



Synthesis and physico-chemical studies of a novel noncentrosymmetric heptacoordinated cadmium(II) compound containing a tripodal amine, $\text{CdCl}_2[\text{N}(\text{C}_2\text{H}_6\text{N})_3]_2$

M. Ben Nasr^a, K. Kaabi^a, P. S. Pereira Silva^b, F. Lefebvre^c, C. Ben Nasr^{a*}

^aLaboratoire de Chimie des Matériaux, Faculté des Sciences de Bizerte, 7021 Zarzouna, Tunisie,

^bCEMDRX, Department of Physics, University of Coimbra, P-3004-516 Coimbra, Portugal.

^cLaboratoire de Chimie Organométallique de Surface (LCOMS), Ecole Supérieure de Chimie Physique Electronique, 69622 Villeurbanne Cedex, France.

* Corresponding author: cherif_bennasr@yahoo.fr

ABSTRACT

A new noncentrosymmetric Cd(II) complex with the tripodal amine tris(2-aminoethyl)amine, $\text{CdCl}_2[\text{N}(\text{C}_2\text{H}_6\text{N})_3]_2$, has been prepared and characterized by single crystal X-ray diffraction, solid state NMR and IR spectroscopies. In the complex, the Cd(II) ion is surrounded by seven nitrogen atoms. The organic molecule acts as both a tri- and a tetradentate ligand. The cationic complexes are linked to each other forming layers parallel to the (a, b) plane. The Cl⁻ counter ions occupy the cavities created inside these layers. The ¹³C CP-MAS NMR spectra are in agreement with the X-ray structure. DFT calculations allow the attribution of the carbon peaks to the different atoms. The vibrational absorption bands were identified by infrared spectroscopy and DFT calculations allowed their attributions.

Indexing terms/Keywords

X-ray diffraction; heptacoordinated cadmium complex; IR spectroscopy; CP-MAS NMR; DFT calculations.

Council for Innovative Research

Peer Review Research Publishing System

Journal: Journal of Advances in Chemistry

Vol. 10, No. 10

editorjaconline@gmail.com

www.cirjac.com



INTRODUCTION

Mono-, di- and polynuclear coordination compounds of cadmium(II) [1–6] are of great interest for the preparation of functional materials with specific electronic and optoelectronic properties [7, 8]. Recently, different cadmium(II) compounds with interesting molecular properties using multidentate N-donor Schiff bases in combination with halides/pseudohalides were isolated [9-13]. The coordination behaviors of Schiff bases [14, 15] are of great interest because of their ease of preparation, structural variety, varied denticities and subtle steric and/or electronic effects leading to complexes of different dimensionalities. Halides [16–19] and pseudohalides [20–23] are suitable terminal/bridging units which in combination with organic ligands result in different mono-, di-, or polynuclear coordination molecules and supramolecular entities. Cadmium(II) with its d^{10} configuration permits a wide range of symmetries and coordination numbers and reports on hexacoordinated cadmium(II) complexes are well documented [24-27]. However, heptacoordinated cadmium(II) complexes are scarce [28-30]. This work stems from our interest to build new molecular and crystalline architecture of cadmium(II) in combination with the tris(2-aminoethyl)amine as a Schiff base.

2. Experiment

2.1. Chemical preparation

An aqueous solution of CdCl_2 (0.19 g, 1 mmol) in water (10 mL) was added dropwise to a solution of tris(2-aminoethyl)amine (0.29 g, 2 mmol) in ethanol (10 mL). After stirring for 30 min, the resultant mixture was evaporated at room temperature. Crystals of the title compound, which remained stable under normal conditions of temperature and humidity, were isolated after several days and subjected to X-ray diffraction analysis (yield 52%).

2.2. Investigation techniques

2.2.1. X-ray diffraction

Single-crystal X-ray diffraction data were collected at room temperature on a Bruker APEX2 CCD area-detector diffractometer equipped with graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). The structure was solved by direct methods using SHELXS-97 [31] and refinement was performed on F^2 by full-matrix least-squares techniques using SHELXL 2013 [32]. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms isotropically. The drawings were made with Diamond [33]. The experimental conditions of data collection, the strategy followed for the structure determination and the final results are given in Table 1.

2.2.2. Infrared spectroscopy

The IR spectrum was recorded in the range $4000\text{-}400 \text{ cm}^{-1}$ on a “Nicolet 6700” spectrophotometer (resolution = 2 cm^{-1} , number of scans = 256).

2.2.3. DFT calculations

The infrared spectrum and the ^{13}C NMR chemical shifts were calculated with the Gaussian 09 software. For this purpose a molecule containing one Cd atom surrounded by one tetracoordinated $\text{N}(\text{CH}_2\text{-CH}_2\text{-NH}_2)_3$ organic cation and three $\text{N-CH}_2\text{-CH}_2\text{-N}(\text{CH}_3)_2$ groups mimicking the three cations linked by only one nitrogen was studied. All calculations were made with the B3LYP method. For all atoms the 6-31+G* basis was chosen except for cadmium for which the LanL2DZ pseudopotential was used. In all cases the positions of the atoms were those determined by the X-ray diffraction study except for the hydrogen atoms which were first optimized at the above level of theory. Indeed the positions determined by X-ray do not correspond to the location of the proton but to that of the barycenter of charges. The ^{13}C NMR chemical shifts were then calculated by use of the GIAO method. The infrared spectrum was also calculated and the absence of imaginary frequencies was checked.

Table 1. Experimental details of $[\text{CdCl}_2(\text{N}(\text{C}_2\text{H}_6\text{N})_3)_2]$.

Crystal data	
Chemical formula	$\text{C}_{12}\text{H}_{36}\text{CdN}_8 \cdot 2(\text{Cl})$
M_r	475.79
Crystal system, space group	Trigonal, $P31c$
Temperature (K)	293
a, c (Å)	7.9706 (2), 17.7771 (7)
V (Å ³)	978.08 (5)
Z	2
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	1.40
Crystal size (mm)	0.31 × 0.27 × 0.22
Data collection	
Diffractometer	Bruker APEX2 CCD area-detector diffractometer
Absorption correction	Multi-scan
T_{\min}, T_{\max}	0.631, 0.735
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18683, 1524, 1517
R_{int}	0.021
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.651
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.023, 0.063, 1.12
No. of reflections	1524
No. of parameters	70
No. of restraints	1
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.30, -0.57

3. Results and discussion

3.1. Structure description

The ortep view of the title noncentrosymmetric coordination compound, $\text{CdCl}_2[\text{N}(\text{C}_2\text{H}_6\text{N})_3]_2$ (Fig. 1), shows that the crystal structure contains four crystallographically independent nitrogen atoms. The N1, N2 and N4 atoms are coordinated to cadmium, while N3 is not coordinated. In the atomic arrangement, the distorted polyhedral Cd environment contains seven nitrogen atoms (Fig. 2) belonging to two independent ligands. The first ligand, having N3 as central nitrogen atom, is tricoordinated to the Cd(II) cation via N4, N4ⁱ and N4ⁱⁱ terminal nitrogen atoms (for symmetry code, see Table 2). The second ligand, containing the central nitrogen atom N1, is tetracoordinated to the cadmium atom via its four nitrogen atoms N1, N2, N2ⁱ and N2ⁱⁱ, (for symmetry code, see Table 2). Table 3 shows that the atoms Cd, N1, N3, Cl1 and Cl2 are located on special positions. In the atomic arrangement, the polyhedra are interconnected via the first ligand forming layers parallel to the (a, b) plane (Fig. 3).

Table 2. Selected bond distances and angles (\AA , $^\circ$) in $[\text{CdCl}_2(\text{N}(\text{C}_2\text{H}_6\text{N})_3)_2]$.

Cd1—N2	2.429 (3)	Cd1—N4	2.496 (3)
Cd1—N2 ⁱ	2.429 (3)	Cd1—N4 ⁱ	2.496 (2)
Cd1—N2 ⁱⁱ	2.429 (3)	Cd1—N1	2.684 (4)
Cd1—N4 ⁱⁱ	2.496 (2)	N2—Cd1—N4 ⁱ	79.70 (10)
N2—Cd1—N2 ⁱ	107.53 (7)	N2 ⁱ —Cd1—N4 ⁱ	166.75 (9)
N2—Cd1—N2 ⁱⁱ	107.53 (7)	N2 ⁱⁱ —Cd1—N4 ⁱ	79.97 (9)
N2 ⁱ —Cd1—N2 ⁱⁱ	107.53 (7)	N4 ⁱⁱ —Cd1—N4 ⁱ	90.93 (10)
N2—Cd1—N4 ⁱⁱ	79.97 (9)	N4—Cd1—N4 ⁱ	90.93 (10)
N2 ⁱ —Cd1—N4 ⁱⁱ	79.70 (10)	N2—Cd1—N1	68.65 (7)
N2 ⁱⁱ —Cd1—N4 ⁱⁱ	166.75 (9)	N2 ⁱ —Cd1—N1	68.65 (7)
N2—Cd1—N4	166.75 (9)	N2 ⁱⁱ —Cd1—N1	68.65 (7)
N2 ⁱ —Cd1—N4	79.97 (9)	N4 ⁱⁱ —Cd1—N1	124.60 (7)
N2 ⁱⁱ —Cd1—N4	79.70 (10)	N4—Cd1—N1	124.60 (7)
N4 ⁱⁱ —Cd1—N4	90.93 (10)	N4 ⁱ —Cd1—N1	124.60 (7)

Symmetry codes: (i) $-x+y, -x+1, z$, (ii) $-y+1, x-y+1, z$, (iii) $-x+y+1, -x+2, z$, (iv) $-y+2, x-y+1, z$.

Table 3. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2).

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cd1	0.3333	0.6667	0.100296 (13)	0.02455 (10)
N1	0.3333	0.6667	-0.0507 (2)	0.0232 (8)
N2	0.0157 (4)	0.4376 (4)	0.05054 (16)	0.0359 (5)
H2A	0.1138	0.4226	0.0586	0.043*
H2B	-0.0634	0.4205	0.0865	0.043*
N3	1.0000	1.0000	0.2733 (2)	0.0225 (7)
N4	0.6220 (4)	0.8739 (4)	0.18003 (16)	0.0349 (5)
H4A	0.6997	0.9919	0.1670	0.042*
H4B	0.5317	0.7969	0.1499	0.042*
C1	0.1424 (4)	0.5127 (4)	-0.07617 (17)	0.0300 (6)
H1A	0.1419	0.3909	-0.0784	0.036*
H1B	0.1176	0.5426	-0.1264	0.036*
C2	-0.0162 (4)	0.4921 (4)	-0.02389 (18)	0.0349 (7)
H2C	-0.0160	0.6138	-0.0211	0.042*
H2D	-0.1413	0.3938	-0.0429	0.042*
C3	0.8086 (4)	0.9562 (4)	0.30021 (16)	0.0271 (5)
H3A	0.8016	1.0742	0.2997	0.033*

H3B	0.7931	0.9117	0.3519	0.033*
C4	0.6434 (4)	0.8040 (5)	0.2537 (2)	0.0326 (6)
H4C	0.6642	0.6951	0.2463	0.039*
H4D	0.5237	0.7575	0.2816	0.039*
Cl1	0.6667	1.3333	0.19100 (9)	0.0362 (3)
Cl2	0.0000	1.0000	0.03650 (10)	0.0438 (3)

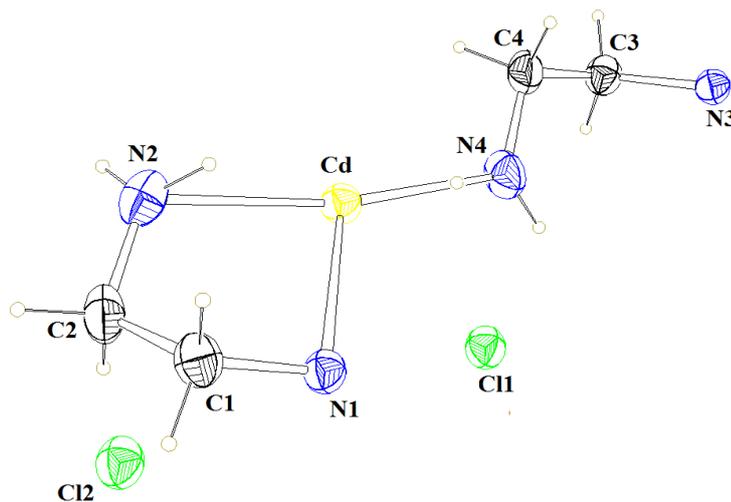


Figure 1. View of the local coordination of the Cd(II) cations in $\text{CdCl}_2[\text{N}(\text{C}_2\text{H}_6\text{N})_3]_2$ showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Inside each layer, the Cl^- counter ions occupy the created cavities and connect the metal complexes by a set of N-H...Cl hydrogen bonds (Fig. 4, Table 4). It is worth noticing that the hydrogen atoms (H1A and H1B), linked to the N1 nitrogen atom, and the Cl2 chlorine atom are not involved in hydrogen bondings (Table 4) while all hydrogen atoms attached to the N2 and N4 nitrogen atoms are hydrogen bonded to Cl1 chlorine atoms.

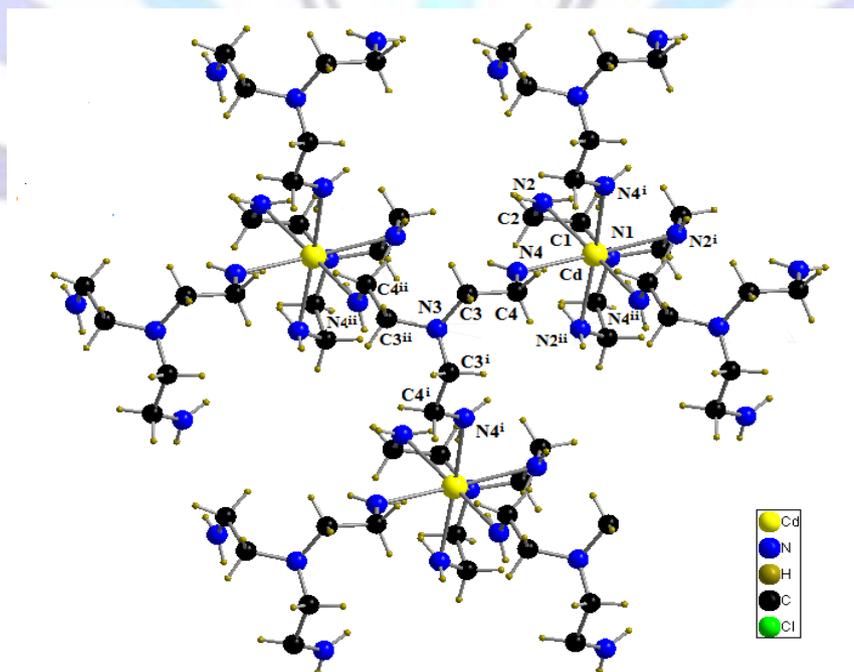
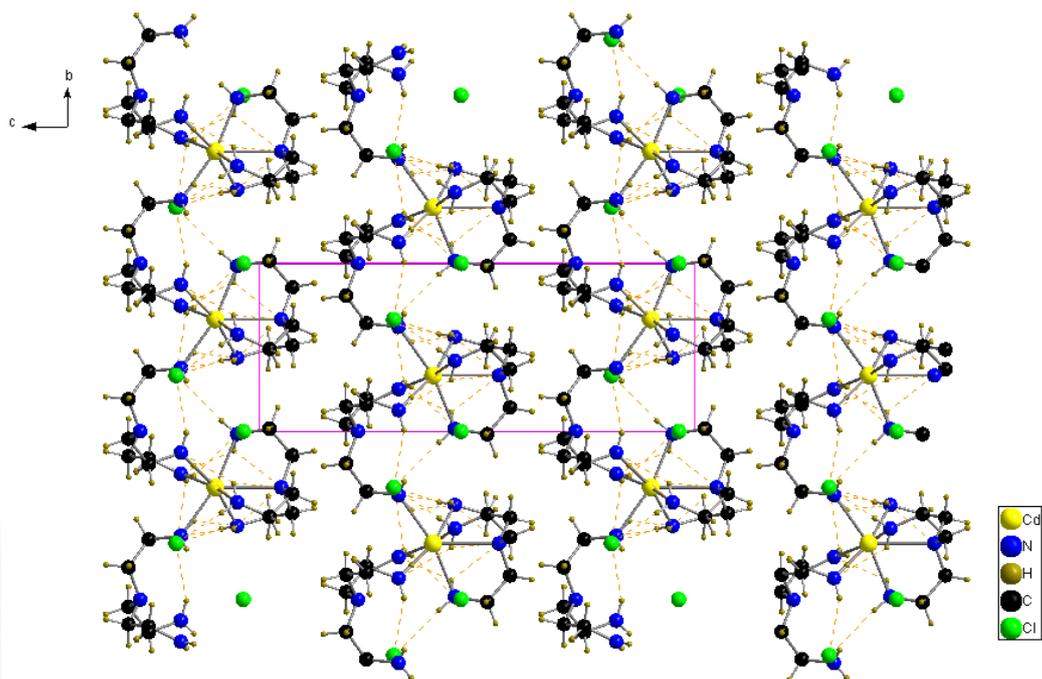
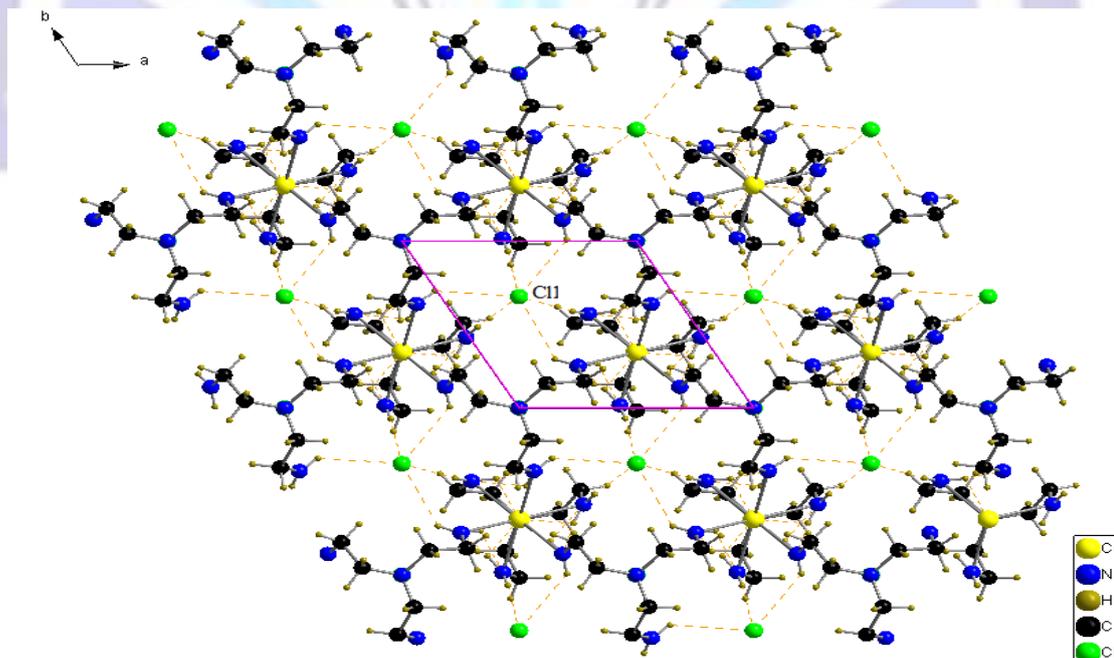


Figure 2. Coordination environment of the Cd(II) atom with atomic labels in $\text{CdCl}_2[\text{N}(\text{C}_2\text{H}_6\text{N})_3]_2$.

Table 4. Hydrogen-bond geometry (Å, °) in [CdCl₂(N(C₂H₆N)₃)₂].

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H2 <i>A</i> ...N4 ⁱ	0.86	2.53	3.157 (4)	131
N2—H2 <i>B</i> ...Cl1 ^v	0.86	2.66	3.515 (3)	174
N4—H4 <i>A</i> ...Cl1	0.86	2.89	3.503 (3)	129
N4—H4 <i>B</i> ...N2 ⁱⁱ	0.86	2.58	3.157 (4)	126

 Symmetry codes: (i) $-x+y, -x+1, z$; (ii) $-y+1, x-y+1, z$; (v) $x-1, y-1, z$.

Figure 3. View of CdCl₂[N(C₂H₆N)₃]₂ along the a axis. The dotted lines indicate hydrogen bonds.

Figure 4. View of a layer in CdCl₂[N(C₂H₆N)₃]₂. The dotted lines indicate hydrogen bonds.

3.2. NMR results

The ^{13}C CP-MAS NMR spectrum of $\text{CdCl}_2[\text{N}(\text{C}_2\text{H}_6\text{N})_3]_2$ is shown in Fig. 5. It exhibits four broad and asymmetric resonances corresponding to the four crystallographically independent carbon atoms. The observed asymmetry and broadening of the lines are caused by the ^{13}C - ^{14}N dipolar coupling perturbed by the ^{14}N quadrupole interaction. This phenomenon is usually observed in the ^{13}C spectra of carbon atoms bonded to nitrogen atoms in organic compounds [34].

Theoretical calculations were undertaken in order to assign the NMR resonances to the different crystallographically independent carbon atoms of the unit cell. The theoretical chemical shifts were subtracted from those of the reference (tetramethylsilane) calculated at the same level of theory. The results are listed on Table 5 and show a very good agreement between theory and experiment.

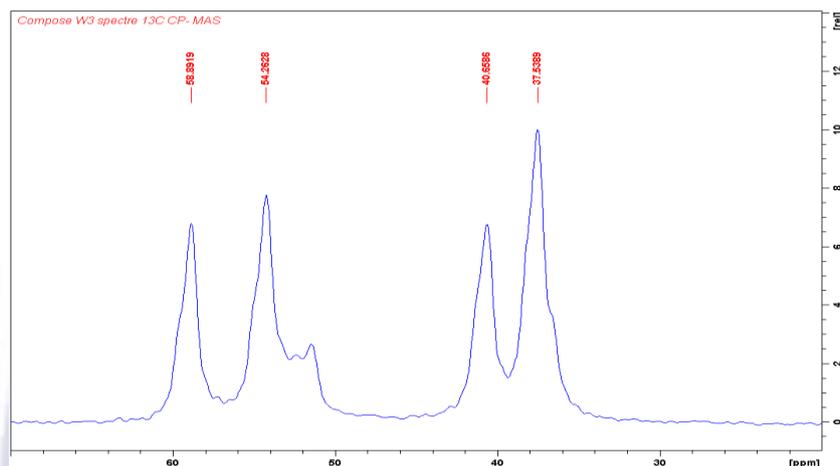


Figure 5. ^{13}C CP-MAS NMR spectrum of $\text{CdCl}_2[\text{N}(\text{C}_2\text{H}_6\text{N})_3]_2$.

Table 5. Comparison of calculated and experimental chemical shift values of the carbon atoms in $\text{CdCl}_2[\text{N}(\text{C}_2\text{H}_6\text{N})_3]_2$.

Atoms	C1	C2	C3	C4
Theory	38.4	53.7	43.4	65.4
	38.5	53.9	43.5	65.7
	38.5	53.9	43.5	65.4
Experiment	37.5	54.2	40.7	59

3.2 IR absorption spectroscopy

FTIR spectroscopy was used to verify the functional groups present in the crystal and their vibrational behavior in the solid state. Hydrogen bonding interactions are able to affect both frequency as well as intensity and width of the vibrations. The IR spectrum of crystalline $\text{CdCl}_2[\text{N}(\text{C}_2\text{H}_6\text{N})_3]_2$ is shown in Figure 6. The characteristic vibrational modes of the compound can be compared to those of similar materials [35-37]. In the high-frequency region, the stretching vibrations of the amino groups can be found. Hydrogen bonding interactions are able to affect frequency as well as intensity and width of these vibrations. The bands observed at (3442 - 3154 cm^{-1}) can be assigned to the asymmetric and symmetric stretching modes of the NH_2 group, respectively. The bands between 2963 and 2807 cm^{-1} can be attributed to the stretching vibrations of the CH_2 alkyl groups [38]. The adjacent carbon atoms attached to the CH_2 groups were also involved in the wagging, twisting and rocking modes of these groups. This induces a coupling between the adjacent CH_2 groups. The bands observed at (1400 - 1317 cm^{-1}) can thus be assigned to wagging modes and those observed at (1287 - 1107 cm^{-1}) to the CH_2 twisting modes and to the C-N and C-C stretching vibrations. Finally, those observed at 1065 - 743 cm^{-1} correspond to the CH_2 rocking modes [39].

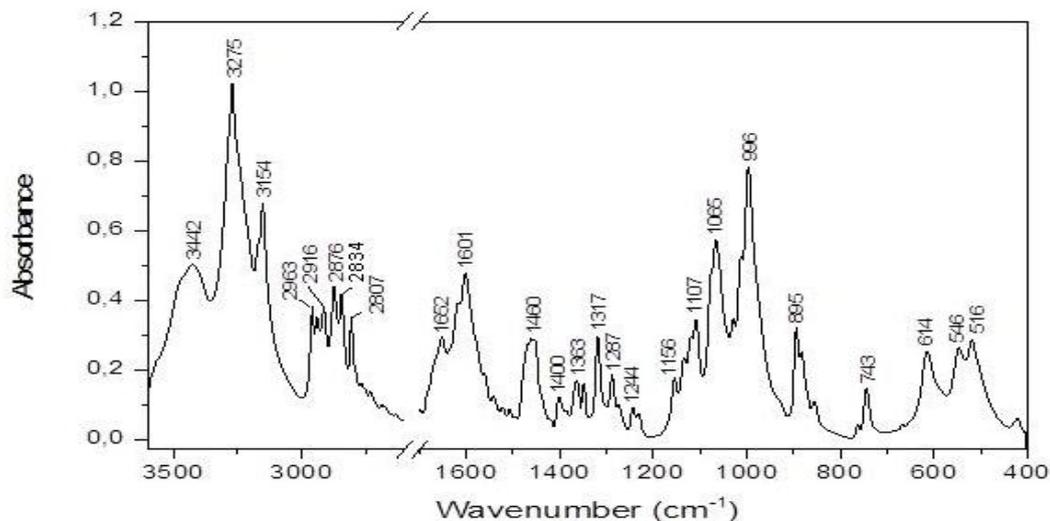


Figure 6. Infrared absorption spectrum of $\text{CdCl}_2[\text{N}(\text{C}_2\text{H}_6\text{N})_3]_2$.

DFT calculations showed that the inorganic entities lead to vibrations below 500 cm^{-1} which are not observed experimentally in our conditions. So we focused only on the vibrations of the organic cation. X-ray diffraction data give C-H or N-H distances which are too small compared to what is usually observed (typically below 0.1 nm) due to the fact that this method is not sensitive to the nuclei but to the electrons and so gives values corresponding to distances between the barycenters of electronic charges. As a consequence the positions of protons were first optimized, the Cd, C and N atoms being located at the positions given by the X-ray study. The resulting C-H and N-H distances corresponded to what is usually obtained (typically 0.109 nm for C-H and 0.104 nm for N-H) and the frequencies calculation was made on the semi-optimized geometry. The resulting IR spectra, calculated by the same method than the NMR chemical shifts, are shown on Figure 7 and is very similar to the experimental spectrum allowing a good correlation between the experimental and theoretical data as shown on Figure 8. Thus, the precision is well-sufficient to assign the experimental frequencies and to confirm the attributions proposed above.

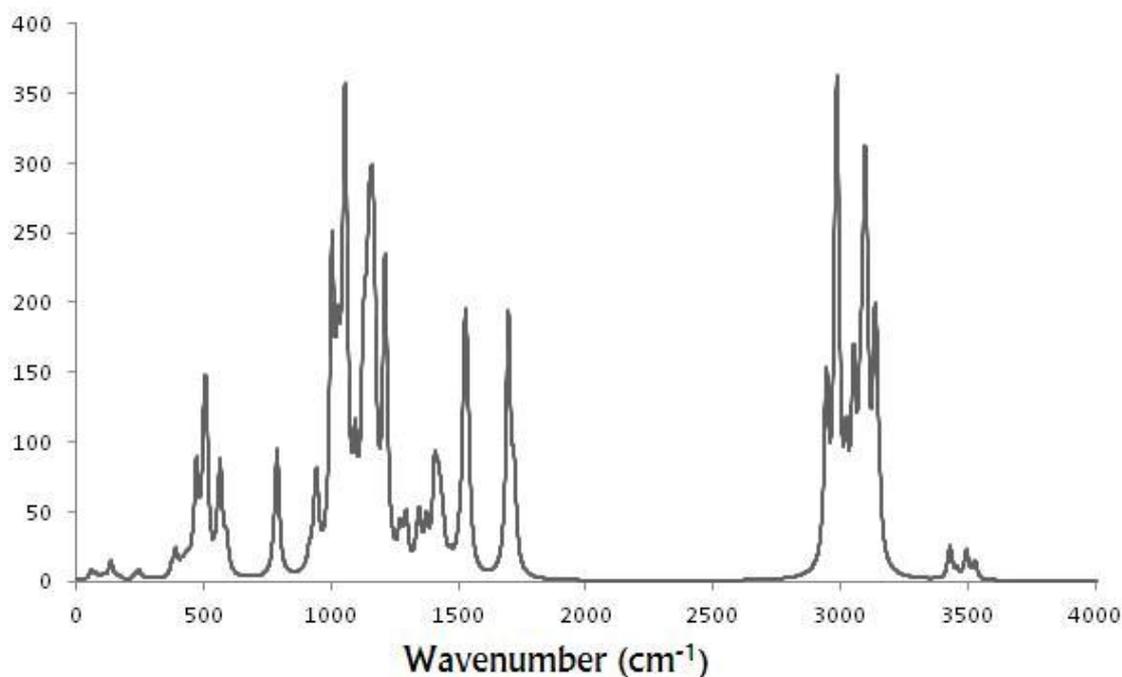


Figure 7. Calculated IR absorption spectrum of $\text{CdCl}_2[\text{N}(\text{C}_2\text{H}_6\text{N})_3]_2$.

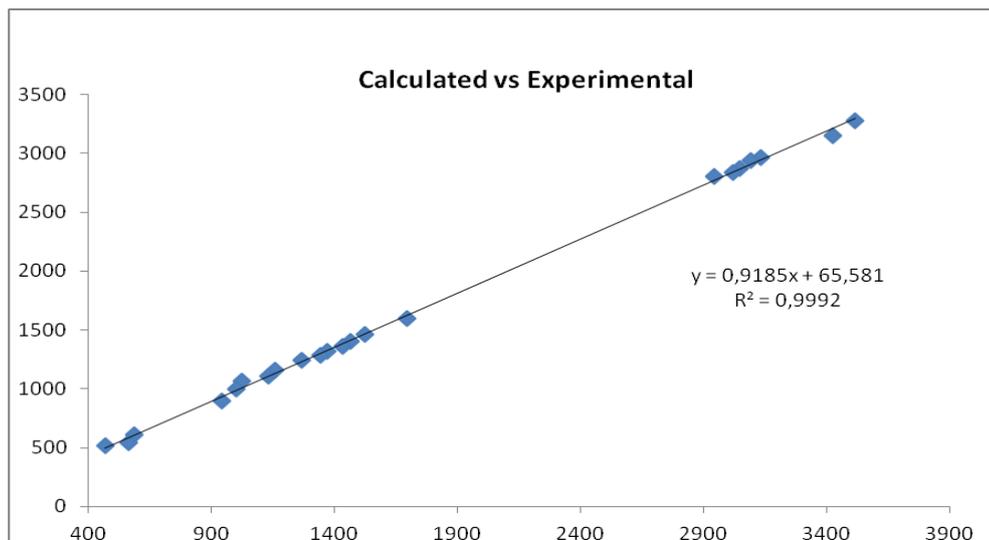


Figure. 8 Comparison between experimental and calculated IR frequencies of $\text{CdCl}_2[\text{N}(\text{C}_2\text{H}_6\text{N})_3]_2$.

4. Conclusions

In the crystal structure of the complex, the Cd(II) ion is heptacoordinated to seven nitrogen atoms belonging to two crystallographically independent tris(2-aminoethyl)amine ligands. One of them acts as a tetradentate while the other is a tridentate ligand. The cationic complexes are linked to each other forming layers parallel to the (a, b) plane. The Cl⁻ counter ions occupy the cavities created inside these layers. The crystal packing is stabilized by N-H...N and N-H...Cl hydrogen bonds. The vibrational properties of this structure were studied by infrared spectroscopy. The number of ¹³C CP-MAS NMR lines is in full agreement with the crystallographic data.

Acknowledgements

We would like to acknowledge the support provided by the Secretary of State for Scientific Research and Technology of Tunisia.

Supplementary data

CCDC 1034564 contains the supplementary crystallographic data for the title complex. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: (+44) 01223-336-033; e-mail: deposit@ccdc.cam.ac.

References

- [1] H. Zhang, X. Wang, K. Zhang, B.K. Teo, *Coord. Chem. Rev.* 183 (1999) 157.
- [2] Q.-G. Zhai, X.-Y. Wu, S.-M. Chen, C.-Z. Lu, W.-B. Yang, *Cryst. Growth Des.* 6(2006) 2126.
- [3] H. Deng, Y.-C. Qiu, Y.-H. Li, Z.-H. Liu, R.-H. Zeng, M. Zeller, S.R. Batten, *Chem. Commun.* (2008) 2239.
- [4] P. Cui, Z. Chen, D. Gao, B. Zhao, W. Shi, P. Cheng, *Cryst. Growth Des.* 10 (2010) 4370.
- [5] J. Yang, B. Wu, F. Zhuge, J. Liang, C. Jia, Y.-Y. Wang, N. Tang, X.-J. Yang, Q.-Z. Shi, *Cryst. Growth Des.* 10 (2010) 2331.
- [6] G. Wei, Y.-F. Shen, Y.-R. Li, X.-C. Huang, *Inorg. Chem.* 49 (2010) 9191.
- [7] V. Balzani, A. Credi, M. Venturi, *Molecular Devices and Machines*, Wiley-VCH, Weinheim, 2003.
- [8] M. Petty, *Molecular Electronics: From Principles to Practice*, Wiley, Chichester, 2008.
- [9] S.H. Rahaman, R. Ghosh, G. Mostafa, B.K. Ghosh, *Inorg. Chem. Commun.* 8(2005) 700.
- [10] S.H. Rahaman, D. Bose, R. Ghosh, G. Mostafa, H.-K. Fun, B.K. Ghosh, *Struct. Chem.* 18 (2007) 237.
- [11] H. Chowdhury, S.H. Rahaman, S.K. Sarkar, H.-K. Fun, B.K. Ghosh, *J. Mol. Struct.* 826 (2007) 170.



- [12] S. Das, B.N. Sarkar, K. Bhar, S. Chattopadhyay, H.-K. Fun, P. Mitra, B.K. Ghosh, *Inorg. Chem. Commun.* 13 (2010) 353.
- [13] B.N. Sarkar, K. Bhar, S. Chattopadhyay, S. Das, P. Mitra, B.K. Ghosh, *J. Mol. Struct.* 963 (2010) 35.
- [14] V. Alexander, *Chem. Rev.* 95 (1995) 273.
- [15] P.A. Vigato, S. Tamburini, L. Bertolo, *Coord. Chem. Rev.* 251 (2007) 1311.
- [16] G. Wu, X.-F. Wang, T. Okamura, W.-Y. Sun, N. Ueyama, *Inorg. Chem.* 45 (2006) 8523.
- [17] A. Lan, L. Han, D. Yuan, F. Jiang, M. Hong, *Inorg. Chem. Commun.* 10 (2007) 993.
- [18] T. Chattopadhyay, A. Banerjee, K.S. Banu, E. Suresh, M. Netahji, G. Birarda, E. Zangrando, D. Das, *Polyhedron* 27 (2008) 2452.
- [19] B. Hollo, Z.D. Tomic, P. Pogany, A. Kovacs, V.M. Leovac, K.M. Szecsenyici, *Polyhedron* 28 (2009) 3881.
- [20] A.M. Golub, H. Kohler, V.V. Skopenko (Eds.), *Chemistry of Pseudohalides*, Elsevier, Amsterdam, 1986.
- [21] D.A. Buckingham, *Coord. Chem. Rev.* 135–136 (1994) 587.
- [22] J. Ribas, A. Escuer, M. Monfort, R. Vicente, R. Cortes, L. Lezama, T. Rojo, *Coord. Chem. Rev.* 193–195 (1999) 1027.
- [23] Y.-Q. Sun, D.-Z. Gao, W. Dong, D.-Z. Liao, C.-X. Zhang, *Eur. J. Inorg. Chem.* (2009) 2825.
- [24] T.K. Maji, G. Mostafa, S. Sain, J.S. Prasad, N.R. Chaudhuri, *Cryst. Eng. Commun.* 37 (2001) 1.
- [25] X. Shi, G. Zhu, Q. Fang, G. Wu, G. Tian, R. Wang, D. Zhang, M. Xue, S. Qiu, *Eur. J. Inorg. Chem.* (2004) 185.
- [26] C.-D. Wu, W. Lin, *Inorg. Chem.* 44 (2005) 1137.
- [27] Y. Jin, P. Yoon, J. Seo, J.-E. Lee, S.T. Moon, J. Kim, S.W. Han, K.-M. Park, L.F. Lindoy, S.S. Lee, *Dalton Trans.* 4 (2005) 788.
- [28] H. Zhang, X. Wang, K. Zhang, B.K. Teo, *Coord. Chem. Rev.* 183 (1999) 157.
- [29] S.H. Rahaman, R. Ghosh, G. Mostafa, B.K. Ghosh, *Inorg. Chem. Commun.* 8 (2005) 700.
- [30] V. Haber, I. Cisaova, J. Fabry, *Polyhedron* 22 (2003) 3451.
- [31] G. M. Sheldrick, *Acta Cryst.*, (2008) A64, 112-122.
- [32] G. M. Sheldrick, *SHELXL 2013*, University of Göttingen, Germany, (2013).
- [33] K. Brandenburg, *Diamond Version 2.0 Impact GbR*, Bonn, Germany, (1998).
- [34] A. Naito, S. Ganapathy, C.A. McDowell, *J. Magn. Reson.*, 48 (1982) 367.
- [35] M. Belhouchet, M. Bahri, J. M. Savariault, T. Mhiri, *Spectrochim. Acta A* 61 (2005) 387.
- [36] N. L. Calve, F. Romain, M. H. Limage, A. Novak, *J. Mol. Struct.* 200 (1989) 131.
- [37] S. Shanmuga Sundara Raj, H. K. Fun, P. S. Zhao, F. F. Jian, L. D. Lu, X. J. Yang, X. Wang, *Acta Cryst.* C56 (2000) 742.
- [38] B. Chenon, C. Sandorfy, *Can. J. Chem.* 36 (1958) 1181.
- [39] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley-Interscience, New York, 1986.