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TWO SUPRAMOLECULAR COMPLEXES OF GALLIUM(III) WITH DIFFERENT ADDUCT ION PAIRS CONTAINING PYRIDINE-2,6-DICARBOXYLIC ACID: SYNTHESSES, CHARACTERIZATION, CRYSTAL STRUCTURES AND COMPUTATIONAL STUDY**J. Soleimannejad¹, S. Sheshmani², M. Solimannejad³, E. Nazarnia⁴, F. Hosseinabadi⁴**

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Two complexes of gallium(III) with adduct ion pair compounds containing pyridine-2,6-dicarboxylic acid and two different Lewis bases are synthesized. The chemical formulae are $(\text{dmpH})[\text{Ga}(\text{pydc})_2] \cdot 2\text{H}_2\text{O}$, (**1**) and $(\text{bpyH}_2)_{1/2}(\text{pydcH}_2)_{1/2}[\text{Ga}(\text{pydc})_2] \cdot 4\text{H}_2\text{O}$, (**2**) where pydc, dmp, and bpy are pyridine-2,6-dicarboxylate, 2,9-dimethyl-1,10-phenanthroline, and 4,4'-bipyridine respectively. The two crystal structures illustrate that the Ga^{III} ion is six-coordinated by two pyridine-2,6-dicarboxylates. Hydrogen bonds as well as other noncovalent interactions such as ion-pairing, $\text{C}—\text{O} \cdots \pi$, $\text{C}—\text{H} \cdots \pi$, and $\pi \cdots \pi$ stacking play an important role in the formation of supramolecular systems. Particular attention is given to the molecular geometries and NMR properties of the complexes from the computational point of view. The electronic properties of the complexes are analysed using the parameters derived from the atoms in molecules (AIM) and natural bond orbital (NBO) methodologies at the B3LYP/6-311++G(2d,2p) computational level.

Keywords: gallium(III), pyridine-2,6-dicarboxylic acid, 2,9-dimethyl-1,10-phenanthroline, 4,4'-bipyridine, X-ray structure determination, DFT, supramolecular chemistry.

INTRODUCTION

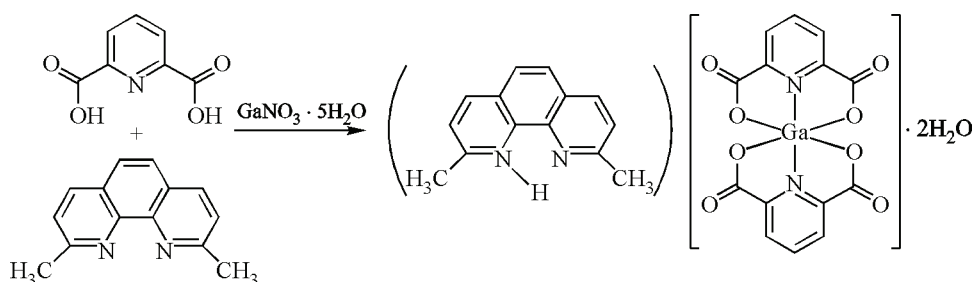
Noncovalent interactions form the backbone of supramolecular chemistry and include hydrogen bonds, π — π stacking, ion pairing, hydrophobic and hydrophilic interactions [1, 2]. Among these interactions, hydrogen bonds play a major role in the structure, function, and dynamics of chemical and biological systems [3]. The design of new supramolecular architectures tests and refines our understanding of the fundamental principles of molecular self-organization. The process of self-assembly and self-organization involves the noncovalent interactions of two or more molecular subunits to form a supramolecular arrangement whose novel structure and properties are determined by the nature and positioning of the components [4]. Recently, the synthesis and characterization of self-assembled ion pairs have been reported and their complexation behavior with different metal ions has been studied [5—10]. The main goal of this study is the complexation behavior of a gallium(III) ion with different adduct ion pairs. Also, the present work reports a detailed examination of the molecular geometries, electronic structure, and NMR properties of the title complexes at the B3LYP/6-311++G(2d,2p) computational level.

EXPERIMENTAL

Reagents. All chemicals were of commercial suppliers and used without any further purification. Doubly distilled deionized water was used in the procedures when needed.

Apparatus. Melting points were determined with Electrothermal IA-9100 and were not corrected. IR spectra were recorded on a 843Perkin-Elmer spectrophotometer using KBr discs. Elemental analysis was obtained from a Perkin Elmer 2400 analyzer. The mass and NMR spectra were determined with Agilent Technology (HP) and Bruker 400 MHz, respectively. X-ray structure analysis of suitable single crystals was carried out on a Bruker-AXS SMART diffractometer with an APEX CCD area detector (MoK_α radiation, graphite monochromator, $\lambda = 0.71073 \text{ \AA}$). The data were corrected for polarization and Lorentz effects, and an empirical absorption correction (SADABS) was applied [11]. The structures were solved by SHELXS-97 [12]. The non-hydrogen atoms were refined anisotropically by the full matrix least squares method based on F^2 using SHELXL-97 [12]. CIF file containing complete information on the studied structure was deposited with CCDC, deposition numbers 865074 for the complex (1), and CCDC 865075 for complex (2), and is freely available upon request from the following web site: www.ccdc.cam.ac.uk/data_request/cif.

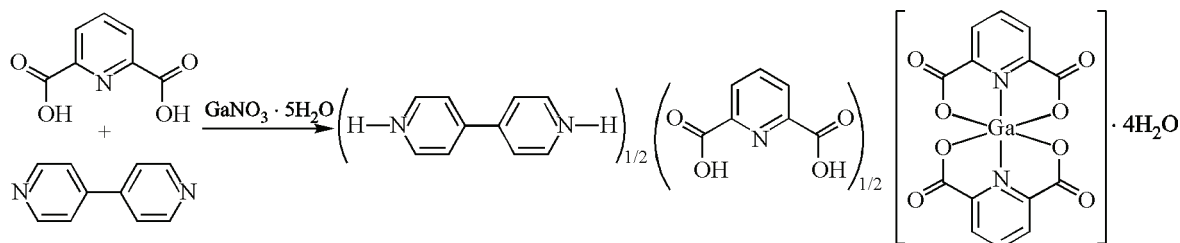
Synthesis of $(\text{dmpH})[\text{Ga}(\text{pydc})_2] \cdot 2\text{H}_2\text{O}$ complex (1). An aqueous solution of pyridine-2,6-dicarboxylic acid (56 mg, 0.34 mmol) and 2,9-dimethyl-1,10-phenanthroline (70 mg, 0.34 mmol) in water (6 ml) which was already stirred for 10 minutes at $60 \text{ }^\circ\text{C}$, was added to a solution of $\text{GaNO}_3 \cdot 5\text{H}_2\text{O}$ (58 mg, 0.17 mmol) in ethanol (2 ml). Colorless crystals of the complex were obtained by slow evaporation of the solution at room temperature after one day. The procedure adopted in the synthesis of complex (1) is outlined in Scheme 1. mp: $331\text{--}335 \text{ }^\circ\text{C}$, yield: 67 %. IR (KBr): 3492—3397 br, 3089—3054 br, 1723 s, 1677 vs, 1663 vs, 1599 s, 1548 m, 1535 m, 1494 s, 1467 m, 1427 m, 1370 vs, 1325 vs, 1297 w, 1260 w, 1175 s, 1083 vs, 1038 w, 1005 w, 914 s, 887 w, 864 w, 819 m, 746 cm^{-1} . $^1\text{HNMR}$ (400 MHz, DMSO): $\delta = 3.02$ (6H, s, 2CH_3), 8.06 (2H, d, 2 CH dmp), 8.23 (2H, s, 2 CH dmp), 8.46 (4H, d, 4 CH pydc), 8.69 (2H, t, 2 CH pydc), 8.88 (2H, d, 2 CH dmp); $^{13}\text{CNMR}$ (400 MHz, DMSO): 23.38 (C-dmp), 125.58 (C-dmp), 126.96 (C-dmp), 126.98 (C-pydc), 128.07 (C-dmp), 137.55 (C-dmp), 141.64 (C-pydc), 144.60 (C-dmp), 147.77 (C-pydc), 159.50 (C-dmp) and 162.26 (C-pydc) ppm. Anal. Calcd. for $\text{C}_{28}\text{H}_{23}\text{GaN}_4\text{O}_{10}$: C, 51.88; H, 3.25; N, 8.63; Found: C, 52.07; H, 3.56; N, 8.68. MS (m/z , %): 208 (100), 236, 398, 608, and 646.



Scheme 1. Method for the synthesis of complex (1)

Synthesis of $(\text{bpyH}_2)_{1/2}(\text{pydcH}_2)_{1/2}[\text{Ga}(\text{pydc})_2] \cdot 4\text{H}_2\text{O}$ complex (2). To a solution of 4,4'-bipyridine (100 mg, 0.64 mmol) and pyridine-2,6-dicarboxylic acid (107 mg, 0.64 mmol) in water (8 ml) heated for one hour at $90 \text{ }^\circ\text{C}$, a solution of $\text{GaNO}_3 \cdot 5\text{H}_2\text{O}$ (111 mg, 0.32 mmol) in water (2 ml) was added. Light yellow crystals were obtained after one day by slow evaporation of the solvent at room temperature. The procedure adopted in the synthesis of complex (2) is shown in Scheme 2. mp: $311\text{--}316 \text{ }^\circ\text{C}$, yield: 81 %. IR (KBr): 3484—3419 br, 3090—3055 br, 3086 w, 3054 w, 2773—2552 m, 2360 w, 1703 s, 1677—1663 vs, 1600 s, 1599 m, 1500 m, 1494 m, 1430 m, 1370 s, 1336 vs, 1260 w, 1260 w, 1228 w, 1166 s, 1083 s, 1039 w, 953 w, 916 m, 870 m, 826 m, 782 s, 749 cm^{-1} . $^1\text{HNMR}$ (400 MHz, DMSO): $\delta = 6.53\text{--}6.97$ (4 H, br-s, 2 NH and 2 COOH), 8.18—9.29 ppm (17 H, m, CH-all of pyridine rings containing $(\text{pydc})^{2-}$ and bpy). $^{13}\text{CNMR}$ (400 MHz, DMSO): 124.61 (C-bpy), 125.60

(C-pydc), 128.03 (C-pydc), 139.73 (C-bpy), 144.61 (C-bpy), 146.17 (C-pydc), 147.77 (C-pydc), 148.59 (C-pydc), 162.28 (C-pydc) and 165.95 (C-pydc) ppm. Anal. Calcd. for $C_{22.50}H_{22.50}GaN_{3.50}O_{13.50}$: C, 43.72; H, 2.92; N, 7.97; Found: C, 43.29; H, 2.96; N, 7.86. MS (m/z , %): 77, 123, 156 (100), and 398.



Scheme 2. Method for the synthesis of complex (2)

Computational details. The structures of pyridine-2,6-dicarboxylate ligand and $[Ga(pydc)_2]^-$ anionic complex were optimized using gradient-corrected density functional theory with the Becke—Lee—Young—Parr exchange correlation functional (B3LYP) [13] with the 6-311++ G(2d,2p) basis set. All calculations were performed using the Gaussian 03 system of codes [14]. The natural bond orbital (NBO) method [15] at the B3LYP/6-311++G(2d,2p) computational level has been used to analyze the interaction of occupied and empty orbitals with the Gaussian 03 system of codes. These kinds of interactions are of main importance in the formation of charge transfer complexes. The electron densities of the isolated ligand and anionic complexes were analyzed within the atoms in molecules (AIM) methodology [16] implemented in the AIM2000 program [17].

RESULTS AND DISCUSSION

Characterization of (dmpH)[Ga(pydc)₂]·2H₂O complex (1). The IR spectra contained several indicative peaks, such as the absorption bands at 1677 cm^{-1} and 1723 cm^{-1} which refer to the stretching vibration of C=O pyridine-2,6-dicarboxylate. The strong absorption band at 1083 cm^{-1} is assigned to C—O pyridine-2,6-dicarboxylate. The stretching frequencies of C=C aromatic rings appeared at 1427 cm^{-1} . Furthermore, the stretching and bending frequencies of C—H aromatic rings are assigned to $3054\text{—}3089\text{ cm}^{-1}$ and $746\text{—}914\text{ cm}^{-1}$ respectively. The adsorption peaks at 1370 cm^{-1} and 1467 cm^{-1} are due to symmetric and asymmetric bending frequencies of CH₃ in the 2,9-dimethyl-1,10-phenanthroline cation. Lattice water normally appears in the $3300\text{—}3500\text{ cm}^{-1}$ (antisymmetric and symmetric OH stretchings) and 1600 cm^{-1} regions (HOH bending). The strong broad peaks in the range $3397\text{—}3492\text{ cm}^{-1}$ are attributed to the existence of the N—H stretching vibrational mode coupled with hydrogen bonding between water molecules. In the (dmpH)[Ga(pydc)₂]·2H₂O complex, the ¹H NMR spectrum showed some characteristic sets of resonances at 3.02 ppm, 8.06 ppm, 8.23 ppm and 8.88 ppm, which are due to the 2,9-dimethyl-1,10-phenanthroline cation, and 8.46 ppm and 8.69 ppm resulted from the pyridine-2,6-dicarboxylate fragments. The ¹³C NMR spectrum showed 11 resonances at 23.38 ppm, 125.58 ppm, 126.96 ppm, 126.98 ppm, 128.07 ppm, 137.55 ppm, 141.64 ppm, 144.60 ppm, 147.77 ppm, 159.50 ppm, and 162.26 ppm, as expected. Considering the peak assignments reported for (pydc)²⁻ at 126.98 ppm, 141.64 ppm, 147.77 ppm, and 162.26 ppm, the remaining resonances can be definitely attributed to the 2,9-dimethyl-1,10-phenanthroline cation. From the integration in ¹H NMR signals it is quite clear that the (dmpH)⁺ to pydc²⁻ molar ratio is 1:2. The MS data showed a fragment at m/e 208 as a base peak that obviously indicates the presence of 2,9-dimethyl-1,10-phenanthroline in the complex. The other peaks that worth noting were at m/e 236, 398, 608, and 646, which corresponds to [Ga(pydcH₂)], [Ga(pydc)₂], (dmpH)[Ga(pydc)₂], and (dmpH)[Ga(pydc)₂]·2H₂O respectively.

X-ray crystallographic structure of (dmpH)[Ga(pydc)₂]·2H₂O complex (1). The molecular structure of this complex is presented in Fig. 1. A summary of the crystallography data are presented

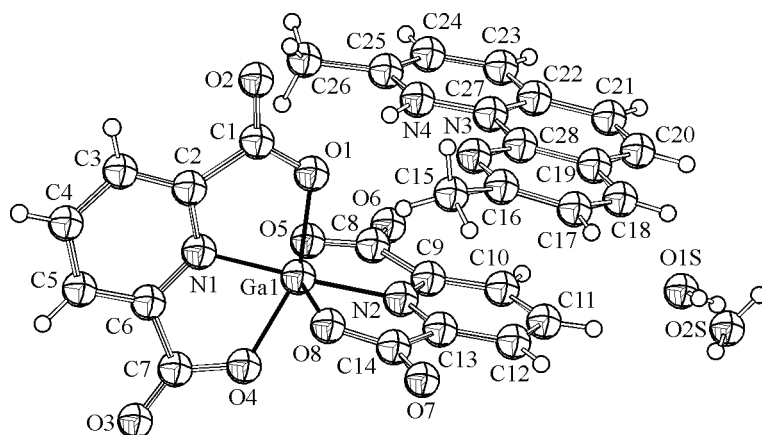


Fig. 1. Molecular structure of the (dmpH)[Ga(pydc)₂]·2H₂O complex with atom numbering

in Table 1. Table 2 shows the selected bond lengths and bond angles. Table 3 reports the intermolecular hydrogen bonds. This complex crystallizes in the space group $P2_1/n$ of the monoclinic system and contains four molecules per unit cell. It can be seen in Fig. 1 that the Ga^{III} ion is six-coordinated by two nitrogen atoms N1 and N2 and four oxygen atoms O1, O4, O5, and O8 of two (pydc)²⁻ groups as tridentate ligands. The Ga^{III} atom is located in the center of a distorted octahedral arrangement (Fig. 1 and Table 2). The N1—Ga1—N2 angle is 171.27(6)°, which shows a 8.73° deviation from linearity (Table 2). The summation of O1—Ga1—O5, O1—Ga1—O8, O4—Ga1—O5, and O4—Ga1—O8

Table 1

Crystallography data for complexes 1 and 2

Parameters	Complex 1	Complex 2
Deposition number	865074	865075
Empirical formula	C ₂₈ H ₂₃ GaN ₄ O ₁₀	C _{22.50} H _{18.50} GaN _{3.50} O _{13.50}
Formula weight; <i>T</i> , K	645.22; 296(2)	1283.29; 296(2)
Crystal system	Monoclinic	Monoclinic
Space group; <i>Z</i>	$P2_1/n$; 4	$C2/c$; 8
Unit cell dimensions <i>a</i> , <i>b</i> , <i>c</i> , Å; β, deg.	8.9715(9), 18.4950(17), 18.4950(17); 94.725(2)	22.0817(9), 28.0738(13), 8.2609(4); 106.995(2)
Unit cell volume, Å ³	2584.4(4)	4897.44
Calculated density, g/cm ³	1.658	1.703
Absorption coefficient	1.136	1.206
Crystal dimensions, mm	0.43×0.32×0.21	0.32×0.20×0.20
Crystal description / Color	Block / colorless	Needle / pale-yellow
<i>F</i> (000); θ range	1320; 2.53—27.44	2567; 2.58—27.57
Limiting indices	-11 ≤ <i>h</i> ≤ 11, -23 ≤ <i>k</i> ≤ 23, -20 ≤ <i>l</i> ≤ 20	-28 ≤ <i>h</i> ≤ 28, -28 ≤ <i>k</i> ≤ 36, -10 ≤ <i>l</i> ≤ 10
Reflections collected	5050	4715
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Goodness-of-fit on <i>F</i> ²	1.059	0.931
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0390, <i>wR</i> 1 = 0.0846	<i>R</i> 1 = 0.0436, <i>wR</i> 1 = 0.0967
<i>R</i> indices (all data)	<i>R</i> 2 = 0.0313, <i>wR</i> 2 = 0.0806	<i>R</i> 2 = 0.0333, <i>wR</i> 2 = 0.0901
Largest diff. peak and hole, e/Å ³	0.000 and 0.001	0.000 and 0.002

Table 2

Selected bond lengths (Å) and bond angles (deg.) for complex 1

Ga1—N1	1.9787(15)	O1—Ga1—O4	157.37(5)	O4—Ga1—N1	79.74(6)
Ga1—N2	1.9775(15)	O1—Ga1—O5	90.62(5)	O5—Ga1—N1	107.59(5)
Ga1—O1	2.0430(13)	O1—Ga1—O8	94.63(6)	O8—Ga1—N1	94.93(5)
Ga1—O4	1.9907(12)	O4—Ga1—O5	93.06(5)	O1—Ga1—N2	97.32(5)
Ga1—O5	1.9977(12)	O4—Ga1—O8	90.47(5)	O4—Ga1—N2	105.31(5)
Ga1—O8	2.0384(13)	O5—Ga1—O8	157.47(5)	O5—Ga1—N2	79.52(5)
		O1—Ga1—N1	77.86(6)	O8—Ga1—N2	78.09(5)
				N1—Ga1—N2	171.27(6)

angles is 368.78° , which reveals that oxygen atoms form a flattened tetrahedron around the central atom and the Ga^{III} atom is out of plane (Table 2). On the other hand, the planes of two tridentate ligands are quasi-perpendicular.

There are varieties of O—H \cdots O and N—H \cdots O hydrogen bonds between the H₂O molecules, cationic and anionic moieties in the compound, which are classified as a strong hydrogen bond O(2S)—H(2B) \cdots O(7) ($x+1/2, -y+1/2, z+1/2$) and a weak hydrogen bond O2S—H2A \cdots O2 ($x-1/2, -y+1/2, z+1/2$) (Table 3). There are two uncoordinated water molecules, one of them (O1s) is hydrogen bonded to oxygen (O4) of the (pydc)²⁻ group. The second water molecule (O2s) is hydrogen bonded to oxygen (O2) of the (pydc)²⁻ group of the adjacent complex in addition to the first water molecule (Table 3). Also, in the crystal structure, C—O \cdots π and C—H \cdots π interactions between the [Ga(pydc)₂]⁻ complex and the aromatic ring in 2,9-dimethyl-1,10-phenanthroline with 3.371 Å and 3.335 Å distances and $\pi\cdots\pi$ stacking between the cationic and anionic aromatic rings with a distance of 3.460 Å were observed (Fig. 2).

Table 3

Hydrogen bonds for complexes 1 and 2

D—H \cdots A	<i>d</i> (D—H)	<i>d</i> (H \cdots A)	<i>d</i> (D \cdots A)	\angle DHA	Symmetry code
Complex 1					
N4—H4A \cdots O1	0.85	2.00	2.807(2)	158	
O1S—H1B \cdots O4	0.85	1.99	2.8199(19)	166	$-x+1, -y, -z+1$
O1S—H1A \cdots O2S	0.85	2.00	2.849(2)	173	
O2S—H2B \cdots O7	0.85	1.96	3.7942(19)	166	$x+1/2, -y+1/2, z+1/2$
O2S—H2A \cdots O2	0.85	2.11	2.9270(19)	161	$x-1/2, -y+1/2, z+1/2$
Complex 2					
O9—H9A \cdots O1S	0.90	1.69	2.564(2)	166	
N4—H4A \cdots N3	0.85	2.02	2.870(3)	180	$x, y, z+1$
N5—H5A \cdots O3S	0.85	1.81	2.655(3)	180	
O1S—H1B \cdots O2	0.85	1.95	2.787(2)	168	$x, y, z+1$
O1S—H1A \cdots O7	0.85	2.01	2.853(2)	171	
O2S—H2B \cdots O6	0.85	2.02	2.818(2)	155	
O2S—H2A \cdots O4	0.85	2.10	2.881(2)	153	$x, y, z-1$
O3S—H3A \cdots O2S	0.85	1.90	2.755(2)	180	$-x+1/2, y-1/2, -z+1/2$
O4SA—H41B \cdots O6	0.85	2.03	2.840(6)	159	$-x+1/2, -y+1/2, -z$
O4SA—H41A \cdots O10	1.04	2.31	3.303(7)	159	

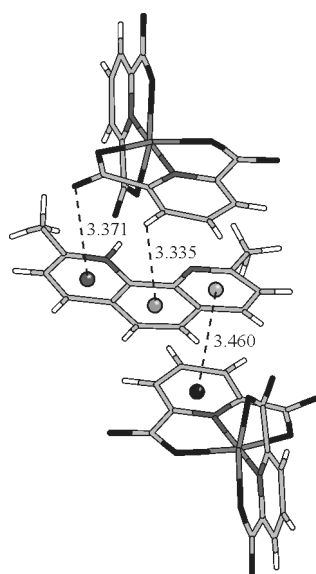


Fig. 2. C—O···π, C—H···π, and π···π interactions in the (dmpH)[Ga(pydc)₂]·2H₂O complex

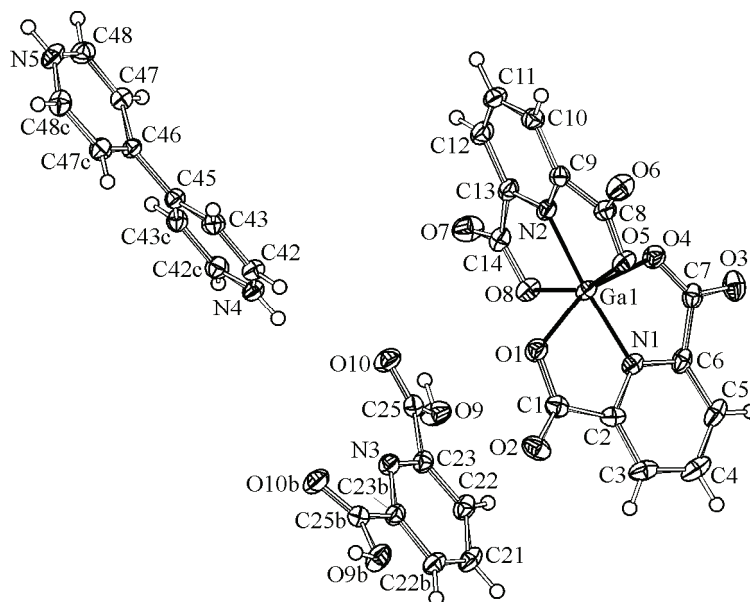


Fig. 3. Molecular structure of the (bpyH₂)_{1/2}(pydcH₂)_{1/2}[Ga(pydc)₂]·4H₂O complex (water molecules are omitted for clarity)

Characterization of (bpyH₂)_{1/2}(pydcH₂)_{1/2}[Ga(pydc)₂]·4H₂O complex (2). In the IR spectroscopy of the complex there are broad bands, and those at 3419—3484 cm⁻¹ and 3055—3090 cm⁻¹ were due to N—H stretching vibrations in the 4,4'-bipyridinium fragment and C—H in the aromatic rings. Absorption bands at 2552—2773 cm⁻¹ refer to the OH stretching vibration of free pyridine-2,6-dicarboxylic acid. The strong absorption band at 1663—1677 cm⁻¹ was attributed to C=O pyridine-2,6-dicarboxylate. The asymmetric and symmetric carboxylate stretching frequencies appeared at 1494 cm⁻¹ and 1336 cm⁻¹ respectively. Also, C—N stretching vibrations at 1599 cm⁻¹, C=C of the aromatic ring at 1370—1430 cm⁻¹ and the bending vibration of aromatic C—H at 749—916 cm⁻¹ appeared. The ¹H NMR spectrum showed some resonances at 6.53—6.97 ppm due to NH and pyridine-2,6-dicarboxylic acid and at 8.18—9.29 ppm due to CH of all pyridine rings. Carbon resonances of this complex have appeared at 124.61 ppm, 125.60 ppm, 128.03 ppm, 139.73 ppm, 144.61 ppm, 146.17 ppm, 147.77 ppm, 148.59 ppm, 162.28 ppm, and 165.95 ppm. In the ¹³C NMR spectrum, the resonances at 124.61 ppm, 139.73 ppm, and 144.61 ppm are assigned to 4,4'-bipyridine, and the remaining ¹³C NMR resonances (125.60 ppm, 128.03 ppm, 146.17 ppm, 147.77 ppm, 148.59 ppm, 162.28 ppm, and 165.95 ppm) clearly indicate the presence of (pydc)²⁻ and pydcH₂. The MS data resulted in a fragment at *m/e* 156 that is due to the presence of 4,4'-bipyridine in the complex. The other peaks at *m/e* 77, 123, and 398 are attributed to (bpy-H)_{1/2}, (pyridine-2-carboxylic acid) and [Ga(pydc)₂] respectively.

X-ray crystallographic structure of (bpyH₂)_{1/2}(pydcH₂)_{1/2}[Ga(pydc)₂]·4H₂O complex (2). The molecular structure is presented in Fig. 3. The crystallographic data, selected bond distances, bond angles, and intermolecular hydrogen bonds are listed in Tables 1, 3, and 4. The shortest distance between the closest parallel π-rings of the structure as well as C—O···π, C—H···π and π···π are shown in Fig. 4. This complex crystallizes in the space group *C2/c* of the monoclinic system with eight molecules per unit cell. According to the crystal structure of complex (2), the asymmetric units consist of an anionic hexacoordinated complex, [Ga(pydc)₂]⁻, half 4,4'-bipyridinium, half free pyridine-2,6-dicarboxylic acid, and four uncoordinated water molecules. In the anionic complex, the metal center lies in a pseudo-octahedral environment with four oxygen atoms O1, O4, O5, and O8 and two pyridine nitrogen atoms N1 and N2 of two (pydc)²⁻ anions (Fig. 3 and Table 4). With respect to the bond angles

Table 4

Selected bond lengths (Å) and bond angles (deg.) for complex 2

Ga1—N1	1.9611(17)	O1—Ga—O4	158.72(6)	O4—Ga1—N1	78.93(7)
Ga1—N2	1.9661(17)	O1—Ga—O5	88.99(6)	O5—Ga1—N1	101.00(6)
Ga1—O1	1.9954(15)	O1—Ga—O8	93.14(6)	O8—Ga1—N1	100.95(6)
Ga1—O4	2.0239(14)	O4—Ga1—O5	95.24(6)	O1—Ga1—N2	106.74(6)
Ga1—O5	2.0163(14)	O4—Ga1—O8	90.69(6)	O5—Ga1—N2	78.93(6)
Ga1—O8	1.9929(14)	O5—Ga1—O8	157.97(6)	O8—Ga1—N2	79.46(7)
		O1—Ga1—N1	79.79(6)	N1—Ga1—N2	173.45(7)

in N1—Ga1—N2, it shows a 6.55° deviation from linearity (Table 4). The summation of O1—Ga1—O5, O1—Ga1—O8, O4—Ga1—O5 and O4—Ga1—O8 angles is 368.06°, which reveals that Ga^{III} atom is out of plane (Table 4). Also, the planes of two tridentate ligands are quasi-perpendicular.

The intermolecular forces in this complex consist of hydrogen bonding and ion pairing. Four uncoordinated water molecules increase the number of hydrogen bonds in the structure. A wide range of hydrogen bonds (of the type O—H···O, N—H···O and N—H···N) with D···A distances ranging from 2.564(2) Å to 3.303(7) Å make an extended network based on H-bonding interactions (Table 3). The uncoordinated water molecules contribute to the formation of this network and increase the number of hydrogen bonds in the structure (Table 3). The strongest hydrogen bonds are between the uncoordinated water molecules and the carboxylate groups. Therefore, dipole-dipole and van der Waals interactions as well as hydrogen bonding seem to be effective in stabilizing the crystal structure.

The C—O··· π interaction in [Ga(pydc)₂][−] with the 4,4'-bipyridinium aromatic ring and free pydcH₂ with 3.045 Å and 3.498 Å distances, the C—H··· π interaction between [Ga(pydc)₂][−] and the aromatic ring in 4,4'-bipyridinium with a distance of 3.150 Å, and π ··· π stacking between the aromatic rings with a distance of 3.405 Å were observed (Fig. 4).

Optimized structure of the [Ga(pydc)₂][−] anion. Optimized geometrical parameters of the studied ligand and the anionic complexes at the B3LYP/6-311++G(2d,2p) computational level are shown in Table 5. The calculated values are in good agreement with the experimental results. The optimized geometry confirms that the C—O_(bonded) bond length of the (pydc)^{2−} ligand in the complex has been increased comparing with the free form. This evidence shows that C—O_(bonded) is weakened upon the complexation, while the C—O_(free) bond order is increased. Structures of the anionic complex and free ligand are shown in Fig. 5.

NBO analysis. In order to derive conclusions about the direction and magnitude of the charge transfer (CT) interaction, the natural bond orbital (NBO) analysis [13] was performed. The present complex formation is associated with an orbital interaction along with CT between the lone pairs of oxygen and nitrogen atoms of the ligand with LP* and Ry*(extra valence) of Ga. The excess electron density of Ga through back-bonding from LP* of Ga is mainly sent to the BD* of C—O_(bonded) and also C's Ry* orbitals of carboxylate groups (Tables 6 and 7).

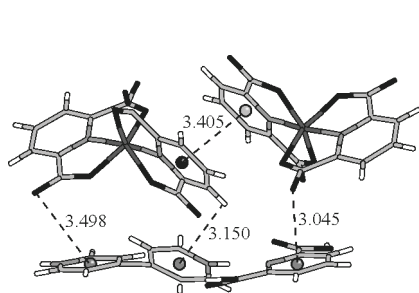


Fig. 4. C—O··· π , C—H··· π , and π ··· π interactions in (2)

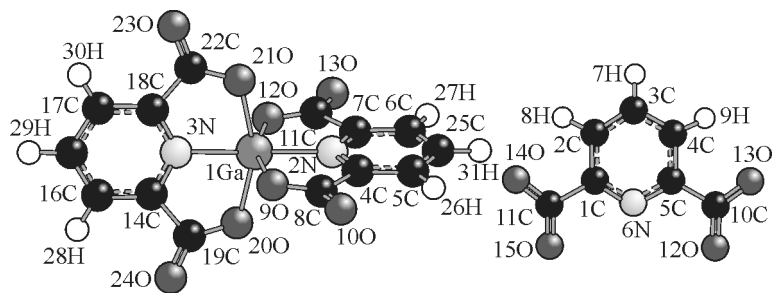


Fig. 5. Optimized structures of the [Ga(pydc)₂][−] anionic complex and the free (pydc)^{2−} ligand

Table 5

Selected experimental and B3LYP/6-31++G(d,p) calculated geometrical parameters of the (pydc)²⁻ ligand and the [Ga(pydc)₂]⁻ complex

Bond, Å	Complex		Ligand (calculated)	Bond, Å	Complex		Ligand (calculated)
	Calculated	Experimental ^a			Calculated	Experimental ^a	
Ga—N	2.002	1.979	—		1.288	1.316	1.248
Ga—O	2.002	1.977	—		1.288	1.295	1.248
	2.035	2.043	—	C—O _(free)	1.288	1.286	1.248
	2.035	2.038	—		1.223	1.234	1.262
	2.035	1.998	—		1.223	1.229	1.262
C—N	2.035	1.991	—		1.223	1.222	1.262
	1.326	1.335	1.343	Angle, deg.			
	1.326	1.334	1.343	N—Ga—N	179.981	176.90	—
C—O _(bonded)	1.326	1.333	1.343	O2—Ga—O6	91.90	90.59	—
	1.288	1.305	1.248				

^a Obtained for the (dmp)[Ga(pydc)₂]·2H₂O compound.

The natural charges and electron configurations on the atoms of the complex and the free (pydc)²⁻ ligand, which have been calculated by the NBO analysis, are gathered in Table 8. A part of negative charge over free oxygen atoms is located among carbon and oxygen atoms, in order to form the C=O bond. A small amount of the negative charge density over carbon atoms of the ring and the carboxylate carbon atom is due to complexation [16]. The natural charge of the nitrogen atom has increased to -0.57 in the complex from -0.46 in the free ligand due to back-bonding. Due to a more negative charge of nitrogen and more positive charge of adjacent carbon in the complex compared with the free ligand, the C—N_(ring) bond order is increased. This case is evident in a decrease in the C—N bond length (Table 5). Also, the natural charge of the oxygen atom bonded to Ga has increased to -0.76 compared to -0.77 in the free (pydc)²⁻ ligand. A part of the electron density of the C=O_(bonded) bond is transferred to the oxygen atom and its bond order decreases. These results verify that in the complexation process, the oxygen atom acts as a donor, on the other hand, the nitrogen atom as an acceptor.

AIM Analysis. In the present study, several basic parameters arising from Bader's theory of atoms in molecules (AIM [16]), characterizing the interactions were calculated in order to analyze the metal-ligand bond within the [Ga(pydc)₂]⁻ complex. The AIM study included the search for the (3, -1) bond critical points (BCPs), the calculation of charge densities $\rho(r_c)$ and the corresponding density Laplacians $\nabla^2\rho(r_c)$ at (3, -1) BCPs [18, 19].

The calculated values for the AIM quantities (at the B3LYP/6-31++G(2d,2p) level of theory) are given in Table 9. Table 9 shows that interactions of Ga and the coordinated atoms of the ligands are of the closed-shell type. As expected for the closed-shell interactions, this contact is characterized by small $\rho(r_c)$ values and $\nabla^2\rho(r_c) > 0$ [15]. The molecular graph of the studied complex is shown in Fig. 6.

¹³C NMR study. The ¹³C NMR chemical shifts of carbons were calculated on the optimized structures of the complex using the GIAO/DFT method with the 6-311++G(2d,2p) basis set for all atoms. The calculated ¹³C chemical shifts are tabulated in Table 10. On an absolute scale, the computed NMR chemical shifts at the DFT level of theory are in acceptable agreement with the experimental data. Differences between the calculated and measured values may be a result of solvent interactions. The relation between the experimental ¹³C chemical shifts and the computed (GIAO/DFT method) magnetic isotropic shielding tensors are shown in Fig. 7. The correlation is linear and it is described by the equation $\delta_C^{13} = -0.9\sigma_C + 178.71$.

Table 6

Results from the second-order perturbation theory analysis of the Kohn—Sham analog of the Fock matrix within the NBO basis for the $[\text{Ga}(\text{pydc})_2]^-$ complex at the B3LYP/6-311++G(2d,2p) level of theory

Donor orbital	Acceptor orbital	E^2 , kcal/mol	$(E_{\text{acc}} - E_{\text{don}})$, a.u.	$\langle \Psi_{\text{don}}^* F \Psi_{\text{acc}} \rangle$, a.u.	$Q_{\text{donor} \rightarrow \text{acceptor}}$	$Q_{\text{donor} \rightarrow \text{acceptor}}$
BD N2—C4	LP* Ga	2.84	0.81	0.049	0.00731901	0.030835669
		10.7	1.15	0.104	0.0163569	
		1.16	0.52	0.022	0.00357988	
		1.14	0.52	0.022	0.00357988	
BD N2—C7	LP* Ga	2.84	0.81	0.049	0.00731901	0.023675906
		10.7	1.15	0.104	0.0163569	
BD C8—O9	LP* Ga	2.17	0.88	0.045	0.00522986	0.023166718
		5.48	1.12	0.075	0.00896843	
		5.6	1.12	0.075	0.00896843	
BD O11—C12	LP* Ga	2.17	0.88	0.045	0.00522986	0.023166718
		5.48	1.12	0.075	0.00896843	
		5.6	1.12	0.075	0.00896843	
CR N2	LP* Ga	1.03	14.09	0.124	0.0001549	0.001339887
		9.53	14.42	0.351	0.00118499	
CR O9	LP* Ga	1.15	18.79	0.151	0.00012916	0.000901926
		4.01	19.03	0.263	0.000382	
		4.09	19.03	0.266	0.00039077	
CR O12	LP* Ga	1.15	18.79	0.151	0.00012916	0.000901926
		4.01	19.03	0.263	0.000382	
		4.09	19.03	0.266	0.00039077	
LP N2	LP* Ga	64.56	0.34	0.142	0.34885813	0.488871936
		57.36	0.67	0.176	0.13800847	
LP O9	Ry* Ga	2.19	2.91	0.076	0.00136418	0.525713035
		1.89	5.25	0.094	0.00064116	
		3.76	0.45	0.041	0.01660247	
LP O12	LP* Ga	10.02	0.69	0.078	0.02555766	0.524988319
		10.23	0.69	0.079	0.02621718	
		52.67	0.39	0.137	0.24679816	
		34.89	0.63	0.133	0.0891358	
		35.63	0.63	0.135	0.09183673	
		2.37	0.72	0.037	0.00528164	
		3.2	0.43	0.034	0.01250406	
		3.1	0.43	0.033	0.01177934	
		3.76	0.45	0.041	0.01660247	
		10.02	0.69	0.078	0.02555766	
10.22	0.69	0.079	0.02621718			
52.68	0.39	0.137	0.24679816			
34.92	0.63	0.133	0.0891358			
35.58	0.63	0.135	0.09183673			
2.37	0.72	0.037	0.00528164			
3.15	0.43	0.033	0.01177934			
3.15	0.43	0.033	0.01177934			

Table 7

Results from the second-order perturbation theory analysis of the Kohn—Sham analog of the Fock matrix within the NBO basis for the $[\text{Ga}(\text{pydc})_2]^-$ complex at the B3LYP/6-311++G(2d,2p) level of theory

Donor orbital	Acceptor orbital	E^2 , kcal/mol	$(E_{\text{acc}} - E_{\text{don}})$, a.u.	$\langle \Psi_{\text{don}}^* F \Psi_{\text{acc}} \rangle$, a.u.	$q_{\text{donor} \rightarrow \text{acceptor}}$	$q_{\text{donor} \rightarrow \text{acceptor}}$
CR Ga	BD* N2—C4	0.56	7.68	0.059	0.00011804	0.000118035
CR Ga	BD* N2—C7	0.56	7.68	0.059	0.00011804	0.000118035
LP* Ga	Ry* N2	0.72	0.76	0.06	0.01246537	0.040313374
		2.06	1	0.118	0.027848	
LP* Ga	BD* C8—O9	0.67	0.57	0.033	0.0067036	0.094525284
		0.88	0.33	0.039	0.02793388	
		0.86	0.33	0.038	0.02651974	
		0.75	0.24	0.031	0.03336806	
LP* Ga	BD* C11—O12	0.67	0.57	0.033	0.0067036	0.094525284
		0.86	0.33	0.038	0.02651974	
		0.88	0.33	0.039	0.02793388	
		0.75	0.24	0.031	0.03336806	
LP* Ga	Ry* C4	0.8	1.29	0.085	0.00868337	0.008683372
LP* Ga	Ry* C7	0.8	1.29	0.085	0.00868337	0.008683372
LP* Ga	Ry* O9	0.58	1.67	0.082	0.00482197	0.004821973
LP* Ga	Ry* O12	0.58	1.67	0.082	0.00482197	0.004821973

Table 8

B3LYP/6-311++G(2d,2p) calculated natural configurations and natural charges for the atoms of $[\text{Ga}(\text{pydc})_2]^-$ and the free $(\text{pydc})^{2-}$ ligand

Atom	Complex		Ligand	
	Natural Electron Configuration	Natural charge	Natural Electron Configuration	Natural charge
Ga	[core]4S(0.48)4p(0.71)4d(0.01)7p(0.01)	1.78	—	—
O _(bonded)	[core]2S(1.68)2p(5.06)3d(0.02)4p(0.01)	-0.76	[core]2S(1.72)2p(5.02)3p(0.01)3d(0.02)	-0.77
O _(free)	[core]2S(1.71)2p(4.92)3d(0.02)	-0.65	[core]2S(1.73)2p(5.06)3p(0.01)3d(0.02)	-0.82
N	[core]2S(1.29)2p(4.25)3d(0.01)4p(0.02)	-0.57	[core]2S(1.36)2p(4.06)3p(0.01)3d(0.02)	-0.46
C8	[core]2S(0.74)2p(2.44)3S(0.01)4p(0.03)4d(0.01)	0.78	[core]2S(0.75)2p(2.45)4p(0.03)4d(0.01)	0.75
C4	[core]2S(0.89)2p(2.91)4p(0.02)	0.17	[core]2S(0.91)2p(2.91)3d(0.01)4p(0.02)	0.15
C5	[core]2S(0.96)2p(3.22)4p(0.01)	-0.20	[core]2S(0.95)2p(3.29)4p(0.01)	-0.27
C25	[core]2S(0.96)2p(3.17)4p(0.01)	-0.15	[core]2S(0.95)2p(3.25)3p(0.01)4p(0.01)	-0.21
C6	[core]2S(0.96)2p(3.22)4p(0.01)	-0.20	[core]2S(0.95)2p(3.29)4p(0.01)	-0.27
C7	[core]2S(0.89)2p(2.91)4p(0.02)	0.17	[core]2S(0.91)2p(2.91)3d(0.01)4p(0.02)	0.15

CONCLUSIONS

It was shown that how good proton donors and acceptors can result in supramolecular metal complexes. We have demonstrated that the reaction between a proton donor, a proton acceptor, and a Ga^{III} ion can be used to synthesize a variety of interesting metal-organic compounds. Different non-covalent interactions such as ion-pairing, π — π stacking, and hydrogen bonding play important roles in the construction of extended networks in the crystal systems. By comparing the calculated geometrical parameters with the experimental values, the reliability of the DFT method (B3LYP) in the study of the title complexes is revealed.

Table 9

Results from the AIM analysis
of the relevant BCPs of the
[Ga(pydc)₂] complex

Bond	$\rho(r_c)$	$\nabla^2\rho(r_c)$
Ga—O	0.075	0.277
Ga—N	0.092	0.299

Table 10

Carbon chemical shifts (ppm) and calculated magnetic
isotropic shielding tensors

Atoms	δ_C (Exp) ^a	σ_C (Cal)	Atoms	δ_C (Exp) ^a	σ_C (Cal)
C8	165.96	16.25	C5	128.03	57.03
	162.28			125.60	
C16	147.77	37.58	C4	148.59	30.01
	146.17				

^a Obtained for the (bipyH₂)[Ga(pydc)₂]-2H₂O compound in DMSO.

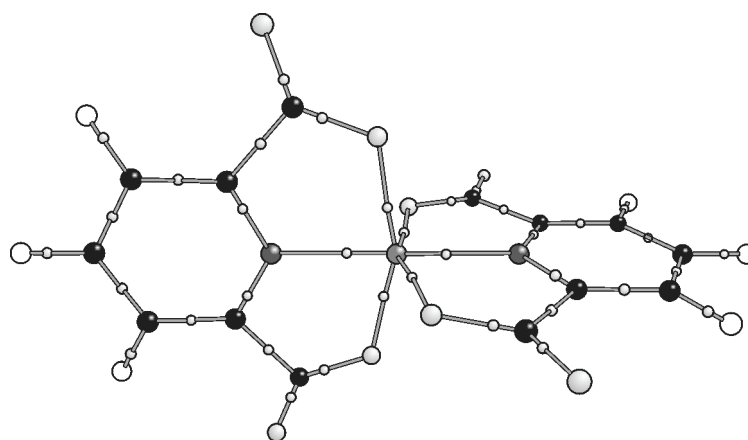


Fig. 6. Molecular graph indicating BCPs in the [Ga(pydc)₂]⁻ complex

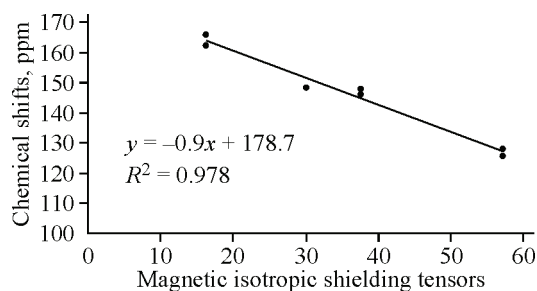


Fig. 7. Plot of experimental chemical shifts vs. magnetic isotropic shielding tensors from the B3LYP/6-311++G(2d,2p) calculation

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