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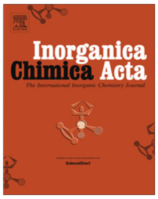

Synthesis and characterization of new Mn(II) and Cd(II) Schiff base complexes containing homopiperazine moiety: Spectral, X-ray crystal structural and theoretical studies

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ABSTRACT

Two new symmetrical Mn(II) and Cd(II) pentaaza macrocyclic Schiff base complexes were prepared via templated [1 + 1] cyclocondensation of 2,6 diacetylpyridine and an amine containing homopiperazine moiety in the presence of related metal ions. These complexes have been characterized by elemental analysis, IR spectra, EI-MS, conductivity measurements and in the case of Cd(II) complex by ^1H and ^{13}C NMR spectroscopy. In addition, Crystal structures of complexes have been determined by X-ray crystallographic technique. This reveals that in the solid state both complexes adopt a distorted pentagonal pyramidal geometry, with the pentaaza macrocycle positioned in the equatorial plane and the chloride ion in the axial site. Also, the bonding situation between the $[MCl]^+$ ($M = Mn^{2+}$, Cd^{2+}) fragment and Ligand (L) in $[MLCl]^+$ (M = Mn, Cd) complexes, were carried out by NBO and energy-decomposition analysis (EDA), as well as its natural orbitals for chemical valence variation (EDA-NOCV). The results confirmed that the contribution of the electrostatic interactions in the $M \leftarrow L$ bonds of the complexes is predominantly more than 50%.

1. Introduction

The macrocyclic chemistry of metals is developing very rapidly because of its applications [1,2] and importance in the area of coordination chemistry [3] Schiff base macrocycles were among the first artificial metal macrocyclic complexes to be synthesized [4]. Studies on Schiff base macrocyclic complexes with different size, number and donor atoms for coordination with a variety of metal centers have been published [5–7]. These macrocyclic complexes have potential applications in a variety of areas such as stabilization of unusual oxidation states [8], magnetic resonance imaging contrast enhancing agents [9,10], sensor technology [11–13], catalysts [14–16] and models for biological structures and functions [17–19].

Diimine [1 + 1] Schiff base macrocyles have generally been prepared via the cyclocondensation of the appropriate dicarbonyl and diamine precursors using metal template reactions [20–22]. We have been interested for some times in the synthesis of Schiff base macrocyclic ligands and related complexes from metal ion templated [1 + 1] cyclocondensation of 2,6-diacetylpyridine or 2,6-diformylpyridine and various polyamines [5,23,24]. Since 2008, we have been interested to work on synthesis of Schiff base macrocyclic complexes having piperazine moiety [25–33]. Recently we have synthesised new macrocyclic schiff base complexes using dialdehyde containing homopiperazine and different diamines [34].

The present work, describes the Mn(II) and Cd(II) templated [1 + 1] cyclocondensation of 2,6-diacetylpyridine with a linear tetraamines having a homopiperazine moiety, paying special attention to their X-ray crystal structures, spectral and theoretical studies.

2. Experimental

2.1. Starting materials

1,4-Bis(3-aminopropyl)-l,4-diazacycloheptane was prepared according to the literature procedure [35]. Solvents, 2,6-diacetylpyridine, and metal salts were purchased from Merck and were used without further purification.

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Caution! Perchlorate salts are potentially explosive. Only small amount of material should be prepared and handled with great care

2.2. Physical measurements

Infrared spectra were collected using KBr pellets on a BIO-RAD FTS-40A spectrophotometer (4000–400 cm^{-1}). CHN analyses were carried out using a Perkin-Elmer, CHNS/O elemental analyzer model 2400 series 2. Conductance measurements were performed using a Hanna HI 8820 conductivity meter. ^1H and ^{13}C NMR spectra were taken in DMSO-d_6 on a Bruker Avance 400 MHz spectrometer using $Si(CH_3)_4$ as an internal standard. Mass spectra were recorded on an Agilent technologies (HP) 5973 mass spectrometer operating at an ionization potential of 70 eV.

2.3. X-ray crystallography

The brown crystals of $[MnLCl]ClO_4$ and yellow crystals of $[CdLCl]ClO_4$ were grown by the slow evaporation of a 3:1 methanol/acetonitrile solution of the complex. X-ray data for complexes were collected on a STOE IPDS-II diffractometer with graphite monochromated Mo Kα radiation. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of diffraction data. Data were collected at a temperature of 298(2) in a series of ω scans in 1° oscillations and integrated using the Stoe X-AREA [36] software package. A numerical absorption correction was applied using the X-RED [37] and X-SHAPE [37] software's. The data were corrected for Lorentz and Polarizing effects. The structures were solved by direct methods using SIR2004 [38]. The non-hydrogen atoms were refined anisotropically by the full matrix least squares method on F^2 using SHELXL [39]. All hydrogen atoms were added at ideal positions and constrained to ride on their parent atoms. Crystallographic data for complexes are listed in Table 1. Selected bond distances and angles are summarized in Table 3.

2.4. Computational methods

The geometries of the compounds have been optimized without symmetry constraints at the BP86 [40,41]/def2-SVP [42] level of theory using the GAUSSIAN 03 [43] in conjunction with Turbomole 5 [44] energies and gradients. Vibrational frequency analyses, 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 geometry of [CdLCl] ClO_4 and $[MnLCl]ClO_4$ complexes, as determined by the X-ray crystal structure analysis (see Figs. 2 and 3), was fully optimized at above mentioned level of theory. We considered both high spin d^5 (sextet spin multiplicity) and low spin d^5 (doublet spin multiplicity) for Mn(II) complexes. The result show that the stability of high spin Mn(II)complex is about 14.6 kcal mol^{-1} more than corresponding low spin complex. Thus further calculations including structural analysis, NBO and EDA analyses was done on high spin complex of Mn(II). The bonding analyses in the terms of energy-decomposition analysis, were carried out at BP86/TZP(ZORA)// BP86/def2-SVP with C_1 symmetry. The basis sets for all elements have triple-ζ quality augmented by one set of polarization functions (ADF basis set TZP(ZORA)) with the program package ADF2009.01. EDA calculations were carried out in order to analyze the nature of the bonding. In the EDA, bond formation between the interacting fragments is divided into three steps, which can be interpreted in a plausible way. In the first step, the fragments, which are calculated with the frozen geometry of the entire molecule, are superimposed without electronic relaxation to yield the quasiclassical electrostatic attraction ΔE_{elstat}. In the second step,

Table 1
Crystal data and structure refinement for $[MnLCl]ClO_4$and $[CdLCl]ClO_4$ complexes.

	$[MnLCl]ClO_4$	$[CdLCl]ClO_4$
Formula	$C_{20}H_{31}Cl_2MnN_5O_5$	$C_{20}H_{31}CdCl_2N_5O_4$
Identification code	*m+p21c*	*m+p21c*
Formula weight	547.34	588.80
T (K)	298(2)	298(2)
λ (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
space group	$P2(1)/c$	$P2(1)/c$
Unit cell dimensions		
a (Å)	14.146(3)	10.946(2)
b (Å)	14.461(3)	25.744(5)
c (Å)	13.696(3)	8.6893(17)
α (°)	90(3)	90
β (°)	112.60(3)	95.33(3)
γ (°)	90(3)	90
V ($Å^3$)	2586.6(11)	2438.0(8)
Z	4	4
Calculated density ($Mg/m^{-3)}$	1.406	1.604
Absorption coefficient (mm^{-1})	0.756	1.151
$F(000)$	1140	1200
θ (°)	2.82–26.00	2.84–29.16
Limiting indices	$-17 \leqslant h \leqslant 17$, $-16 \leqslant k \leqslant 17$, $-15 \leqslant l \leqslant 16$	$0 \leqslant h \leqslant 14$, $-35 \leqslant k \leqslant 0$, $-11 \leqslant l \leqslant 11$
Reflections collected/unique [$R_{(int)}$]	14758/5071(0.0386)	6540/6540(0.0412)
Completeness to θ = 25.00 (%)	99.8	99.5
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5071/0/309	6540/0/291
Goodness-of-fit on F^2	0.923	0.882
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0664$, $wR_2 = 0.1975$	$R_1 = 0.0397$, $wR_2 = 0.1111$
R indices (all data)	$R_1 = 0.0984$, $wR_2 = 0.2141$	$R_1 = 0.0570$, $wR_2 = 0.1154$
Largest diff. peak and hole (e $Å^{-3}$)	0.881 and −0.661	0.928 and −0.623

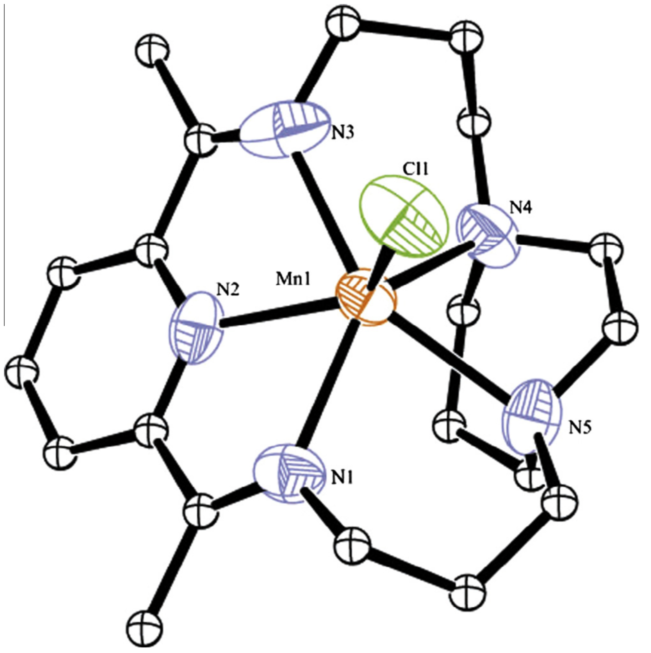

Fig. 1. ORTEP representation of $[MnLCl]ClO_4$. Displacement ellipsoids are drawn at the 50% probability level. The H atoms and counter ion (ClO_4) is omitted for clarity.