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Synthesis and Characterization of Mn(II), Ni(II), Cu(II), Zn(II) and Cd(II) Complexes of Heptadentate Asymmetrical Tripodal Schiff Base

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Bis(2-aminoethyl)(3-aminopropyl)amine, 2-pyridinecarboxaldehyde and a number of metal ions were used to prepare metal complexes of tripodal Schiff base ligand (L_{322}). The resulting complexes, $[M(L_{322})](ClO_4)_2$ [M = Mn(II), Ni(II), Cu(II), Zn(II) and Cd(II)]; $L_{322} = N[CH_2CH_2CH_2N{=}CH(C_5H_4N)][(CH_2CH_2N{=}CH(C_5H_4N)]_2$, were characterized by microanalysis and IR spectra in all cases and by ^1H NMR spectra in the case of Zn(II) and Cd(II) complexes. In the ^1H NMR spectrum of the cadmium complex the signals of imine protons having two clear satellite peaks (^3J = 44.41–47.64 Hz) with rarely observed intensities in the ratio 1 : 6 : 1 due to coupling with neighbouring $^{111/113}Cd$. The *ab initio* studies on $[Zn(L_{322})]^{2+}$ and $[Cd(L_{322})]^{2+}$ complexes were also reported. The results show that the most bonding interaction between the metal ion and the bridging tertiary nitrogen atom of ligand occurs in the Cd(II) complex.

Key Words: ***Ab initio*****, Heptadentate ligands, Schiff bases, Seven-coordinate, Tripodal complexes.**

INTRODUCATION

The most studied potentially heptadentate (N_7) tripodal Schiff base compounds are the transition metal complexes of tripodal Schiff base ligand L_{222}, $N[CH_2CH_2N = CH(C_5H_4N)]_2$, which is derived from the tris(2-aminoethyl)amine, tren[1–6]. X-ray crystal structure analysis has shown that all of the reported $[M(L_{222})]^{2+}$ (M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Tc(II)) complexes are six- or pseudo-seven-coordinated[3, 4]. The authors were interested in exploring the usage of symmetrical and asymmetrical tripodal aliphatic tetramines to synthesis of new heptadentate (N_7) tripodal ligands and also related complexes and comparing these to L_{222} and their complexes. The authors have already used tris(3-aminopropyl)amine, tpt and bis(3-aminopropyl)(2-aminoethyl)amine, ppe, tetraamine ligands and 2-acetyl pyridine in template synthesis of symmetrical Ni(II) and Cd(II) Schiff base complexes of former ligand and asymmetrical Cd(II) Schiff base complex of latter ligand[7, 8]. In this research an asymmetrical tripodal tetraamine ligand, 2-pyridine carboxaldehyde and a number of metal ions [Mn(II), Ni(II), Cu(II), Zn(II) and Cd(II)] are used to simply prepare a new series of asymmetrical tripodal Schiff base complexes of a new ligand L_{322} (Fig. 1). An *ab initio* RHF and a density functional B3LYP calculations on Zn(II) and Cd(II) complexes synthesized here are also reported.

EXPERIMENTAL

2-pyridine carboxaldehyde and metal salts were obtained from Aldrich and used without further purification. The asymmetrical tripodal tetraamine ligand $N[(CH_2)_3NH_2][(CH_2)_2NH_2]_2$ (pee), as tetrahydrochloride salt, was synthesized according to literature method[9]. IR and ^1H NMR spectra were measured on Perkine Elmer FT-IRGX, Shimadzu UV-265 FW and Bruker FT-NMR 500 Hz spectrometers respectively.

Theoretical calculations

The geometries of both $[Zn(L_{322})]^{2+}$ and $[Cd(L_{322})]^{2+}$ species at gas phase were fully optimized at both the Hartree-Fock and DFT (B3LYP)[10] levels of theory using Gaussian 98 set of programs[11]. Both complexes were optimized using the standard LanL2MB basis set[12]. This basis set includes effective core potential (ECP) for zinc and cadmium atoms. Vibrational frequency analyses, calculated at the same level of theory, indicate that optimized structures are at the stationary points corresponding to local minima without any imaginary frequency. Calculations were performed on a Pentium-PC computer with 2400 MHz processor. A starting molecular mechanics structure for the *ab initio* calculations was obtained using the HyperChem 5.02 program[13].

General procedure for synthesis of $[M(L_{322})](ClO_4)_2$ complexes

All the complexes were readily prepared by the following general procedure. 2-Pyridine carboxaldehyde (0.321 g, 3 mmol) was added to a mixture of $pee{\cdot}4HCl{\cdot}1.5H_2O$ (0.333 g, 1 mmol) and NaOH (0.160 g, 4 mmol) dissolved in 20 mL of ethanol. After stirring for 1 h, the ethanolic solution was filtered to remove the produced NaCl. To the resulting clear solution was added the required metal salt (usually nitrate, chloride or perchlorate salts), dissolved in 20 mL methanol, in an equimolar ratio. The resulting solution was allowed to evaporate at room temperature to a volume of approximately 15 mL. Upon addition of excess amount of $NaClO_4$ usually a powder was formed which was filtered off and was collected. All complexes were recrystallized in 1 : 1 acetonitrile-methanol solution and were dried in vacuum. The IR data for all complexes are given in Table-1. For NMR numbering see Fig. 1.

Caution: Perchlorate salts can be dangerously explosive. The compounds described here have never detonated in our hands, but they should be treated with care.

TABLE-1

IR DATA (cm^{-1}) FOR THE $[M(L_{322})](ClO_4)_2$ COMPLEXES

Compound[a]	ν(C═N)[b]	ν(C═N)[c]	ν(C═C)[c, d]
(1)	1661	1597	1571
(2)	1645	1600	1571
(3)	1645, 1663 sh	1598	1571
(4)	1659	1598	1569
(5)	1666	1595	1572

[a]For all complexes absorptions attributable to ionic perchlorate were found at *ca.* 1095 and 622 cm^{-1}. [b]Schiff base. [c]Pyridine ring. [d]Weak band.

$[Mn(L_{322})](ClO_4)_2$ (1): Yield: 0.53 g (78%); Anal. Calcd. (Found) for $C_{25}H_{29}N_7O_8Cl_2Mn$: C, 44.9 (44.6), H, 4.5 (4.3), N, 14.1 (14.0).

$[Ni(L_{322})](ClO_4)_2$ (2): Yield: 0.53 g (77%); Anal. Calcd. (Found) for $C_{25}H_{29}N_7O_8Cl_2Ni$: C, 44.6 (44.4), H, 4.4 (4.5), N, 14.0 (13.6).

$[Cu(L_{322})](ClO_4)_2$ (3): Yield: 0.55 g (80%); Anal. Calcd. (Found) for $C_{25}H_{29}N_7O_8Cl_2Cu$: C, 44.4 (44.1); H, 4.4 (4.3), N, 13.9 (13.7).

$[Zn(L_{322})](ClO_4)_2$ (4): Yield: 0.49 g (71%); Anal. Calcd. (Found) for $C_{25}H_{29}N_7O_8Cl_2Zn$: C, 44.2 (44.0), H, 4.4 (4.5), N, 13.9 (13.5).

^1H NMR (500MHz, CD_3CN). 2.08 (m, 2H, 2-H), 2.71 (m, 1H), 2.80 (m, 1H), 2.93 (m, 3H), 3.03 (m, 1H), 3.45 (m, 3H), 3.68 (m, 1H), 3.76 (m, 1H), 3.80 (m, 1H), 7.21 (d, 1H, J = 4.66 Hz, py-H) 7.32 (d, 1H, J = 4.77 Hz, py-H), 7.58 (q, 2H, py-H), 7.68 (m, 1H, py-H), 7.74 (m, 1H, H-py), 8.00 (m, 2H, py-H), 8.05 (d, 1H, J = 7.68 Hz, py-H), 8.22 (t, 2H, py-H), 8.30 (t, 1H, py-H), 8.70 (s, 2H, H-7 and H-8), 8.77 (s, 1H, H-6).

$[Cd(L_{322})](ClO_4)_2$ (5): Yield: 0.51 g (69%); Anal. Calcd. (Found) for $C_{25}H_{29}N_7O_8Cl_2Cd$: C, 41.5 (41.1), H, 4.1 (4.0), N, 13.0 (12.5).

^1H NMR (500MHz, CD_3CN). 2.02 (m, 1H, 2-H_α), 2.14 (m, 1H, 2-H_β), 2.72 (m, 2H), 2.97 (m, 2H), 3.07 (m, 2H), 3.73 (m, 3H), 3.80 (m, 1H), 4.00 (m, 2H), 7.30 (d, 1H, J = 3.98 Hz, py H), 7.53 (m, 2H, py-H), 7.58 (bt, 1H, py-H), 7.65 (bt, 1H, py-H), 7.80 (m, 1H, H-py), 7.92 (d, 1H, J = 7.69 Hz, py-H), 7.98 (d, 2H, J = 7.53 Hz, py-H), 8.20 (m, 3H, py-H), 8.67 (s, 1H, with two satellite peaks at ratio 1 : 6 : 1 relative to main signal, $^3J(^{111/113}Cd\text{-}^1H) = 44.41$ Hz, 6-H), 8.75 (s, 1H, with two satellite peaks at ratio 1 : 6 : 1 relative to main signal, $^3J(^{111/113}Cd\text{-}^1H) = 47.64$ Hz, 7-H or 8-H), 8.78 (s, 1H, with two satellite peaks at ratio 1 : 6 : 1 relative to main signal, $^3J(^{111/113}Cd\text{-}^1H) = 45.39$ Hz, 7-H or 8-H).

RESULTS AND DISCUSSION

The IR spectra of all resulting complexes contain three bands in the 1666–1569 cm^{-1} region as expected for pyridine containing Schiff bases[7, 8]. Complete condensation of all primary amino groups of initial tetraamine ligand, tpt, was confirmed by lack of N—H stretching bands in the IR region 3450–3150 for all compounds. Furthermore, no bands attributable to (C═O) groups are detectable.

The ^1H NMR spectra of zinc and cadmium complexes confirm the formation of fully condensed Schiff base complexes. The fourteen protons of methylene groups appear as more than eight peaks at the region 2–4 ppm indicating that the protons of each methylene group are probably diastereotopic due to formation of six- and five-membered chelate rings (Figs. 1 and 2). It should be noted that in the case of previously known cadmium complex of L_{222}, $[Cd(L_{222})]^{2+}$, only the protons of one methylene group of each arm confirmed to be diastereotopic. On the other hand, it hase already been observed that the *geminal* coupling for diastereotopic protons of a similar symmetrical tripodal complex $[Cd(N\{(CH_2CH_2CH_2N = C(CH_3)(C_5H_4N)\}_3)]^{2+}$ in which the strong coordination of bridging tertiary nitrogen atom to the metal ion and formation of six-membered chelate rings was confirmed by X-ray crystal structure analysis[8].

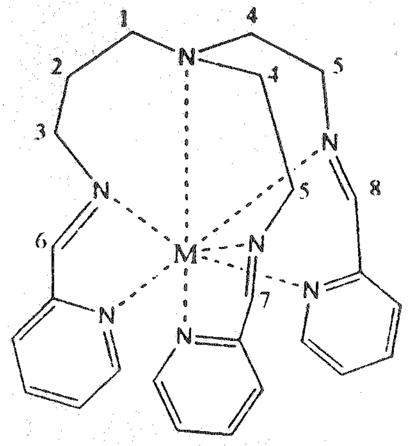
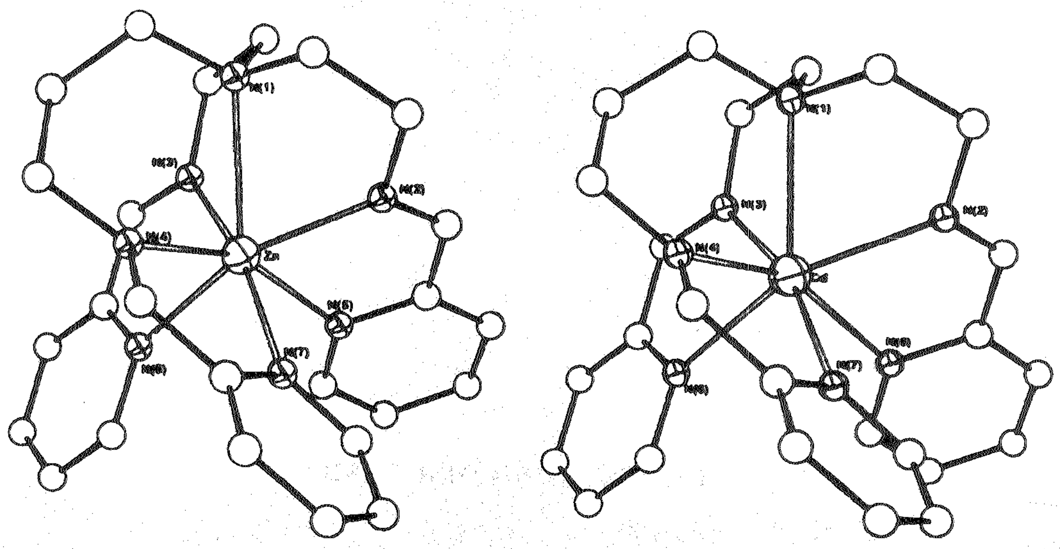


Fig. 1. Proposed chemical structure of metal complexes along with NMR numbering for zinc and cadmium complexes



(a) (b)

Fig. 2. Calculated molecular structure of (a) $[Zn(L_{322})]^{2+}$ and (b) $[Cd(L_{322})]^{2+}$ complexes, at the B3LYP level of theory, using standard LanL2MB basis set. Hydrogen atoms are omitted for clarity

In addition to the above observations, in the ^{1}H NMR spectrum of the cadmium complex synthesized here the signal of imine protons having two satellite peaks (^{3}J = 44.41–47.64 Hz) with rarely observed intensities in the ratio 1 : 6 : 1 due to coupling with neighbouring $^{111/113}$Cd at natural abundance (^{111}Cd, 12.81; ^{113}Cd, 12.22%). The similar magnetogyric ratios of ^{113}Cd and ^{111}Cd, –5.93330 and -5.6720×10^{-7} rad/Ts, respectively, lead to satellite overlap at the splittings observed here. Similar observations were reported about $^{111/113}$Cd–^{1}H heteronuclear coupling[14–18]. The observed value for ^{3}J($^{111/113}$Cd, ^{1}H) coupling constant in this research is similar with those that have been reported for two cadmium(II) complexes of macrocyclic Schiff base ligand[17]. The observation of this coupling and related satellites suggests that the Cd-N$_{im}$ bond remains in solution and supports the formation of six- and five-membered chelate rings in the cadmium complex.

Ab initio and DFT studies

The geometries of Zn(II) and Cd(II) complexes were also fully optimized at both the Hartree-Fock (HF) and density functional B3LYP levels of theory. Among the metals investigated in this research only the Zn(II) and Cd(II) metal ions have closed shell configuration and therefore calculations will be made without SCF convergence problems.

Selected bond lengths and bond angles of the Zn(II) and Cd(II) complexes are given in Table-2. The results show that the three imine, three pyridine and unique tertiary nitrogen donor atoms are arranged at apices of a distorted capped trigonal antiprism (Fig. 2(a) and (b)). If we compare the calculated (Cd—N) and (Zn—N) bond distances it will be understood that with increase in the size of metal ion the tertiary nitrogen atom of the ligand L_{322} will more easily coordinate to it. The authors expect that the (Cd—N$_{im}$) and (Cd—N$_{py}$) bond lengths are longer than the corresponding (Zn—N$_{im}$) and (Zn—N$_{py}$) bond lengths but Cd—N$_T$ (Cd—N(1)) bond length is shorter than (Zn—N$_T$) bond length.

For all complexes the other (M—N) bond lengths and also (N—M—N) bond angles are in the normal range for this type of compounds. The (Cd—N$_{im}$) and (Zn—N$_{im}$) bond lengths are shorter than the (Cd—N$_{py}$) and (Zn—N$_{py}$) bond lengths, respectively, as was previously confirmed by X-ray crystal structure analysis for similar complexes[3, 8].

Conclusions

The syntheses of fully condensed tripodal Schiff base complexes of Mn(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes were confirmed with elemental analysis, IR and electronic spectra. The authors suggest that the N$_T$ donor atom of the potentially heptadentate ligand L_{333} may be coordinated to both the Zn(II) and Cd(II) metal ions in related complexes, but surely more bonding interaction exists in the cadmium complex.

TABLE-2
SELECTED THEORETICAL BOND LENGTHS (Å) AND BOND ANGLES (°) OF THE CALCULATED STRUCTURES

	$[Cd(L_{322})]^{2+}$		$[Zn(L_{322})]^{2+}$	
Bond Lengths:				
M—N(1)	2.57	**2.56**	2.63	**2.59**
M—N(2)	2.32	**2.36**	2.19	**2.22**
M—N(3)	2.31	**2.33**	2.16	**2.18**
M—N(4)	2.34	**2.37**	2.22	**2.24**
M—N(5)	2.49	**2.48**	2.37	**2.38**
M—N(6)	2.42	**2.44**	2.27	**2.30**
M—N(7)	2.40	**2.40**	2.26	**2.27**
Bond Angles:				
N(1)—M—N(2)	68.3	**68.4**	67.4	**67.9**
N(1)—M—N(3)	69.6	**70.0**	69.2	**70.1**
N(1)—M—N(4)	77.0	**77.2**	74.2	**74.8**
N(1)—M—N(5)	126.9	**127.8**	126.6	**127.1**
N(1)—M—N(6)	130.3	**131.0**	131.3	**131.9**
N(1)—M—N(7)	123.7	**122.3**	123.0	**122.6**
N(2)—M—N(3)	104.6	**104.7**	104.3	**105.1**
N(2)—M—N(4)	120.1	**121.9**	116.9	**118.2**
N(2)—M—N(5)	70.0	**69.7**	73.2	**73.0**
N(2)—M—N(6)	151.8	**151.2**	156.1	**155.4**
N(2)—M—N(7)	89.0	**89.0**	86.0	**85.5**
N(3)—M—N(4)	106.9	**105.4**	106.3	**106.0**
N(3)—M—N(5)	91.5	**92.3**	87.9	**87.8**
N(3)—M—N(6)	70.8	**70.8**	75.3	**75.0**
N(3)—M—N(7)	164.4	**164.8**	166.9	**166.4**
N(4)—M—N(5)	154.5	**153.8**	158.6	**157.7**
N(4)—M—N(6)	87.1	**85.9**	85.4	**84.4**
N(4)—M—N(7)	71.4	**71.6**	75.2	**75.3**
N(5)—M—N(6)	82.5	**81.9**	82.9	**82.4**
N(5)—M—N(7)	86.0	**86.2**	87.4	**87.3**
N(6)—M—N(7)	93.6	**94.0**	92.0	**91.8**
C(2)—N(1)—C(3)	108.1	**106.8**	109.0	**107.7**
C(2)—N(1)—C(4)	110.4	**109.6**	110.6	**109.5**
C(3)—N(1)—C(4)	109.8	**108.4**	110.4	**108.8**
C(2)—N(1)—M	119.4	**120.1**	120.6	**121.4**
C(3)—N(1)—M	106.1	**107.7**	105.2	**107.4**
C(4)—N(1)—M	102.7	**103.8**	100.5	**101.4**

The parameters obtained at the HF level are given as plain text, those for the B3LYP level are in bold.

The present data, still, are not enough to say that the Mn(II), Cu(II) and Ni(II) complexes of L_{322}, in contrast to similar complexes of L_{222}, are seven-coordinated.

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