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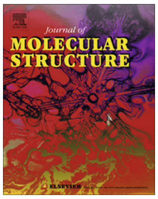

Synthesis, structure and characterization of two new Zn(II) and Cd(II) complexes with the bidentate ligand 2-[(2-aminoethyl)amino]ethanaminium (AEEA)

Wijdene Nbili [a], Matthias Zeller [b], Frédéric Lefebvre [c], Cherif Ben Nasr [a,*]

[a] Laboratoire de Chimie des Matériaux, Faculté des Sciences de Bizerte, 7021 Zarzouna, Tunisia
[b] Youngstown State University, Department of Chemistry, One University Plaza, Youngstown, OH 44555-3663, USA
[c] Laboratoire de Chimie Organometallique de Surface (LCOMS), Ecole Superieure de Chimie Physique Electronique, 69622 Villeurbanne Cedex, France

HIGHLIGHTS

- Two new Zn(II) and Cd(II) complexes with the bidentate ligand 2-[(2-aminoethyl)amino]ethanaminium were synthesized.
- The crystal structure of (1) is described by $ZnCl_2N_2$ tetrahedra.
- In (2), the CdN_2Cl_4 entities form polymeric chains of edge-sharing octahedra.
- The crystal packing stabilized by a set of hydrogen bonds.
- ^{13}C and ^{15}N CP–MAS NMR spectra are in good agreement with the X-ray data.

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ABSTRACT

Two new Zn(II) and Cd(II) complexes with the bidentate ligand 2-[(2-aminoethyl)amino]ethanaminium (AEEA), $[ZnCl_2(C_4H_{14}N_3)]ClO_4$ (**1**) and $[CdCl_2(C_4H_{14}N_3)]ClO_4$ (**2**), have been prepared and were characterized by single crystal X-ray diffraction, elemental analysis, CP–MAS-NMR and IR spectroscopies. The basic coordination patterns of the AEEA coordinated metal cations is highly distorted tetrahedral in (**1**) and distorted octahedral in (**2**). The crystal structure of (**1**) is characterized by $ZnCl_2N_2$ tetrahedra interconnected via N–H···Cl hydrogen bonds to form layers parallel to the (*b*, *a* + *c*) plane. In (**2**), the CdN_2Cl_4 entities form polymeric chains of edge-sharing octahedra extending along the *a*-axis direction. The crystal structures are stabilized by sets of hydrogen bonds, some of which are bi or trifurcated. The ^{13}C and ^{15}N CP–MAS NMR spectra are discussed and the vibrational absorption bands were identified by infrared spectroscopy.

Introduction

Design and fine tuning of ligands are an extremely important aspect of coordination chemistry. Variable bonding, such as the ligands' ability to coordinate to a metal atom in mono-, bi- or polydentate fashions, their ability to bridge between metal ions, or to steer the coordination environment of the central atom are what allows for the immense structural possibilities in metal coordination chemistry, which in turn is central to the extremely diverse use of metal complexes in all kinds of applications [1,2]. Among ligands commonly used in coordination chemistry, Schiff bases are an extremely important class, thanks to their facile synthesis, and their easily tunable steric and electronic properties [3,4]. They are known to be a class of versatile ligands, capable of generating a variety of molecular architectures and coordination polyhedra [5–7]. The metal complexes of such Schiff bases have been extensively used as biological probes [8], DNA cleaving agents [9], catalysts [10,11], sensing materials [12,13] and corrosion inhibitors [14]. In recent years, the coordination chemistry of N coordinated ligands has also received a lot of attention because of their relevance to biological systems [15].

As part of our continued involvement in the investigation of metal complexes of nitrogen containing ligands such as, e.g., Schiff bases [16], we report here the synthesis and characterization of two new Zn(II) and Cd(II) complexes with the bidentate ligand

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* Corresponding author.
E-mail address: cherif_bennasr@yahoo.fr (C. Ben Nasr).

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2-[(2-aminoethyl)amino]ethanaminium, AEEA. It is worth noticing that some compounds containing the same bidentate cationic ligand have been reported [17–19].

Experimental

Chemical preparation

All reagents used were of analytical grade and used without further purification. Perchlorate salts are potentially explosive and should only be handled with utmost care and only in small quantities.

*Preparation of [ZnCl$_2$(C$_4$H$_{14}$N$_3$)]ClO$_4$ (**1**)*

A solution of perchloric acid (28.70 mg, 0.2 mmol) in water (6 mL) was added dropwise to 10 mL of a solution of diethylenetriamine (20.63 mg, 0.2 mmol) in ethanol. Then, 6 mL of an aqueous solution of zinc chloride (27.2 mg, 0.2 mmol) was added, drop by drop, to this mixture. After stirring for 30 min, the mixture was filtered. Colorless crystals suitable for X-ray analysis were obtained after five days by slow evaporation of the filtrate at room temperature [44 mg (0.13 mmol), yield = 65%]. *Anal.* Calc.: C, 14.12; H, 4.11; N, 12.53. Found: C, 14.53; H, 4.26; N, 12.32%.

*Preparation of [CdCl$_2$(C$_4$H$_{14}$N$_3$)]ClO$_4$ (**2**)*

Compound (**2**) was prepared at room temperature by dropwise addition of perchloric acid (28.70 mg, 0.2 mmol) in water (6 mL) to a solution of diethylenetriamine (20.63 mg, 0.2 mmol) in ethanol (10 mL). To this mixture, was added, drop by drop, 6 mL of an aqueous solution of CdCl$_2$·5/2H$_2$O (45.672 mg, 0.2 mmol) under continuous stirring during 30 min. Then, the mixture was filtered. Colorless crystals suitable for X-ray analysis were obtained after one week by slow evaporation of the filtrate at room temperature [38 mg (0.10 mmol), yield = 50%]. *Anal.* Calc.: C, 12.40; H, 3.61; N, 10.85. Found: C, 10.46; H, 3.42; N, 10.58%.

Investigation techniques

The characterization of the investigated compounds was performed using X-ray diffraction, solid state NMR and IR spectroscopy techniques.

X-ray single crystal structural analysis

Single crystals were carefully selected under a microscope and mounted on a Mitegen micromesh mount with the help of a trace of mineral oil. X-ray diffraction data were collected at 100 K on a Bruker Smart APEX CCD area-detector diffractometer using the ω scan technique with Mo Kα radiation (λ = 0.7107 Å). Data were collected, the unit cells determined, and the data integrated and corrected for absorption and other systematic errors using the Apex2 suite of programs [20]. SHELXS-97 [21] was used to solve the structures using direct methods and SHELTXL6.14 [22], SHELXL2013 [23] and SHELXLE [24] were used for refinement. The drawings were made with Diamond [25]. Crystal data and experimental parameters used for the intensity data collection are summarized in Table 1.

NMR and IR measurements

The NMR spectra were recorded on a solid-state high-resolution Bruker DSX-300 spectrometer operating at 75.49 MHz for ^{13}C and 30.30 MHz for ^{15}N with a classical 4 mm probehead allowing spinning rates up to 10 kHz. ^{13}C and ^{15}N NMR chemical shifts are given relative to tetramethylsilane and liquid ammoniac, respectively (precision 0.5 ppm). The spectra were recorded by use of cross-polarization (CP) from protons (contact time 5 ms) and magic angle spinning (MAS). Before recording the spectrum it was checked that there was a sufficient delay between the scans allowing a full relaxation of the nuclei. The IR spectra were recorded in the range 4000–400 cm^{-1} with a "Perkin–Elmer FTIR" spectrophotometer 1000 using samples dispersed in spectroscopically pure KBr pressed into a pellet.

Table 1
Experimental details of compounds (**1**) and (**2**).

Complexes	**1**	**2**
Chemical formula	C$_4$H$_{14}$Cl$_2$N$_3$Zn·ClO$_4$	C$_4$H$_{14}$CdCl$_2$N$_3$·ClO$_4$
Crystal system, space group	Monoclinic, $P2_1/n$	Triclinic, $P\bar{1}$
M_r	339.90	386.93
Temperature (K)	100	100
a (Å)	10.5137 (13)	6.6302 (12)
b (Å)	10.0294 (12)	7.4573 (13)
c (Å)	11.5104 (14)	12.986 (2)
α (°)	90	75.934 (2)
β (°)	100.577 (2)	84.201 (2)
γ (°)	90	77.106 (2)
V (Å^3)	1193.1 (3)	606.37 (18)
Z	4	2
Radiation type	Mo Kα	Mo Kα
μ (mm^{-1})	2.73	2.46
Crystal size (mm)	0.27 × 0.26 × 0.23	0.42 × 0.15 × 0.08
Absorption correction	Multi-scan	Multi-scan
$T_{\min}$, $T_{\max}$	0.619, 0.746	0.551, 0.746
No. of measured reflections	14,291	11,503
No. of observed reflections [$I > 2\sigma(I)$]	3697	3634
No. of independent reflections	3574	3577
R_{int}	0.023	0.022
$(\sin\theta/\lambda)_{\max}$ (Å^{-1})	0.734	0.736
$R[F^2 > 2\sigma(F^2)]$, wR(F^2), S	0.020, 0.055, 1.07	0.017, 0.045, 1.08
No. of reflections	3697	3634
No. of parameters	146	148
No. of restraints	3	3
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.63, −0.33	0.70, −0.57

Results and discussion

X-ray diffraction study

*Structure description of [ZnCl$_2$(C$_4$H$_{14}$N$_3$)]ClO$_4$ (**1**)*

The main geometrical features of the different chemical entities of the coordination compound [ZnCl$_2$(C$_4$H$_{14}$N$_3$)]ClO$_4$ (**1**) are reported in Tables 2 and 3.

The asymmetric unit of (**1**) consists of one complex cation and one not coordinated interstitial perchlorate anion. The coordination geometry around the Zn(II) atom can be described as distorted tetrahedral. The Zn(II) center is tetracoordinated by two nitrogen atoms (N1 and N2) of the bidentate ligand 2-[(2-aminoethyl)amino]ethanaminium (AEEA) and two chloride ligands (Cl1 and Cl2) (Fig. 1). The Zn(II) ion is tetracoordinated by two nitrogen atoms (N1 and N2) of the AEEA ligand and two chlorine atoms (Cl1 and Cl2). The detailed geometry of the ZnCl$_2$N$_2$ tetrahedron

Table 2
Selected bond distances and angles (Å,°) in [ZnCl$_2$(C$_4$H$_{14}$N$_3$)]ClO$_4$.

ZnCl$_2$N$_2$					
Zn–N1	2.0216(10)	N1–Zn–N2	86.90(4)	N1–Zn–Cl1	113.23(3)
Zn–N2	2.0849(9)	N1–Zn–Cl2	128.06(3)	N2–Zn–Cl1	108.10(3)
Zn–Cl2	2.2393(4	N2–Zn–Cl2	110.39(3)	Cl2–Zn–Cl1	107.123(12)
Zn–Cl1	2.2520(4)				
ClO$_4^-$					
Cl3–O3	1.4447(9)	O3–Cl3–O4	109.71(6)	O3–Cl3–O1	109.78(5)
Cl3–O4	1.4458(9)	O3–Cl3–O2	108.60(6)	O4–Cl3–O1	109.19(5)
Cl3–O2	1.4459(9)	O4–Cl3–O2	109.61(6)	O2–Cl3–O1	109.96(5)
Cl3–O1	1.4459(8)				