

# Crystal and molecular structure and properties of tetrakis-(dichloroacetato)bis( $\mu$ -pyridine-*N*-oxide)bis(pyridine-*N*-oxide)-dicopper(II)

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*Dedicated to Associate Professor Ing. F. Hanic, DrSc.,  
in honour of his 60th birthday*

The title compound  $\text{Cu}_2(\text{Cl}_2\text{CHCOO})_4(\text{pyO})_4$  was synthesized and its crystal structure was solved at room temperature. It crystallized in the triclinic space group  $P\bar{1}$  with  $a = 0.8807$  nm,  $b = 1.0657$  nm,  $c = 1.1628$  nm,  $\alpha = 73.43^\circ$ ,  $\beta = 74.62^\circ$ ,  $\gamma = 68.55^\circ$ , and  $Z = 1$ . Least-squares refinement of the structure led to a conventional  $R$  factor of 0.0455. The crystal structure is composed of well separated centrosymmetric binuclear molecules in which the geometry around each copper ion approximates a square-based pyramid. The copper atoms are linked by two *N*-oxide bridges from an apical coordination site of one Cu(II) to a basal site of another. Variable temperature magnetic susceptibility measurements did not detect down to 93 K an effective exchange coupling within the copper(II) ion pair of the dimer. The IR spectrum clearly manifests that the *N*-oxide ligands are coordinated both in bridged and nonbridged forms; the carboxylato ligand in monodentate form only.

Синтезировано заглавное соединение  $\text{Cu}_2(\text{Cl}_2\text{CHCOO})_4(\text{pyO})_4$  и определена его кристаллическая структура при комнатной температуре. Соединение кристаллизуется в триклинной пространственной группе  $P\bar{1}$  с  $a = 0,8807$  нм,  $b = 1,0657$  нм,  $c = 1,1628$  нм,  $\alpha = 73,43^\circ$ ,  $\beta = 74,62^\circ$ ,  $\gamma = 68,55^\circ$  и  $Z = 1$ . Уточнение структуры с помощью метода наименьших квадратов дало величину условного  $R$  фактора равную 0,0455. Кристаллическая структура состоит из хорошо отделенных, centrosymmetрических двухъядерных молекул, в которых геометрическое расположение атомов вокруг каждого иона меди приближается к тетрагональной пирамиде. Атомы меди связаны двумя *N*-окисными мостиками между апикальным координационным центром одного Cu(II) и базальным центром другого. Измерения магнитной восприимчивости при разных температурах не обнаружили при высших температурах

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чем 93 К значительных обменных взаимодействий в ионной паре Cu(II) димера. Из ИК-спектра ясно видно, что *N*-окисные лиганды координированы как в мостиковой, так и в немостиковой форме; карбоксилатный лиганд присутствует только в монодентатной форме.

Aromatic *N*-oxides and carboxylate anions are often coordinated as exchange coupling effective bridge ligands in the copper(II) dimeric complexes [1—6]. Systematic studies of the structural and magnetic properties of several related series of exchange coupled  $S = 1/2$  copper(II) dimers show that exchange coupling varies in a rational way with the changes in chemical and structural features, of the molecules in each series [7]. Complexes of the tetrakis( $\mu$ -acetato-*O,O'*)bis(pyridine-*N*-oxide)dicopper(II) type [8—12] contain carboxylate bridges favourable for an effective intradimer exchange coupling and monodentate axially coordinated *N*-oxide ligands. On the other hand, it is known that pyridine-*N*-oxide (pyO) and its derivatives in many cases form *O*-atom bridges which are responsible for superexchange interaction in copper(II) dimers. The singlet-triplet splitting depends in these cases on bridge geometry and was found to be in a wide range changing from  $-800 \text{ cm}^{-1}$  in  $[\text{Cu}_2\text{Cl}_4(\text{pyO})_4]$  [8] to near zero in  $[\text{Cu}_2(\text{NO}_3)_4(\text{pyO})_4]$  [7, 13—15], so that assignment of the structure on the basis of the magnetic susceptibility data only may be dubious. For instance, on the basis of the overspin value of the room temperature magnetic moment of  $\text{Cu}(\text{Cl}_2\text{CHCOO})_2$  a distorted octahedral mononuclear structure was proposed [16] for this complex.

In order to elucidate this problem further, we have determined the crystal and molecular structure of the  $\text{Cu}(\text{Cl}_2\text{CHCOO})_2(\text{pyO})_2$  complex and studied its cryomagnetic properties to 93 K, ESR and IR spectra.

## Experimental

### Synthesis

A solution of 3.0 g of  $\text{Cu}(\text{Cl}_2\text{CHCOO})_2(\text{H}_2\text{O})_4$  in  $50 \text{ cm}^3$  of acetone was slowly added to a solution of 1.8 g of pyridine-*N*-oxide in  $50 \text{ cm}^3$  of acetone. Well formed, green crystals which appeared within some days were filtered out, washed with diethyl ether and air-dried. For  $\text{C}_{14}\text{H}_{12}\text{CuN}_2\text{O}_8$   $w_i(\text{calc.})$ : 12.47 % Cu, 33.00 % C, 5.49 % N, 2.37 % H;  $w_i(\text{found})$ : 12.5 % Cu, 33.00 % C, 5.5 % N, 2.3 % H.

### Crystal data

$M_r(\text{C}_{28}\text{H}_{24}\text{Cl}_8\text{Cu}_2\text{N}_2\text{O}_{12}) = 1019.2$ , triclinic, space group  $P\bar{1}$ ,  $a = 0.8807(2) \text{ nm}$ ,  $b = 1.0657(3) \text{ nm}$ ,  $c = 1.1628(3) \text{ nm}$ ,  $\alpha = 73.43(2)^\circ$ ,  $\beta = 74.62(2)^\circ$ ,  $\gamma = 68.55(2)^\circ$ ,  $Z = 1$ ,

$\rho_m = 1.77(2)$ ,  $\rho_c = 1.77 \text{ g cm}^{-3}$ ,  $F(000) = 510$ ,  $\text{CuK}\alpha$ ,  $\lambda = 0.15418 \text{ nm}$ ,  $\mu = 6.9 \text{ mm}^{-1}$ , room temperature.

### *Data collection and structure determination*

The crystal used for structure determination was of prismatic form with approximate dimensions  $0.35 \text{ mm} \times 0.20 \text{ mm} \times 0.15 \text{ mm}$ . The density was measured by flotation in a mixture of  $\text{CHBr}_3$  and  $\text{CHCl}_3$ . Preliminary unit-cell data and triclinic symmetry were obtained from rotational and Weissenberg's photographs and refined by a least-squares fit of angular positions of 11 independent reflections measured on the diffractometer.

The intensities of 2614 independent reflections ( $0 < 2\theta < 115^\circ$ ) were collected on Syntex P2<sub>1</sub> diffractometer with graphite monochromated  $\text{CuK}\alpha$  radiation and the  $\theta - 2\theta$  scan technique at a scan rate varying from 4.88 to  $29.3^\circ \text{ min}^{-1}$  in  $2\theta$ . The background was measured at each end of the scan for one half of the scan time. To check stability, two standard reflections were measured after every 98 reflections. The net count of these reflections did not change significantly during data collections. The 2461 reflections with  $I > 1.96 \sigma(I)$  were considered observed. The intensities were corrected for Lorentz and polarization factors but not for absorption or extinction. A centrosymmetry was determined by intensity statistics. The structure was solved by the Patterson and Fourier methods and refined by full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms. Hydrogen atoms were included in their calculated positions and refined with isotropic temperature parameters and C—H bond lengths constrained to 0.09 nm. The function  $\sum w(|F_o| - |F_c|)^2$  was minimized, a weighting scheme  $w^{-1} = \sigma^2(|F_o|) + C \cdot |F_o|^2$ , where  $\sigma^2(|F_o|)$  is derived from counting statistic and  $C = 0.0003$ , was employed.  $C$  was adjusted so that a constant value of  $\langle w(|F_o| - |F_c|)^2 \rangle$  was obtained in different  $|F_o|$  intervals. The final  $R = \sum |\Delta F| / \sum |F_o| = 0.0455$  and  $R_w = \sum \sqrt{w} |\Delta F| / \sum \sqrt{w} |F_o| = 0.0490$  for observed reflections used in refinement. The maximum electron density peak in the final difference synthesis was  $750 \text{ e nm}^{-3}$  (near Cl(4) atom). Scattering factors for neutral atoms were taken from *International Tables for X-Ray Crystallography* [17]. All calculations were performed with *SHELX76 Program* [18] on an ES 1033 computer. The refined positional parameters and coefficients of anisotropic temperature factors for the nonhydrogen atoms are given in Table 1. The  $F_o$  and  $F_c$  tables can be obtained on request from the authors.

### *Magnetic susceptibility and spectral measurements*

The magnetic susceptibilities of the title complex were measured in the temperature range from 90 to 340 K using a magnetic balance of the Guy type (Newport Instruments) calibrated with  $\text{HgCo}(\text{NCS})_4$ . The magnetic susceptibility of the calibrant was taken as  $\chi = 20.66 \times 10^{-11} \text{ m}^3/\text{kg}$  at 293 K. The effective absence of the ferromagnetic impurities was indicated by the invariance of the observed susceptibilities to the used four different field strengths (0.4 to 0.7 T). The molar susceptibility  $\chi_m$  was corrected for diamagnetism using Pascal's constants,  $\sum \chi_{\text{dia}} = -271 \times 10^{-11} \text{ m}^3/\text{mol}$  and a value of  $75 \times 10^{-11} \text{ m}^3/\text{mol}$  was assumed for the temperature-independent paramagnetism (TIP) of Cu(II).

Table 1

Fractional atomic coordinates ( $\times 10^4$ ) and coefficients of anisotropic temperature factors ( $\times 10^4$ ) for the nonhydrogen atoms with  $\sigma$  in parentheses. The temperature factor is of the form:

$$T = \exp [-2\pi^2(U_{11} \cdot a^2h^2 + \dots + 2U_{23}b^*c^*kl \dots)]$$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>23</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>12</sub>
Cu(1)	4330(1)	3598(1)	5300(1)	337(4)	271(3)	191(3)	- 85(2)	- 41(2)	- 61(2)
Cl(1)	2761(2)	563(1)	9827(1)	732(8)	535(7)	386(6)	- 37(5)	- 23(6)	- 243(6)
Cl(2)	1508(2)	3526(1)	9416(1)	889(11)	534(8)	435(7)	- 109(6)	184(7)	45(7)
Cl(3)	4829(2)	3289(1)	1208(1)	527(7)	780(9)	341(6)	- 185(6)	- 195(5)	49(6)
Cl(4)	8345(1)	2060(2)	1237(1)	405(7)	1039(11)	315(6)	- 159(6)	12(5)	- 175(7)
O(1)	6391(3)	3945(2)	5274(2)	351(15)	273(14)	237(13)	- 16(11)	- 106(12)	- 57(12)
O(2)	2086(3)	3668(3)	5269(3)	345(16)	517(18)	414(17)	- 273(15)	- 33(13)	- 84(13)
O(3)	3740(4)	3399(3)	7051(3)	683(22)	679(22)	224(15)	- 107(15)	- 4(14)	- 416(18)
O(4)	5049(3)	3351(3)	3623(2)	360(15)	318(15)	230(14)	- 126(11)	- 44(11)	- 29(12)
O(5)	4027(6)	1191(4)	7224(3)	1163(34)	439(21)	357(19)	- 162(17)	- 22(20)	63(20)
O(6)	7005(4)	1316(3)	4005(3)	736(22)	360(17)	328(17)	- 111(14)	- 226(16)	86(16)
N(1)	7303(4)	3205(3)	6150(3)	351(18)	219(16)	210(16)	- 19(13)	- 87(14)	- 58(14)
N(2)	1859(4)	3069(3)	4473(3)	298(17)	341(19)	281(17)	- 115(15)	- 28(14)	- 93(15)
C(1)	3697(5)	2205(5)	7642(4)	348(23)	505(28)	298(23)	- 102(22)	- 43(19)	- 80(21)
C(2)	3217(6)	2104(4)	9033(4)	482(27)	373(24)	278(22)	- 56(19)	- 59(20)	- 87(21)
C(3)	6136(5)	2257(4)	3350(3)	386(23)	285(21)	217(20)	- 71(17)	- 47(18)	- 82(19)
C(4)	6339(5)	2067(4)	2046(4)	352(23)	383(24)	255(21)	- 128(18)	- 30(17)	- 51(19)
C(5)	8517(5)	2026(4)	5946(4)	386(24)	279(22)	318(23)	- 40(18)	- 55(19)	- 57(19)
C(6)	9525(5)	1300(5)	6786(4)	323(24)	332(24)	506(29)	- 17(22)	- 100(21)	- 2(20)
C(7)	9286(6)	1754(5)	7832(5)	532(30)	493(30)	448(30)	44(24)	- 270(25)	- 77(25)
C(8)	8041(7)	2941(5)	8021(4)	721(34)	424(27)	344(25)	- 47(21)	- 233(24)	- 100(25)
C(9)	7041(6)	3659(5)	7166(4)	485(27)	289(23)	362(26)	- 106(20)	- 149(21)	63(21)
C(10)	770(5)	3835(4)	3727(4)	402(24)	322(24)	415(25)	- 81(20)	- 83(20)	- 61(19)
C(11)	496(6)	3244(5)	2919(4)	503(28)	503(29)	385(26)	- 81(22)	- 177(23)	- 113(23)
C(12)	1390(6)	1887(5)	2870(4)	626(31)	483(28)	378(26)	- 161(23)	- 121(23)	- 218(24)
C(13)	2463(6)	1135(5)	3658(4)	446(26)	290(24)	525(29)	- 148(21)	- 39(22)	- 86(20)
C(14)	2670(5)	1735(4)	4473(4)	339(23)	309(23)	358(23)	- 61(19)	- 76(20)	- 60(19)

X-Band ESR spectra of polycrystalline sample were recorded on a Varian E4 spectrometer at 77 K and at room temperature using a quartz liquid nitrogen insertion Dewar. Infrared spectra in KBr pellets were recorded on a Specord 75-IR spectrometer.

## Results and discussion

A perspective view of the molecular structure is in Fig. 1. Interatomic distances and angles are in Table 2. The crystal structure consists of discrete molecules of centrosymmetric dimeric complex  $[\text{Cu}_2(\text{Cl}_2\text{CHCOO})_4(\text{pyO})_4]$  held together by van der Waals forces.

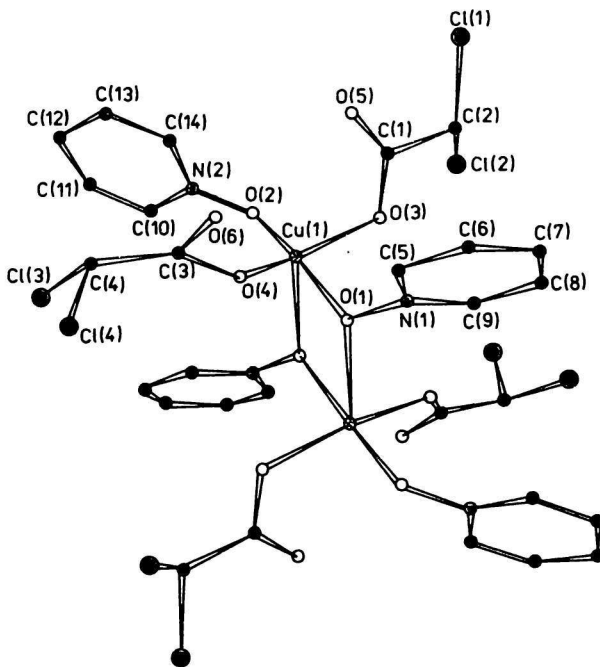


Fig. 1. A perspective view and the numbering scheme of the structure  $[\text{Cu}_2(\text{Cl}_2\text{CHCOO})_4(\text{pyO})_4]$ . All hydrogen atoms have been omitted for clarity.

The copper atom has a distorted tetragonal pyramidal environment of five oxygen atoms. In the basal plane of the pyramid two dichloroacetato ligands are in *trans* position. Bridging pyO ligand forms one basal and one apical bond (Fig. 1). The  $\text{Cu}(1) \dots \text{Cu}(1')$  distance is 0.3429 nm. The apical  $\text{Cu}-\text{O}$  bond length 0.2391 nm is longer than the basal bonds 0.1972 nm, 0.1960 nm, respectively, and the angle in the bridge is 76.8°. The base of pyramid is tetrahedrally deformed. The pyO oxygen atoms are displaced by 0.0204 nm and 0.0213 nm,

Table 2

Selected interatomic distances and angles with  $\sigma$  in parentheses

Interatomic distances		$d/(10^{-10} \text{ m})$	
Cu(1)—Cu(1 <sup>i</sup> )	3.429(2)	Cu(1)—O(1)	1.972(3)
Cu(1)—O(2)	1.960(3)	Cu(1)—O(3)	1.932(3)
Cu(1)—O(4)	1.946(3)	Cu(1)—O(1 <sup>i</sup> )	2.391(3)
Cl(1)—C(2)	1.770(4)	Cl(2)—C(2)	1.767(4)
Cl(3)—C(4)	1.764(4)	Cl(4)—C(4)	1.766(4)
O(1)—N(1)	1.348(4)	O(2)—N(2)	1.353(4)
O(3)—C(1)	1.271(5)	O(4)—C(3)	1.268(5)
O(5)—C(1)	1.219(6)	O(6)—C(3)	1.218(5)
N(1)—C(5)	1.353(5)	N(1)—C(9)	1.335(5)
N(2)—C(10)	1.344(5)	N(2)—C(14)	1.338(5)
C(1)—C(2)	1.541(6)	C(3)—C(4)	1.542(5)
C(5)—C(6)	1.367(6)	C(6)—C(7)	1.373(7)
C(7)—C(8)	1.366(7)	C(8)—C(9)	1.374(6)
C(10)—C(11)	1.381(6)	C(11)—C(12)	1.380(7)
C(12)—C(13)	1.364(7)	C(13)—C(14)	1.364(6)
Bond angles		$\varphi/^\circ$	
O(1)—Cu(1)—O(2)	168.2(1)	O(1)—Cu(1)—O(3)	91.4(1)
O(1)—Cu(1)—O(4)	91.9(1)	O(2)—Cu(1)—O(3)	89.1(1)
O(2)—Cu(1)—O(4)	90.2(1)	O(3)—Cu(1)—O(4)	167.1(1)
O(1 <sup>i</sup> )—Cu(1)—O(1)	76.8(1)	O(1 <sup>i</sup> )—Cu(1)—O(2)	91.5(1)
O(1 <sup>i</sup> )—Cu(1)—O(3)	99.0(1)	O(1 <sup>i</sup> )—Cu(1)—O(4)	93.9(1)
Cu(1)—O(1)—Cu(1 <sup>i</sup> )	103.2(1)	Cu(1)—O(1)—N(1)	119.8(2)
Cu(1)—O(2)—N(2)	119.6(2)	Cu(1)—O(3)—C(1)	115.0(5)
Cu(1)—O(4)—C(3)	121.6(2)	O(1)—N(1)—C(5)	118.0(3)
O(1)—N(1)—C(9)	120.3(3)	C(5)—N(1)—C(9)	121.6(3)
O(2)—N(2)—C(10)	118.3(3)	O(2)—N(2)—C(14)	119.9(3)
C(10)—N(2)—C(14)	121.7(4)	O(3)—C(1)—O(5)	127.0(4)
O(3)—C(1)—C(2)	112.9(4)	O(5)—C(1)—C(2)	120.1(4)
Cl(1)—C(2)—Cl(2)	109.0(2)	Cl(1)—C(2)—C(1)	112.6(3)
Cl(2)—C(2)—C(1)	111.7(3)	O(4)—C(3)—O(6)	127.9(4)
O(4)—C(3)—C(4)	116.2(3)	O(6)—C(3)—C(4)	115.8(3)
Cl(3)—C(4)—Cl(4)	110.1(2)	Cl(3)—C(4)—C(3)	114.8(3)
Cl(4)—C(4)—C(3)	109.7(3)	N(1)—C(5)—C(6)	119.2(4)
C(5)—C(6)—C(7)	120.1(4)	C(6)—C(7)—C(8)	119.5(4)
C(7)—C(8)—C(9)	119.6(5)	N(1)—C(9)—C(8)	120.0(4)
N(2)—C(10)—C(11)	119.5(4)	C(10)—C(11)—C(12)	119.1(4)
C(11)—C(12)—C(13)	119.7(4)	C(12)—C(13)—C(14)	119.9(4)
N(2)—C(14)—C(13)	120.0(4)		

respectively, from mean plane O(1), O(2), O(3), O(4) towards apex and carboxylic oxygen atoms by 0.0210 nm and 0.0206 nm in opposite direction. The Cu atom lies approximately on the least-square plane (the displacement is 0.0006 nm). This is different from usual tetragonal pyramidal coordination in which central atom is shifted from the base towards the apex of pyramid. Reason for this can be found in two weak Cu(1)—O(5) and Cu(1)—O(6) interactions on the opposite side of the pyramid apex with distances 0.2922(9) nm and 0.3123(3) nm, respectively. Resulting coordination thus can be described as 4 + 1 + 2.

The geometry of binuclear coordination polyhedron is very similar to that found in bis(pyO)copper(II) nitrate [19]. The only difference is in the lengths of apical bond which is 0.244 nm in nitrate complex. This lengthening is compensated by shortening of two weak Cu...O interactions to 0.280 nm.

Pyridine rings are planar. The O(2) atom (unbridged) lies in the plane of pyridine ring within standard deviation, but bridge atom O(1) is displaced by 0.008(2) nm from mean pyridine plane, which seems to be significant.

*Table 3*  
Results of magnetic measurements  
Temperature, molar magnetic susceptibility, and magnetic moment

<i>T</i> /K	$\chi_m/\text{mm}^3 \text{mol}^{-1}$	$\mu_{\text{eff}}/\mu_B$	<i>T</i> /K	$\chi_m/\text{mm}^3 \text{mol}^{-1}$	$\mu_{\text{eff}}/\mu_B$
93	60.1	1.87	221	25.9	1.88
102	55.8	1.89	240	23.7	1.87
122	46.3	1.88	251	22.7	1.87
132	42.9	1.88	271	21.2	1.88
152	37.0	1.87	280	20.5	1.87
163	35.2	1.89	299	19.0	1.86
182	31.1	1.87	310	18.5	1.87
191	30.3	1.89	322	17.9	1.87
211	26.6	1.86	340	17.1	1.88

The O(1)—N(1) bond has an angle 55.7° with a normal to the Cu(1), O(1), Cu(1<sup>i</sup>), O(1<sup>i</sup>) plane, which suggests *sp*<sup>3</sup> hybridization on *N*-oxide oxygen as well as no  $\pi(p, d)$  orbital interaction between Cu and O atoms. This is supported by torsion angles C(5)—N(1)—O(1)—Cu(1) and C(5)—N(1)—O(1)—Cu(1<sup>i</sup>) with values 91° and -137°, respectively.

The magnetic moment ( $\mu_{\text{eff}} = 1.87(2) \cdot \mu_B$ ) of the title compound is practically temperature-independent (Table 3) down to 93 K. Its cryomagnetic properties obey the Curie—Weiss law  $\chi_m - \chi_{\text{dia}} - \text{TIP} = C/(T - \Theta)$  with  $\Theta = 3$  K,  $C = 5.46 \times 10^{-6} \text{ m}^3/\text{kmol}$ , and  $g = 2.152$  (from  $C$ ). Thus the cryomagnetic

properties of  $[\text{Cu}_2(\text{Cl}_2\text{CHCOO})_4(\text{pyO})_4]$  in the range 93—340 K did not reveal a perceptible magnetic coupling between the  $\text{Cu}^{2+}$  ions in the oxygen-bridged dimeric complex molecules.

The ESR spectrum of powdered sample represents the axial type with  $g_{\parallel} = 2.308$  and  $g_{\perp} = 2.071$  at liquid nitrogen temperature. The value of average  $g$ -factor 2.153 is very close to the Landé splitting factor resulting from Curie—Weiss law. Down to the liquid nitrogen temperature no triplet state signals were observed.

The IR spectrum of  $[\text{Cu}_2(\text{Cl}_2\text{CHCOO})_4(\text{pyO})_4]$  indicates two N—O stretching vibrations at  $\tilde{\nu} = 1211 \text{ cm}^{-1}$  and  $\tilde{\nu} = 1204 \text{ cm}^{-1}$  which correspond to nonbridging and bridging N-oxide groups similarly to the  $[\text{Cu}_2(\text{NO}_3)_4(\text{pyO})_4]$  [20]. Two very strong and broad absorption bands of the antisymmetric COO frequency are at  $\tilde{\nu} = 1651 \text{ cm}^{-1}$  and  $\tilde{\nu} = 1629 \text{ cm}^{-1}$ , one strong band of the symmetric COO frequency is at  $\tilde{\nu} = 1368 \text{ cm}^{-1}$ . The difference between antisymmetric and symmetric COO vibrations ( $283 \text{ cm}^{-1}$  and  $261 \text{ cm}^{-1}$ ) shows the monofunctional coordination of the carboxylic groups with some differences between carboxyls.

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