

Synthesis, Crystal Structure and Vibrational Spectra of Di- μ -aqua-bis[(nitrato)(phenanthroline)(pyridinium-4-carboxylato)-copper(II)]dinitrate; $[\{\text{Cu}(\text{NO}_3)(\text{INA})(\text{phen})\}_2(\mu\text{-H}_2\text{O})_2](\text{NO}_3)_2$

Introduction

In order to combine the rare earth metals with d-elements to form heterometallic complexes we synthesized a new copper complex. Crystals of $[\{\text{Cu}(\text{NO}_3)(\text{INA})(\text{phen})\}_2(\mu\text{-H}_2\text{O})_2](\text{NO}_3)_2$ could be obtained from water-methanol solution by the reaction of the metal nitrates, phenanthroline and isonicotinic acid. Its crystal structure has been determined by single-crystal X-ray diffraction. The title compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 10.353(1)$, $b = 9.254(1)$, $c = 20.383(2)$ Å, $\beta = 96.27(1)^\circ$, $Z = 2$ (referred to the "dimeric building blocks") and $V_{EZ} = 1941.1(3)$ Å³. Herein, copper shows a strongly distorted octahedral coordination sphere with phenanthroline, protonated isonicotinate as pyridinium-4-carboxylate, nitrate and two water molecules as bridging ligands. Two edge-sharing CuN_2O_3 polyhedra form "dimeric building blocks". The structure shows different non-covalent stabilizing interactions which are typically observed in supramolecular assemblies, especially aromatic π - π , lone-pair- π , anion- π and C-H- π interactions. Therefore, the "dimeric building blocks" are connected by aromatic π - π -contacts with phenanthroline and pyridinium-4-carboxylate and stacked as a 1D-chain-like manner along b -axis. Furthermore an extended hydrogen bond network with O-H- \cdots O, N-H- \cdots O and C-H- \cdots O contacts are stabilizing this structure. From the literature only some structures are known, where the copper atoms are bridged by heterocyclic aromatic molecules like isonicotinate and nicotinate and additionally coordinated with chelating ligands such as phenanthroline or bipyridine [1-3].

Structure description

Two edge-sharing CuN_2O_3 polyhedra and their corresponding ligands form the "dimeric building blocks" (Fig. 1). Herein, Cu-Cu distances are 3.644(5) Å. The water molecules are acting as bridging ligands and involved in a hydrogen bond network with the carboxylate and ionic-pair nitrate group. These hydrogen bonds exhibit well accepted distances (Tab. 2). In the middle of the edge of bridging water molecules the crystallographic centre of inversion is located. It is known that aromatic heterocycles containing nitrogen are electron poor rings [4]. Therefore, in the present structure pyridinium-4-carboxylate and phenanthroline have an electron deficient π -system. π -Interactions which increase the electron density of phenanthroline allow a very stable face-to-face stacking between both electron poor partners wherein phenanthroline acts as π -donor and pyridinium-4-carboxylate acts as π -acceptor. The aromatic-aromatic packing of π - π -interactions are parallel displaced with distances of 3.62(2) Å. Another striking feature of this structure is the protonated pyridine ring of the pyridinium-4-carboxylate [5]. This proton is bonded to N1 and involved in a hydrogen network. Furthermore, this structure is stabilized and partly constructed by C-H- \cdots O contacts. The ionic-pair nitrate and the copper coordinating nitrate group are embedded in a hydrogen bonding network and are mainly relevant for sheet buildings and sheet connections (Fig. 2 and 3). The C-H- \cdots O hydrogen bond lengths have expected values (Tab. 2). Unusual short distance of the ionic pair nitrate group and N3 of the phenanthroline as well as between O7 also O8 and N1^{vi} of the pyridinium ring are detected without any suggestion of a hydrogen bond. Besides these forces, lone-pair- π -interactions of the non-coordinating O2 atom of the carboxylate is observed. The distance of 3.189(2) Å and an angle of C1^v-O2^v-Cg3 which exhibit a value of 87.9(2) are reflecting a significant interaction as well as a nearly ideal parallel stacking on the ring plane. In this structure also anion- π -interactions can be observed between the ionic-pair nitrates and the phenanthroline rings which have values of 3.682(3) and 4.024(3) Å. These distances can be compared to literature [6]. Another π -stacking interaction between the pyridinium ring and the hydrogen bond interface of coordinated nitrate group and phenanthroline is observed and show a distance of 3.244(2) Å [7].

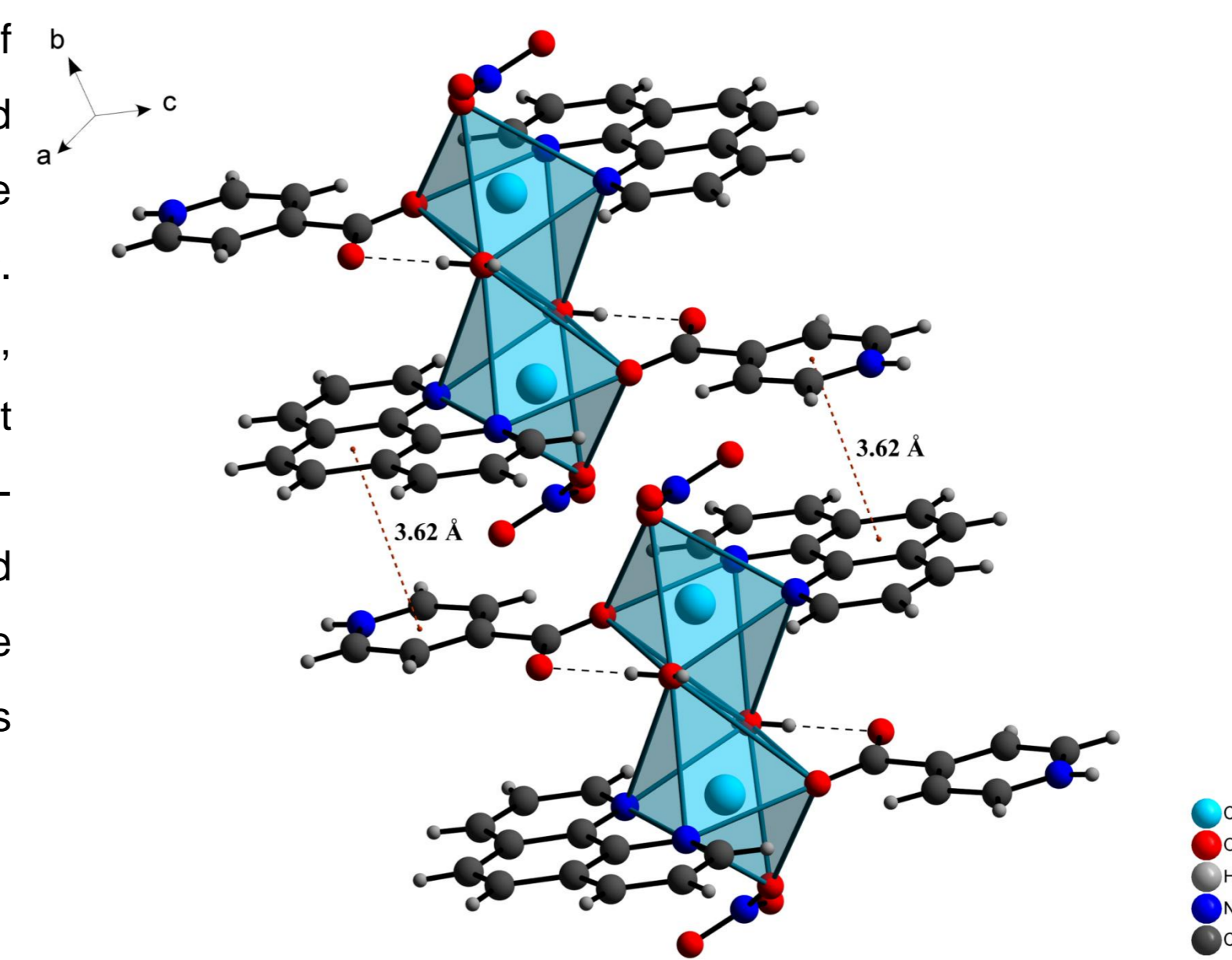


Fig. 1 Edge-sharing CuN_2O_3 -polyhedra and π - π connected "dimeric building blocks" (dotted lines represent hydrogen bonds and π - π -interactions).

Tab. 1 Crystallographic data of the title compound

Crystal system	monoclinic
Space group	$P2_1/c$
a [Å]	10.353(1)
b [Å]	9.254(1)
c [Å]	20.383(2)
β	96.27(1)
V [Å ³]	1941.1(3)
Z	2 ("dimeric building blocks")
D_{calc} [g cm ⁻³]	1.741
μ (MoK α) [mm ⁻¹]	1.192
$F(000)$ [e]	1036
Temperature [K]	223(2)
Diffractometer	Stoe IPDS II
Monochromator	Graphite
Wavelength [Å]	0.71073
2θ range [°]	1.00 – 25.68
Index range	$-11 \leq h \leq 12$ $-11 \leq k \leq 11$ $-24 \leq l \leq 24$
Unique reflections	3685
Data / refined parameters	3685 / 358
Goodness-of-fit on F^2	1.064
R_1 [$I \geq 2\sigma(I)$]/ R_1 (all data)	0.0361 / 0.0451
wR_2 [$I \geq 2\sigma(I)$]/ wR_2 (all data)	0.0854 / 0.0895
$\Delta\rho_{\text{max}}/\text{min}$ [e Å ⁻³]	0.832 / -0.590
Deposition number	CCDC-789277

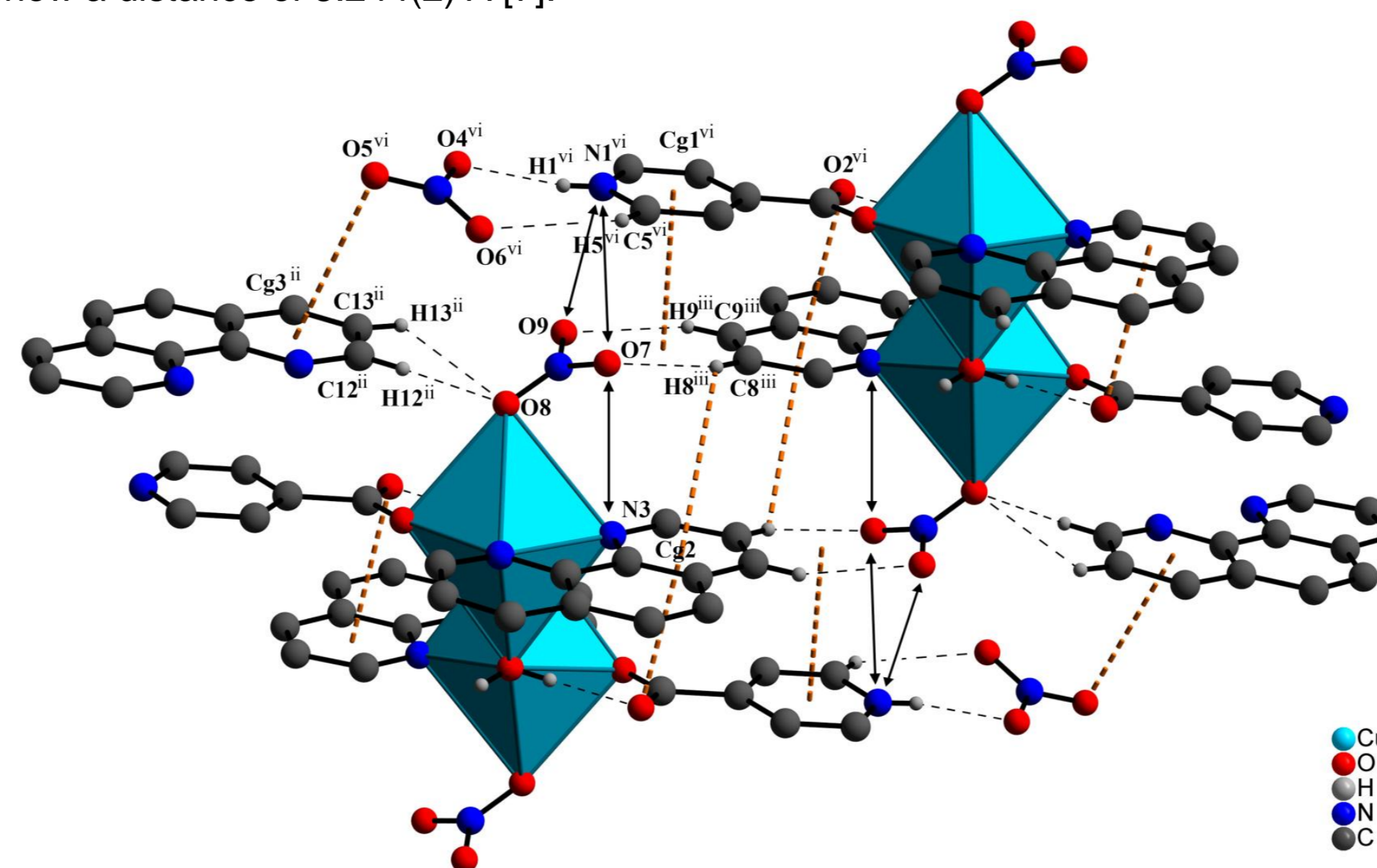


Fig. 2 Sheet connections by C-H- \cdots O hydrogen bonds and π -interactions (thin dotted lines represent hydrogen bonds; thick dotted lines represent π -interactions).

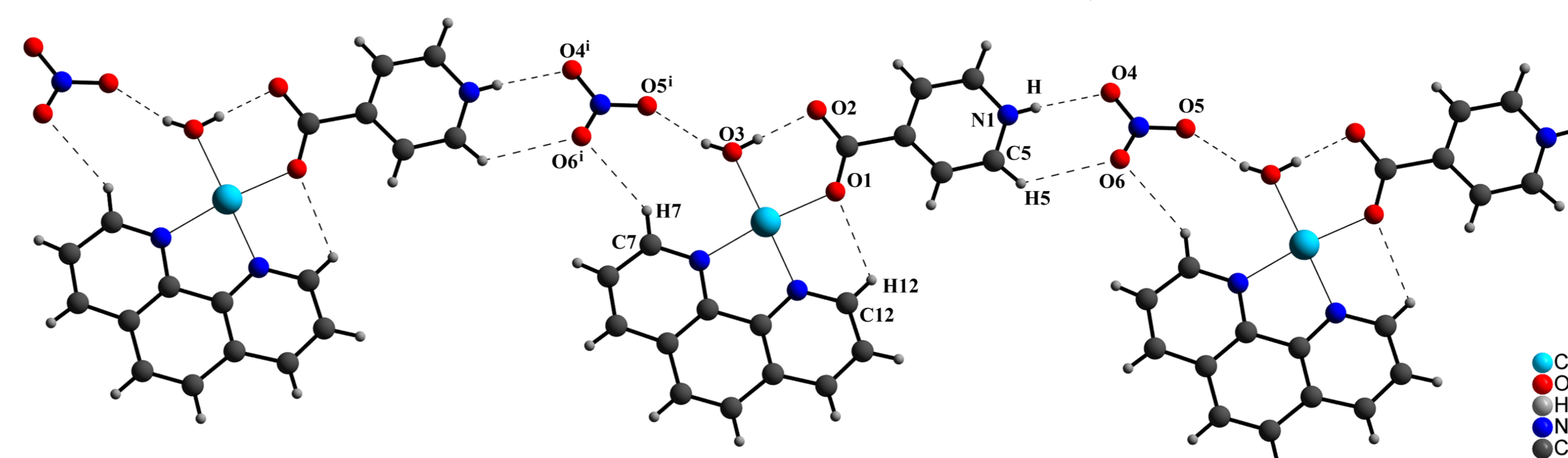


Fig. 3 Representation of a sheet with extended hydrogen bonding network including ionic pair nitrate group as well as O-H- \cdots O, N-H- \cdots O and C-H- \cdots O contacts (dotted lines represent hydrogen bonds).

Tab. 2 Selected hydrogen bond lengths (Å) and angles (°) of $[\{\text{Cu}(\text{NO}_3)(\text{INA})(\text{phen})\}_2(\mu\text{-H}_2\text{O})_2](\text{NO}_3)_2$

O-H- \cdots O and N-H- \cdots O hydrogen bonds			
N1- \cdots O4	2.760(4)	N1-H- \cdots O4	170.4(4)
O3- \cdots O5 ⁱ	2.758(3)	O3-HW2- \cdots O5 ⁱ	165.4(4)
O3- \cdots O2	2.582(3)	O3-HW1- \cdots O2	179.3(2)
C-H- \cdots O hydrogen bonds			
C5- \cdots O6	3.261(4)	C5-H5- \cdots O6	125.7(3)
C6 ^{iv} - \cdots O6	3.528(4)	C6 ^{iv} -H6 ^{iv} - \cdots O6	126.4(2)
C7- \cdots O6 ⁱ	3.316(4)	C7-H7- \cdots O6 ⁱ	138.9(3)
C8 ⁱⁱⁱ - \cdots O7	3.244(4)	C8 ⁱⁱⁱ -H8 ⁱⁱⁱ - \cdots O7	162.9(3)
C9 ⁱⁱⁱ - \cdots O9	3.466(6)	C9 ⁱⁱⁱ -H9 ⁱⁱⁱ - \cdots O9	129.9(2)
C12 ⁱⁱ - \cdots O1	2.996(3)	O12 ⁱⁱ -H12 ⁱⁱ - \cdots O1	113.6(2)
C12 ⁱⁱ - \cdots O8	3.146(4)	O12 ⁱⁱ -H12 ⁱⁱ - \cdots O8	118.2(2)
C13 ⁱⁱ - \cdots O8	3.125(4)	O13 ⁱⁱ -H13 ⁱⁱ - \cdots O8	120.9(3)

Symmetry codes: (i) 1+x, 1+y, z; (ii) 1-x, -y, 1-z; (iii) 2-x, 1-y, 1-z; (iv) -x, -y, 1-z; (v) 1-x, 1-y, 1-z; (vi) 1+x, y, z; (vii) -x, -1-y, 1-z; (viii) x, -1+y, z; (ix) -1+x, -1+y, z.

Vibrational Spectra and Discussion

The broad absorption band in the infrared spectrum at 3358 cm^{-1} is due to the stretching vibration of coordinated water molecules. The weak but sharp absorption band at 3273 cm^{-1} as well as the shoulder at 3114 and the band at 3104 cm^{-1} are attributed to the N-H stretching modes and the deformation of these groups is located at 1635 cm^{-1} (Fig. 4). The occurrence of the bands at 1321, 1292 and 1256 cm^{-1} may result from deformations and combination modes involving the N-H deformation frequencies. Several absorption bands in the region of 3080 – 3000 cm^{-1} being due to the stretching vibrations of aromatic C-H bonds. The stretching vibrations of the carboxylate are located at 1594 cm^{-1} for the asymmetric and at 1386 cm^{-1} for the symmetric mode corresponding to the literature [8]. The difference between the asymmetric and symmetric stretching vibrations of COO^- is 208 cm^{-1} which indicates a monodentate carboxylate group to copper. Deformation vibration of CO_2^- which are absent in Raman spectrum can be found at 767 and 722 cm^{-1} . Corresponding to the literature of transition metal complexes with 1,10-phenanthroline as ligand, the region between 1590 – 1400 cm^{-1} is dominated by aromatic C=C and C=N stretching modes. Absorption between 1250 – 1000 cm^{-1} can be assigned to the aromatic in-plane C-H deformation vibrations and are followed by aromatic out-of-plane C-H as well as the out-of-plane ring vibrations in the region between 900 – 650 cm^{-1} . Nitrate absorption bands for the ionic nitrate group occur at 1056 cm^{-1} and 834 cm^{-1} . Absorption at 722 cm^{-1} is a combination band of NO_2 stretching mode and deformation vibrations of CO_2^- . The bands at 1292, 1041, 1026 and 909 can be assigned to the NO and NO_2 stretching vibrations and absorption at 770, 740 and 700 cm^{-1} is attributed to the symmetric and asymmetric bending modes of the coordinated nitrate group.

References

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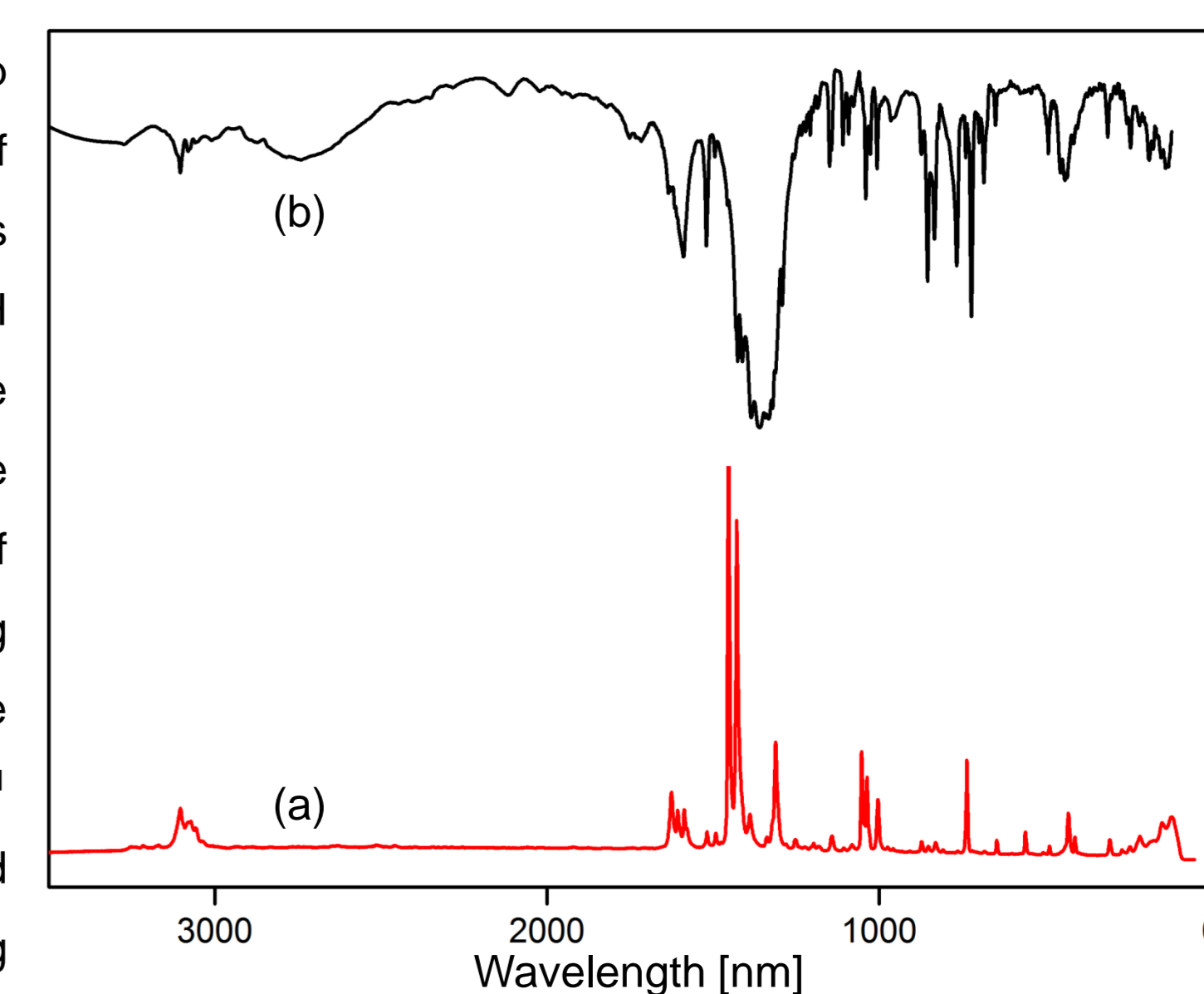


Fig. 4 (a) Raman ($\lambda_{\text{exc}} = 473$ nm) and (b) FT-IR / FIR spectra of crystalline title compound.