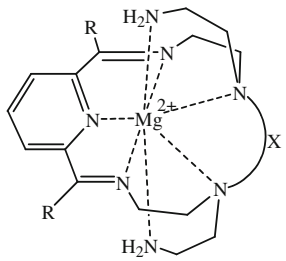


L	R	R′	X
L′	H	H	$-CH_2CH_2-$
L″	CH_3	H	$-CH_2CH_2-$
L^1	H	$CH_2CH_2NH_2$	$-CH_2CH_2-$
L^2	CH_3	$CH_2CH_2NH_2$	$-CH(CH_3)CH_2-$
L^3	CH_3	$CH_2CH_2NH_2$	$-CH_2CH_2-$
L^4	CH_3	$CH_2CH_2NH_2$	$-CH_2C(CH_3)_2CH_2-$



X	
ten	$-CH_2CH_2-$
tmen	$-CH(CH_3)CH_2-$
tdmtn	$-CH_2C(CH_3)_2CH_2-$

(b)



Compounds		R	X
1	$[MgL^1]^{2+}$	H	$-CH_2CH_2-$
2	$[MgL^2]^{2+}$	CH_3	$-CH(CH_3)CH_2-$
3	$[MgL^3]^{2+}$	CH_3	$-CH_2CH_2-$
4	$[MgL^4]^{2+}$	CH_3	$-CH_2C(CH_3)_2CH_2-$

Scheme 1 (**a**) Polyaza Schiff base macrocycles; (**b**) Compounds under discussion in this paper

various microorganisms such as *Escherichia coli* (*E. Coli*), *Staphylococcus aureus* (*S. aureus*), and *candidia albicans* (C. A.). The Mg(II) templated [1 + 1] cyclocondensation of DFP and DAP with ten and tmen yield to $[MgL^1](ClO_4)_2$ (**1**) and $[MgL^2](ClO_4)_2$ (**2**), respectively (Scheme 1(b)). The **1** and **2** are based on the [15] pydieneN_5 macrocycles, L′ and L″ (Scheme 1(a)), but in addition having two 2-aminoethyl arms coordinated at the axial sites.

The results show that the newly prepared complexes, **1** and **2**, as well as the previously prepared similar complex, **3**, which are containing a 15-membered pentaaza ring had no activity against microorganisms studied here. Where as the compound **4** (Scheme 1(b)), which contains two methyl groups in the central chain of a 16-membered pentaaza ring, had remarkable inhibition zone on the culture of *S. aureus* and *E. coli* as compared with standard drugs. The results of this study may be useful to researchers attempting to understand the mechanisms of action of Schiff base compounds against microorganisms studied here.

On the other hand, the comparison between experimental and theoretical NMR data may be helpful in making correct assignments and understanding the relationship between chemical shielding and molecular structure. Therefore, nowadays the GIAO/DFT (Gauge Independent Atomic Orbitals/Density Functional Theory) [18, 19] and CSGT/DFT (Continuous Set of Gauge Transformations/Density Functional Theory) [20, 21] approaches are widely used for the calculation of chemical shifts for a variety of heterocyclic compounds [22–25]. According to our knowledge, there are only few computational NMR studies on polyaza macrocyclic complexes [26]. At this work, the ^1H and ^{13}C NMR isotropic chemical shieldings of gas phase complexes were systematically studied by the GIAO and CSGT methods at the level of density functional theory (DFT). The performance of the effective core potentials (ECP) of CRENBL [27] basis set for metal atom was compared to LanL2DZ [28–30]. The computed ^1H and ^{13}C NMR chemical shieldings for all complexes are compared with the experimental data.

Experimental

General information

All of the reagents and solvents used were of analytical grade and purchased commercially. 2,6-diformylpyridine and 2,6-diacetylpyridine were obtained from Aldrich and used without further purification. *N*,*N*,*N*′,*N*′-tetrakis(2-aminoethyl)ethane-1,2-diamine hexahydrobromide (ten · 6HBr) was prepared as described previously [31]. ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained on a Bruker AV 300 MHz spectrometer. IR spectra were recorded as pressed KBr discs, using Unicom Galaxy Series FTIR 5000 spectrophotometer (400–4,000 cm^{-1}). C, H, N analyses were performed on a Vario EL III elemental analyzer.

Theoretical calculations

The structures and NMR chemical shifts of the complexes were calculated using Gaussian-98 [32] series of programs.

A starting molecular mechanics structure for the DFT calculations was obtained using the HyperChem 5.02 program [33]. The geometry of all complexes were fully optimized at the B3LYP/6-311++G* level. Vibrational frequency analyzes, calculated at the same level of theory, indicate that the optimized structures are at the stationary points corresponding to local minima without any imaginary frequency. The calculations of ^{1}H and ^{13}C NMR chemical shieldings were performed using GIAO/DFT [18, 19] and CSGT/DFT [20, 21] methods at the following basis set combinations: basis set **I**, H, C and N atoms 6-311++G* and Mg(II) ion LanL2DZ and basis set **II**, H, C and N atoms 6-311++G* and Mg(II) ion CRENBL. The ^{1}H and ^{13}C NMR chemical shifts were referenced to TMS.

Antibacterial and antifungal study

Compounds **1–4** were screened for their activity against *E. coli*, *S. aureus*, and C. A. strains by the disc diffusion method as gram negative, gram positive and fungal organisms, respectively. The Muller Hinton agar and sabouraud dextrose agar were used to culture bacteria and fungal, respectively. The culture media was poured into sterile plates and microorganisms were introduced on the surface of agar plates individually. The blank sterile discs measuring 6.4 mm in diameter were soaked in a known concentration of the test compounds. Then the soaked discs were implanted on the surface of the plates. A blank disc was soaked in the solvent (DMSO) and implanted as negative control on each plate along with the standard drugs. The plates were incubated at 37°C (24 h) and 27°C (48 h) for bacterial and fungal strain, respectively. The inhibition zones were measured and compared with the standard drugs.

Safety note

Perchlorate complexes 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.

Synthesis of *N*,*N*,*N*′,*N*′-tetrakis(2-aminoethyl) propane-1,2-diamine hexahydrobromide (tmen · 6HBr)

tmen · 6HBr was prepared by reaction of 1,2-propylendiamine with N-tosylaziridine (1:4) in benzene at room temperature for 5 days followed by detosylation with HBr/AcOH as described previously for ten · 6HBr [31]. Overall Yield: 55%. Anal. Calcd. for $C_{11}H_{36}N_6Br_6$: C, 18.05; H, 4.92; N, 11.47. Found: C, 17.8; H, 4.7; N, 11.6%. ^{1}H NMR (D_2O, ppm): δ 1.2 (d, 3H), 2.8–3.4 (m, 19H). $^{13}C\{^{1}H\}$ NMR (D_2O, ppm): δ 55.8, 55.6, 50.1, 47.2, 36.2, 35.5 and 12.3.

General procedure for the synthesis of complexes

A solution of KOH (3 mmol) in absolute EtOH (10 ml) was added to a suspension of hexamine. 6HBr (0.5 mmol) in absolute EtOH (10 ml) and the mixture was stirred at room temperature for 15 min. The mixture was filtered and precipitate was washed well with absolute EtOH (10 ml). This solution was added dropwise to a hot solution of $Mg(NO_3)_2 \cdot 6H_2O$ (0.5 mmol) and DFP and/or DAP (0.5 mmol) in absolute EtOH (20 ml) over a period of 2 h. After refluxing for 15 h the solution was filtered whilst hot and $NaClO_4$ (1 mmol) added to the filtrate. On cooling, the product was recovered as powder.

*$[MgL^1](ClO_4) \cdot 0.5H_2O$ (**1**)*

The product was dissolved in acetonitrile/ethanol (3:1) and the solution was diffused with diethyl ether to afford **1** as colourless microcrystals.

Yield 0.19 g (66%). Anal. Calcd. for $C_{17}H_{30}N_7Cl_2O_{8.5}$ Mg: C, 36.20; N, 17.39; H, 5.32. Found: C, 36.2; N, 17.5; H, 5.1%. IR (KBr, cm^{-1}); 3,540, 3,336, 3,290, 1,653, 1,595, 1,089, 1,016, 666 and 623.

*$[MgL^2](ClO_4)_2$ (**2**)*

The product was dissolved in acetonitrile and the solution was diffused with diethyl ether to afford **2** as greenish microcrystals.

Yield: 40%. Anal. Calcd. for $C_{20}H_{35}N_7Cl_2O_8$ Mg: C, 40.27; H, 5.87; N, 16.43. Found: C, 40.5; H, 6.0; N, 16.6%. IR (KBr, cm^{-1}); 3,339, 3,287, 1,651, 1,593, 1,102, 1,017, 662 and 623.

Results and discussion

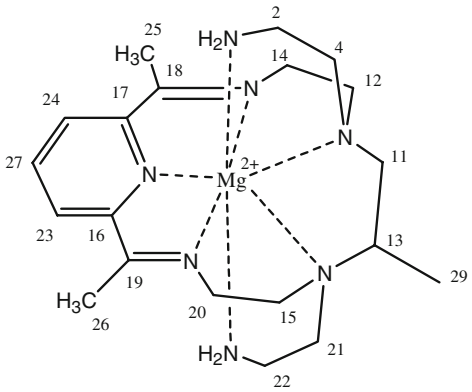
The condensation of aldehydes or ketones with amines is a rout to imines, functional groups with carbon–nitrogen double bond. By increasing the functionality of the precursors, one can obtain polymers, oligomers, or macrocycles. The diimine macrocyclic complexes, **1** and **2**, were synthesized by the metal templated cyclocondensation of 2,6-diformylpyridine and 2,6-diacetylpyridine with ten and tmen in the presence of appropriate Mg(II) salt in ethanol (Scheme 1). The prepared complexes were fully characterized by microanalysis, IR and NMR (^{1}H, ^{13}C, DEPT135, COSY(H, H) and HMQC and/or HETCOR(C, H)) spectroscopy. While it is theoretically possible for these hexaamines to condense with DFP and/or DAP to

give either bis(12-memberedtetraaza)macrocycles, like bis(14-memberedtetraaza) macrocycle, [34, 35] or an 15-membered pentaaza macrocycle, with two pendant 2-aminoethyl arms, only one product containing the pentaaza ring was observed. Absence of the 12-membered macrocycle probably derives from it being of too small a ring size to form around the Mg(II) template ion. The complexes are air stable solids, moderately soluble in CH_3CN and DMSO.

IR spectra

The infrared spectra of **1** and **2** were taken in the region 4,000 − 400 cm^{-1} and provide some information

Table 1 ^{1}H NMR and ^{13}C {^{1}H}NMR spectral assignments for **1** and **2** recorded at 300 MHz in d_6-DMSO



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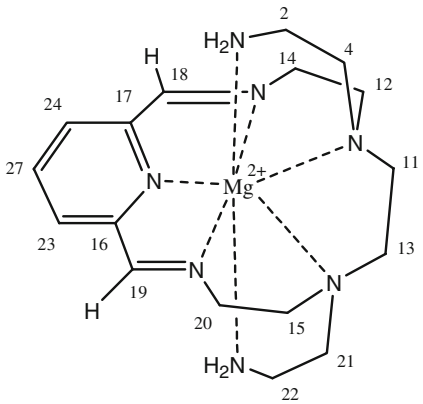

(1)

Hydrogen atom	δ_H (ppm)	J (Hz)	Carbon atom	δ_C
1				
H_{27} (1H)	8.43(dd)	^{3}J (H_{27}, $H_{(23,24)}$) ≈ 7.80	C_{27} (1C)	143.1
$H_{(23,\ 24)}$ (2H)	8.08(d)		$C_{23,\ 24}$ (2C)	127.6
$H_{(18,\ 19)}$ (2H)	8.73(t)	^{4}J ($H_{(18,19)}$, $H_{(14,\ 20)}$) ≈ 2.10	$C_{16,\ 17}$ (2C)	149.7
$H_{(14,20)}$ (4H)	4.02(dm)		$C_{18,\ 19}$ (2C)	161.7
$H_{(12,15)}$ (4H)	3.16(m)		$C_{14,\ 20}$ (2C)	49.7
$H_{(11,13)\alpha}$ (2H)	3.09(d)	^{2}J ($H_{(11,13)\alpha}$, $H_{(11,13)\beta}$) ≈ 9.6	$C_{12,\ 15}$ (2C)	58.2
$H_{(11,13)\beta}$ (2H)	2.82(d)	^{2}J ($H_{(11,13)\alpha}$, $H_{(11,13)\beta}$) ≈ 9.6	$C_{11,\ 13}$ (2C)	54.5
$H_{(4,21)}$ (4H)	2.91(m)		$C_{4,\ 21}$ (2C)	57.0
$H_{(2,22)\alpha}$ (2H)	2.77(m)		$C_{2,\ 22}$ (2C)	40.0
$H_{(2,22)\beta}$ (2H)	2.47(m)			
H_{NH2}(4H)	1.90–2.60(br)			
2				
H_{27} (1H)	8.27(m)		C_{27}	142.8
$H_{(23,24)}$ (2H)	8.17(m)		C_{23} and C_{24}	124.9
$H_{(25,26)}$ (6H)	2.40 and 2.41 (s)		C_{16} and C_{17}	150.6
H_{13} (1H)	3.15(m)		C_{18} and C_{19}	167.8 and 167.9
$H_{(14,20)}$ (4H)	3.67–3.75(m)		C_{14} and C_{20}	47.2 and 47.7
$H_{(12,15)\ \alpha}$ (2H)	3.54(m)		C_{12} and C_{15}	56.2 and 57.6
$H_{(12,15)\ \beta}$ (2H)	3.10(m)		C_4 and C_{21}	55.1
H_{11}, H_2, H_4, H_{22} and H_{21} (10H)	2.51–2.85 (m)		C_2 and C_{22}	44.1
H_{29} (3H)	0.96(d)	^{3}J (H_{29}, H_{13}) ≈ 6.43	C_{25} and C_{26}	15.9
H_{NH2}(4H)	2.30–2.60		C_{11}	62.5
			C_{13}	59.0
			C_{29}	10.7

regarding the bonding in the complexes. The total absence of carbonyl stretching mode in the IR spectra of each macrocyclic complexes together with the appearance of new imine (C=N) stretching mode in the range of 1,651–1,653 cm^{-1} clearly indicated that a cyclic Schiff base had formed in each case.

The IR spectra of **1** and **2** exhibit strong bands at 1,593–1,595 cm^{-1} as expected for the high energy ring vibrations of the coordinated pyridine [36]. The bonding of the pyridine nitrogen atom is also shown by the presence of the band at 1,016–1,017 cm^{-1} and 662–666 cm^{-1} attributable to the ring breathing frequency and the low energy pyridine ring vibrations, respectively [16, 17, 36]. The presence of unreacted pendant primary amino groups and the non-macrobicyclic nature of complexes are indicated by the appearance of two strong bands at ca. 3,290 and ca. 3,340 cm^{-1} assigned to the symmetric and asymmetric NH_2 stretching modes. The IR spectra exhibit a strong absorption band centered at ca. 1,095 cm^{-1}, suggesting the presence of non-coordinated perchlorate groups [37].

NMR studies

To assess whether or not the structures proposed for **1** and **2** are the same as **3** [16] and **4** [17], a detailed ^{1}H and $^{13}C\{H\}$ NMR study of the complexes was undertaken. The NMR spectra of **1** and **2** at ambient temperature in d_6-DMSO, was consistent with the macrocycle adopting a solution conformation similar to that proposed for **3** and **4** in DMSO solution. Hydrogen and carbon atoms were assigned, as far as possible, by various techniques such as DEPT(135), COSY(H, H) and HMQC and/or HETCOR(C, H). The chemical shift assignments are summarized in Table 1.

The ^{1}H NMR spectra of **1** and **2** exhibit a doublet of doublets (δ_H 8.27–8.43) and a doublet (δ_H 8.08–8.17) assigned to the *para*-(H_{27}) and *meta*-($H_{23,24}$) pyridyl protons, respectively (Fig. 1). Only one single imine resonance (δ_H 8.73 ppm) in the proton spectrum of **1** is observed, which demonstrate the equivalence of the two imine environment in solution, that has triplet character as a result of coupling with the methylene group adjacent to imine

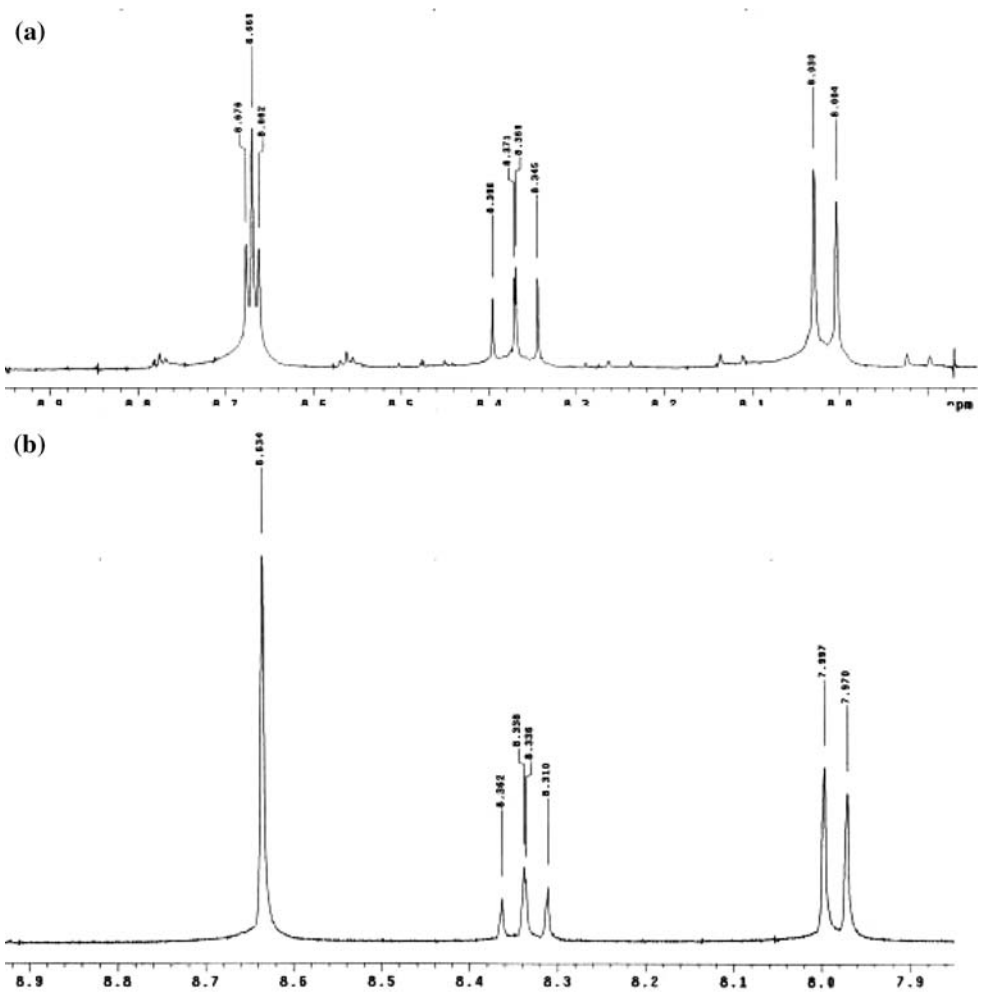

Fig. 1 (**a**) Expansion of the pyridine region of 1-D ^{1}H NMR spectrum of **1**. (**b**) The pyridine region of 1-D ^{1}H NMR spectrum of **1** after irradiation of methylene signal at 4.02 ppm

nitrogen atom ($^4J_{(H(18,19),\ H(14,20))} \approx 2.10$ Hz). The triplet pattern of imine proton signal is simplified after irradiation of $H_{(14,20)}$ signal at $\delta_H \approx 4.02$ (Fig. 1).

In the ^{1}H NMR spectrum of **1**, the broad signal at δ_H 1.90–2.60 may be assigned to the NH_2 groups, as was confirmed by deuterium exchange when D_2O was added to d_6-DMSO solution. In the ^{1}H NMR spectrum of **2**, new additional signals belonging to methyl protons were recorded at δ_H 2.39–2.42 and 1.0 ppm. The doublet pattern of signal at 1 ppm indicates that the signal belongs to the methyl group appended to the central component of the 15-membered pentaaza macrocycle. Compound **2** shows two ^{1}H methyl resonances at ca 2.39–2.42 ppm demonstrating the inequivalance of the two head unit methyl (H_{25} and H_{26}) environments. The complex nature of the aliphatic region signals of complexes, **1** and **2**, could stem from the magnetic inequivalence of the geminal hydrogen pairs which is due to the restricted rotation about the C–C bonds and also in pendant arms this restriction could possibly be due to the coordination of the primary amine nitrogen atoms to the Mg(II) ion [16, 17, 38, 39] (Table 1).

Although the overall pattern of the ^{1}H NMR spectrum of **2** is similar to that of **1**, their ^{13}C NMR spectral features are significantly different. According to the symmetrical structure of **1**, the ^{13}C NMR spectrum contains nine signals and shows its displaying C_2 symmetry in solution. However, the ^{13}C NMR spectrum of **2** exhibits 15 signals for 20 different carbons. Among them the signals of the azomethine carbons lie at δ_C 167.8 and δ_C 167.9 ppm, the signals of the pyridine carbons at δ_C 124.9 to δ_C 150.6 ppm and the signals of the 10 alkyl-carbons between δ_C 15.9 and δ_C 62.5 ppm. The discrepancy between the number of expected and observed signals can be explained by the overlapping of resonance frequencies of some carbon atoms.

Computational studies

In spite of our many efforts, single crystals suitable for X-ray crystallography have not been obtained for newly

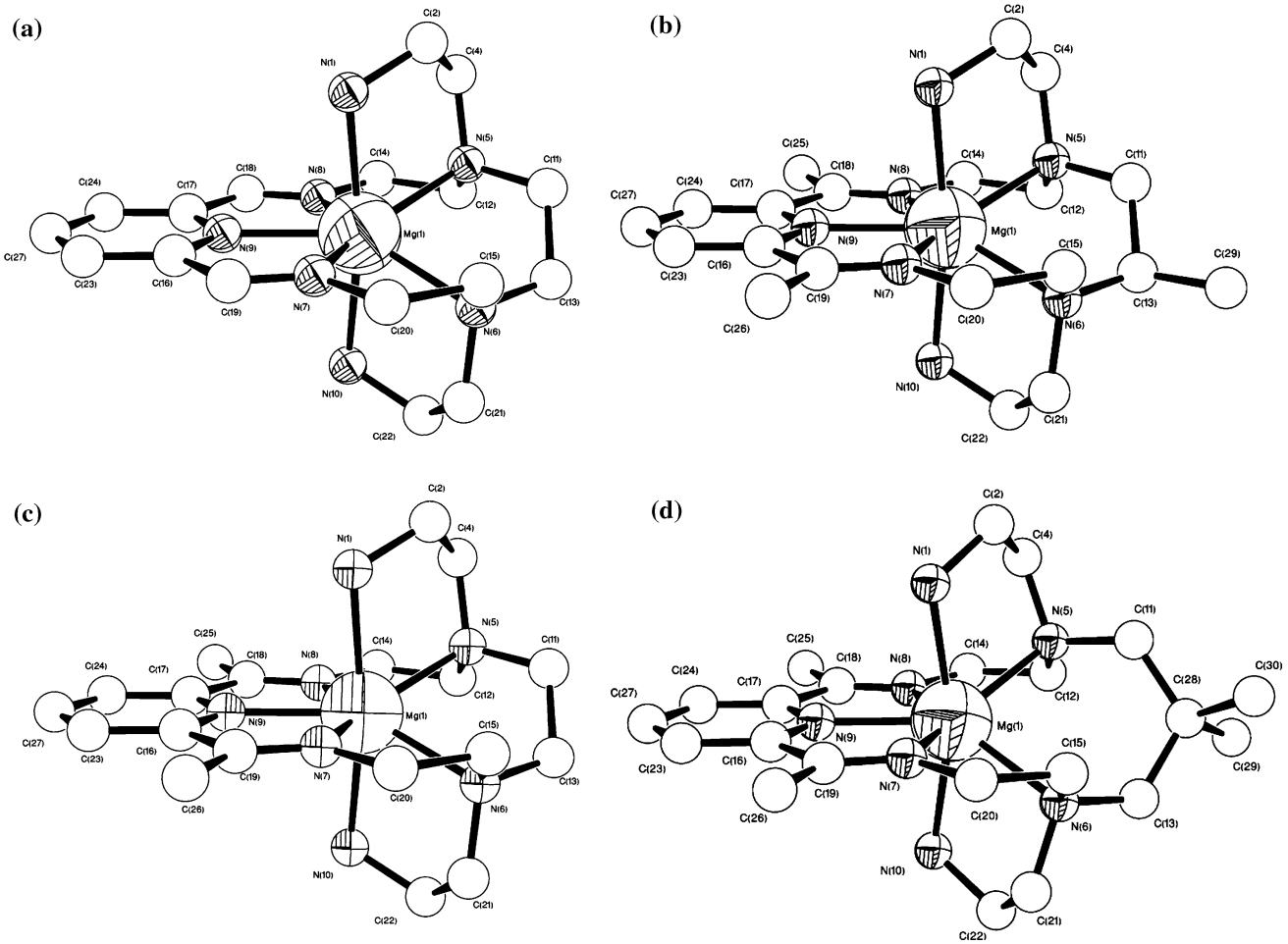

Fig. 2 B3LYP/6-311++G* optimized structure of **1**(**a**), **2**(**b**), **3**(**c**) and **4**(**d**)

Table 2 Selected calculated bond length (Å), bond angles (deg) and torsion angles (deg) for **1**–**4**

	1	**2**	**3**	**3** (XRD)	**4**	**4** (XRD)
Bond length						
M–N(1)	2.346	2.350	2.351	2.184(4)	2.376	2.179(4)
M–N(5)	2.315	2.309	2.325	2.344(4)	2.343	2.426(3)
M–N(6)	2.315	2.352	2.325	2.314(5)	2.343	2.399(4)
M–N(7)	2.235	2.223	2.228	2.245(5)	2.247	2.296(4)
M–N(8)	2.235	2.237	2.228	2.266(5)	2.247	2.296(4)
M–N(9)	2.193	2.188	2.181	2.211(5)	2.210	2.276(3)
M–N(10)	2.346	2.332	2.351	2.197(4)	2.376	2.170(4)
Bond angles						
N(1)–M–N(5)	75.087	75.029	74.683	76.89(15)	74.590	77.19(14)
N(1)–M–N(6)	112.131	111.792	112.051	97.16(18)	117.326	100.69(15)
N(1)–M–N(7)	84.832	84.858	85.033	89.03(17)	81.368	83.46(15)
N(1)–M–N(8)	92.425	92.548	92.460	91.57(17)	93.732	96.58(16)
N(1)–M–N(9)	85.547	85.507	85.879	94.03(16)	82.293	87.44(14)
N(1)–M–N(10)	171.095	171.323	171.758	174.9(2)	164.587	172.95(16)
N(5)–M–N(6)	79.553	78.432	78.523	75.93(16)	87.748	85.32(13)
N(5)–M–N(7)	137.917	137.588	137.193	144.5(2)	138.036	147.63(14)
N(5)–M–N(8)	74.363	74.730	74.771	72.87(17)	73.353	71.05(13)
N(5)–M–N(9)	140.223	140.323	140.739	141.26(19)	136.126	134.43(13)
N(5)–M–N(10)	112.131	112.257	112.051	101.57(16)	117.325	109.35(14)
N(6)–M–N(7)	74.363	75.022	74.772	73.66(17)	73.353	72.97(13)
N(6)–M–N(8)	137.917	137.343	137.139	144.68(16)	138.036	146.74(14)
N(6)–M–N(9)	140.223	141.246	140.739	142.81(17)	136.126	140.05(13)
N(6)–M–N(10)	75.087	75.084	74.681	77.73(18)	74.590	77.67(13)
N(7)–M–N(8)	144.185	144.222	144.635	140.92(18)	143.031	137.60(13)
N(7)–M–N(9)	72.094	72.288	72.317	71.19(18)	71.517	69.18(12)
N(7)–M–N(10)	92.427	92.102	92.459	89.57(17)	81.368	89.51(14)
N(8)–M–N(9)	72.094	71.936	72.317	69.79(17)	71.517	68.47(12)
N(8)–M–N(10)	84.832	85.152	85.033	92.62(18)	81.368	88.22(14)
N(9)–M–N(10)	85.547	85.825	85.879	90.17(16)	82.294	89.55(13)
Torsion angles						
M–N(5)–C(11)–C(13)	32.477	34.012	33.007	−39.3(5)	–	–
M–N(5)–C(12)–C(14)	52.739	53.293	52.998	50.0(5)	54.040	49.0(4)
M–N(6)–C(13)–C(11)	32.477	32.836	33.007	−41.2(5)	–	–
M–N(6)–C(15)–C(20)	52.737	52.536	52.996	48.7(5)	54.038	51.5(4)
M–N(7)–C(19)–C(16)	−0.633	0.000	0.000	−10.4(6)	0.633	1.2(5)
M–N(7)–C(20)–C(15)	2.722	3.118	2.591	17.8(5)	−3.637	16.4(5)
M–N(8)–C(14)–C(12)	2.722	2.532	2.591	14.0(5)	−3.623	2.6(6)
M–N(8)–C(18)–C(17)	−0.633	−0.316	0.000	−0.9(6)	0.633	3.3(5)
M–N(9)–C(16)–C(19)	−0.448	−0.775	−0.547	−2.2(5)	−0.316	−7.6(4)
M–N(9)–C(17)–C(18)	−0.448	−0.316	−0.547	2.0(5)	−0.316	0.7(4)
N(5)–C(11)–C(13)–N(6)	−45.859	−46.611	−46.214	55.4(5)	–	–
N(5)–C(12)–C(14)–N(8)	−38.506	−38.917	−39.118	43.3(6)	−35.757	−35.7(6)
N(6)–C(15)–C(20)–N(7)	−38.504	−39.777	−39.115	−44.2(5)	−35.757	−46.6(5)
N(7)–C(19)–C(16)–N(9)	0.706	0.448	0.448	8.2(6)	0.000	4.1(5)
N(8)–C(18)–C(17)–N(9)	0.706	0.448	0.448	0.7(6)	0.000	−2.5(5)

XRD; X–ray diffraction solid–state experimental results

prepared complexes (**1** and **2**). However, based on the composition of these complexes, their IR and NMR spectra and the crystal structures of the analogous complexes (**3** and **4**) [16, 17], the new complexes (**1** and **2**) are proposed to have a slightly distorted pentagonal bipyramid structure with the metal ion located within a pentaaza macrocycle and two pendant amines coordinating on opposite sides.

The structural parameters of **1** and **2** were assessing by undertaking density functional theory calculations. This was done by undertaking a full geometry optimization at the B3LYP/6-311++G* level of theory, using LanL2DZ and/or CRENBL basis sets for Magnesium(II) ion. For all complexes, except **2**, the calculations predicate structure with C_2 symmetry axis, which is closely related to the solid-state structure of **3** and **4** as well as solution studies of these complexes [16, 17]. The resulting optimized structures and atom numbering are displayed in Fig. 2. The selected bond lengths, bond angles and torsion angles of the minimum energy structures are given in Table 2 along with the corresponding values obtained for **3** and **4** by X-ray diffraction (XRD) analysis [16, 17], for comparison. Overall, the calculated values of the bond lengths and angles for **3** and **4** agree well with those deduced from the X-ray diffraction study of complexes. The slightly differences between the calculated and measured values may be a result of solid-state interactions. In common with other pyridine containing macrocycles the Mg–N(9) bond of **1** and **2** is the shortest equatorial bond [16, 17, 40]. As indicated by calculated torsion angles (Table 2) the two5-member rings, which include the two imine bonds [Mg–N(9)–C(17)–C(18)–N(8) and Mg–N(9)–C(16)–C(19)–N(7)] are nearly planner in all complexes.

^{1}H and ^{13}C NMR chemical shifts were calculated on the optimized structures (C_2 for **1**, **3**, **4** and C_1 for **2**) using two methods (GIAO/DFT and CSGT/DFT) with different basis sets. The following basis set combinations were used: basis **I**, LanL2DZ basis set for the metal atom and 6-311++G* for the other atoms; basis **II**, the same as basis **I**, but LanL2DZ of the metal atom was replaced by CRENBL. Calculated and measured ^{1}H and ^{13}C chemical shifts of selected atoms in the complexes are tabulated in Table 3 and Table 4.

The following conclusions can be straight forwardly derived based on presented data. On an absolute scale, the computed NMR chemical shifts for **1**–**4** at the DFT level of theory are in acceptable agreement with the experimental data. Differences between the calculated and measured values may be a result of solvent interactions, particularly in the case of hydrogen-bonding atoms (NH_2 groups). The computed GIAO relative ^{1}H shift values of all complexes correlate better with the experimental ones than the CSGT ones (Table 4). Regarding the method for achievement of

Table 3 ^{13}C NMR data for selected carbons of **1**–**4**

Carbons		1	2	3	4
C14 and C20	a	49.7	47.2 or 47.7	47.1	46.5
	b	53.9	51.2	51.3	51.7
	c	47.0	44.6	44.7	44.8
	d	51.3	50.5	49.1	49.2
	e	47.9	45.5	45.6	45.7
C29 and C30		–	10.7	–	29.1
			14.7		35.5
			9.1		30.3
			14.6		32.7
			10.1		31.3
C25 and C26		–	15.9	15.4	15.8
			20.5	20.7	20.5
			13.6	3.7	13.4
			19.8	18.1	17.9
			14.8	14.9	14.7
C16 and C17		149.7	150.6	150.9	150.5
		157.6	159.6	159.6	159.1
		146.3	148.0	148.0	147.9
		155.1	158.2	157.3	156.9
		147.5	149.2	149.2	149.1
C18 and C19		161.7	169.7 or 169.8	168.2	167.9
		172.1	184.8	184.6	183.7
		162.4	174.2	174.4	173.8
		168.7	183.5	181.2	180.3
		163.6	175.3	175.4	174.9
C23 and C24		124.7	124.9	124.7	124.5
		135.9	135.5	135.9	135.7
		129.5	125.4	125.5	125.4
		137.2	135.4	133.1	132.8
		130.6	127.2	126.6	126.5
C27		143.1	142.8	142.6	142.5
		156.0	155.4	155.7	156.1
		145.5	144.4	144.5	144.3
		153.7	154.9	153.3	153.8
		146.6	145.5	145.7	145.4

[a] Experimental

[b] Computed data at GIAO, LanL2DZ for Mg(II) and B3LYP/6-311++G* for other atoms

[c] Computed data at CSGT, LanL2DZ for Mg(II) and B3LYP/6-311++G* for other atoms

[d] Computed data at GIAO, CRENBL for Mg(II) and B3LYP/6-311++G* for other atoms

[e] Computed data at CSGT, CRENBL for Mg(II) and B3LYP/6-311++G* for other atoms

^{13}C chemical shifts, for the present case, at the B3LYP level, the CSGT algorithm is slightly superior to GIAO. It is clear that (Tables 3 and 4) in common with previous reports [41, 42], if the LanL2DZ basis set, for Mg(II) ion,

Table 4 ^{1}HNMR data for selected hydrogens of **1–4**

Hydrogen		**1**	**2**	**3**	**4**
NH_2(1) and NH_2(**10**)	a	1.90–2.60	2.15–2.60	2.18	2.60
	b	0.25, 0.93	0.27, 0.82	1.15, −0.03	−0.15, 0.84
	c	−0.40, −0.1	−0.47, −0.18	−0.43, −0.13	−0.60, −0.20
	d	0.78, 0.33	0.71, 0.37	0.38, 0.80	0.14, 0.80
	e	−0.40, −0.1	−0.47, −0.16	−0.44, −0.12	−0.61, −0.18
H_{18} and H_{19}		8.73	–	–	–
		8.89			
		6.99			
		8.84			
		7.05			
H_{23} and H_{24}		8.08	8.17	8.16	8.20
		8.31	8.35, 8.43	8.13	8.17
		6.30	6.44	6.44	6.43
		8.23	8.21, 8.39	8.12	8.13
		6.34	6.48	6.49	6.48
H_{27}		8.43	8.27	8.34	8.30
		8.94	8.85	8.95	9.03
		6.94	6.89	6.91	6.89
		8.91	8.79	8.97	9.05
		6.98	6.94	6.95	6.94
H_{25} and H_{26}		–	2.40	2.46	2.48
			2.77	2.77	2.71
			1.59	1.60	1.56
			2.68	2.78	2.74
			1.60	1.60	1.60
H_{29} and H_{30}		–	0.97	–	1.09
			0.72		0.78
			1.47		1.42
			0.69		0.76

[a] Experimental

[b] Computed data at GIAO, LanL2DZ for Mg(II) and B3LYP/6-311++G* for other atoms

[c] Computed data at CSGT, LanL2DZ for Mg(II) and B3LYP/6-311++G* for other atoms

[d] Computed data at GIAO, CRENBL for Mg(II) and B3LYP/6-311++G* for other atoms

[e] Computed data at CSGT, CRENBL for Mg(II) and B3LYP/6-311++G* for other atoms

was replaced by CRENBL, the ^{1}H and ^{13}C absolute shieldings are slightly better. Namely, except for the carbons 18(19), 23(24) and 27 the CSGT/B3LYP/6-311++G* (CRENBL for Mg) ^{13}C isotropic shieldings agree acceptable with the experimentally measured ones (Table 3). The relation between the experimental ^{13}C chemical shifts and the computed (CSGT/DFT method) magnetic isotropic shielding tensors for **2** is shown in Fig. 3. The correlation is linear and it is described by the equation:

$$\delta_{exp} = a + b\sigma$$

Parameters a and b for all complexes are:

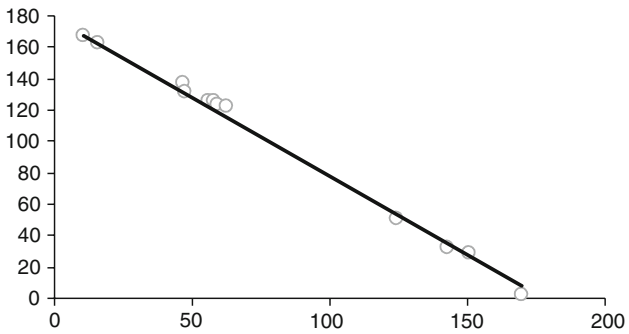

Fig. 3 Plot of experimental chemical shifts *vs* the magnetic isotropic shielding tensors from the CSGT B3LYP/6-311++G* calculation for **2**

$$\delta_{13C} = -0.9898\sigma + 177.4\left(R^2 = 0.9794\right) \quad \text{for } \mathbf{1},$$
$$\delta_{13C} = -0.9955\sigma + 177.4\left(R^2 = 0.9931\right) \quad \text{for } \mathbf{2},$$
$$\delta_{13C} = -1.0106\sigma + 177.4\left(R^2 = 0.9927\right) \quad \text{for } \mathbf{3}$$

and

$$\delta_{13C} = -1.0083\sigma + 177.4\left(R^2 = 0.9943\right) \quad \text{for } \mathbf{4}$$

Biological activities

The results showed that the compounds **1**, **2** and **3**, which are macrocyclic complexes of Mg(II) containing 15-membered pentaaza ring, had no antimicrobial activity against bacteria (*E. Coli* and *S. aureus*) and fungi (C. A.). Where as, compound **4** that is a macrocyclic complex of Mg(II) containing 16-membered pentaaza ring had inhibition zone of 25 and 19 mm on the culture of *S. aureus* and *E. Coli*, respectively. No biological activity were observed when the lateral unit of DAP containing complexes (**2** and **3**) was changed from ten to tmen. In addition, the replacement of DFP (in **1**) instead of DAP (in **3**) did not affect the antibacterial activity of the complex. Thus, as the result showed, we may conclude that neither replacement of head unit nor lateral unit could not affect the biological activity of heptaaza [15] pydieneN_5-based complexes of Mg(II). The observed antibacterial activity in **4** may be due to reduce the polarity of the metal ion because of partial sharing of its positive charge with the donor atoms of 16-membered methyl containing macrocycle ring [43]. Furthermore the mode of action of the compound **4** may involve formation of hydrogen bonds through the azomethine (C = N) groups with the active centres of cell constituents, resulting in interference with the normal cell processes [44]. Although the compound **4** showed highest activity against *S. aureus* and *E. coli*, it is inactive against C.A. The variation in the effectiveness of the different compounds against different organisms depends on the impermeability of the microbial cells or on the difference in the ribosome of the microbial cells [45, 46]. We propose more investigations to understand the mechanisms involve in the biological activity of this compound.

Conclusion

The Mg^{2+} ion is an effective template ion for the Schiff base condensation of DFP and DAP with hexadentate hexaamines yielding heptaaza macrocyclic complexes based on the [15] pydieneN_5 rings. The antimicrobial screening of newly prepared complexes, **1** and **2**, as well as previously prepared similar complexes, **3** and **4**, against *E. coli*, *S. aureus* and C. A. showed that the macrocyclic complexes of Mg(II) containing 15-membered pentaaza ring (**1**, **2** and **3**) have no activity. Where as the compound **4** which contain 16-membered pentaaza ring, had remarkable inhibition zone on the culture of *S. aureus* and *E. coli* as compared with standard drugs. The antibacterial activity of heptaaza complex of Mg(II) containing 16-membered pentaaza macrocycle ring may be due to reduce the polarity of the metal ion because of partial sharing of its positive charge with the donor groups and/or the formation of hydrogen bonds through the azomethine (–C=N–) groups of bigger size macrocycle with the active centres of cell constituents.

The ^{1}H and ^{13}C NMR chemical shieldings of gas phase complexes were systematically studied by the GIAO/DFT and CSGT/DFT methods. The CSGT ^{13}C relative shift values correlate better with the experimental ones than the GIAO, where as the ^{1}H relative shift values with respect to both methods was reverse. The comparison of the theoretical results from the LanL2DZ and CRENBL basis sets for metal atom show that the absolute shieldings are slightly better when the CRENBL basis set was used. The proposed approach can be potentially useful in an extended way to predict the chemical shifts of the polyaza macrocyclic complexes.

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References

1. Radecka-Paryzek, W., Patroniak, V., Lisowski, J.: Metal complexes of polyaza and polyoxaaza Schiff base macrocycles. Coord. Chem. Rev. **249**, 2165–2175 (2005)
2. Vigato, P.A., Tamburini, S.: The challenge of cyclic and acyclic schiff bases and related derivatives. Coord. Chem. Rev. **248**, 1717–2128 (2004)
3. Vigato, P.A., Tamburini, S., Bertolo, L.: The development of compartmental macrocyclic Schiff bases and related polyamine derivatives. Coo rd. Chem. Rev. **251**, 1311–1492 (2007)
4. Zhang, Z., Mikkola, S., Lönnberg, H.: Preparation of hexaaza and heptaaza macrocycles functionalized with a single aminoalkyl pendant arm. Org. Biomol. Chem. **1**, 854–858 (2003)
5. Costamagna, J., Ferraudi, G., Matsuhiro, B., Campos-Vallette, M., Canales, J., Villagran, M., Vargas, J., Aguirre, M.J.: Complexes of macrocycles with pendant arms as models for biological molecules. Coord. Chem. Rev. **196**, 125–164 (2000)
6. Wainwright, K.P.: Synthetic and structural aspects of the chemistry of saturated polyaza macrocyclic ligands bearing pendant coordinating groups attached to nitrogen. Coord. Chem. Rev. **166**, 35–90 (1997)
7. He, Y., Kou, H., Li, Y., Chuan Zhou, B., Xiong, M., Li, Y.: One-pot template synthesis and crystal structure of two new polyaza Copper(II) complexes. Inorg. Chem. Commun. **6**, 38–42 (2003)
8. Vicente, M., Bastida, R., Lodeiro, C., Macías, A., Parola, A.J., Valencia, L., Spey, S.E.: Metal complexes with a new N_4O_3 amine pendant-armed macrocyclic ligand: synthesis, characterization, crystal structures, and fluorescence studies. Inorg. Chem. **42**, 6768–6779 (2003)
9. Raimondi, A.C., de Souza, V.R., Toma, H.E., Mangrich, A.S., Hasegawa, T., Nunes, F.S.: An unusual Vanadium(II) promoted

hydrogenation of a magnesium tetraiminediphenolate compound yielding an asymmetric oxovanadium(IV) macrocyclic complex. Polyhedron **23**, 2069–2074 (2004)
10. Dutta, S.K., Flörke, U., Mohanta, S., Nag, K.: Stoichiometric and metal-deficient Copper(II) complexes of a dinucleating macrocyclic ligand. Structural studies. Inorg Chem. **37**, 5029–5032 (1998)
11. Collinson, S.R., Fenton, D.E.: Metal complexes of bibracchial Schiff base, macrocycles. Coord. Chem. Rev. **148**, 19–40 (1996)
12. Nelson, S.M.: Developments in the synthesis and coordination chemistry of macrocyclic Schiff base ligands. Pure Appl. Chem. **52**, 2461–2476 (1980)
13. Fenton, D.E.: Metallobiosites and their synthetic analogues—a belief in synergism 1997–1998 Tilden lecture. Chem. Soc. Rev. **28**, 159–168 (1999)
14. Mohamed, G.G.: Synthesis, characterization and biological activity of bis(phenylimine) Schiff base ligands and their metal complexes. Spectrochim. Acta Part A **64**, 188–195 (2006)
15. Mohamed, G.G., Abd El-Wahab, Z.H.: Mixed ligand complexes of bis(phenylimine) Schiff base ligands incorporating pyridinium moiety: Synthesis, characterization and antibacterial activity. Spectrochim. Acta Part A **61**, 1059–1068 (2005)
16. Keypour, H., Khanmohammadi, H., Wainwright, K.P., Taylor, M.R.: Synthesis, crystal structure, NMR and ab initio molecular-orbital studies of some Magnesium(II) macrocyclic Schiff-base complexes, with two 2-aminoethyl pendant arms. Inorg. Chim. Acta **357**, 1283–1291 (2004)
17. Khanmohammadi, H., Amani, S., Lang, H., Rüeffer, T.: Synthesis and characterization of Mg(II), Mn(II), Zn(II) and Cd(II) complexes with a new heptaaza Schiff base pendant-armed macrocycle: X-ray crystal structure, NMR and computational study. Inorg. Chim. Acta **360**, 579–587 (2007)
18. Ditchfield, R.: Self-consistent perturbation theory of diamagnetism. Mol. Phys. **27**, 789–807 (1974)
19. Wolinski, K., Hinton, J.F., Pulay, P.: Efficient implementation of the gauge-independent atomic orbital method for NMR chemical shift calculations. J. Am. Chem. Soc. **112**, 8251–8260 (1990)
20. Keith, T.A., Bader, R.F.W.: Calculation of magnetic response properties using atoms in molecules. Chem. Phys. Lett. **194**, 1–8 (1992)
21. Keith, T.A., Bader, R.F.W.: Calculation of magnetic response properties using a continuous set of gauge transformations. Chem. Phys. Lett. **210**, 223–231 (1993)
22. Prakash Reddy, V., Rasul, G., Surya Prakash, G.K., Olah, G.A.: ^{13}C NMR/DFT/GIAO studies of phenylene bis(1,3-dioxolanium) dications and 2,4,6-triphenylene tris(1,3-dioxolanium) trication. J. Org. Chem. **68**, 3507–3510 (2003)
23. Katritzky, A.R., Akhmedov, N.G., Güven, A., Doskocz, J., Akhmedova, R.G., Majumder, S., Dennis Hall, C.: GNMR simulated ^{1}H and proton-coupled ^{13}C NMR spectra of substituted 3-nitropyridines. GIAO/DFT calculated values of proton and carbon chemical shifts and coupling constants. J. Mol. Struct. **787**, 131–147 (2006)
24. Meng, Z., Carper, W.R.: GIAO NMR calculations for atrazine and atrazine dimers: comparison of theoretical and experimental ^{1}H and ^{13}C chemical shifts. J. Mol. Struct. **588**, 45–53 (2002). (THEOCHEM)
25. Gallant, A.J., Hui, J.K.H., Zahariev, F.E., Wang, Y.A., MacLachlan, M.J.: Synthesis, structure, and computational studies of soluble conjugated multidentate macrocycles. J. Org. Chem. **70**, 7936–7946 (2005)
26. Gomila, R.M., Garau, C., Frontera, A., Quiñonero, D., Ballester, P., Costaa, A., Deyà, P.M.: Applicability of the ^{1}H NMR chemical shifts computed by the ab initio/GIAO-HF methodology to the study of geometrical features of Zn-porphyrin dimers. Tetrahedron Lett. **45**, 9387–9391 (2004)
27. Basis set was obtained from the extensible computational chemistry Environment basis set database, Version 11/29/01, as developed and distributed by the Molecular Science
28. Dobbs, K.D., Hehre, W.J.: Molecular orbital theory of the properties of inorganic and organometallic compounds. 6. Extended basis sets for second-row transition metals. J. Comp. Chem. **8**, 880–893 (1987)
29. Hay, P.J., Wadt, W.R.: Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals. J. Chem. Phys. **82**, 299–310 (1985)
30. Hariharan, P.C., Pople, J.A.: The influence of polarization functions on molecular orbital hydrogenation energies. Theor. Chim. Acta **28**, 213–222 (1973)
31. Wagnon, B.K., Jackels, S.C.: Synthesis, characterization, and aqueous proton relaxation enhancement of a Manganese(II) heptaaza macrocyclic complex having pendant arms. Inorg. Chem. **28**, 1923–1927 (1989)
32. Frich, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Zakrazewski, V.G., Montgomery, J.A., Startmann Jr., R.E., Burant, J.C., Dapprich, S., Millam, J.M., Daniels, A.D., Kudin, K.N., Strain, M.C., Farkas, O., Tomasi, J., Barone, V., Cossi, M., Cammi, R., Mennucci, B., Adamo, C., Clifford, S., Ochterski, J., Petersson, G.A., Ayala, P.Y., Cui, Q., Morokuma, K., Malik, D.K., Rabuck, A.D., Raghavachar, K., Foresman, J.B., Cioslowski, J., Ortiz, J.V., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Gomperts, R., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanyakkara, A., Gonzalez, C., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Andres, J.L., Head-Gordon, M., Replogle, E.S., Pople, J.A.: GAUSSIAN 98 (Revision A.3). Gaussian Inc, Pittsburgh, PA, USA (1998)
33. HyperChem, Release 5.02, Hypercube, Inc., Gainesville (1997)
34. Mochizuki, K., Ikeda, Y.: Synthesis and square planar-octahedral equilibrium of bis macrocyclic dinickel(II) complexes with polymethylene bridges of various lengths. Bull. Chem. Soc. Jpn **63**, 1587–1591 (1990)
35. Mochizuki, K., Endoh, Y.: synthesis of heterobinuclear Cu(II)Ni(II)complexes with bis(tetraazamacrocycle). Bull. Chem. Soc. Jpn **62**, 936–938 (1989)
36. Radecka-Paryzek, W., Patroniak-Krzyminiewska, V., Litkowska, H.: The template synthesis and characterization of the yttrium and lanthanide complexes of new 19-membered pentadentate azaoxa macrocycle. Polyhedron **17**, 1477–1480 (1998)
37. Nakamoto, K.: Infrared and Raman Spectra of Inorganic and Coordination Compounds. New York, Wiley-Interscience (1978)
38. Adams, H., Bailey, N.A., Dwyer, M.J.S., Fenton, D.E., Hellier, P.C., Hempstead, P.D., Latour, J.M.: Synthesis and crystal structure of a first-generation model for the trinuclear copper site in ascorbate oxidase and of a dinuclear silver precursor. J. Chem. Soc. Dalton Trans, 1207–1216 (1993)
39. Bailey, N.A., Rodriguez de Barbarin, C.O., Fenton, D.E., Hellier, P.C., Hempstead, P.D., Kanesato, M., Leeson, P.B.: Attempted functionalisation of a mononuclear barium complex of a 24-membered bibracchial tetraimine Schiff-base macrocycle derived from tris(2-aminoethyl)amine using salicylaldehyde. J. Chem. Soc. Dalton Trans, 765–770 (1995)
40. Othman, A.H., Ng, S.W.: Diaqua[2,13-dimethyl-3,12,18-triaza-6,9-dioxa-bicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene] Magnesium(II) Diperchlorate. Acta Crystallogr. Sect. **C 51**, 1059–1060 (1995)
41. Cai, S.-H., Chen, Z., Wan, H.-L.: Theoretical investigation of 19f NMR chemical shielding of alkaline-earth-metal and alkali-metal fluorides. J. Phys. Chem. A **106**, 1060–1066 (2002)
42. Cai, S.-H., Chen, Z., Chen, Z.-W., Wan, H.-L.: ^{19}F NMR chemical shielding for metal fluorides MF_2 (M=Zn, Cd, Pb), MF_3 (M=Al, Ga, In) and SnF_4. Chem. Phys. Lett. **362**, 13–18 (2002)

43. Tweedy, B.G.: Phytopathology **55**, 910 (1964)
44. Dharmaraj, N., Viswanathamurthy, P., Natarajan, K.: Ruthenium(II) complexes containing bidentate Schiff bases and their antifungal activity. Trans. Met. Chem. **26**, 105–109 (2001)
45. Dharmaraj, N., Viswanathamurthy, P., Natarajan, K.: Ruthenium(II) complexes containing bidentate Schiff bases and their antifungal activity. Trans. Met. Chem. **26**, 105–109 (2001)
46. Balasubramanian, K.P., Parameswari, K., Chinnusamy, V., Prabhakaran, R., Natarajan, K.: Synthesis, characterization, electro chemistry, catalytic and biological activities of Ruthenium(III) complexes with bidentate N, O/S donor ligands. Spectrochim. Acta Part A **65**, 678–683 (2006)