Synthesis, Crystal Structure and Vibrational Spectra of Di-$\mu$-aquabis[(nitrato)(phenanthroline)(pyridinium-4-carboxylato)-copper(II)]dinitrate; [{Cu(NO$_3$)(INA)(phen)}$_2$(H$_2$O)$_2$(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 [{Cu(NO$_3$)(INA)(phen)}$_2$(H$_2$O)$_2$(NO$_3$)$_2$] could be obtained from water-methanol solution by the reaction of the metal nitrates, phenanthroline and isonicotinate 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 $a = 10.35(1)$ Å, $b = 9.25(4)$ Å, $c = 20.38(2)$ Å, $\beta = 96.27(1)$°, $Z = 2$ (refined to the "dimeric building blocks") and $V_{tot} = 1941.13$ Å$^3$. 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 Cu$_2$O$_2$polyhedra form "dimeric building blocks". The structure shows different non-covalent stabilizing interactions which are typically observed in supramolecular assemblies, especially aromatic $\pi$- $\pi$, lone-pair $\pi$-acceptor $\pi$ and C–H–O interactions. Therefore, the "dimeric building blocks" are connected by aromatic $\pi$-contacts with phenanthroline and pyridinium-4-carboxylate and stacked as a 1:2 chain-like manner along b-axis. Furthermore an extended hydrogen bond network with O–H–O, N–H–O and C–H–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 bipyrindine [1-3].

Structure description
Two edge-sharing Cu$_2$O$_2$polyhedra and their corresponding ligands form the "dimeric building block" (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 amino-pair nitrate group. These hydrogen bonds exhibit well accepted distances (Tab. 2). In the middle of the bridging of 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 system. $\pi$-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 n-acceptor and pyridinium-4-carboxylate acts as n-acceptor. The aromatic-atomic packing of n-interactions are parallel displaced with distances of 3.622(2) Å. Another striking feature of this structure is the protonated pyridinium 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 contributed by C–H–O contacts. The amino-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–O hydrogen bond lengths have expected values (Tab. 2). Unusual short distance of the amino-pair nitrate group and N3 of the phenanthroline as well as between O7 also O8 and N10 of the pyridinium ring are detected without any suggestion of a hydrogen bond. Besides these forces, lone-pair $\pi$-interactions of the non-coordinating O2 atom of the carboxylate is observed. The distance of 3.189(2) Å and an angle C1–O2–C3 which exhibit a value of 97.9(2)° are reflecting a significant interaction as well as a nearly ideal parallel stacking on the ring plane. In this structure also amino $\pi$-interactions are observed between the amino-pair nitrate and the phenanthroline rings which have values of 3.668(2) and 4.024(2) Å. These distances can be compared to literature (6). Another amino $\pi$-interaction between the pyridinium ring and the hydrogen bond interface of coordinated nitrate group and phenanthroline is observed and show a distance of 3.044(2) Å [7].

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 vibrations. Several absorption bands in the region of 3080 - 3000 cm$^{-1}$ are due to the stretching vibrations of aromatic C–H bonds. The stretching vibrations of the carboxylate are located at 1594 cm$^{-1}$ for the aromatic and at 1386 cm$^{-1}$ for the symmetric mode corresponding to the literature [6]. The difference between the asymmetric and symmetric stretching vibrations of COO$^-$ at 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 the C–H deformation vibrations of ligand, the region between 1599 - 1400 cm$^{-1}$ is dominated by aromatic C=C and C=O stretching modes. Absorption between 1250 - 1500 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 iron nitrate group occur at 1561 cm$^{-1}$ and 834 cm$^{-1}$. Absorption at 722 cm$^{-1}$ is a combination band of NO$_3^-$ stretching and mode deformation vibrations of CO$_2$$. The bands at 1092, 1041, 1026 and 900 can be assigned to the NO and NO$_3^-$ 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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