

## Research Article

# Nitrate-Bridged One-Dimension Coordination Polymer Self-Assembled from a $N_4O_2$ -Tetraiminodiphenolate Dicopper(II) Macrocyclic Complex

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Herein we report on the synthesis and single crystal X-ray structure characterization of  $[\{Cu_2(tidf)(\mu-NO_3)\}_\infty]ClO_4$  ( $tidf$  = a Robson type macrocyclic ligand obtained upon condensation of 2,6-diformyl-4-methylphenol and 1,3-diaminopropane). The coordination geometry around the copper(II) is square-pyramidal and has  $[Cu_2(tidf)]^{2+}$  units connected to each other through nitrate bridges extending as a one-dimension coordination polymer. The compound exhibits an extensive supramolecular structure supported by nonclassic hydrogen bonding between  $C-H \cdots O_{perchlorate}$  and  $C-H \cdots O_{nitrate}$ .

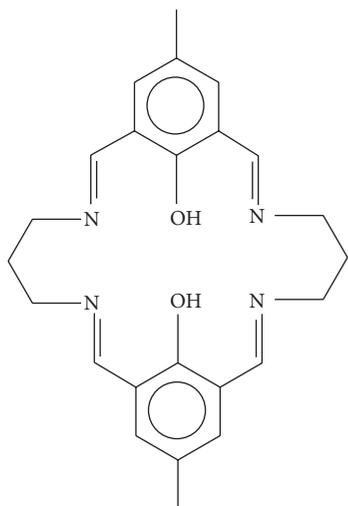
## 1. Introduction

Robson type ligands, obtained on condensation of 2,6-diformyl-4-methylphenol and diamines, have been investigated over the years as their coordination compounds show interesting magnetic, redox, and structural properties [1–11].

These molecules are able to self-assemble through metal-ligand interactions rendering 1D, 2D, or 3D supramolecular assemblies with interesting structural properties, which are intimately related to the nature of the building blocks, their relative orientation in the crystal lattice, and interactions such as H-bonding and van der Waals contacts. This subject gained importance due to the innumerable possibilities to prepare novel extended lattices and is a major challenge in current coordination and synthetic inorganic chemistry [12, 13].

A vast number of crystallographic studies on coordination polymers are known and have provided valuable information about metal-base interactions and preferred coordination sites. However, there is very little structural information regarding the specific binding of nitrate as a bridging ligand in macrocyclic chemistry.

Dutta and coworkers reported on the  $[Pb_2L(NO_3)_2]$  (where L is the same tetraiminodiphenolated ligand used in our work) that exhibits a 2D structural network and contains parallel chains of two independent  $[Pb_2L]_2$  units. The nitrate anions interact with those units in an unusual mode: one oxygen atom is coordinated to two symmetry-equivalent metal centers, another oxygen atom is coordinated to a single lead ion, and the third oxygen atom is free [14]. In another example of the Robson family, the crystal structure of  $[Zn_2L(NO_3)(H_2O)](ClO_4)$  (L = template condensation of the 2,6-diformyl-4-methylphenol and 2,2'-dimethyl-1,3-diaminopropane) was described by Mohanta and coworkers. A 2D polymer is formed through complex hydrogen bonds, three  $O-H \cdots O$ , and two  $C-H \cdots O$ . One hydrogen atom of the coordinated water forms bifurcated hydrogen bonds with two nitrate oxygen atoms [15]. Bartoli and coworkers investigated the crystal structure of  $[Cu_8L_4(\mu-OH)_8(\mu-NO_3)_3](NO_3)_5 \cdot 32H_2O$  (L = an acridine moiety inserted in a polyamine cycle) which is formed from two individual tetranuclear clusters  $[Cu_4L_2(\mu-OH)_4(\mu-NO_3)_x]^{(4-x)+}$  ( $x = 1$  or 2) linked by hydroxide and nitrate anions bridging two



SCHEME 1: Ligand tidf.

copper(II) ions. The nitrate anions  $[\text{Cu}_2(\mu\text{-OH})_2]$  cores belonging to adjacent metallomacrocyclic units producing an infinite zigzag chain [16]. More recently, Choi et al. isolated the 1D hydrogen-bonded polymer  $[\text{Cu}(\text{L})(\text{NO}_3)_2]$  from the self-assembly of  $[\text{CuL}]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  ( $\text{L} = 3,14$ -dimethyl-2,6,13,17-tetraazatricyclo[14,4,0<sup>1,18</sup>,0<sup>7,12</sup>]docosane) with polycarboxylate and  $\text{KNO}_3$ . In here, nitrate is mono-coordinated through one oxygen atom, while the two uncoordinated oxygen atoms form intermolecular hydrogen bonds to adjacent amines of the macrocycle [17].

Continuing our general synthesis of metal complexes of the tetraaminodiphenolate macrocyclic ligand (Scheme 1), we have recently reported on a copper coordination polymer connected by piperazine bridges [2] and on the structural, magnetic, and spectroelectrochemical properties of the pentanuclear complex  $[\{\text{Cu}_2(\text{tidf})(\text{H}_2\text{O})\}_2(\mu\text{-CN})_2\text{Fe}(\text{CN})_4] \cdot 6\text{H}_2\text{O}$  [3].

In this work we report on the preparation, characterization, and properties of a new coordination polymer of the Robson family. Our results show the self-assembly of the building molecules into an extended structure maintained by intricate hydrogen-bonding interactions.

## 2. Materials and Methods

Reagent grade commercial chemicals were used in this work.  $[\text{Mg}_2(\text{tidf})](\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  was prepared as described elsewhere [18].

**2.1. Synthesis.** In a round bottom flask, 2.0 g (3.1 mmol) of  $[\text{Mg}_2(\text{tidf})](\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  was dissolved in 30 mL of hot MeOH under stirring. To the yellow solution formed, 1.15 g (3.1 mmol) of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  was added and a dark green color appeared instantaneously. The system was kept at reflux for 4 h and a green solid was recovered by filtration after cooling to room temperature, washed with cold MeOH, and dried under vacuum. Single crystals suitable to X-ray diffractometry were obtained after recrystallization from

acetonitrile solutions. Infrared spectrum in KBr ( $\text{cm}^{-1}$ ): 1639vs  $\nu(\text{C}=\text{N})$ , 1568s  $\nu(\text{C}=\text{C})$ , and 1323m  $\nu(\text{C}-\text{O})$ , characteristics of the tetraaminodiphenolate macrocycle. The bands at 525 and 489  $\text{cm}^{-1}$  were assigned to the vibrational modes  $\nu\text{Cu}-\text{N}$  and  $\nu\text{Cu}-\text{O}$ . Nitrate exhibited bands at 1385w, 1274w, and 1068w  $\text{cm}^{-1}$  and perchlorate at 1100s and 623m  $\text{cm}^{-1}$  [7, 15].

**2.2. Instruments.** Infrared spectra were obtained with a FTS3500GX Bio-Rad Excalibur series spectrophotometer in the region 4000–400  $\text{cm}^{-1}$  in KBr pellets. A Bruker CCD X8 Kappa APEX II diffractometer operated using graphite monochromator and Mo- $\text{K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) was used for the X-ray structure analyses. The molecular crystal structures were solved by direct methods with SHELXS [19]. The final structure was refined with SHELXL [19] with anisotropic displacement parameters for all nonhydrogen atoms; hydrogen atoms were refined isotropically as riding atoms at their theoretical ideal positions. Drawings were made with the ORTEP-3 for Windows [20]. More detailed information about the structure determinations is given in Table 1.

The positional sites of atoms O21A, O21B, O23A, O23B, and O24A and O24B of the perchlorate anion and those related to atoms C45A and C45B of the complex cation were determined based on a positional disorder modeling, respectively. The final refinement cycles including the disordered nonhydrogen atoms were performed assigning all variables free and anisotropic thermal parameters to all nonhydrogen atoms. The site-occupation fractions adding one for each pair of the disordered nonhydrogen atoms are given in parentheses: O21A (0.415), O21B (0.485), O23A (0.415), O23B (0.485), O24A (0.415), O24B (0.485), C45A (0.515), and C45B (0.485).

The positional parameters of the H atoms bonded to C atoms were obtained geometrically, with the C-H lengths fixed (0.96  $\text{\AA}$  for  $\text{Csp}^3$  methyl; 0.97  $\text{\AA}$  for  $\text{Csp}^3$  methylene), and refined as riding on their respective C atoms, with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{Csp}^3 \text{ methyl})$  and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{Csp}^3 \text{ methylene})$ .

Attempts restraining the distance between H atoms to remove short contacts observed between atoms H44A and H45C, H46B and H45C, H46B and H45D, and H44A and H45D have not been successful. The unexpected short contacts observed between the above related H atom pairs were attributed to the positional disorder atoms C45A and C45B refined with anisotropic displacement parameters.

## 3. Results and Discussion

The macrocyclic ligand tidf was prepared by the condensation of 2,6-diformyl-4-methylphenol and 1,3-diaminopropane in the presence of magnesium acetate and magnesium nitrate according to the procedure of Mohanta and coworkers [21].

In an attempt to prepare the mononuclear copper(II) complex,  $[\text{Cu}(\text{tidf}-\text{H}_2)(\text{H}_2\text{O})_2](\text{ClO}_4)$ , equimolar amounts of copper(II), and  $[\text{Mg}_2(\text{tidf})](\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  were mixed. Much to our surprise, upon recrystallization from acetonitrile, the coordination polymer  $[\{\text{Cu}_2(\text{tidf})(\mu\text{-NO}_3)\}_\infty]\text{ClO}_4$  was

TABLE 1: Crystal data and structure refinement for  $[\{\text{Cu}_2(\text{tidf})(\mu\text{-NO}_3)\}_\infty]\text{ClO}_4$ .

Empirical formula	$\text{C}_{24}\text{H}_{27}\text{ClCu}_2\text{N}_5\text{O}_9$
Formula weight	692.04
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P(-1)$
Unit cell dimensions	$a = 8.9071(3)$ Å, $\alpha = 93.936(2)^\circ$ . $b = 11.9325(5)$ Å, $\beta = 107.870(2)^\circ$ . $c = 13.6743(5)$ Å, $\gamma = 105.530(2)^\circ$ .
Volume	1314.59(9) Å <sup>3</sup>
Z	2
Density (calculated)	1.748 Mg/m <sup>3</sup>
Absorption coefficient	1.783 mm <sup>-1</sup>
$F(000)$	706
Crystal size	0.93 × 0.27 × 0.19 mm <sup>3</sup>
Theta range for data collection	1.59 to 28.34°.
Index ranges	$-11 \leq h \leq 11$ , $-15 \leq k \leq 15$ , $-18 \leq l \leq 18$
Reflections collected	43374
Independent reflections	6536 [ $R(\text{int}) = 0.0207$ ]
Completeness to theta = 28.34°	99.7%
Max. and min. transmission	0.7281 and 0.2878
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	6536/0/362
Goodness-of-fit on $F^2$	1.048
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0482$ , $wR2 = 0.1431$
$R$ indices (all data)	$R1 = 0.0538$ , $wR2 = 0.1494$
Extinction coefficient	0.0000(6)
Largest diff. peak and hole	1.849 and $-1.000$ e.Å <sup>-3</sup>

TABLE 2: Selected bond lengths/Å and angles/° for  $[\{\text{Cu}_2(\text{tidf})(\mu\text{-NO}_3)\}_\infty]\text{ClO}_4$ .

Cu1-N1	1.947(3)
Cu1-N2	1.984(3)
Cu1-O1	1.982(2)
Cu1-O1'	1.975(2)
Cu1-O3'	2.237(3)
Cu2-N3	1.960(3)
Cu2-N4'''	1.952(3)
Cu2-O2	1.975(2)
Cu2-O2'''	1.964(2)
Cu2-O4''	2.290(3)
Cu1...Cu1'	3.113
O4-N5	1.255(4)
O3-N5	1.250(4)
O5-N5	1.213(5)
Cu1-O1-Cu1	103.75(9)
O1'-Cu1-N1	165.85(12)
O1-Cu1-N2	165.56(10)
O1'-Cu1-O1	76.25(9)
N1-Cu1-N2	96.71(12)
O1-Cu1-N1	92.68(11)
O1'-Cu1-N2	92.64(10)
O1-Cu1-O3'	98.12(11)
O1'-Cu1-O3'	86.37(11)
N1-Cu1-O3'	104.13(14)
N2-Cu1-O3'	90.22(12)
Cu1-O11-N5	128.6(2)
O3-N5-O4	116.7(3)
O3-N5-O5	121.5(3)

Symmetry code: ('):  $-x, 2 - y, 1 - z$ ; (''):  $1 - x, -1 + y, z$ ; ('''):  $-x, 1 - y, -z$ .

isolated. Unfortunately, our many attempts to reproduce the synthesis were not successful, suggesting that the product might be a byproduct. As a consequence, it was characterized only structurally and by its vibrational spectrum. It crystallizes in the triclinic space group  $P\bar{1}$  and contains  $[\text{Cu}_2(\text{tidf})]^{2+}$  units bridged to each other through nitrate anions. The polymer extends in one dimension and shows the cationic  $[\text{Cu}_2(\text{tidf})(\mu\text{-NO}_3)]^+$  complex as the monomeric repeating unit. The representation of the crystal structure of  $[\{\text{Cu}_2(\text{tidf})(\mu\text{-NO}_3)\}_\infty]\text{ClO}_4$  is shown in Figure 1 and Table 2 lists selected bond distances and angles. The compound is a diphenolate-bridged dinuclear copper(II) complex and each metal ion is five-coordinated to two imine and two endogenous phenolate groups in the equatorial plane. The nitrate connects copper(II) ions of two  $[\text{Cu}_2(\text{tidf})]^{2+}$  units by O3 and O4 atoms at the axial positions of Cu1 and Cu2 centers, respectively.

In a previous report [3], we showed that the copper(II) ions of the coordination polymer  $[\{\text{Cu}_2(\text{tidf})(\text{H}_2\text{O})_2\}_2(\mu\text{-CN})_2\text{Fe}(\text{CN})_4]$  are slightly out of the  $\text{N}_2\text{O}_2$  equatorial planes

in opposite directions by 0.162(1) Å for Cu2 and 0.287(1) Å for Cu1, because of the strong bonding to the cyanobridges. The complex also exhibited a square-pyramidal geometry around the metal ion with the longest Cu-Cu distance at 9.780 Å and the shortest at 3.133 Å.

In contrast,  $[\{\text{Cu}_2(\text{tidf})(\mu\text{-NO}_3)\}_\infty]\text{ClO}_4$  shows a fairly planar geometry and *in-plane* copper(II) ions due to the weak interaction with the nitrate ligand. On the other hand, additional evidences point out to some distortions of the copper(II) coordination site as given by the *transoid* angles N1-Cu1-O1' 165.85(12)°, O1-Cu1-N2 165.56(10)°, N3-Cu2-O2' 163.74(11)°, and N4'''-Cu(2)-O(2) 167.75(11)° and the *cisoid* angles N1-Cu1-O1 92.68(11)°, N1-Cu1-N2 96.71(12)°, and O1-Cu1-O1' 76.25(9)°.

Main bond distances for  $[\{\text{Cu}_2(\text{tidf})(\mu\text{-NO}_3)\}_\infty]\text{ClO}_4$  are Cu1-O1(phenolate) 1.982(2) Å, Cu1-N1 1.947(3) Å, Cu1-O3(nitrate) 2.237(3) Å, and Cu2-O4(nitrate) 2.290(3) Å. Intermolecular bond distance between the copper(II) ions bridged by the nitrate anion is 6.442 Å, while the intramolecular metal ions connected through the diphenolate oxygen are 3.113 Å apart from each other. Furthermore,

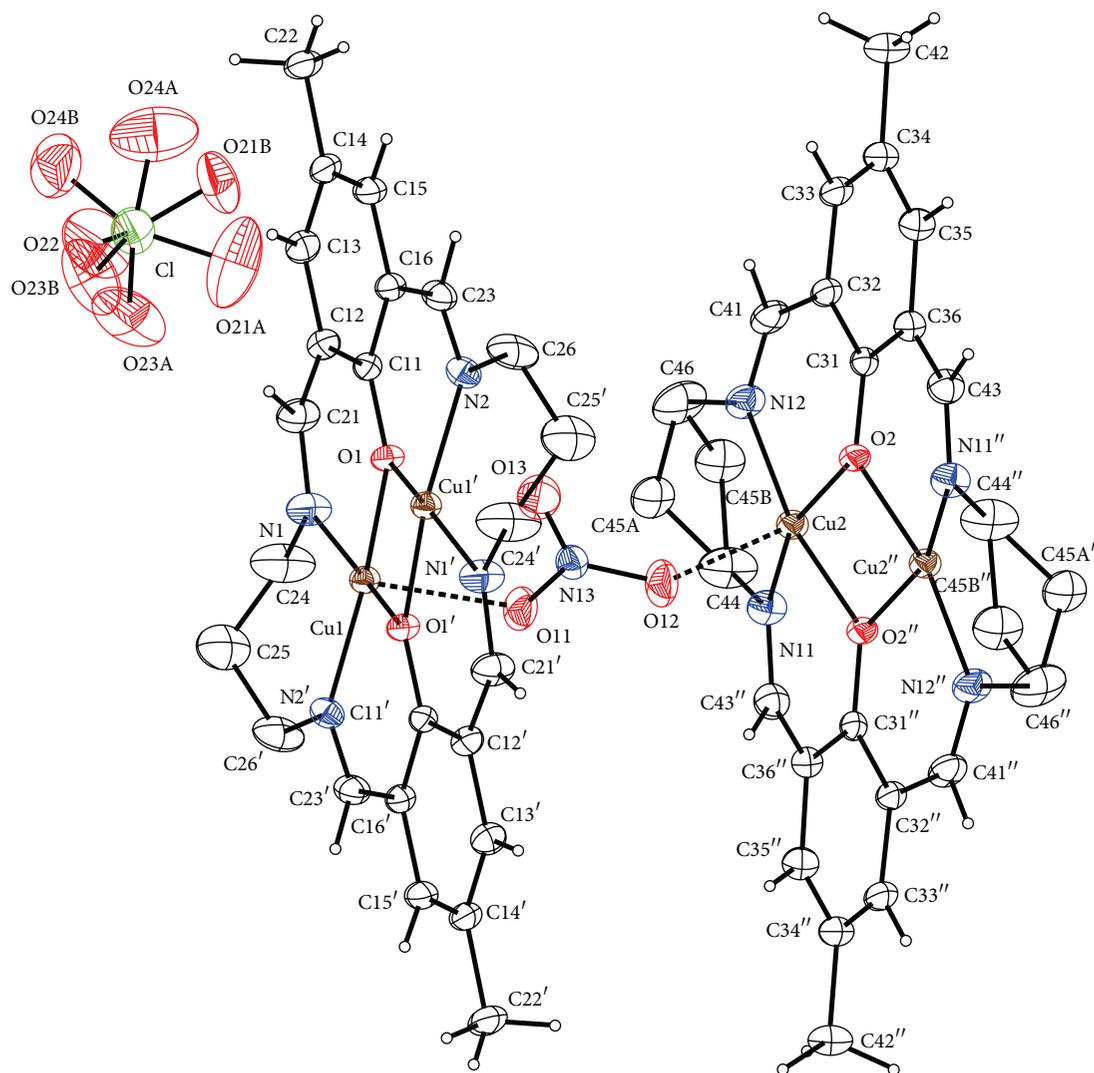


FIGURE 1: The molecular structure of  $[\{Cu_2(tidf)(\mu-NO_3)\}_\infty]ClO_4$  showing the atom-labeling scheme. Displacement ellipsoids drawn at the 30% probability level. H atoms of methylene groups omitted for clarity [symmetry codes ('):  $-x, 2 - y,$  and  $1 - z$ ; (''):  $1 - x, 2 - y,$  and  $2 - z$ ].

diphenolate bridge angles  $Cu(1)'\text{-O}(1)\text{-Cu}(1)$  and  $Cu(2)'''\text{-O}(2)\text{-Cu}(2)''$  are  $103.75(9)^\circ$  and  $103.63(9)^\circ$ , respectively. Mandal and coworkers reported the crystal structure of the dicopper complex  $[Cu_2(tidf)(ClO_4)_2(H_2O)_2]$  [18]. The structure has two different molecules in the unit cell: one pseudooctahedral and the other square-pyramidal. The bond distances and angles found for  $[\{Cu_2(tidf)(\mu-NO_3)\}_\infty]ClO_4$  are comparable to those found for pentacoordinated metal center core of  $[Cu_2(tidf)(ClO_4)_2(H_2O)_2]$  [18].

The complex exhibits supramolecular three-dimensional (3D) assembling formed through nonclassical hydrogen bond between  $C\text{-H}\cdots O$ (perchlorate) and  $C\text{-H}\cdots O$ (nitrate). The nitrate molecule coordinated to copper atom formed interactions such as  $C5\text{-H}5\cdots O5'$  with bond distance for  $H\cdots A$  at  $2.5295(1)\text{ \AA}$ , symmetry code ('):  $1 - x, -y, 1 - z$ , which extended along the  $a$  crystallographic axis. Also,

the perchlorate ion formed nonclassical hydrogen bond such as  $C3\text{-H}3\cdots O6''$  ( $1 - x, 1 - y, 1 - z$ ) at  $2.5433(1)\text{ \AA}$ ,  $C12\text{-H}12A\cdots O6'''$  ( $x, -1 + y, z$ ) at  $2.5656(1)\text{ \AA}$ ,  $C12\text{-H}12B\cdots O6'$  ( $1 - x, -y, 1 - z$ ) at  $2.5437(1)\text{ \AA}$ ,  $C20\text{-H}20\cdots O7$  at  $2.5690(1)\text{ \AA}$ , and  $C22\text{-H}22A\cdots O8^1$  ( $1 + x, y, z$ ) at  $2.4581(1)\text{ \AA}$ , extended along the  $bc$  crystallographic plane as seen in Figure 2, and the selected bond distances and angles are listed in Table 3.

#### 4. Conclusion

The coordination polymer  $[\{Cu_2(tidf)(\mu-NO_3)\}_\infty]ClO_4$  was prepared from the reaction between  $[Mg_2(tidf)](NO_3)_2\cdot 4H_2O$  and  $Cu(ClO_4)_2\cdot 6H_2O$  in methanol. Structural analysis showed square-pyramidal copper(II) ions bridged by covalently bonded nitrate anions through two distinct oxygen atoms. Significant hydrogen bonding expands intermolecular

TABLE 3: Hydrogen-bonding geometric parameters (Å and °) of  $[\{\text{Cu}_2(\text{tidf})(\mu\text{-NO}_3)\}_\infty]\text{ClO}_4$ .

$D\text{-H}\cdots A$	$D\text{-H}$	$\text{H}\cdots A$	$D\cdots A$	$D\text{-H}\cdots A$	Symmetry code
C5-H5 $\cdots$ O5'	0.930	2.5295	3.447(1)	169	$1-x, -y, 1-z$
C3-H3 $\cdots$ O6''	0.930	2.5433	3.459(1)	168	$1-x, 1-y, 1-z$
C12-H12A $\cdots$ O6'''	0.970	2.5656	3.345(1)	137	$x, -1+y, z$
C12-H12B $\cdots$ O6'	0.970	2.5437	3.4821(1)	163	$1-x, -y, 1-z$
C20-H20 $\cdots$ O7	0.930	2.5690	3.4606(1)	161	$x, y, z$
C22-H22A $\cdots$ O8	0.970	2.4581	3.333(1)	150	$1+x, y, z$

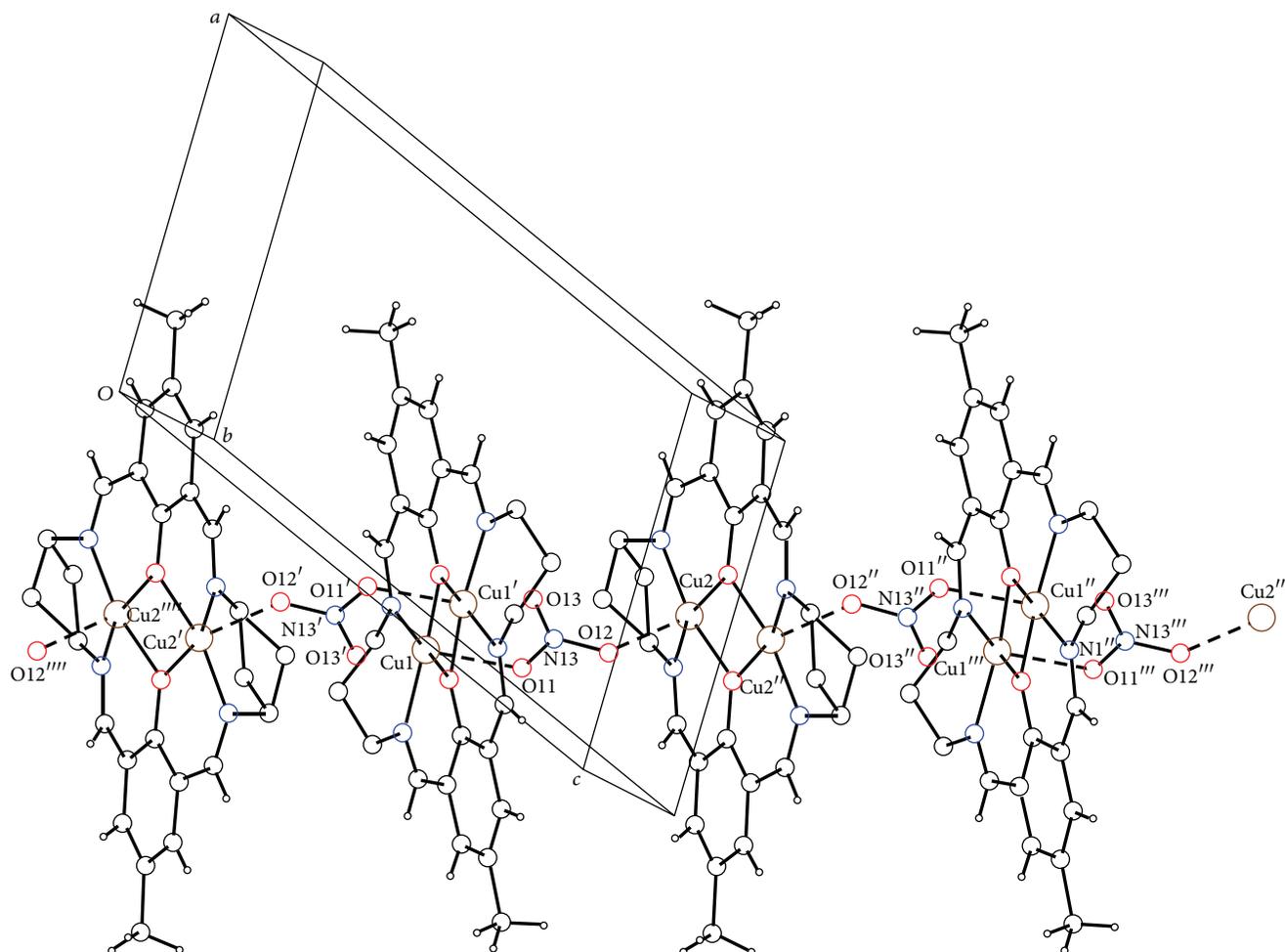


FIGURE 2: A partial view of the crystal packing of  $[\{\text{Cu}_2(\text{tidf})(\mu\text{-NO}_3)\}_\infty]\text{ClO}_4$  showing the  $\text{Cu}\cdots\text{O}-\text{N}(\text{=O})-\text{O}\cdots\text{Cu}$  interactions (dashed lines) resulting in a one-dimensional polymeric arrangement along the  $[101]$  crystallographic direction [symmetry codes ('):  $-x, 2-y, 1-z$ ; ('' ):  $1-x, 2-y, 2-z$ ; (''' ):  $1+x, y, 1+z$ ; ('''') :  $-1+x, y, -1+z$ ]. Perchlorate anion and H atoms of methylene groups omitted for clarity.

interactions affording an interesting supramolecular architecture.

### Supporting Information

CCDC-990913 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html)

(or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; email: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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