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Structural, spectral and thermal properties of 2-(2-pyridylamino)pyridinium trihydrogen pyromellitate

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Abstract: The title compound, (Hdipya)(H$_3$pyr), where Hdipya is protonated 2,2′-dipyridilamine and H$_3$pyr is the monoanion of pyromellitic acid (H$_4$pyr), was obtained from a reaction mixture containing Zn(II) ions, dipya, Na$_4$pyr (in the mole ratio 2:2:1) and HNO$_3$. The products (micro- and single-crystalline) were characterized by X-ray structure determination, FT-IR spectroscopy and TG/DSC analysis. The most striking structural feature of (Hdipya)(H$_3$pyr) are short inter- and extremely short intramolecular hydrogen bonds. These bonds mutually connect cations and anions making thin layers parallel to the crystallographic (223) plane. In addition, quite unusual, linear proton-bound polymeric $\{H(H_2pyr)^-\}_n$ were identified in the structure. The results of crystal structure determination are compared with FT-IR and TG/DSC data. The low position of the ν_{as}(COO) vibration at 1660 cm^{-1} is in accordance with strong hydrogen bonding. This value could be used as a measure of the C=O bond order, which was calculated to be 1.81.

Keywords: pyromellitic acid; 2,2′-dipyridylamine; crystal structure; FT-IR spectra; TG/DSC analysis.

INTRODUCTION

Pyromellitic or 1,2,4,5-benzenetetracarboxylic acid (H$_4$pyr), one of 12 benzenepolycarboxylic acids, is used in the production of polyesters and polyamides. Anions of H$_4$pyr, in particular pyr^{4-}, are well-known as very prospective ligands in coordination chemistry due to the presence of eight O atoms as potential ligating sites that can coordinate up to ten metal centers.[1] The crystal structure of

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H$_4$pyr was published in 1971,[2] and earliest transition metal (TM) complexes with the tetra-anion of H$_4$pyr were published just after that.[3] The first structurally characterized complexes were described at the beginning of the 1990s.[4] Later, during structural studies of TM complexes, it was shown that the tetra-anion pyr^{4-} usually acts as a centrosymmetric bridging ligand and can build discrete,[5] chain,[6] layered,[7] or framework[8] structures. A survey of the Cambridge Structural Database, CSD,[9] showed that the partially deprotonated forms: Hpyr^{3-}, H$_2$pyr^{2-} and H$_3$pyr$^-$ are, as a rule, not coordinated.

Binary and ternary TM complexes with anions of aromatic polycarboxylic acids have been studied for a long time.[10] In line with this subject, attempts were made to prepare mixed ligand Mn(II) and Zn(II) complexes with pyr^{4-} and 2,2'- -dipyridylamine (dipya) as an *N,N'* ligand. Surprisingly, the title compound containing only potential ligands was obtained instead. Such compounds can be classified into two major groups, as co-crystals (adducts) or organic salts (proton-transfer complexes),[11] but between them there are so-called "disordered solid forms",[12,13] where hydrogen atoms are not undoubtedly located or they are disordered. Although such compounds are much less frequent in comparison with single-component organics or the corresponding complexes, the number of studied examples permanently increases since their possible importance for pharmaceutical chemistry was recognized.[14,15] Even ferroelectric properties were found in some compounds.[16] Therefore, it seemed worthwhile to study the obtained compound in detail.

In the CSD[9] there is a very limited number of structurally characterized compounds concerning molecule of H$_4$pyr or its partially deprotonated ions. There are, however, several similar organic salts: (Hpy)(H$_3$pyr), where py is pyridine,[13] (NMe$_4$)(H$_3$pyr),[17] a series of H$_2$pyr^{2-} salts with different pyridinium derivatives,[18] (cytosinium)$_2$(H$_2$pyr)·H$_2$O,[19] and (Hbipy)$_2$(H$_2$pyr)(H$_4$pyr), where bipy is 2,2'-bipyridine, which was characterized structurally[20] and by FT-IR and NMR spectroscopy.[21]

On the other hand, dipya is well known as a chelating ligand. A search of the CSD revealed some 170 compounds containing dipya.[9] Most of them were TM complexes, and there were no examples of uncoordinated dipya in its neutral form. At the same time, there were only eight compounds containing protonated dipya, which can be present as monoprotonated 2-(2-pyridylamino)pyridinium, Hdipya, or diprotonated 2,2'-iminodipyridinium(2+), H$_2$dipya. Such protonated forms are not coordinated, and in five out of eight cases tetrahalidometalates, [MX$_4$]$^{2-}$ (M = Co, Cu or Hg; X = Cl or Br), were present as counter ions.[9]

Herein, crystal structure of the title compound, (Hdipya)(H$_3$pyr), together with its FT-IR spectral and thermal properties are described and correlated with each other.

EXPERIMENTAL

The starting reagents pyromellitic acid (> 95 %), 2,2′-dipyridylamine (98 %), Mn(II) nitrate solution, 45–50 % in dilute nitric acid (all Sigma–Aldrich) and $Zn(NO)_3 \cdot 6H_2O$ (*p.a.* Kemika, Zagreb) were used without any purifications.

Preparation of the microcrystalline product. Into 100 cm^3 of an aqueous solution containing 0.74 g (2.5 mmol) of $Zn(NO_3)_2 \cdot 6H_2O$, first 5 cm^3 of HNO_3 solution ($c = 1$ mol dm^{-3}), then 0.43 g of dipya (2.5 mmol) dissolved in 10 cm^3 of an EtOH/H$_2$O mixture (3:1 volume ratio) was added. The pH value of this mixture was 2. Then, 50 cm^3 of an aqueous solution of Na$_4$pyr (0.32 g; 1.25 mmol) was slowly added under stirring. The final pH value was 4. After standing for 24 h, the obtained precipitate was filtered and rinsed with H$_2$O, EtOH and Et$_2$O. Yield: 84.6 %; Anal. Calcd. for $C_{20}H_{15}N_3O_8$: C, 56.48; H, 3.55; N, 9.88 %. Found: C, 56.27, H, 3.62, N, 9.91 %; FT-IR (KBr, cm^{-1}): 3470 (*bw*), 3117 (*m*), 3097 (*m*), 3061 (*m*), 3024 (*m*), 2993 (*m*), 2920 (*w*), 1715 (*m*), 1660 (*s*), 1604 (*s*), 1562 (*s*), 1451 (*s*), 1311 (*w*), 1292 (*w*), 1270 (*w*), 1250 (*w*), 1170 (*m*), 1151 (*m*), 1005 (*m*), 955 (*m*), 901 (*m*), 771 (*s*), 748 (*s*), 594 (*m*), 559 (*w*), 532 (*m*). The compound was soluble in DMSO but insoluble in H$_2$O and EtOH.

A similar procedure using Mn(II) instead of Zn(II) ions resulted in a white microcrystalline powder in a comparable yield (78.9 %). As revealed by elemental analysis and FT-IR spectroscopy, this product was identical to the product obtained in the presence of Zn(II) ions.

Preparation of single-crystals. Into 50 cm^3 of an aqueous suspension containing 0.25 g (1 mmol) of H$_4$pyr was added 0.17 g of dipya (1 mmol) dissolved in 5 cm^3 of EtOH. Then, 50 cm^3 of an aqueous solution containing 0.30 g (1 mmol) of $Zn(NO_3)_2 \cdot 6H_2O$ was added dropwise under continuous stirring. The mixture was gently heated at 50 °C for 3 h, filtered to remove a small quantity of unreacted H$_4$pyr, and left standing under ambient conditions. The first crystals appeared after 24 h, but single-crystals of appropriate size were collected after 10 days.

Characterization. The FT-IR spectra were recorded on a Bomem MB-100 (Hartmann Braun) spectrophotometer (4000–600 cm^{-1} region) using KBr pellets. The thermal properties of the compound were examined from room temperature up to 380 °C using an SDT Q600 TGA/DSC instrument (TA Instruments) in a dry nitrogen atmosphere (flow rate: 100 cm^3 min^{-1}) at a heating rate of 20 °C min^{-1}. The sample mass was 8.14 mg.

Room temperature (22 °C) single-crystal X-ray diffraction data were collected on an Oxford Gemini S diffractometer equipped with CCD detector, using monochromatized Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). A multi-scan correction for absorption was applied. The structure was solved by direct methods (SIR97)[22] and refined on F^2 by full-matrix least-squares using the programs SHELXL97[23] and WinGX.[24] All non-hydrogen atoms were refined anisotropically. The positions of the C- and N2-bonded H atoms were calculated geometrically and refined by the riding model with $U_{iso} = 1.2U$(C,N). H atoms from OH groups were found in ΔF maps and refined with the $U_{iso} = 1.5U$(O) constraint. The Hdipya cation was disordered over a centre of symmetry with congener atoms having 0.5 site occupancies; the individual pyridyl groups were refined using the FLAT constraint with equal displacement parameters for the corresponding A and B atoms. Attempts to determine the H atom that protonates dipya were unsuccessful, very likely because this atom was spread over four positions (N1A, N1B and their centrosymmetric counterparts, see Fig. 1. Selected crystal data and refinement results are listed in Table I. CCDC 948070 contains supplementary crystallographic data for this paper. This data can be obtained free of charge at http://www.ccdc.cam.ac.uk/cgi--bin/catreq.cgi.
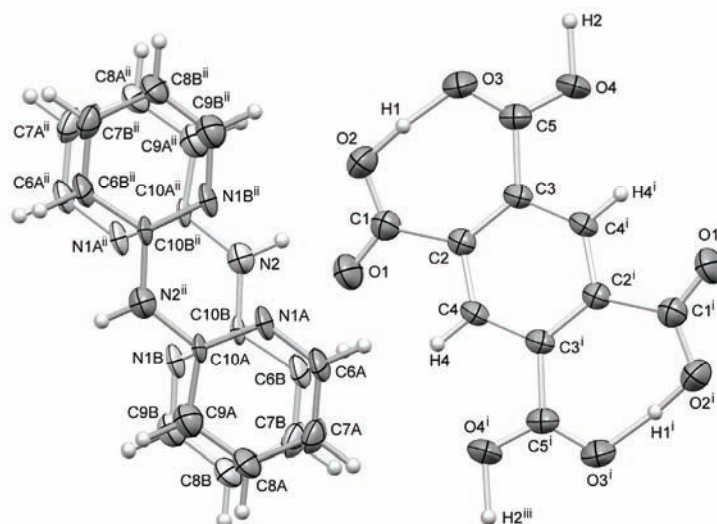
Fig. 1. Molecular structure of (Hdipya)(H$_3$pyr) with atomic numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level. Disordered Hdipya ions are marked by different shades of gray. Symmetry codes: (*i*) 1 − *x*, 1 − *y*, 1 − *z*; (*ii*) 1 − *x*, 1 − *y*, −*z*; (*iii*) 1 + *x*, 1 + *y*, −*z*.

TABLE I. Crystal data and structure refinement for (Hdipya)(H$_3$pyr)

Empirical formula	C$_{20}$H$_{15}$N$_3$O$_8$
M / g mol^{-1}	425.35
Crystal system	Triclinic
Space group	$P\bar{1}$
a, b, c / Å	3.8268(2), 9.2726(6), 13.3494(8)
α, β, γ / °	74.761(6), 81.845(5), 82.935(6)
V / Å^3	450.59(5)
Z	1
ρ_c / g cm^{-3}	1.568
μ / mm^{-1}	1.056
F(000)	220
Crystal dimensions, mm	0.09×0.10×0.31
θ_{max} / °	72.12
Range of h, k, l	−4 ≤ h ≤ 3, −11 ≤ k ≤ 11, −16 ≤ l ≤ 16
Reflections collected	7605
Independent reflections	1770 (R_{int} = 0.0361)
Completeness, %	99.6
Data/restraints/parameters	1770/6/169
$(\Delta/\sigma)_{max}$	0.001
S	1.116
R indices ($I > 2\sigma (I)$)	R_1 = 0.0533, wR_2 = 0.1282
R indices (all data)	R_1 = 0.0631, wR_2 = 0.1341
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (both in e Å^{-3})	0.150, −0.205

<div style="text-align:center">RESULTS AND DISCUSSION</div>

Synthesis

As described in the Experimental, the title compound was obtained during attempts to synthesize ternary Zn(II)–dipya-pyr complexes or their Mn(II) analogues. This demonstrates the difficulties in the preparation of such complexes, in spite of being known.[9] A similar experience was already published by Ha,[25] when (Hdipya)$_2$[MnCl$_4$] was obtained instead of the expected Mn(II)–dipya complex, and it was not reported previously for Zn(II) complexes. Such behavior can be partly explained by an increase on the thermodynamic stability of the protonated dipya in respect to the neutral molecule,[26] but since dipya complexes of many TMs are known, the specific role of Zn(II)/Mn(II) ions and the pH of the reaction mixture should not be neglected.

Crystal structure

In the structure of (Hdipya)(H$_3$pyr), both the Hdipya and H$_3$pyr ions are positioned around the symmetry centre, and only half of each species belongs to the asymmetric unit (Fig. 1). Besides, Hdipya is disordered over a centre of symmetry with equal allocation of both entities. A comparable disorder was found in some organostannates,[26] and in the analogous (Hdipya)(Hpht), where Hpht is the hydrogen phthalate ion.[27] One of pyridyl N atoms has to be protonated, but it was not possible to locate the corresponding H atom. Both N atoms from the pyridyl rings could be protonated because N1A···O1 and N1B···O1 distances are 3.018(7) and 3.121(5) Å, respectively, *i.e.*, they could form hydrogen bonds. Therefore, the H atom is very likely spread over four possible positions.

The whole Hdipya is practically perfectly planar with a negligible dihedral angle between the mean-planes of the two pyridyl rings. In three known dipya polymorphs and five crystallographically different dipya molecules, this angle varied between about 4 and 40°.[28] A very similar variety of angles was also found in some TMs–dipya complexes.[10] The planarity of Hdipya might be explained by symmetry constraints or by extended delocalization of the π electrons. However, the influence of intramolecular (intra-H) and intermolecular (inter-H) hydrogen bonds could also be important. According to Haddad *et al.*,[29] weak intra-H bonding is also possible between the protonated and unprotonated N atom from adjacent pyridyl rings (Fig. 1, atoms N1A and N1B). As usual, pyridyl rings are less regular than benzene rings.

At first sight, the H$_3$pyr ion (Fig. 1) is fully protonated, *i.e.*, it should be described as a neutral H$_4$pyr molecule, not as a monoanion. However, the H2 atom is in special position (site symmetry: $\bar{1}$) and with a 0.5 site occupancy factor. The geometry data for the H$_3$pyr anion are listed in Table II. While the C–C bond distances are as expected, the angles, in particular C1–C2–C3 and C2–C3–C5, strongly deviate from the values found in H$_4$pyr·2H$_2$O (max. 121.7°).[30] This is the consequence of the stress caused by the presence of the

intra-H bond O2–H1···O3 and the formation of seven-membered, S(7), pseudo--rings. In respect to the aromatic ring, the C–COO groups are inclined in the opposite sides, with the corresponding angles of 13.3° for the C2C1O1O2 group and 73.6° for the C3C5O3O4 group. This intra-H bond is extremely short and clearly asymmetrical (Table III, Fig. 1). Very similar geometries were already found in H_2pyr and H_3pyr anions.[13,18–20] and in some Hpht complexes.[31,32]

TABLE II. Bond distances and angles in H_3pyr ion (For O–H bond distances, see Table III)

Bond distance, Å			
O1–C1	1.202(4)	O2–C1	1.297(3)
O3–C5	1.225(3)	O4–C5	1.251(3)
C1–C2	1.527(3)	C2–C3	1.406(3)
C2–C4	1.391(3)	C3–C4	1.391(3)
C3–C5	1.513(3)		
Bond angle, °			
O1–C1–O2	121.2(3)	O1–C1–C2	118.9(2)
O2–C1–C2	119.9(2)	C1–C2–C3	129.2(2)
C1–C2–C4	113.0(2)	C3–C2–C4	117.8(2)
C2–C3–C4	118.0(2)	C2–C3–C5	126.8(2)
C4–C3–C5	115.2(2)	C2–C4–C3	124.2(2)
C2–C4–H4	117.9(2)	C3–C4–H4	117.9(2)
O3–C5–O4	122.2(3)	O3–C5–C3	121.9(2)
O4–C5–C3	115.8(2)		

TABLE III. Geometry of hydrogen bonds in (Hdipya)(H_3pyr); Symmetry codes: (iv) $-x$, $-y + 2$, $-z + 1$; (v) $x - 1$, y, z

D–H···A	d(D–H) / Å	d(H···A) / Å	Angle (DHA) / °	d(D···A) / Å
O2–H1···O3	1.11(4)	1.34(4)	167(3)	2.435(3)
O4–H2···O4[iv]	1.24[a]	1.24[a]	180[a]	2.477(2)
N2–H2A···O1[v]	0.86	1.87	165	2.706(4)

[a]Atom H2 is in a special position and its coordinates were fixed during refinement

Another, inter-H bond O4–H2···O4[iv] ((iv) $-x$, $-y + 2$, $-z + 1$) is symmetrical and also very short, but a little longer than the intra-H bond (Table III). In comparison to typical O···O distances found in related Hpht compounds,[27] the intra-H bond is slightly longer, whereas inter-H bond is shorter than expected. This shows how strong the inter-H bond is in this case. Being that the inter-H bond is symmetrical, H_3pyr could also be viewed as a polymeric proton-bound trihydrogen pyromellitate anion, $\{H(H_2pyr)^-\}_n$ (Fig. 2). Again, there is great similarity with Hpht compounds, in which proton-bound anions are also found.[33–35] The main difference is that $\{H(H_2pyr)^-\}_n$ is polymeric, while $[H(Hpht)_2]^-$ ions are only dimeric. This is because H_4pyr could be considered as developed from H_2pht by mirroring two COOH groups in the *ortho*-position to another pair of COOH groups. Thus, only H_3pyr^- and H_2pyr^{2-} can make polymeric proton-bound anions,

while Hpht$^-$ is restricted to dimeric forms.[36] To the best of our knowledge, a similar polyanion was found only in (NMe$_4$)(H$_3$pyr), described by Rodriguez-Cuamatzi *et al.*[17] However, those chains were of a zig–zag type, while here the presented chains are linear (Fig. 2) and so could be regarded as unprecedented.
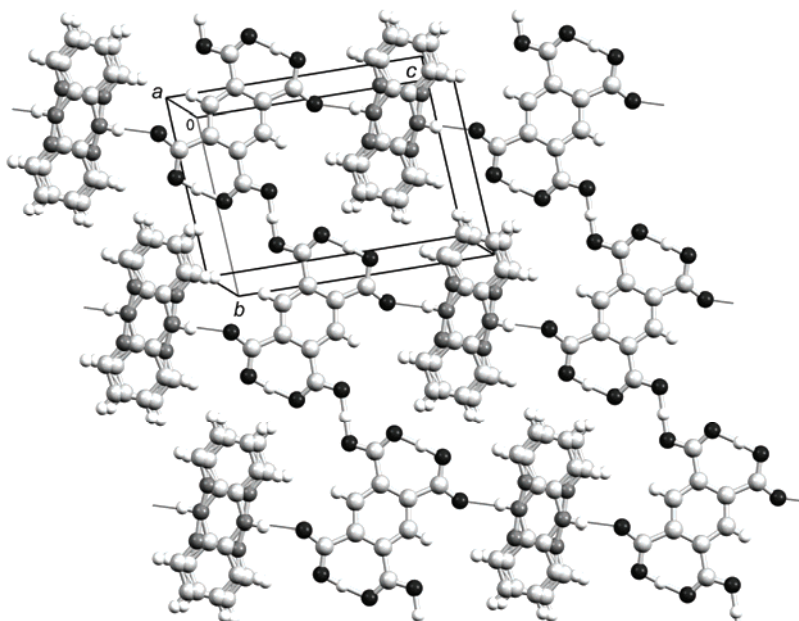

Fig. 2. Motif of hydrogen bonds (thin dark lines) in the (223) crystallographic plane. Color codes for atoms: H – white, C – light gray, N – dark gray and O – black.

In the structure, there is another hydrogen bond between the amine N2 atom and O1 (Fig. 1, Table III). Since all hydrogen bonds are concentrated in one plane, thin layers approximately parallel to the crystallographic (223) plane are formed (Fig. 2). The {H(H$_2$pyr)$^-$}$_n$ and Hdipya ions are assembled in alternating rows making a non-rectangular grid. The layers are stacked together by short parallel--displaced π–π interactions. For example, all distances between the plane of one benzene ring and benzene C atoms from the nearest layer are 3.490(5) Å. Analogous layers also exist in (cytosinium)$_2$(H$_2$pyr)·H$_2$O,[19] and in (NMe$_4$)(H$_3$pyr).[17]

Spectral and thermal properties

A sequence of weak and sometimes broad IR bands between 3500 and 3200 cm^{-1} is indicative for numerous hydrogen bonds. According to the literature,[21] even weak and very broad bands centered at 2900, 2430 and 1900 cm^{-1} could also be ascribed to strong hydrogen bonding. In some cases, they could be extremely strong and broad.[37] Bands between about 3120 and 2990 cm^{-1} are characteristic for stretching N–H and C–H vibrations in secondary amines and aromatic rings.

It seems that the stretching N–H band was shifted from 3244 cm^{-1} in dipya to 3117 or 3097 cm^{-1} in (Hdipya)(H$_3$pyr), suggesting stronger hydrogen bonding.

In the "fingerprint" region, there are bands of different origin typical for substituted benzene rings and secondary amines; they agree with the bands in the individual components. Especially characteristic for dipya is a prominent doublet due to N–H out of plane bending at 771 and 748 cm^{-1}. Both vibrations were slightly shifted with respect to pure dipya (768 and 735 cm^{-1}) and very likely overlap with the corresponding C–H vibrations.[38]

The most interesting part of the FT-IR spectrum is the 1720–1250 cm^{-1} region (Fig. 3), where many strong bands are expected: asymmetrical and symmetrical stretching vibrations of COOH and the corresponding COO groups, C–C and C–N stretching vibrations of aromatic rings and N–H bending in a secondary aromatic amine.[39] (Asymmetrical ν_{as}(COOH) vibrations, characteristic for organic acids, are often labelled ν(C=O) and called carbonyl, due to the presence of double C=O bond). Consistent to the literature,[37] ν_{as}(COOH) and ν_s(COOH) frequencies for H$_4$pyr are at 1710 and 1266 (as doublet at 1278 and 1255) cm^{-1}, respectively, and the present experimental data agree within ±5 cm^{-1} with these values. These bands are broad and usually the most intense in the spectrum.[38] Surprisingly, the corresponding bands in the FT-IR spectrum of (Hdipya)(H$_3$pyr) are medium to weak, but one additional very prominent band at 1660 cm^{-1} appeared. At first sight, this band could be attributed to the secondary amine N–H bending group frequency, which is located at 1604 cm^{-1} in dipya. However, such high wavenumbers are observed only in the case of coordinated dipya and the band is typically very sharp.[10] Therefore, the band at 1660 cm^{-1} should be ascribed to the ν_{as}(COOH) or carbonyl C=O vibrations. Such a low position of ν_{as}(COOH) is not expected,[38] and, together with no unambiguous identification of ν_s(COOH) vibrations, has to be correlated to the extremely short and strong hydrogen bonds involving all O atoms from H$_3$pyr. In (Hbipy)$_2$(H$_2$pyr)(H$_4$pyr),[20,21] just the opposite behavior was observed, ν_{as}(COOH) is shifted to the higher wavenumbers (1726 cm^{-1}), which was explained by the absence of hydrogen bonds.

In the tetrathiafulvalene–*p*-chloranil (TTF–CA) complex, which is a widely studied charge-transfer organic compound,[40] the position of C=O vibrations was used to determine the degree of charge transfer from TTF to CA. In other words, ν_{as}(COOH)/ν(C=O) could be related to the C=O bond order. For H$_4$pyr ν_{as}(COOH) was at 1710 cm^{-1},[39] and this corresponds to a bond order of 2. In alkali metal salts, the COOH groups are ionized and, due to delocalization of the electrons in COO groups, the bond order should be 1.5. The available data for the two alkali metal salts K$_4$pyr[39] and Na$_4$pyr (this study) give an identical value, 1580 cm^{-1} for ν_{as}(COO). From these values, it is easy to calculate the C=O bond order in (Hdipya)(H$_3$pyr), which was 1.81. By analogy to the "degree of charge transfer" this quantity could be used to measure the "degree of proton transfer",[41] and should be correlated to the geometry of hydrogen bonding in (Hdipya)(H$_3$pyr).

However, the observed geometry of H_3pyr ions (Table II) does not enable a simple explanation of the calculated value. For O1–C1 and O2–C1 pair, bond distances can be judged as normal when compared to the H_4pyr and common COOH values.[2] Nevertheless, O3–C5 bond is longer than expected and O4–C5 bond distance corresponds to the typical values found in ionized COO groups.[9] This could be a possible cause for the low value of v_{as}(COOH), although an extensive coupling of vibrational modes should also be kept in mind.
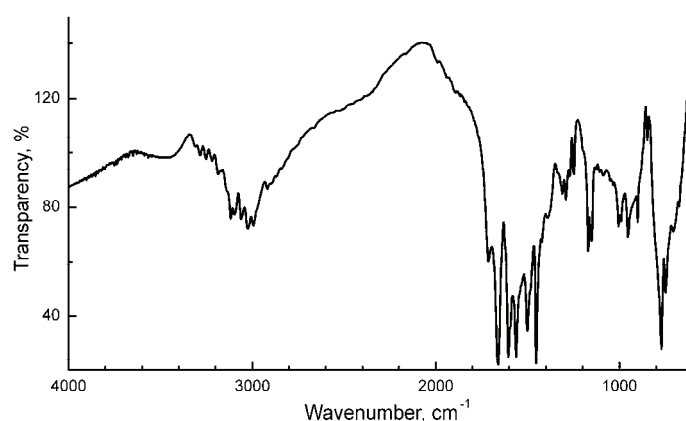

Fig. 3. FT-IR spectrum (KBr pellets) of (Hdipya)(H_3pyr).

As shown in Fig. 4, the decomposition of (Hdipya)(H_3pyr) began at 237 °C (onset temperature) and ended at about 325 °C with a total mass loss. No melting
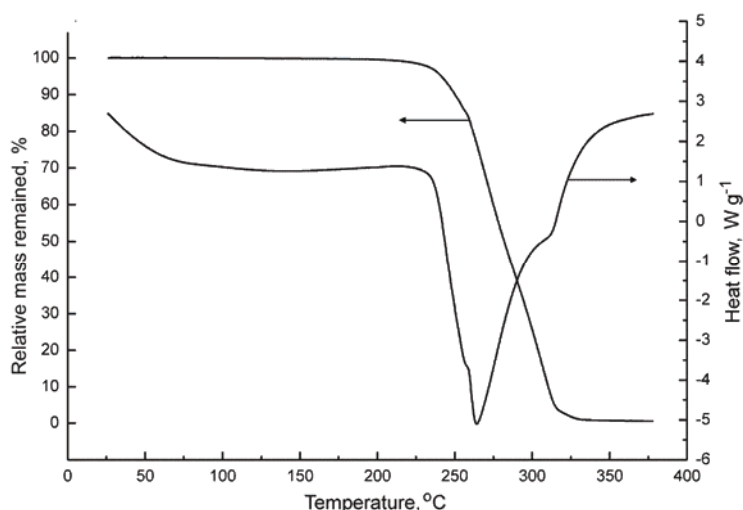

Fig. 4. TG/DSC curves of (Hdipya)(H_3pyr) under a dynamic N_2 atmosphere at a heating rate of 20 °C min^{-1} (exotherm up).

was observed and the decomposition started around the boiling point of dipya (222 °C), suggesting that this molecule escaped first. Although the TG curve decreased rapidly, the shape of the DSC curve indicated that the disintegration occurred in at least three, probably four, highly overlapped steps, which could not be resolved. The total molar decomposition enthalpy was relatively high, $\Delta_{dec}H_m^o = 461.2$ kJ mol^{-1}. In comparison to TM complexes with dipya and some polycarboxylate ligands,[10] the initial decomposition temperature of (Hdipya)(H$_3$pyr) was lower, very likely owing to the absence of coordinative bonds. In analogous systems (py)$_2$(H$_2$tpht), where H$_2$tpht is terephthalic acid, and (py)$_3$(H$_3$tms), where H$_3$tms is trimesic acid, the total degradation was found to be at 339 and 366 °C, respectively.[13] There, however, loss of py molecules started just above room temperature, although the boiling point of py is 115 °C.

CONCLUSIONS

A new organic salt (Hdipya)(H$_3$pyr) was prepared unpredictably during efforts to obtain ternary Zn(II) or Mn(II) complexes with dipya and pyr ligands. Besides the higher stability of Hdipya with respect to dipya,[26] the presence of Zn^{2+} or Mn^{2+} ions, as well as a starting mixture pH value of 4 most likely affected the reaction mechanism and the formation of (Hdipya)(H$_3$pyr). The compound consisted of disordered Hdipya cations and H$_3$pyr anions connected by hydrogen bonds. There were short inter- and extremely short intra-H bonds. In this way, thin layers parallel to the (223) plane were formed. Due to the very strong and symmetrical inter-H bond, the H$_3$pyr anions could furthermore be regarded as polymeric {H(H$_2$pyr)$^-$}$_n$ anions. The position and shape of the characteristic bands revealed by FT-IR spectroscopy undoubtedly confirmed the structural findings in (Hdipya)(H$_3$pyr), and the value of v_{as}(COO) vibration was used for measuring the "degree of proton transfer", which was calculated to be 1.81. The TG/DSC analysis proved that (Hdipya)(H$_3$pyr) decomposed in several overlapping steps and a total molar decomposition enthalpy of 461.2 kJ mol^{-1} was calculated.

SUPPORTING INFORMATION

Crystallographic data can be obtained free of charge at http://www.ccdc.cam.ac.uk/cgi--bin/catreq.cgi.

ИЗВОД

СТРУКТУРНА, СПЕКТРАЛНА И ТЕРМИЧКА СВОЈСТВА
2-(2-ПИРИДИЛАМИНО)ПИРИДИНИЈУМ-ТРИХИДРОГЕНПИРОМЕЛИТАТА

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Описано једињење, (Hdipya)(H$_3$pyr), где је Hdipya протоновани 2,2′-дипиридил-амин, а H$_3$pyr моноанјон пиромелитне киселине (H$_4$pyr), добијено је из реакционе смеше која је садржала Zn(II) јоне, dipya, Na$_4$pyr (молски однос 2:2:1) и HNO$_3$. Производи (микро- и монокристални) окарактерисани су рендгеном структурном анализом, FT-IR спектроскопијом и TG/DSC анализом. Врло необично структурно својство (Hdipya)(H$_3$pyr) јесте присуство кратких интер- и екстремно кратких интрамолекулских водоничних веза, које међусобно повезују катјоне и анјоне градећи танке слојеве паралелне кристалографској равни (223). Такође, у структури су нађени до сада веома ретки, линеарни полимерни анјони {H(H$_2$pyr)$^-$}$_n$ настали повезивањем преко протона. Резултати рендгенске структурне анализе упоређени су са подацима добијеним FT-IR спектроскопијом и TG/DSC анализом. Ниска фреквенција ν_{as}(COO) вибрације на 1660 cm^{-1} у сагласности је са постојањем јаких водоничних веза. Ова вредност искоришћена је за одређивање реда C=O везе ("степена преноса протона") и израчунато је да он износи 1,81.

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