Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Molecular Structure 785 (2006) 54–62

Journal of
MOLECULAR
STRUCTURE

www.elsevier.com/locate/molstruc

Metal complexes of a new potentially heptadentate(N_7) tripodal Schiff base ligand. Synthesis, NMR studies and ab initio calculations

Sadegh Salehzadeh *, Seyed Amrollah Javarsineh, Hassan Keypour

Department of Chemistry, Bu-Ali Sina University, Hamadan 65174, Iran

Received 17 July 2005; received in revised form 12 September 2005; accepted 22 September 2005
Available online 16 November 2005

Abstract

Tris(3-aminopropyl)amine, 2-pyridinecarboxaldehyde and a number of metal ions were used to prepare metal complexes of a new fully condensed potentially heptadentate(N_7) tripodal Schiff base ligand (L_{333}). The resulting complexes, $[M(L_{333})](ClO_4)_2$ {M= Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II); $L_{333}=[N(CH_2CH_2CH_2N{=}CH(C_5H_4N))_3]$}, were characterized by microanalysis, IR and electronic spectra in all cases and by NMR spectra in the case of Zn(II) and Cd(II) complexes: these two are both seven-co-ordinate. The ^{1}H NMR, COSY and HMQC spectra of these complexes show two kinds of protons for each methylene group. The COSY spectrum confirms the geminal coupling of the two protons of each methylene group, indicating that the protons are diastereotopic in rigid six-membered rings. In the ^{1}H NMR spectrum of the cadmium complex the signal of the imine proton has two clear satellites peaks ($^3J=41.9$ Hz) with intensities in the ratio 1:6:1 due to coupling with neighbouring $^{111/113}$Cd. This coupling constant was confirmed by ^{113}Cd NMR spectroscopy. Ab initio studies on $[Fe(L_{333})]^{2+}$, $[Zn(L_{333})]^{2+}$ and $[Cd(L_{333})]^{2+}$ and also on the previously known complex, $[Cd(L_{Me333})]^{2+}$ are also reported. The results show that the shortest bonding interaction between the metal ion and the bridging tertiary nitrogen atom of the ligand is occurs in the Cd(II) complexes.

Keywords: Ab initio; Heptadentate ligands; Schiff bases; Seven-coordinate; Tripodal complexes

1. Introduction

The most thoroughly studied tripodal Schiff base compounds are the transition metal complexes of potentially heptadentate(N_7) Schiff base ligand L_{222} (Fig. 1) [1–6] and lanthanide derivatives of a range Schiff base ligands of the type $N[CH_2CH_2N{=}CH(2\text{-}OH\text{–}3\text{-}R^1\text{–}5\text{-}R^2C_6H_2)]_3$, [7–13]: both types are derived from the tris(2-aminoethyl)amine (tren). X-ray crystal structure analysis has shown that these complexes are six- or pseudo-seven-coordinate while the lanthanide complexes are all seven-coordinate [3,4]. We are interested in exploring the usage of symmetrical and asymmetrical tripodal aliphatic tetramines in synthesis of new heptadentate(N_7) tripodal ligands and their complexes to compare with the L_{222} complexes.

In addition to tren, a number of other tripodal tetraamine ligands containing three aliphatic N-donor atoms have been synthesized [14–18], but only those having ethylene and/or propylene chains, producing five- or six-membered chelate rings, are suitable for synthesis of heptadentate(N_7) ligands. We have already investigated template synthesis using 2-acetyl pyridine with tris(3-aminopropyl)amine (tpt), to produce symmetrical tetraamine-ligand complexes of Ni(II) and Cd(II) complexes or with bis(3-aminopropyl)(2-aminoethyl) amine (ppe) to give an asymmetrical Cd(II) complex [19,20]. X-ray crystal structure analysis of the symmetrical cadmium complex, $[Cd(L_{Me333})](ClO_4)_2$, has confirmed that this is the first example of a real seven-co-ordinate complex containing a heptadentate(N_7) tripodal Schiff base ligand [20].

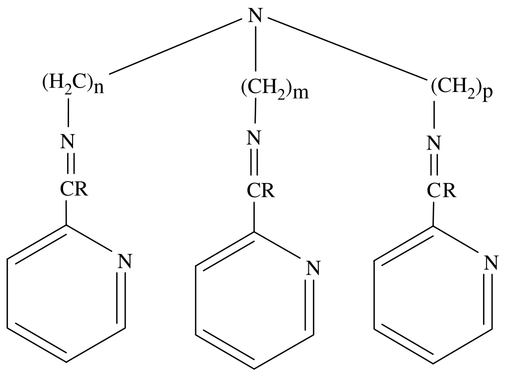
In this research the tpt, 2-pyridine carboxaldehyde and a number of metal ions {Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)} are used to successfully prepare a new series of symmetrical tripodal Schiff base complexes of a new ligand L_{333} (Fig. 1).

Although, the behavior of the potentially heptadentate(N_7) tripodal Schiff bases derived from tren as a function of metal ion size has been already investigated by X-ray crystal structure analysis of a series of d-block metal complexes [1–6], there is no similar experimental or theoretical study on a series of complexes of heptadentate(N_7) tripodal ligands derived from tpt. Thus, ab initio RHF and density-functional B3LYP calculations on the Fe(II), Zn(II) and Cd(II) complexes

---

* Corresponding author. Tel.: +98 811 8270900; fax: +98 811 8272404.
E-mail address: saleh@basu.ac.ir (S. Salehzadeh).

0022-2860/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2005.09.033



n=m=p=2, R=H	L_{222}	Refs. 1-6
n=m=p=3, R=CH_3	L_{Me333}	Refs. 19,20
n=m=3,p=2, R=CH_3	L_{Me332}	Ref. 20
n=m=p=3, R=H	L_{333}	This work

Fig. 1. Structures of tripodal heptadentate (N_7) ligands.

synthesized here and on the previously known Cd(II) complex, $[Cd(L_{Me333})]^{2+}$, are also reported.

2. Experimental

2.1. General information

2-Pyridinecarboxaldehyde and metal salts were obtained from Aldrich and used without further purification. The tripodal tetraamine ligand $N\{(CH_2)_3NH_2\}_3$ (tpt), as the tetra hydrochloride salt was synthesized as previously described [14]. IR, UV and NMR spectra were measured on Perkin Elmer FT-IRGX, Shimadzu UV-265 FW and Bruker FT-NMR 500 HZ spectrometers, respectively. The NMR spectra of Ligand L_{333} was obtained on a Jeol 90 MHz FT NMR spectrometer.

2.2. Theoretical calculations

The geometries of all $[ML]^{2+}$ species in the gas phase were fully optimized at both the Hartree–Fock and DFT (B3LYP) [21] levels of theory using the Gaussian 98 set of programs [22]. At first, all complexes were optimized using the standard LanL2MB basis set [23] and resulting structures were then used for further calculations using standard 3-21G* basis set for ligand atoms and LanL2DZ for metal ion [24,25]. The structures resulting from this were also used for similar calculations using 6-31G* basis set for ligand atoms [26]. Therefore, all complexes were fully optimized by six different methods. 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 [27].

2.3. General procedure for synthesis of $[M(L_{333})](ClO4)_2$ complexes

All complexes were readily prepared by following general procedure. 2-pyridinecarboxaldehyde (0.321 g, 3 mmol) was added to a mixture of tpt·4HCl·H_2O (0.352 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. The required metal salt (usually nitrate, chloride or perchlorate), dissolved in 20 ml methanol, was added in 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 $NaClO_4$ a powder was usually formed which was filtered off and collected. All complexes were recrystallized 1:1 acetonitrile–methanol and were dried in vacuum. It should be noted that Fe(II) and Co(II) complexes were prepared under nitrogen atmosphere. The IR data (Nujol mull, cm^{-1}) for all complexes are given in Table 1. For NMR numbering see Fig. 2. CAUTION: Perchlorate salts can be dangerously explosive. The compounds described here have never detonated in our hands, but they should be treated with care.

$[Mn(L_{333})](ClO_4)_2$ (**1**). Yield 0.44 g (62%). Anal. Calc. for $C_{27}H_{33}N_7Cl_2O_8Mn$: C, 45.7; H, 4.6; N, 13.8. Found: C, 45.4; H, 4.5; N, 13.7%.

$[Fe(L_{333})](ClO_4)_2$ (**2**). Yield 0.50 g (70%). Anal. Calc. for $C_{27}H_{33}N_7Cl_2O_8Fe$: C, 45.7; H, 4.6; N, 13.8. Found: C, 45.4; H, 4.5; N, 13.7%.

$[Co(L_{333})](ClO_4)_2$ (**3**). Yield 0.30 g (42%). Anal. Calc. for $C_{27}H_{33}N_7Cl_2O_8Co$: C, 45.7; H, 4.6; N, 13.8. Found: C, 45.4; H, 4.5; N, 13.7%.

$[Ni(L_{333})](ClO_4)_2$ (**4**). Yield 0.48 g (67%). Anal. Calc. for $C_{27}H_{33}N_7Cl_2O_8Ni$; C, 45.4; H, 4.6; N, 13.7. Found: C, 45.5; H, 4.5; N, 13.5%.

$[Cu(L_{333})](ClO_4)_2$ (**5**). Yield 0.42 g (58%). Anal. Calc. for $C_{27}H_{33}N_7Cl_2O_8Cu$; C, 45.1; H, 4.3; N, 13.6. Found: C, 44.9; H, 4.5; N, 13.5%.

$[Zn(L_{333})](ClO_4)_2$ (**6**). Yield 0.36 g (50%). Anal. Calc. for $C_{27}H_{33}N_7Cl_2O_8Zn$; C, 45.0; H, 4.6; N, 13.1. Found: C, 44.9; H, 4.5; N, 13.0%. ^1H NMR (500 MHz, CD_3CN) δ: 1.87 (m, 6H,

Table 1
IR data (cm^{-1}) for the new ligands and related complexes

Compound[a]	ν (C=N)[b]	ν (C=N)[c]	ν (C=C)[c,d]
L_{333}	1650	1589	1568
(**1**)	1654	1595	1568
(**2**)	1615	1590	1556
(**3**)	1642	1598	1568
(**4**)	1652	1600	1570
(**5**)	1651	1598	1570
(**6**)	1653	1595	1568
(**7**)	1660	1594	1569

[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.