

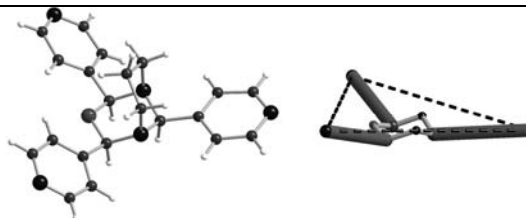
A NEW *EXO*-TRIDENTATE TRIS-PYRIDINE LIGAND DERIVED FROM 3-OXA-1,5-DIAZABICYCLO[3.3.1]NONANE AND ITS DINUCLEAR CU(II) COMPLEX. SYNTHESIS AND CRYSTAL STRUCTURES

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A new *exo*-tridentate tris-pyridine ligand (L), derived from 3-oxa-1,5-diazabicyclo[3.3.1]nonane, has been synthesized and structurally characterized by X-ray diffraction on single crystal. A dinuclear complex, $[\{Cu(acac)(phen)\}_2(L)](ClO_4)_2 \cdot 5H_2O$, was obtained using this bridging ligand and also structurally characterized by X-ray diffraction on single crystal.



INTRODUCTION

The development of new building blocks for constructing coordination polymers is of current interest in crystal engineering. The growing interest for designing coordination polymers with pre-established dimensionalities and network topologies is justified by the potential applications in catalysis, gas storage, magnetism, luminescence, non-linear optics or sensing.

In the “node and spacer” approach, defined by Robson in 1990,² the formation of coordination polymers consists on self-assembly processes involving metal ions (nodes, connectors) and *exo*-dentate ligands (spacers, linkers). The growth of the extended structures takes place following different possible pathways: (i) initial formation of the node with a pre-established nuclearity and subsequent reaction with the spacer; (ii) formation of the nodes through interactions of the metal ions and spacer (usually a polycarboxylato ligand), or (iii) serendipitous assembly of the metal ions into clusters with various nuclearities, and their subsequent interaction with the spacer.³

In this paper the synthesis and crystal structure of a new *exo*-tridentate tris-pyridine ligand, derived from 3-oxa-1,5-diazabicyclo[3.3.1]nonane, is reported. Its coordination ability as bridging ligand was studied toward a monocationic building-block, $[Cu(acac)(phen)(H_2O)]^+$, (acac = acetylacetonate anion, phen = 1,10-phenanthroline). This cationic building-block has been used because the water molecule from the apical position of the copper(II) ion can be easily replaced by various neutral ligands or anionic complexes, while the aromatic ligands attached to copper(II) favor the intermolecular π - π stacking interactions, which play an important role sustaining supramolecular solid-state architectures.⁴

RESULTS AND DISCUSSION

By reacting 4-pyridinecarboxaldehyde with 1,3-diaminopropane a new *exo*-tridentate tris-pyridine derivative was obtained. Its molecular structure determined by X-ray diffraction on single crystal consists in a 3-oxa-1,5-diazabicyclo[3.3.1]nonane core functionalized by three 4-pyridine fragments (Fig. 1a).

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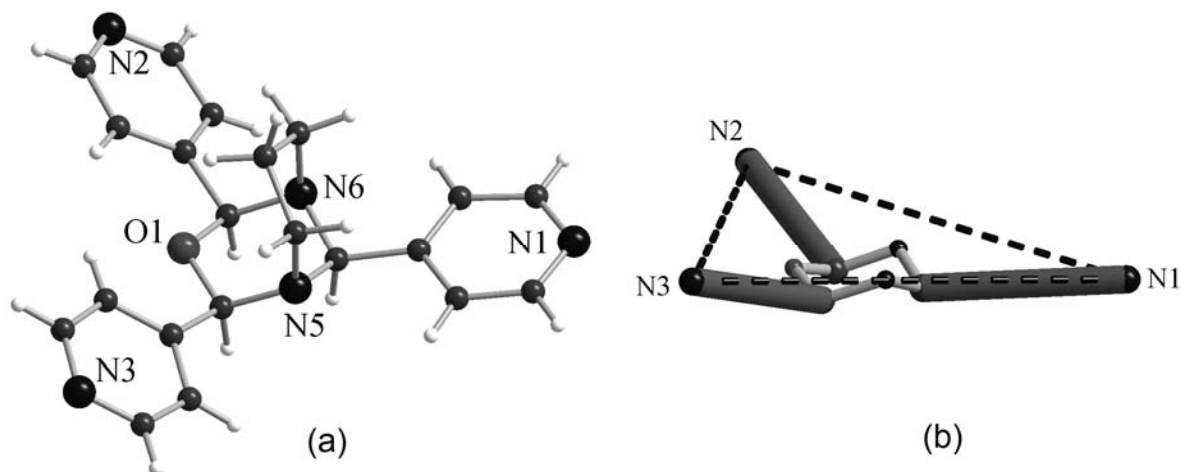


Fig. 1 – Perspective view of the molecular structure of the ligand L (a) and schematic representation of the coordination directions as *exo*-tridentate ligand (b).

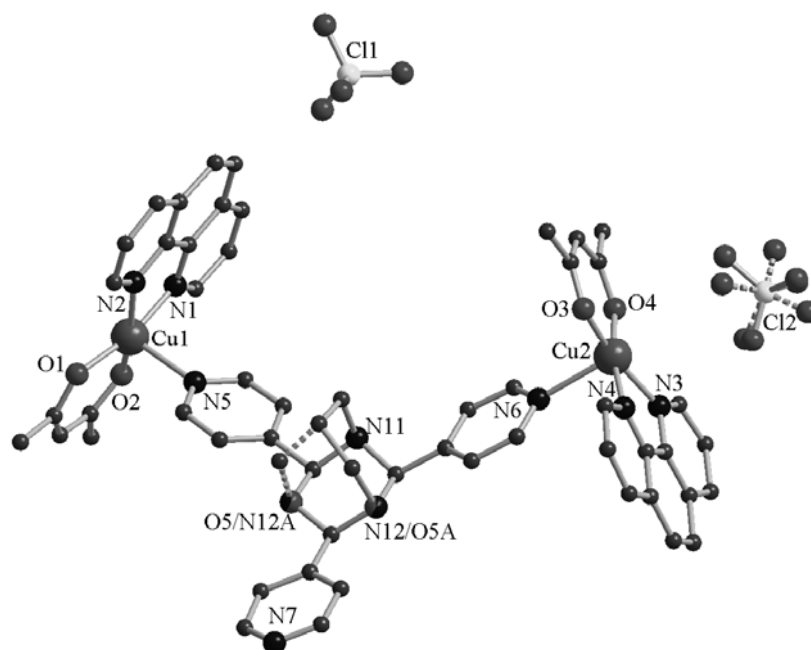


Fig. 2 – Perspective view of the crystal structure of the complex $[\{Cu(acac)(phen)\}_2(L)](ClO_4)_2$ (the hydrogen atoms were omitted for clarity).

The pyridine fragments are located in the equatorial positions of the carbon atoms from the six-member ring with a chair conformation containing the heteroatoms N5, N6 and O1. Two pyridine fragments, which contain the atoms labelled with N2 and N3, are almost coplanar with the dihedral angle between their mean planes of 5.6° . The coordination directions as *exo*-tridentate ligand are not coplanar (Fig. 1b) and form between them angles of 73.9° ($N2 \cdots N3$), 61.6° ($N1 \cdots N2$) and 57.8° ($N1 \cdots N3$).

In order to test the bridging capability of the ligand L, this was reacted with a mononuclear

copper(II) complex, $[Cu(acac)(phen)(H_2O)](ClO_4)$, in the molar ratio 1:3, expecting formation of a trinuclear compound by a replacement of the water molecules from the apical positions with pyridine fragments. The crystallographic investigation of the green crystals obtained in this reaction revealed the formation of a dinuclear compound, $[\{Cu(acac)(phen)\}_2(L)](ClO_4)_2 \cdot 5H_2O$. Only two pyridine rings of the ligand L are involved in coordination to the Cu(II) ions (Fig. 2).

The copper(II) ions are pentacoordinated with square-pyramidal geometries. The chelatic ligands (acetylacetonate anion and 1,10-phenanthroline)

form the basal planes [Cu1-N1 = 2.021(4), Cu1-N2 = 2.022(5), Cu1-O1 = 1.926(4), Cu1-O2 = 1.911(4), Cu2-N3 = 2.017(5), Cu2-N4 = 2.009(5), Cu2-O3 = 1.908(5) and Cu2-O4 = 1.912(4) Å], while in the apical positions are coordinated pyridine fragments of the ligand L. The apical bond lengths Cu-N with the pyridine rings are longer [Cu1-N5 = 2.280(5) and Cu2-N6 = 2.288(4) Å]. The intramolecular Cu...Cu distance is 13.70 Å. The 3-oxa-1,5-diazabicyclo[3.3.1]nonane core is disordered on two crystallographic positions with site occupancy factors of 0.58 and 0.42 respectively. One perchlorate ion is disordered also on two crystallographic positions

with site occupancy factors of 0.63 and 0.37 respectively.

The chelatic ligands, acac and phen, are involved in intermolecular π - π stacking interactions generating supramolecular chains (Fig. 3). The separation between the aromatic fragments is 3.28-3.42 Å for the ligands coordinated to Cu1 and Cu1' ($' = 1-x, 1-y, -z$) and 3.28-3.58 Å for the ligands coordinated to Cu2 and Cu2'' ($'' = 1-x, 2-y, 1-z$).

The analysis of the packing diagrams reveals formation of channels along the crystallographic a axis, where are located the crystallization water molecules (Fig. 4).

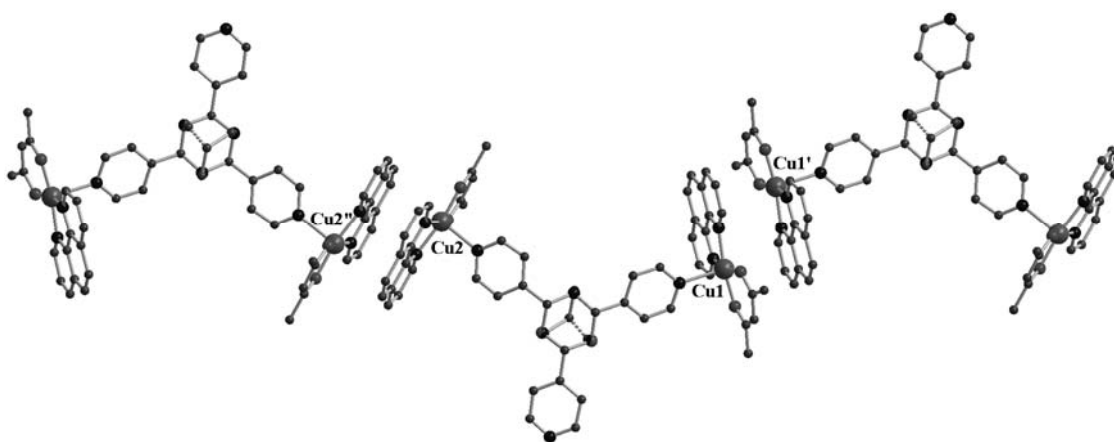


Fig. 3 – View of a supramolecular chain formed by π - π stacking interactions between the $\{\text{Cu}(\text{acac})(\text{phen})\}$ moieties.

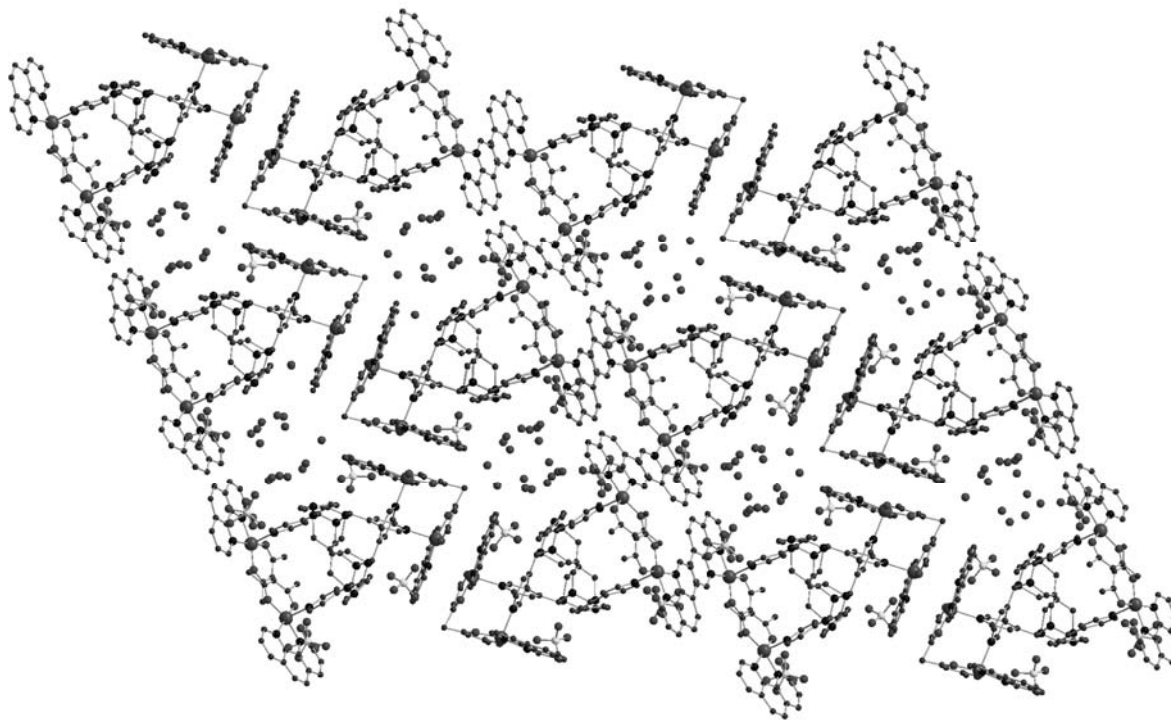


Fig. 4 – View of the packing diagram in crystal $[\{\text{Cu}(\text{acac})(\text{phen})\}_2(\text{L})](\text{ClO}_4)_2 \cdot 5\text{H}_2\text{O}$ along the crystallographic a axis.

EXPERIMENTAL

Materials and methods

All the chemicals used as well as all the solvents were purchased from commercial sources. All manipulations were performed under aerobic conditions.

Synthesis of ligand L: 2 mmol of 4-pyridinecarboxaldehyde were refluxed with 1 mmol of 1,3-diaminopropane in 100 mL ethanol for three hours. The resulting solution was evaporated under reduced pressure and the solid was washed several times with a mixture ethanol – diethyl ether and diethyl ether. Further the ligand L was recrystallized from ethanol. Yield 67 % (reported to 4-pyridinecarboxaldehyde). IR data (KBr, cm^{-1}): 3027m, 2978w, 2946m, 2872m, 1600s, 1561w, 1460w, 1445w, 1411m, 1381w, 1348s, 1325w, 1297w, 1226m, 1163m, 1144m, 1091w, 1047s, 1005s, 969m, 892m, 864w, 826m, 802m, 777m, 731w, 606m, 586m, 539w, 502w, 470w. ^1H NMR (CDCl_3), δ (ppm): 8.740 (d, $J = 5.6$, 4H), 8.710 (d, $J = 5.6$, 2H), 7.673 (d, $J = 5.6$, 4H), 7.607 (d, $J = 4.8$, 2H), 6.233 (s, 2H), 5.620 (s, 1H), 3.086-3.002 (m, 2H), 2.697-2.644 (m, 2H), 2.125-1.993 (m, 1H), 0.769-0.711 (m, 1H).

Synthesis of $[\{\text{Cu}(\text{acac})(\text{phen})\}_2(\text{L})](\text{ClO}_4)_2 \cdot 5\text{H}_2\text{O}$: 0.15 mmol of $[\text{Cu}(\text{acac})(\text{phen})(\text{H}_2\text{O})](\text{ClO}_4)$ dissolved in 50 ml of acetonitrile were mixed for 30 minute with 0.05 mmol of ligand L dissolved in 25 ml methanol. The green crystals of

$[\{\text{Cu}(\text{acac})(\text{phen})\}_2(\text{L})](\text{ClO}_4)_2 \cdot 5\text{H}_2\text{O}$ were obtained by slow evaporation of the resulted solution at room temperature. IR data (KBr, cm^{-1}): 3566 broad, 3067w, 2967w, 1581s, 1518s, 1428m, 1415w, 1379s, 1323w, 1277w, 1252w, 1224w, 1164w, 1146w, 1089vs, 1047m, 1001m, 931w, 908w, 849m, 831w, 777w, 724m, 623m, 592w, 430w. The precursor $[\text{Cu}(\text{acac})(\text{phen})(\text{H}_2\text{O})](\text{ClO}_4)$ was obtained as previous reported.⁵

Physical measurements. The IR spectra (KBr pellets) were collected on a Bruker Tensor 37 spectrophotometer in the 4000–400 cm^{-1} range. The ^1H NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400 MHz.

X-ray crystallography and solution of structures

Single crystals suitable for X-ray diffraction studies were obtained by slow evaporation of the solvent, as described above. Data were collected at 173 K on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo K_α radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct methods and refined by full-matrix least squares techniques based on F^2 . The non-H atoms were refined with anisotropic displacement parameters. A summary of the crystallographic data and the structure refinement is given in Table 1. CCDC reference numbers: 962472-962473.

Table 1

Crystallographic data, details of data collection, and structure refinement parameters for **1** and **2**

Compound	L	$[\{\text{Cu}(\text{acac})(\text{phen})\}_2(\text{L})](\text{ClO}_4)_2 \cdot 5\text{H}_2\text{O}$
Chemical formula	$\text{C}_{21}\text{H}_{21}\text{N}_5\text{O}$	$\text{C}_{55}\text{H}_{61}\text{C}_{12}\text{Cu}_2\text{N}_9\text{O}_{18}$
M (g mol^{-1})	359.43	1334.11
Temperature, (K)	173(2)	173(2)
Wavelength, (\AA)	0.71073	0.71073
Crystal system	<i>Triclinic</i>	<i>Monoclinic</i>
Space group	<i>P-1</i>	<i>P21/a</i>
a (\AA)	8.5170(5)	12.2730(3)
b (\AA)	8.8750(6)	16.8231(7)
c (\AA)	12.0880(7)	30.2518(13)
α ($^\circ$)	87.780(5)	90
β ($^\circ$)	79.780(4)	94.873(2)
γ ($^\circ$)	82.170(3)	90
V (\AA^3)	890.73(9)	6223.5(4)
Z	2	4
D_c (g cm^{-3})	1.340	1.424
μ (mm^{-1})	0.086	0.845
$F(000)$	380	2760
Goodness-of-fit on F^2	0.988	0.961
Final $R1$, wR_2 [$I > 2\sigma(I)$]	0.0583, 0.1231	0.0762, 0.1761
$R1$, wR_2 (all data)	0.1318, 0.1512	0.2193, 0.2198
Largest diff. peak and hole (e\AA^{-3})	0.302, -0.256	0.480, -0.476

CONCLUSIONS

The dinuclear compound described in this paper illustrates that the new *exo*-tridentate tris-pyridine ligand derived from 3-oxa-1,5-diazabicyclo[3.3.1]nonane can be used as spacer in construction of polynuclear compounds and its coordination ability toward other cationic building-blocks follows to be investigated.

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REFERENCES

1. See, for example: (a) M. O’Keeffe, O. M. Yaghi, *Chem. Rev.*, **2012**, *112*, 675; (b) N. Stock, S. Biswas, *Chem. Rev.*, **2012**, *112*, 933; (c) W. L. Leong, J. J. Vittal, *Chem. Rev.*, **2011**, *111*, 688; (d) G. Férey, C. Serre, *Chem. Soc. Rev.*, **2009**, *38*, 1380; (e) S. Horike, S. Shimomura, S. Kitagawa, *Nat. Chem.*, **2009**, *1*, 695; (f) D. J. Tranchemontagne, Z. Ni, M. O’Keeffe, O. M. Yaghi, *Angew. Chem. Int. Ed.*, **2008**, *47*, 5136; (g) X. Lin, J. Jia, P. Hubberstey, M. Schroder, N. R. Champness, *CrystEngComm*, **2007**, *9*, 438; (h) D. Braga, F. Grepioni, *Chem. Commun.*, **2005**, 3635; (i) S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem. Int. Ed.*, **2004**, *43*, 2334; (j) C. Janiak, *Dalton Trans.*, **2003**, 2781; (k) B. Moulton, M. Zaworotko, *J. Chem. Rev.*, **2001**, *101*, 1629; (l) L. K. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne, J. T. Hupp, *Chem. Rev.*, **2012**, *112*, 1105; (m) E. Coronado, M. Espallargos, *Chem. Soc. Rev.*, **2013**, *42*, 1525.
2. (a) R. W. Gable, B. F. Hoskins, R. Robson, *J. Chem. Soc., Chem. Commun.*, **1990**, 1677; (b) B. F. Hoskins, R. Robson, *J. Am. Chem. Soc.*, **1990**, *112*, 1546.
3. (a) M. Andruh, *Chem. Commun.*, **2007**, 2565; (b) M. Andruh, *Chem. Commun.*, **2011**, 3025. (c) M. Andruh, D. G. Branzea, R. Gheorghe, A. M. Madalan, *CrystEngComm*, **2009**, *11*, 2571. (d) M. Andruh, *Pure Appl. Chem.*, **2005**, *77*, 1685.
4. (a) A. M. Madalan, V. C. Kravtsov, D. Pajic, K. Zadro, Y.A. Simonov, N. Stanica, L. Ouahab, J. Lipkowski, M. Andruh, *Inorg. Chim. Acta*, **2004**, *357*, 4151; (b) A. M. Madalan, V. C. Kravtsov, Y. A. Simonov, V. Voronkova, L. Korobchenko, N. Avarvari, M. Andruh, *Cryst. Growth Des.*, **2005**, *5*, 45; (c) A. M. Madalan, M. Noltemeyer, M. Neculai, H. W. Roesky, M. Schmidtman, A. Müller, Y. Journaux, M. Andruh, *Inorg. Chim. Acta*, **2006**, *359*, 459; (d) A. M. Madalan, N. Avarvari, M. Andruh, *Cryst. Growth Des.*, **2006**, *6*, 1671.
5. A. M. Madalan, C. Ruiz-Pérez, E. Melnic, V. Kravtsov, M. Andruh, *Rev. Roum. Chim.*, **2005**, *50*, 11.

