Synthesis, X-ray characterization and DFT study of a novel Fe(III)–pyridine-2,6-dicarboxylic acid N-oxide complex with unusual coordination mode

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Our synthetic approach demonstrates that pyridine-2,6-dicarboxylic acid N-oxide can form a stable FeIII complex with the rare 1:3 metal-to-ligand ratio. This study provides more information about packing features of one crystalline compound, (H9a-acr) 3[Fe(pydco)3]·C16H2O (1) (where H2pydco = pyridine-2,6-dicarboxylic acid N-oxide and 9a-acr = 9-aminoacridine) via proton transfer methodology. The structure of 1 was characterized by IR spectroscopy, X-ray diffraction methods and the elemental analysis was performed to check the purity of the compound. On the basis of crystallographic data, compound 1 contains a monomeric anion with distorted octahedral geometry. The metal center is coordinated to six oxygen atoms by three bidentate pyridine-2,6-dicarboxylic acid N-oxide ligands to form a ceiling fan-shaped entity in which only the N-oxide oxygen and one carboxylate oxygen generate a six-membered chelate ring as seen for other N-oxides. Furthermore, the [Fe(pydco)3]+ and (9a-acr)+ units in 1 form 2D anionic and cationic layers. The intermolecular interactions in this novel system consist of electrostatic attraction between ion pairs, different kinds of H-bonding and π-stacking all of which join the 2D layers to create 3D supramolecular architectures. Since pyridine-2,6-dicarboxylic acid N-oxide and pyridine-2,6-dicarboxylic acid have similar frameworks, we also highlighted some areas of current interest in the coordination behavior of the latter ligand in mononuclear monomeric compounds in the reported structures up to now and investigated the influence of the N-oxide moiety on the coordination mode(s) in the crystal lattice as well.

1. Introduction

In recent years, pyridine dicarboxylic acid derivatives have attracted much interest in designing and synthesis of novel compounds with desirable properties. Also they are a class of organic compounds with variety roles in biology and medicine and they are present in many natural products, such as alkaloids, vitamins, and co-enzymes [1]. Among them, pyridine-2,6-dicarboxylic acid (H2pydc) has been featured in many research fields because of its ability to use different coordination modes with metal ions as well as forming stable chelates through two carboxylate groups that may be completely or partially deprotonated and the nitrogen of the pyridine ring. This specific ligand is also water-soluble, commercially available, cheap and can participate in two important intermolecular interactions; strong hydrogen bond and π–π stacking which are essential for controlling the self-association or aggregation in the crystal structure of metal complexes. In addition, the flexibility of the carboxylate groups is always efficient to form fascinating topologies like mononuclear, binuclear or polynuclear compounds [2]. According to a survey of the Cambridge Structural Database (CSD, Version 5.36, update 2015) for complexation of metal ions by H2pydc, it is clear that extensive studies have been done on this ligand. Presently, we have investigated only mononuclear, monomeric compounds. As shown in Fig. 1, the most common coordination mode for pydc2– in 704 compounds is tridentate by O,N,O donor sites to form stable five-membered chelate rings. Among them, 247 compounds have a 1:2 metal-to-ligand ratio with octahedral coordination environment and 148 compounds have a 1:3 metal-to-ligand ratio with distorted tricapped trigonal prismatic geometry (see Figs. 2 and 3). Also in 20
compounds, pydc\(^2^–\) acted in a bidentate manner through ON chelation through a deprotonated oxygen atom and the nitrogen of the pyridine ring with the second carboxylate group not involved in the coordination (see Fig. 2). Finally, compounds that contain monodentate pydc\(^2^–\) are comparatively less common and only 4 of them have this rare feature (see Scheme 1). It is well known that H\(_2\)pydc and pyridine-2,6-dicarboxylic acid N-oxide (H\(_2\)pydco) have similar frameworks, therefore it is expected that H\(_2\)pydco would show the same features as well as acting as an anti-HIV agent [3]. However, these two structures were found to be quite different from each other in terms of their coordination ability. The reasons are the following: (i) although both ligands have symmetrical carboxylate groups, the N-oxide group of H\(_2\)pydco is a considerably better electron donor than the ring nitrogen atom of H\(_2\)pydc. In fact, this factor could increase coordination capacities and flexibility of the H\(_2\)pydco together with the enrichment of their coordination or bridging modes [4]; (ii) there is steric hindrance between the carboxylate groups and the N-O moiety in pydco\(^2^–\) so one carboxylate group is rotated from the plane of the pyridine ring to reduce this steric hindrance and it is a likely reason for pydco\(^2^–\) acting as a bidentate ligand. On the other hand, the carboxylate groups in pydc\(^2^–\) are sufficiently close to the nitrogen of the pyridine ring that this ligand is able to act in a tridentate fashion. These differences have been motivated our interest in the chemistry of H\(_2\)pydco for investigating the influence of the N-oxide moiety on the coordination mode(s) in the crystal lattice. It should be noted that some differences in many crystal lattices arise from reaction parameters that can play a crucial role in the structure-formation processes and the reaction yield, such as the heterocyclic organic ligands which acted as a linker or auxiliary ligands, the reaction temperature, the nature of the metal ions, the pH value, the solvent concentration and the molar ratio of reactants [5]. It is worth mentioning that the carboxylate groups acids in H\(_2\)pydc and H\(_2\)pydco can adopt various H-bonding linkage modes and can form organic salts when organizing with organic bases such as many amines, in which proton transfer occurs. According to Johnson and Rumon, higher \(\Delta pK\) value (2 or 3) for mixture of organic acids and bases is a customary threshold for salt formation therefor proton transfer will take place [6].

Iron complexes are subjects of extensive research in many different areas because it is the most abundant transition metal in earth’s crust. This biometal is one of the most important elements

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**Fig. 1.** Distribution of different coordination modes of the H\(_2\)pydc ligand in mononuclear monomeric compounds.

**Fig. 2.** Distribution of compounds in which H\(_2\)pydc ligand acted as a bidentate manner.

**Scheme 1.** Representation of coordination behavior of H\(_2\)pydc ligand.

**Fig. 3.** Distribution of compounds that have 1:3 metal-to-ligand ratio with H\(_2\)pydc ligand.
in nature with a plethora of known sources and easy access. Also, it is relatively inexpensive, not very toxic, and environmentally benign [7]. Moreover iron plays effective role in many catalytic applications [8] and biological processes like iron-containing enzymes [9]. Depending upon the complexing ligand attached to the iron, the metal may be divalent, trivalent or be in a redox equilibrium between both states [10]. In the past two decades much attention has been paid to the design and synthesis of iron complexes with carboxylic acids due to the versatile bidentate, tridentate or bridging coordination modes of the ligand. Up to now 54 Fe complexes with H2pydco have been synthesized and in 36 compounds two pydc2− are coordinated around the central metal to generate a monomeric species; indeed there is only one case of a complex in which pydc2− is coordinated in a bidentate manner and it is because of the special conditions of synthesis at various pH [11]. In our previous studies on the synthesis of first row transition metals, it was found that a series of these compounds with synthetically pleasing structures could be generated vis-à-vis employing pyridine-2,6-dicarboxylic acid N-oxide/9a-acr as ligands [4,12]. Herein, we report the successful synthesis and X-ray crystal structure characterization of a novel ([H9a-acr]2[Fe(pydco)2]6H2O (1)) complex with a 1:3 ratio between Fe and pydco− under mild reaction conditions using 2,6-dicarboxylic acid N-oxide/9a-acr, Fe(NO3)3·6H2O, methanol and H2O as reagents. The H2pydco ligand was synthesized according to a literature method [13]. As mentioned above, H2pdco could be coordinated to one metal ion by only the N-oxide moiety and an oxygen atom of one carboxylate groups. Meanwhile, an organic base, 9a-acr, could be protonated to balance the charge of the complexes. Additionally, a CSD search revealed that the metal:ligand ratio observed in 1 is unprecedented, either using H2pdco or H2-pydc ligands (see Fig. 3).

2. Experimental

2.1. General considerations

All reagents were purchased commercially and used without further purification. The infrared spectra were recorded in the range of 4000–600 cm−1 on a Buck 500 scientific spectrometer as KBr discs. The C, H, and N elemental analyses were performed on a Thermo Finnigan Flash model 1112 EA microanalyzer. The X-ray data were obtained using a Bruker D8 VENTURE diffractometer. Melting points determined on a Barnstead Electrothermal 9300 apparatus.

2.2. Synthesis of ([H9a-acr]2[Fe(pydco)2]6H2O (1))

A methanolic solution of 9a-acr (40 mg, 0.2 mmol) was added to an aqueous solution of H2pydco (20 mg, 0.1 mmol) and the mixture was stirred at room temperature for 2 h. Then FeCl2·4H2O (10 mg, 0.05 mmol) was added to the reaction mixture and the stirring was continued for a further 2 h. The resulting solution gave orange plate crystals of the compound by slow evaporation of the solvent over three days at room temperature (m.p. 174 °C). Elemental analysis: Anal. Calc. for C60H54CoN9O21: C, 55.78; H, 3.96; N, 9.62. Found: C, 55.74; H, 4.21; N, 9.75 %. IR bands (KBr pellet, cm−1): ν (s(COO−)) is 283 cm−1 indicating that the carboxylate group is coordinated unidentately to iron(III), in agreement with the crystal structures of 1. Also, the absence of bands in the range 1690–1730 cm−1 indicate that the H2pydco is completely deprotonated in the form of pydco2− anion upon proton transfer reaction [14]. Moreover, the bands in the 1243–1206 cm−1 region can be assigned to the N−O stretching vibrations of the pyridine-N-oxide group. There are also broad absorption bands at 3427–3158 cm−1 attributed to asymmetric and symmetric stretching vibrations of the COO− group, respectively. The separation between νas(COO−) and νs(COO−) is used to diagnose coordination modes. In our case the difference between νas(COO−) and νs(COO−) is 283 cm−1 indicating that the carboxylate group is coordinated unidentately to iron(II), in agreement with the crystal structures of 1. The infrared spectroscopic data and elemental analyses of 1 are fully consistent with its structural characteristics as determined by single-crystal X-ray diffraction.

2.3. X-ray crystallographic analysis

A suitable crystal of 1 was mounted on a Mitegen loop with a drop of Paratone oil and placed in the cold nitrogen stream on the diffractometer. A hemisphere of data was collected under control of the satn2 [18] software and the raw data reduced to F2 values with satn [18] which also performed a global refinement of unit cell parameters using 9826 reflections drawn from the final data set. Correction for absorption and merging of equivalent reflections was accomplished with safrs [18] followed by solution of the structure by direct methods (srafs [19]). Full-matrix, least-squares refinement of the resulting model was performed with srafs [20] with hydrogen atoms attached to carbon being placed in calculated positions. Those attached to nitrogen and oxygen were placed in positions derived from difference maps and their coordinates adjusted to give N−H = 0.91 Å and O−H = 0.84 Å. All hydrogen atoms were included in the refinement as riding contributions with isotropic displacement parameters tied to those of the attached atoms. In the last stages of the refinement, the crystal was determined to be an inversion twin and the refinement was completed on this basis.

2.4. Theoretical methods

The energies of all complexes included in this study were computed at the Bp86-D3/def2TZVP level of theory. We have used the crystallographic coordinates for the theoretical analysis of the non-covalent interactions present in the solid state. The calculations have been performed by using the program TURBOMOLE version 7.0 [21]. The interaction energies were calculated with correction for the basis set superposition error (BSSE) by using the Boys–Bernardi counterpoise technique [22]. For the calculations we have used the DFT-D functional with the latest available correction for dispersion (D3) [23]. In order to reproduce solvent effects, we have used the conductor-like screening model COSMO [24], which is a variant of the dielectric continuum solvation models. We have used water as solvent [25].

3. Results and discussion

3.1. Synthesis and IR spectra

Infrared spectroscopy data show vibrations due to the water, carboxylic acid, and amine fragments of 1. Strong peaks at 1648 and 1365 cm−1 are attributed to asymmetric and symmetric stretching vibrations of the COO− group, respectively. The separation between νas(COO−) and νs(COO−) is used to diagnose coordination modes. In our case the difference between νas(COO−) and νs(COO−) is 283 cm−1 indicating that the carboxylate group is coordinated unidentately to iron(III), in agreement with the crystal structures of 1. Also, the absence of bands in the range 1690–1730 cm−1 indicate that the H2pydco is completely deprotonated in the form of pydco2− anion upon proton transfer reaction [14]. Moreover, the bands in the 1243–1206 cm−1 region can be assigned to the N−O stretching vibrations of the pyridine-N-oxide group. There are also broad absorption bands at 3427–3158 cm−1 attributed to the N−H and N−H 2 groups of the 9-aminoacridinium anion upon proton transfer reaction [14]. Consequently the infrared spectroscopic data and elemental analyses of 1 are fully consistent with its structural characteristics as determined by single-crystal X-ray diffraction.

3.2. Description of the crystal structure

Single crystal X-ray diffraction analysis showed that compound 1 crystallizes with an asymmetric unit consisting of one [Fe(pydco)2]3+ anion, three 9-aminocarboxidim (H9a-acr)7 cations and six uncoordinated water molecules. The molecular structure of 1 with the atom labeling of asymmetric unit, is shown in...
3.3. Comparison to related structures

In our previous work, four isostructural compounds based on 9-aminoacridine, pyridine-2,6-dicarboxylic acid N-oxide and CoII, NiII, CuII and ZnII metal ions with formulas, [[(9a-acr)2–[M(pydco)2(H2O)2]4H2O]} have been synthesized [4,12]. On the basis of crystallographic data, these anionic complexes have the usual 1:2 metal-to-ligand ratios with distorted octahedral coordination geometry about each metal ion consisting of two bidentate pydco2– ligands as well as two coordinated water molecules that are in axial positions. The similarity between these crystals packing suggested that the hydrogen-bonded network of organic ligands would serve as a host lattice in which one metal could be replaced by another metal without disturbing the lattice [16]. To further check this idea, we used another first transition metal, FeII but the result was unexpected in that the resulting complex (1 contains FeIII (note that FeII is readily oxidized to FeIII in aqueous solution unless oxygen is excluded). Moreover, it has the rare 1:3 metal-to-ligand ratio and does not contain coordinated water molecules. Instead, the axial sites are occupied by two carboxylate oxygens and O11 carboxylate oxygens [M(pydco)2(H2O)2]4H2O] have been synthesized [4,12]. On the basis of crystallographic data, these anionic complexes have the usual 1:2 metal-to-ligand ratios with distorted octahedral coordination geometry about each metal ion consisting of two bidentate pydco2– ligands as well as two coordinated water molecules that are in axial positions. The similarity between these crystals packing suggested that the hydrogen-bonded network of organic ligands would serve as a host lattice in which one metal could be replaced by another metal without disturbing the lattice [16]. To further check this idea, we used another first transition metal, FeII but the result was unexpected in that the resulting complex (1)

**Table 1**

Crystallographic data for 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (at 293 K)</th>
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<tbody>
<tr>
<td>Empirical formula</td>
<td>C60H54FeN9O21</td>
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<tr>
<td>M (g mol⁻¹)</td>
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<tr>
<td>T (K)</td>
<td>150</td>
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<tr>
<td>Radiation</td>
<td>Cu Kα</td>
</tr>
<tr>
<td>ψ (Å)</td>
<td>1.54178</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Orthorhombic</td>
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<tr>
<td>Space group</td>
<td>Pca2</td>
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<tr>
<td>a (Å)</td>
<td>25.4446 (4)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>11.5803 (2)</td>
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<tr>
<td>c (Å)</td>
<td>19.2566 (3)</td>
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<tr>
<td>α (°)</td>
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<tr>
<td>β (°)</td>
<td>90</td>
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<tr>
<td>γ (°)</td>
<td>90</td>
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<tr>
<td>V (Å³)</td>
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<tr>
<td>Z</td>
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<tr>
<td>Density (g/cm³)</td>
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<tr>
<td>μ (mm⁻¹)</td>
<td>2.92</td>
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<tr>
<td>Crystal size (Å)</td>
<td>0.19 × 0.15 × 0.05</td>
</tr>
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<td>Ω range for data collection (°)</td>
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<td>Index ranges</td>
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<tr>
<td></td>
<td>–13 ≤ k ≤ 13</td>
</tr>
<tr>
<td></td>
<td>–22 ≤ l ≤ 22</td>
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<td>Reflections collected</td>
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<td>Independent reflections, Rint</td>
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<td>Data/restraints/parameters</td>
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<td>Goodness-of-fit on F²</td>
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<tr>
<td>Final R indexes [I &gt; 2σ(I)]</td>
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</tr>
<tr>
<td></td>
<td>wR2 = 0.0760</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R1 = 0.0419</td>
</tr>
<tr>
<td></td>
<td>wR2 = 0.0792</td>
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<tr>
<td>Largest difference, peak/hole (eÅ⁻³)</td>
<td>0.216/-0.247</td>
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**Fig. 4.** Asymmetric units of compound 1 with the atom numbering scheme.
of multiple π–π stacking interactions between their aromatic rings [17]. However, the alternating cationic layers in 1 are not parallel to each other but are inclined at 61° to one another (see Fig. 7).

Logically, hydrogen bonding interactions are responsible for this difference because the NH and NH+ groups of the cationic layers have to connect with carboxyl groups of the anionic layers via H-bonds to create the 3D network. Thus it appears that the planes of the pyridine rings of the coordinated pydco2–/C0 ligands play an effective role in this case since in the previous compounds they are parallel to each other while in 1 they are not parallel and on average they are inclined at 61° to each other. The average bond distances between the FeIII, CoII, NiII, CuII and ZnII ions and oxygen atoms on the pydco2–/C0 ligands are given in Table 4 and plotted in Fig. 8. Since the amine is more basic than the carboxylate group, the protons are transferred to the 9a-acr molecules and this charge distribution is confirmed by the shorter M–O–carboxylate distances for the deprotonated oxygen atoms coordinated to the former MII metal ions. However, in 1 it is reversed and Fe–O–oxide is shorter than Fe–O–carboxylate. As a result the axial positions in 1 are occupied by two Fe–O–carboxylate oxygen atoms.

3.4. Theoretical studies

The theoretical study is devoted to analyzing the anti-electrostatic p+–p interactions and the crucial role of the countercations in explaining the short p-stacking distances observed between protonated 9-aminoacridine p-systems in the solid state of 1. Fig. 6 shows a fragment of the packing in compound 1 where the alternation of anionic and cationic layers (connected via H-bonding) is highlighted. The [Fe(pydco)3]2– anions are interconnected by means of H-bonding interactions involving bridging water molecules that interact with the carboxylate groups of the pydco ligand (see Fig. 5c). In the cationic layers, the protonated 9-aminoacridine molecules interact with each other by means of...

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### Table 2

Selected bond lengths (Å) and bond angles (°) for 1.

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<tr>
<th></th>
<th>D/H–A</th>
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<td>1.986(3)</td>
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<tr>
<td>Fe1–O3</td>
<td>2.008(3)</td>
<td>1.955(2)</td>
<td>1.996(12)</td>
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<tr>
<td>O1–Fe1–O6</td>
<td>174.85(11)</td>
<td>171.87(11)</td>
<td>176.15(11)</td>
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<tr>
<td>O8–Fe1–O11</td>
<td>166.75(11)</td>
<td>170.31(11)</td>
<td>171.79(12)</td>
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<td>O6–Fe1–O13</td>
<td>90.56(11)</td>
<td>79.09(11)</td>
<td>87.79(12)</td>
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<tr>
<td>O6–Fe1–O15</td>
<td>96.04(10)</td>
<td>96.04(10)</td>
<td>96.04(10)</td>
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### Table 3

Hydrogen bonding parameters for 1.

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<th>H–A</th>
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<td>N4–H4A–O7</td>
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<td>1.86</td>
<td>2.762(4)</td>
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<td>N5–H5A–O15v</td>
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<td>1.98</td>
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<td>N6–H6A–O21v</td>
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<td>2.781(4)</td>
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<td>N7–H7A–O17v</td>
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<td>1.93</td>
<td>2.828(4)</td>
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<td>N8–H8A–O10v</td>
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<td>1.94</td>
<td>2.783(4)</td>
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<tr>
<td>O16–H16A–O9</td>
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<td>O20–H20A–O11</td>
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<td>2.11</td>
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<td>O20–H20B–O4</td>
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<td>2.850(5)</td>
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<td>O21–H21A–O5</td>
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<td>2.07</td>
<td>2.866(4)</td>
<td>159</td>
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Symmetry codes: (i) x, y – 1, z; (ii) –x + 3/2, y, z + 1/2; (iii) –x + 3/2, y, z – 1/2; (iv) x – 1/2, –y + 1, z; (v) x – 1/2, –y, z; (vi) x – 1, y, z; (vii) x, y + 1, z.

**Fig. 5.** (a) Anionic complex with ceiling fan shaped; (b) the role of the water molecules stabilizing the 1D anionic chain along the b axis; (c) 2D anionic layer is generated along the bc plane by the role of the water-bridged between 1D anionic chains as well as (H2O)4 linear water clusters between anionic complexes.
a parallel and two types of antiparallel \( \pi^+ - \pi^+ \) stacking interactions (see Fig. 6, right). First we have used a theoretical model retrieved from the crystallographic coordinates (see Fig. 9A) where the \([\text{Fe(pydco)}_3]^{3-}\) anion simultaneously interacts with three counterions (protonated 9-aminoacridine). This supramolecular system can be used as a minimalist model for the interaction of cationic and anionic layers observed in 1. In this system two antiparallel \( \pi^+ - \pi^+ \) stacking and three electrostatically assisted H-bonding interactions are formed. This supramolecular arrangement is connected with another one in the solid state crystal structure by means of the parallel \( \pi^+ - \pi^+ \) stacking interactions and water molecules (see Fig. 6). We have computed the formation energy of this assembly (tetramer) starting from different trimers (B–D, see Fig. 9) in order to differentiate the energies of the different H bonds. The resulting interaction energies are similar for all combinations, indicating that the assembly is principally stabilized by strong electrostatic (non-directional) interactions and that the \( \pi^+ - \pi^+ \) stacking interactions have a little influence modulating the assembly.

To further explain the formation of the anti-electrostatic \( \pi^+ - \pi^+ \) stacking interactions and the influence of the counterions, we have

**Fig. 6.** 3-D crystal packing of 1 showing its alternating anionic and cationic layers. Protonated 9-aminoacridine molecules are arranged in the both parallel and antiparallel stacking modes in Ap-Ap-P-Ap-P\( ^- \) form (distances are in Å).

**Fig. 7.** The cationic layers of (a) complex 1, (b) isostructural Co, Ni, Cu and Zn compounds.

**Table 4**
Comparison of M–O bond length in five proton transferred compounds.

<table>
<thead>
<tr>
<th>Bond (Å)</th>
<th>M</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>M–O(Oxide)</td>
<td>Fe (1)</td>
<td>1.971</td>
<td>2.048</td>
<td>2.030</td>
<td>1.968</td>
</tr>
<tr>
<td></td>
<td>Co</td>
<td>2.048</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>2.030</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M–O(carboxylate)</td>
<td>Fe (1)</td>
<td>2.003</td>
<td>2.038</td>
<td>2.002</td>
<td>1.933</td>
</tr>
<tr>
<td></td>
<td>Co</td>
<td>2.038</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>2.002</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Zn</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M–O(water)</td>
<td>Fe (1)</td>
<td>–</td>
<td>2.156</td>
<td>2.109</td>
<td>2.412</td>
</tr>
<tr>
<td></td>
<td>Co</td>
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<td></td>
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<tr>
<td></td>
<td>Zn</td>
<td></td>
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</tr>
</tbody>
</table>

**Fig. 8.** Comparison of the distances between metal ions and oxygen atoms on the pydco\(^2-\) ligand.
used several theoretical models. To model the anion we have used the mono-deprotonated ligand [Hpydco]– since in the real assemblies, the carboxylate groups that interact with the π-systems are not coordinated to Fe. This enormously simplifies the calculations since the use of two high spin Fe(III) ions combined with the large size of the systems is computationally too demanding. The theoretical models studied are shown in Fig. 10 along with the interaction energies. For the antiparallel π−−π+ stacking interactions, the interaction energies (ΔE4 and ΔE5) are very different. In contrast the repulsive interaction energy of both stacking complexes in the absence of the anions (see Fig. 10B and D) are very similar (ΔE3 and ΔE7). This is due to the proximity of the anions to the counter-cations, which are closer in the (π−π)1 than in (π−π)2 stacking arrangement. The interaction energy of the parallel π−−π+ stacking interactions (ΔE8) is smaller than the anti-parallel (π−π)1 stacking arrangement (ΔE5) likely indicating that this

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**Fig. 9.** Different reactions used to evaluate the formation of the tetrameric assembly.

**Fig. 10.** Interaction energies of several theoretical models based on the X-ray structure to evaluate the π−−π+ stacking interactions.
Previous investigations have shown that the stoichiometry of the complexes of M = Cu, Ni, Zn, Co with pydco\(^2^−\) ligand is different with respect to 1, i.e. [M(pydco)\(_2\)(H\(_2\)O)\(_2\)]\(^2^−\) [4,12]. We have optimized the geometry of the hypothetical [Fe(pydco)\(_2\)(H\(_2\)O)\(_2\)]\(^2^−\) and compared the energy with the optimized [Fe(pydco)]\(^3^+\) using the energetic balance shown in Fig. 11. It can be observed that the [Fe(pydco)]\(^3^+\) complex is energetically favored in water (we have used water as solvent in the calculations) with respect to the [Fe(pydco)\(_2\)(H\(_2\)O)\(_2\)]\(^2^−\) configuration, in good agreement with the experimental findings.

4. Conclusion

In conclusion, we report the synthesis and X-ray characterization of one new monomeric Fe complex with pyridine-2,6-dicarboxylic acid N-oxide and 9-aminoacridine. One interesting feature of this complex is the rare 1:3 metal-to-ligand ratio. This study demonstrates that compound 1 forms a 3-D supramolecular framework by self-assembling through strong hydrogen bonds between anions, cations, and lattice water molecules together with a variety of π-stacking interactions. We have also reviewed the coordination behavior of pyridine-2,6-dicarboxylic acid in mononuclear monomeric systems and concluded that the tridentate coordination mode is preferred over other possibilities. Also we compared it with pyridine-2,6-dicarboxylic acid N-oxide compounds for investigating the influence of the N-oxide moiety on the coordination mode(s) in the crystal lattice.

Acknowledgements

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Appendix A. Supplementary material

CCDC 1432781 contains the supplementary crystallographic data for compound 1. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2016.04.044.

References