Polyhedron 27 (2008) 3549–3556

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Cd(II) and Mn(II) complexes of a new hexadentate Schiff base ligand derived from an asymmetric tripodal tetraamine and 2-pyridinecarboxaldehyde

Sadegh Salehzadeh [a,*], Reza Golbedaghi [a], Ian S. Tidmarsh [b], Nawal K. Al-Rasbi [b], Harry Adams [b], Michael D. Ward [b]

[a] Faculty of Chemistry, Bu-Ali Sina University, Hamedan, Iran
[b] Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK

ARTICLE INFO

Article history:
Received 16 June 2008
Accepted 21 August 2008
Available online 6 October 2008

Keywords:
Template condensation
Tripodal Schiff base ligands
Cadmium complex
Manganese complex
Ab initio

ABSTRACT

Two new compounds, $[CdL_{22pyfp}(NO_3)](ClO_4)$ (**1**) and $[MnL_{22pyfp}Cl](ClO_4)$ (**2**), were prepared by the template condensation of a previously known ligand, (L_{22py}), and 2-pyridinecarboxaldehyde in the presence of $Cd(NO_3)_2 \cdot 4H_2O$ or $MnCl_2 \cdot 4H_2O$ in equimolar ratios. The resulting compounds were characterized by elemental analysis, IR and single crystal X-ray diffraction, and by NMR in the case of the Cd(II) complex. The Cd(II) ion is in an eight-coordinate environment that is best described as a distorted dodecahedron. The environment around the Mn(II) ion may be described as a distorted pentagonal bipyramid. The ^1H NMR spectrum of the cadmium complex shows the signal of the imine proton to have two satellites ($^3J = 44.4$ Hz) with intensities of 1:6:1 due to coupling with the neighboring $^{111/113}Cd$ atom. The electronic spectra of both complexes, as well as the ligand, is explained on the basis of TD-DFT calculations.

1. Introduction

Schiff base complexes are considered to be among the most important stereochemical models in main group and transition metal coordination chemistry due to their preparative accessibility and structural variety [1,2]. They have played a key role in the development of coordination chemistry, resulting in an enormous number of publications, ranging from pure synthetic work to modern physicochemical and biochemically relevant studies of metal complexes [3]. Recent interest in the design, synthesis and characterization of dissymmetrical Schiff base ligands derived from the appropriate amines for transition metal ion complexes has come from the realization that the coordinated ligands around the central metal ions in natural systems are unsymmetrical [4]. We have been involved in the synthesis of new tripodal tetraamines [5–11], their macrocyclic [6,7] and macroacyclic [8–10] Schiff base complexes, the determination of their stability constants [12] and theoretical studies on their gas phase proton affinities [13,14]. In addition, we have been interested in the ^1H NMR of Cd(II) Schiff base complexes [5,10]. We have recently reported the synthesis and characterization of a number of Cd(II) [5,8,10,11] and Mn(II) [10,11] Schiff base complexes. Herein we report the synthesis and characterization of Cd(II) and Mn(II) complexes with an asymmetric tripodal Schiff base ligand derived from the previously known ligand L_{22py} and 2-pyridinecarboxaldehyde. The resulting complexes were characterized by elemental analysis, IR and single crystal X-ray diffraction and by NMR in the case of the Cd(II) complex.

2. Experimental

2.1. General information

2-Pyridinecarboxaldehyde and the metal salts were obtained from Merck and were used without further purification. The asymmetrical tripodal ligand $N(CH_2CH_2)_2(CH_2C_5H_4N)$ as its hydrochloride salt, $L_{22py} \cdot 3HCl$, was prepared by a literature method [5]. IR and NMR spectra were measured on a Perkin Elmer FT-IRGX and a Bruker DPX 300 spectrometer, respectively.

2.2. X-ray crystal structure determination

All structural determinations were carried out using a Bruker SMART-1000 CCD diffractometer equipped with Mo Kα X-radiation. In all cases, absorption corrections were applied using SADABS, [15] and the structure solution and refinement were carried out using SHELXS-97 and SHELXL-97, respectively [16,17]. The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2. Hydrogen atoms were placed geometrically and refined with a riding model and with U constrained to be 1.2 (1.5 for methyl groups) times U of the carrier atom. The parameters of the crystal structures, data collections, solutions and refinements are given in Table 1.

---

* Corresponding author. Fax: +98 811 8257407.
E-mail addresses: saleh@basu.ac.ir, ssalehzadeh@gmail.com (S. Salehzadeh).

0277-5387/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2008.08.019

2.3. Computational method

The geometry of the resulting complexes $[Mn(L_{22pyfp})Cl]^+$ and $[Cd(L_{22pyfp})NO_3]^+$ in the gas phase were fully optimized at both the Hartree–Fock and DFT (B3LYP) [18] levels of theory using the GAUSSIAN 98 set of program (Figs. 1 and 2) [19]. The atomic coordinates of the complexes in their crystal structures were used for ab initio calculations. Both complexes were optimized using the standard LanL2MB [20] for all atoms, or 3-21G* and/or 6-31G* basis sets [21,22] for ligand atoms, and LanL2DZ for the metal ions [23]. The optimized structures of the ligands of both complexes were used for molecular orbital analysis and time-dependent DFT (TD-DFT) calculations at the B3LYP/LanL2MB level of theory. Calculations were performed on a Pentium-PC computer with a 4400 MHz processor.

2.4. Synthesis

2.4.1. Synthesis of $[Cd(L_{22pyfp})NO_3](ClO_4) \cdot H_2O$ (**1**)

This complex was prepared by the template condensation method [5]. L_{22py}.3HCl (0.1 g, 0.33 mmol) and NaOH (0.039 g, 0.99 mmol) were mixed and heated under reflux for 30 min in EtOH (15 ml). The NaCl which formed upon cooling was filtered off. The filtrate was added to 2-pyridinecarboxaldehyde (0.07 g, 0.66 mmol) in dry EtOH (40 ml) and the solution was stirred. $Cd(NO_3)_2 \cdot 4H_2O$ (0.1 g, 0.33 mmol) dissolved in MeOH (5 ml) was subsequently added. The mixture was stirred at 50–60 °C for 24 h, then $NaClO_4$ (0.92 g, 0.66 mmol) was added. The solution was filtered and the filtrate was reduced to ca. 10 cm^3. A crystalline compound was obtained by slow diffusion of Et_2O vapor into this solution. Yield of the complex $[Cd(L_{22pyfp})NO_3](ClO_4) \cdot H_2O$ (**1**), 0.15 g, 75%. *Anal.* Calc. for ($C_{22}H_{26}CdClN_7O_8$): C, 39.77; H, 3.92; N, 14.75. Found: C, 39.21; H, 3.65; N, 14.17%. IR (KBr, cm^{-1}): 1667 (νC=N schiff base), 1591 (νC=N pyridine), 1568 (νC=C), 1081. ^{1}H NMR (DMSO, ppm, 300 MHz, py = pyridine): δ 2.76 (m, 2H, 1-Hα), 3.12 (m, 2H, 1-H$_\beta$), 3.95 (4H, t, 2-H), 4.24 (s, 2H, CH_2-Py), 7.37 (t, 1H), 7.57 (d, 1H), 7.84 (t, 2H) 7.96 (t, 1H), 8.01 (d, 2H), 8.26 (m, 5H) 8.82 (s, 2H, with two satellite peaks in the ratio 1:6:1 relative to the main signal $^3J(^{111/113}Cd-^1H) = 44.53$ Hz). ^{1}H COSY (DMSO, 300 MHz) δ: 2.76/312 (1-Hα/1-H$_\beta$), 2.76/3.95 (1-Hα/2-Hα), 2.76/3.95 (1-Hα/2-H$_\beta$), 312/3.95 (1-H$_\beta$/2-H$_\alpha$), 312/3.95 (1-H$_\beta$/2-H$_\beta$), ^{13}C NMR (DMSO, ppm, 300 MHz): δ 53.83 (C-1), 54.69 (C-2), 57.66 (C-3), 124.53 (C-8), 125.50 (C-6), 129.28 (C-9 and C-5), 140.17 (C-7), 141.06 (C-13), 147.43 (C-11), 149.39 (C-12), 150.04 (C-10), 156.95 (C-14), 162.47 (C-4).

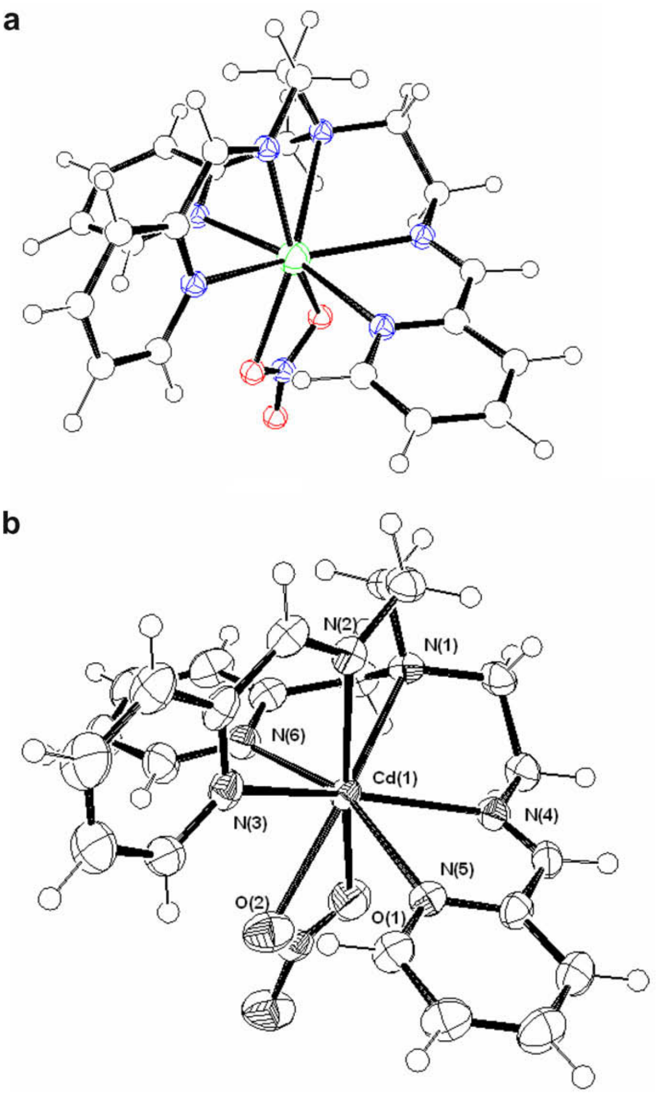

Fig. 1. DFT optimized (a) and crystal structure (b) of compound **1**. The perchlorate anion and solvated H_2O are omitted for clarity.

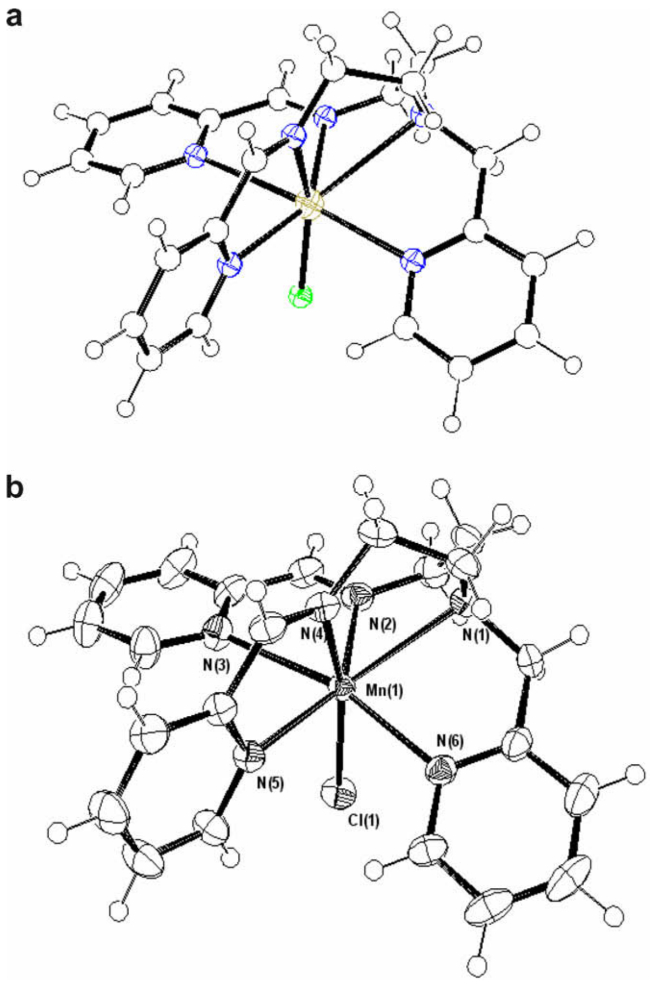

Fig. 2. RHF optimized (a) and crystal structure (b) of compound **2**. The perchlorate anion and solvated MeOH are omitted for clarity.

2.4.2. Synthesis of $[Mn(L_{22pyfp})Cl](ClO_4) \cdot MeOH$ (**2**)

Compound **2** was prepared in an analogous method to **1**. $L_{22py} \cdot 3HCl$ (0.1 g, 0.33 mmol) and NaOH (0.039 g, 0.99 mmol)