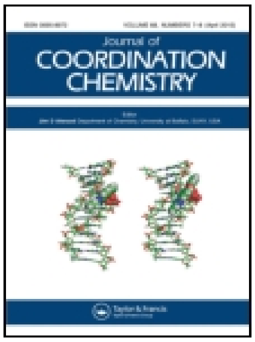

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The first mixed-ligand coordination compound involving 8-aminoquinoline and pyridine-2,6-dicarboxylate: synthesis, X-ray crystal structure, and DFT studies

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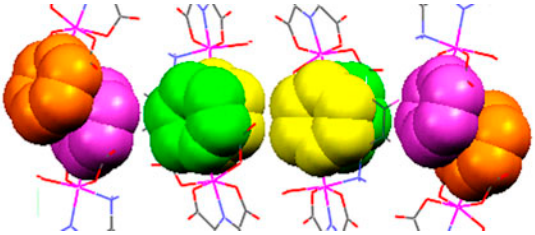

Self-assembly of pyridine-2,6-dicarboxylic acid (H_2py-2,6-dc) and $CrCl_3 \cdot 6H_2O$ in the presence of 8-aminoquinoline as a N-donor co-ligand leads to the formation of a supramolecular coordination compound in which the cationic and anionic complexes differ in composition, namely [Cr(py-2,6-dc)(8-aq)(H_2O)][Cr(py-2,6-dc)$_2$]·$2H_2O$ (**1**). Single-crystal X-ray analysis reveals that the coordination sphere around Cr in the cationic complex consists of one (py-2,6-dc)$^{2-}$, one 8-aq, and one H_2O while the anionic complex is more symmetrical and has two (py-2,6-dc)$^{2-}$ ligands in its coordination environment. Both Cr centers are six coordinate with distorted octahedral geometries. The ionic coordination motifs in **1** are held together by intermolecular O–H···O, N–H···O, and C–H···O hydrogen bonding as well as C–O···π, C–H···π, and π–π stacking interactions to produce extended 2-D architectures. We have analyzed the π–π stacking interactions by DFT calculations focusing our attention on the influence of the anionic/cationic nature of the complex.

Keywords: Mixed-ligand complex; Pyridine-2,6-dicarboxylic acid; 8-Aminoquinoline; Self-assembly; π–π Stacking interaction; Hydrogen bonding

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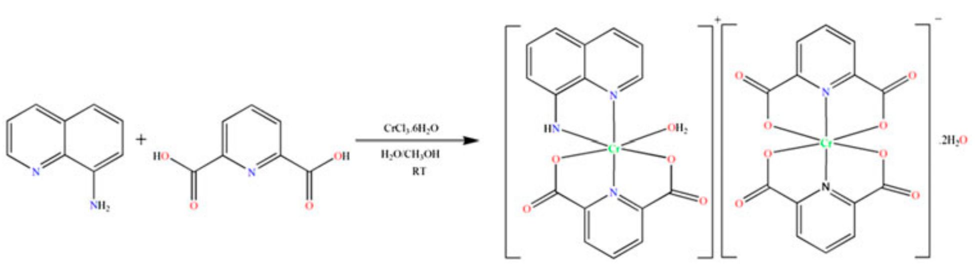
1. Introduction

Supramolecular chemistry elicits considerable attention from chemists due to its function in the design and synthesis of crystalline materials with interesting structures and desired properties such as ion-exchange [1], luminescence [2], catalysis [3], and magnetism [4]. In general, coordination supramolecular complexes can be generated by association and interaction between two main components, a metal ion and an organic ligand [5]. There are many factors which can affect the ultimate structure of these complexes such as the accompanying anion [6], pH [7], and reaction temperature [8], however, the final structure and its properties are strongly dependent on the nature of the organic ligand [9]. Therefore, one synthetic strategy to achieve a new, interesting, and practical crystalline material, based on an organic ligand, is the use of a mixed-ligand system [10–14]. Prior work indicates that polycarboxylate and neutral multidentate N-donor ligands are good candidates for the formation of new mixed-ligand architectures. A survey of the Cambridge Structural Database (CSD: version 5.35/Conquest1.11 May 2014) shows that there is a large number of aromatic polycarboxylic acids which have been used as modular precursors for the construction of coordination networks, in particular H_2py-2,6-dc with 900 coordination compounds is a frequently used precursor. In this context, our research group has focused on preparing supramolecular crystalline coordination compounds based on various dicarboxylic acids such as pyridine-2,3-dicarboxylic acid [15], pyrazine-2,3-dicarboxylic acid [16], pyridine-2,5-dicarboxylic acid [7], and especially pyridine-2,6- dicarboxylic acid [17]. As a ligand, (py-2,6-dc)$^{2-}$ is a symmetrical chelating ligand which can complete the metal coordination sphere and compensate charge [17] as well as providing non-covalent contacts such as hydrogen bonding and aromatic stacking for controlling the growth of supramolecular networks. Also, it can construct multifunctional coordination compounds with new properties in the presence of auxiliary N-donor ligands [18]. As continuation of our efforts to develop systems containing dicarboxylic acids, we have prepared a Cr coordination compound by employing H_2py-2,6-dc and 8-aq ligands, [Cr(py-2,6-dc)(8-aq)(H_2O)][Cr(py-2,6-dc)$_2$]·$2H_2O$ (**1**) (see scheme 1). **1** has been characterized by elemental analysis, IR spectroscopy, and has been structurally determined by single-crystal X-ray diffraction analysis. The X-ray crystallography studies demonstrate that π–π stacking and hydrogen bonding interactions are crucial for the formation and generation of the higher dimensional (D) network. Some counterintuitive non-covalent π–π stacking interactions have been rationalized by means of DFT calculations.



Scheme 1. The synthesis of **1**.

2. Experimental

2.1. *Materials and instrumentation*

All reagents and solvents were purchased from commercial sources and used without purification. The infrared spectrum (4000–600 cm^{-1}) was recorded on a Buck 500 Scientific spectrometer using KBr disks. Elemental analysis was carried out with a Thermo Finnigan Flash-1112EA microanalyzer and Perkin-Elmer 2004(II) apparatus. The X-ray diffraction data were collected with a Bruker AXS D8 Venture Photon 100 CMOS diffractometer equipped with a Cu IμS microsource. The melting point was determined on a Barnstead Electrothermal 9300 apparatus.

2.2. *Synthesis of [Cr(py-2,6-dc)(8-aq)(H_2O)][Cr(py-2,6-dc)$_2$]·2H_2O (1)*

The mixture of H_2py-2,6-dc (50 mg, 0.20 mmol) and 8-aq (10 mg, 0.07 mmol) in 10 mL of methanol was added dropwise to 10 mL of an aqueous solution of $CrCl_3 \cdot 6H_2O$ (50 mg, 0.20 mmol). The red solution was stirred for 3 h. By slow evaporation of the solvent at room temperature, orange plate-like single crystals of **1** were obtained after two weeks. Yield: 58% (based on Cr). IR (KBr pellet, cm^{-1}): 3405(s), 3110(s), 1629(s), 1609(s), 1571 (s), 1540(s), 1521(s), 1388(s), 1368(s), 1247(s), 989(s), 825(s). Anal. Calcd for $C_{30}H_{23}Cr_2N_5O_{15}$: C, 45.14; H, 2.88; N, 8.77. Found: C, 45.88; H, 3.10; N, 9.325%. m.p. 180 °C.

Table 1. Selected crystallographic data and structure refinement parameters of **1**.

Empirical formula	$C_{30}H_{23}Cr_2N_5O_{15}$
Formula weight (g mol^{-})	797.53
Temperature (K)	100(2)
Wavelength, λ (Å)	1.54178
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	8.3383(4)
b (Å)	25.2456(11)
c (Å)	15.2739(7)
α(°)	90
β (°)	102.1350(13)
γ(°)	90
Volume (Å^3)	3143.4(2)
Z	4
D_c (mgm^{-3})	1.685
F(0 0 0)	1624
Crystal size (mm^3)	0.100 × 0.030 × 0.008
θ range for data collection	5.4265–55.8466°
Index ranges	$-8 \le h \le 8$ $-27 \le k \le 27$ $-16 \le l \le 16$
Reflections collected	4055
Refinement method	Full-matrix least-squares on F^2
R_1, $wR_2[I > 2\sigma(I)]$	$R_1 = 0.0390$, $wR_2 = 0.2152$
R_1, wR_2 (all data)	$R_1 = 0.1129$, $wR_2 = 0.2152$
Goodness-of-fit on F^2	1.164
Largest differences peak and hole, e (Å^{-3})	

2.3. *X-ray crystallography*

The crystal of **1** was mounted on a Mitegen loop and flash-frozen to 100 K (Oxford Cryosystems Cryostream cooler). Preliminary examination and intensity data collection were carried out using a D8 Venture Photon 100 CMOS diffractometer, ω scans, and mirror-monochromated Cu–Kα radiation generated from an IμS source operating at 50 kV and 1 mA. Absorption corrections were performed with SADABS [19], the structure solved by direct methods (SHELXT [20]), and refined with SHELXL [20]. It should be mentioned that the crystal used for the measurement was a very thin plate, therefore, we had to use 240-s scans with the microfocus source to get any sort of reasonable data. Even with the longest feasible frame times the extremely small crystal size prevented us from obtaining any measurable data at higher angles than we report (see table 1).

2.4. *Theoretical methods*

The energies of complexes included in this study were computed at the BP86-D3/def2-TZVP level of theory. We have used the crystallographic coordinates for the theoretical analysis of the non-covalent interactions observed in the solid state. This level of theory has been shown useful and reliable to study non-covalent interactions like those analyzed herein [21]. The calculations have been performed using the program TURBOMOLE version 6.5 [22]. For the calculations, we have used the BP86 functional with the latest available correction for dispersion (D3) [23].

3. Results and discussion

3.1. *Spectroscopic studies*

Besides elemental analysis, **1** was initially characterized by its IR spectrum. This compound shows a moderately sharp absorption at 3110–3125 cm^{-1} which is attributed to the asymmetric stretch of coordinated NH_2. The broad bands of medium intensity at 3405 cm^{-1} are

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Cr1–O1	1.993(7)	Cr2–O9	1.999(7)
Cr1–O3	2.001(7)	Cr2–O11	1.985(7)
Cr1–O5	1.994(7)	Cr2–O13	1.969(9)
Cr1–O7	1. 964(7)	Cr2–N3	1.962(9)
Cr1–N1	1.982(8)	Cr2–N4	2.066(10)
Cr1–N2	1.971(9)	Cr2–N5	1.965(11)
N2–Cr1–N1	178.8(4)	N3–Cr2–N4	175.3(4)
O3–Cr1–O5	91.6(3)	O9–Cr2–N5	88.5(4)
O1–Cr1–O7	92.5(3)	O11–Cr2–N4	97.2(3)
O1–Cr1–O5	90.9 (3)	O13–Cr2–N5	172.2(4)
O3–Cr1–O7	93.5(3)	N4–Cr2–N5	83.6(4)
O7–Cr1–N2	79.3(3)	O11–Cr2–O13	90.3(4)
O7–Cr1–N1	99.5(3)	N3–Cr2–N5	92.6(4)
N2–Cr1–O1	101.7(3)	N3–Cr2–O13	94.8(3)
N1–Cr1–O1	78.4(3)	N3–Cr2–O11	80.0(3)
O7–Cr1–O5	158.5(3)	N5–Cr2–O11	90.3(4)
N2–Cr1–O5	79.2(3)	N3–Cr2–O9	78.9(3)
N1–Cr1–O5	102.0(3)	O13–Cr2–O9	90.5(3)
N2–Cr1–O3	101.2(3)	O11–Cr2–O9	158.8(3)
N1–Cr1–O3	78.8(3)	O13–Cr2–N4	89.1(4)
O1–Cr1–O3	157.1(3)	O1–Cr2–N4	97.2(3)
		O9–Cr2–N4	103.7(3)

Table 3. Some of the hydrogen bonding interactions present in **1**.

D–H· · ·A	d(D–H) (Å)	D(H–A) (Å)	d(D–A) (Å)	D–H–A (°)
O15–H15B· · ·O7^{i}	0.84	1.87	2.697(11)	168
O15–H15A· · ·O10^{i}	0.84	2.08	2.669(11)	127
O14–H14B· · ·O1^{ii}	0.84	2.33	3.169(11)	176
O14–H14A· · ·O12^{iii}	0.84	2.00	2.837(11)	171
C28–H28· · ·O2^{ii}	0.95	2.37	3.304(16)	166
C17–H17· · ·O2^{iv}	0.95	2.38	3.219(13)	147
N5–H5B· · ·O14	0.99	2.08	3.010(13)	155
N5–H5A· · ·O6^{v}	0.99	2.09	3.012(12)	154
O13–H13B· · ·O4	0.84	1.80	2.580(11)	154
O13–H13A· · ·O15	0.84	1.64	2.472(11)	170
C5–H5· · ·O4^{vi}	0.95	2.44	3.214(13)	139
C3–H3· · ·O10^{iv}	0.95	2.35	3.191(13)	148

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

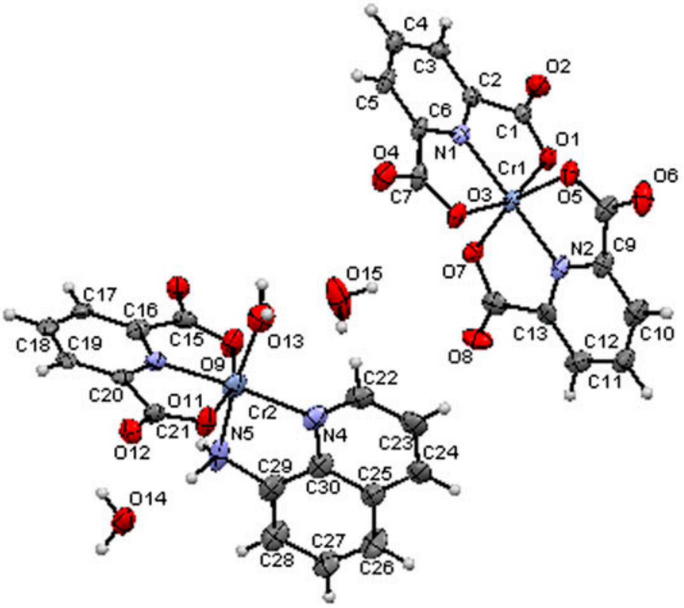


Figure 1. The molecular structure of **1** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

assigned to coordinated H_2O in the cationic complex. Also, bands at 1629 and 1388 cm^{-1} can be assigned to the anti-symmetric $\nu_{as}(COO^{-})$ and symmetric $\nu_{s}(COO^{-})$ stretching vibrations, respectively. The resulting value of $\Delta\nu$ ($\Delta\nu = \nu_{as} - \nu_{s} = 241$ cm^{-1}) is the characteristic of monodentate bonding of the carboxylic group [24]. These findings are also supported by the result obtained from X-ray diffraction measurements.

3.2. *Structure of [Cr(py-2,6-dc)(8-aq)(H_2O)][Cr(py-2,6-dc)$_2$]·2H_2O (1)*

The crystallographic data for **1** are shown in table 1 while selected bond lengths and angles are given in table 2. Hydrogen bond geometries of this compound are shown in table 3. As shown in figure 1, the molecular structure of **1** consists of one cationic [Cr(py-2,6-dc)(8-aq)(H$_2$O)]$^+$, one anionic [Cr(py-2,6-dc)$_2$]$^-$ coordination complex, and two uncoordinated water molecules. In the anionic complex, two (py-2,6-dc)$^{2-}$ ions are tridentate chelating ligands and almost perpendicular to each other. The Cr^{III} ion in the anion is six coordinate and has a distorted octahedral coordination composed of four O (the Cr–O distances range from 1.964 to 2.001 Å) and two N (the Cr–N distances range from 1.971 to 1.982 Å) from two (py-2,6-dc)$^{2-}$ ligands. Although the Cr^{III} in the cationic complex is six coordinate and exhibits a similar distorted octahedral geometry, its coordination sphere is quite different. Here, the Cr^{III} is surrounded by two O [the Cr–O distances are 1.985(7) and 1.999(7) Å] and one N [the Cr–N distance is 1.962(9) Å] from one (py-2,6-dc)$^{2-}$ ligand and two N [the Cr–N distances are 1.965(11) and 2.066(10) Å] belonging to the 8-aq ligand. The remaining site is occupied by coordinated water [the Cr–O distance is 1.969(9) Å]. According to table 4, the bond distances in **1** are in agreement with literature values. The packing of these anionic and cationic complexes is depicted in figure 2.

Covalent connectivity within the coordination compound is supplemented by O–H···O [O/O distances from 2.472(11) to 3.169(11) Å], N–H···O [N/O distances are 3.010(12) and 3.012(13) Å] and C–H···O [C/O distances are 3.191(13)–3.304(16) Å] hydrogen bonds between the amino group of 8-aq, carboxylate groups belonging to (py-2,6-dc)$^{2-}$, and water molecules. The uncoordinated water molecules act as a gluing factor to connect discrete cationic and anionic complexes, generating 1-D chains with the ring having the graph set notation R_4^4 (16) and R_2^2 (14) along the crystallographic *b*-axis. Additionally, infinite 1-D chains join via N–H···O hydrogen bonds between amino and carboxylate groups creating a R_7^7 (28) graph set along the crystallographic *c*-axis (see figure 3). It is worth mentioning that (py-2,6-dc)$^{2-}$ and 8-aq ligands in adjacent chains play an important role in the self-assembly via C–O···π (3.650 Å), C–H···π (3.284, 3585 Å), and π–π (centroid to centroid distances 3.596 (*Cg1*···*Cg2*), 3.635 (*Cg3*···*Cg4*) Å, and dihedral angles (21.32°,

Table 4. Comparison of the bond distances (Å) within some Cr/(py-2,6-dc)$^{2-}$ complexes.

Chemical formula	Cr–O	Ref.
1	2.000, 1.994, 1.964, 1.998, 1.985	This work
[H2,6-dapym]$_2$[Cr(py-2,6-dc)$_2$]·H$_2$py-2,6-dc·6H$_2$O	1.990, 2.005	[25]
[Cr(py-2,6-dc)$_2$(NO)(H$_2$O)$_2$]	2.027	[26]
[H2,9-m-1,10-phen]$_2$[Cr(py-2,6-dc)$_2$]·H$_2$O	1.999, 1.998, 1.990, 1.991	[27]
[Cr(py-2,6-dc)(1,10-phen)(Cl)]·0.5H$_2$O	1.999, 1.975	[28]
[HCreatin][Cr(py-2,6-dc)$_2$]·H$_2$py-2,6-dc·6H$_2$O	1.995, 1.9971.984, 1.994	[29]
[Cr$_2$(py-2,6-dc)$_2$(μ$_2$-OH)$_2$]	2.017	[30]
[Cr(py-2,6-dc)(tpyl)][Cr(py-2,6-dc)$_2$]·4H$_2$O	1.998, 1.980, 1.982, 1.976, 1.955	[31]
[CrNa(μ$_2$-py-2,6-dc)(μ$_3$-py-2,6-dc)(H$_2$O)$_2$]	2.000, 1.999	[32]
[Ag(1H-1,2,4-triazol-5-amine)$_2$][Cr(py-2,6-dc)$_2$][Cr$_2$(py-2,6-dc)$_2$(μ$_2$-OH)$_2$]·2H$_2$O	2.000, 2.003, 1.993, 1.969, 2.011, 1.983	[33]
[Cr(py-2,6-dc)(1,10-phen)(H$_2$O)][Cr (py-2,6-dc)$_2$]·4H$_2$O	2.021, 1.991, 1.989, 1.961, 1.976, 1.964	[34]
Rb[Cr(py-2,6-dc)$_2$]	2.001	[35]
[Cr(η^6-Bz)$_2$][Cr(py-2,6-dc)$_2$]·2H$_2$O	2.001, 1.999, 1.965, 1.984	[36]
[H4-(4-pyr)py][Cr(py-2,6-dc)$_2$]·4H$_2$O	2.017, 1.994, 1.983	[37]
[1H-pyrazol-2-ium][Cr(py-2,6-dc)$_2$]·H$_2$py-2,6-dc·5H$_2$O	1.995, 1.988, 1.984, 1.983	[38]
[Cr(py-2,6-dc)(bpy)(H$_2$O)][Cr(py-2,6-dc)$_2$]·2H$_2$O	2.002, 1.975, 1.972, 1.937, 1.987	[38]
[H2-apym][Cr(py-2,6-dc)$_2$]·2H$_2$O	2.003, 2.018, 1.992, 1.971	[39]

Abbreviations: dapym = diaminopyrimidine, 2,9-m-1,10-phen = 2,9-dimethyl-1,10-phenanthroline, Bz = benzene, tpyl = 2,2′:6′,2″-terpyridyl, H4-(4-pyr)py = 4-(4-pyridyl)pyridine, 2-apym = 2-aminopyrimidine.

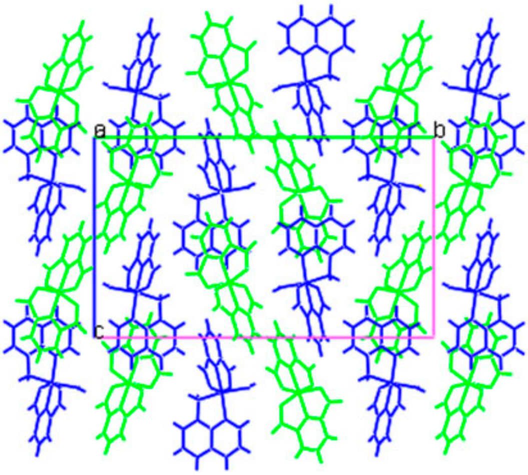


Figure 2. The packing diagram of **1** showing the arrangement of anionic (in green) and cationic (in blue) complexes (see http://dx.doi.org/10.1080/00958972.2015.1077953 for color version).

21.25°) stacking interactions along the crystallographic *c*-axis (see figure 4). These non-covalent interactions make the solid-state structure of **1** more stable and assembled as a 2-D supramolecular network.

Consideration of the structures of **1** and related compounds obtained from the CSD search suggests the following interesting issues. First, there are 540 examples of first row transition metal complexes with the (py-2,6-dc)$^{2-}$ ligand in the CSD with most of them containing Cu, Ni, and Co while those containing Ti and Cr are the least abundant (see figure 5). Second, the CSD search also shows that there are two types of mixed-ligand coordination compounds involving (py-2,6-dc)$^{2-}$ and N-donor chelating ligands. As shown in figure 6, both ligands prefer to coordinate to one metal center to form single-component molecular complexes. Interestingly, we see a reverse trend for Cr and Fe complexes so that they form two component anionic and cationic coordination compounds. This is likely due to the common +3 oxidation state of these metals that facilitates the formation of octahedral monoanions by their coordination to two (py-2,6-dc)$^{2-}$ ligands, as observed in the title compound. The countercation can be then formed simply by metal coordination to one (py-2,6-dc)$^{2-}$ ligand and one or several neutral co-ligands. Third, the most important point in the formation of mixed-ligand complexes is competition between the nucleophilicity and basicity of the organic ligands. For example, the nucleophilicity of 8-aq is greater than that of 8-hydroxyquinoline while its basicity is lower. This statement is confirmed by the results obtained from the CSD search. 8-aq in the presence of carboxylic acids acts as an excellent auxiliary ligand to coordinated metal centers while 8-hydroxyquinoline prefers to be uncoordinated and appears as a counter ion.

3.3. *Theoretical study*

We focused the theoretical study of **1** to the supramolecular 1-D chain found in its solid state that is characterized by π–π interactions of different nature (see figure 7). We have represented those rings that belong to the electron-rich (py-2,6-dc)$^{2-}$ ligand (denoted as π^-)

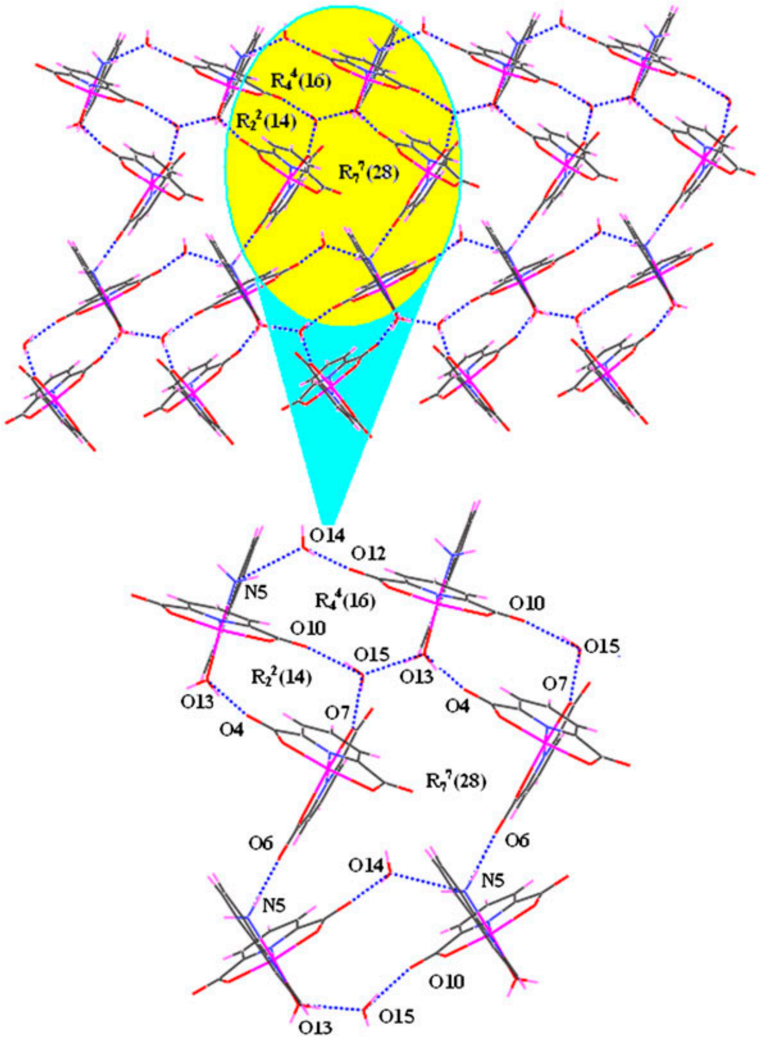


Figure 3. Hydrogen bonds present in **1** that creates the 2-D layer viewed along the *bc* plane with schematic representation of graph sets at the bottom of the figure.

in blue and the neutral 8-aminoquinoline ligand in green. Two different *π*–*π* stacking interactions are observed. In one, the interaction is established between two (py-2,6-dc)$^{2-}$ moieties and, in the other, the interaction is formed between the 8-aminoquinoline and the (pydc)$^{2-}$ ligands. We have evaluated both stacking interactions by DFT calculations. Their interaction energies (ΔE_1 and ΔE_2) are large and negative because they are established between counterions $[Cr(py\text{-}2,6\text{-}dc)(8\text{-}aq)(H_2O)]^{+}\cdots[Cr(py\text{-}2,6\text{-}dc)_2]^{-}$ and consequently strong electrostatic forces dominate the binding. Interestingly, ΔE_2 is 7.5 kcal/mol more favorable than ΔE_1 because, in addition to the strong and non-directional electrostatic effects, the *π*–*π* interaction is formed between electron-rich $[(py\text{-}2,6\text{-}dc)^{2-}]$ and electron-poor (coordinated 8-aq) rings. As a matter of fact, the interaction between both electron-rich

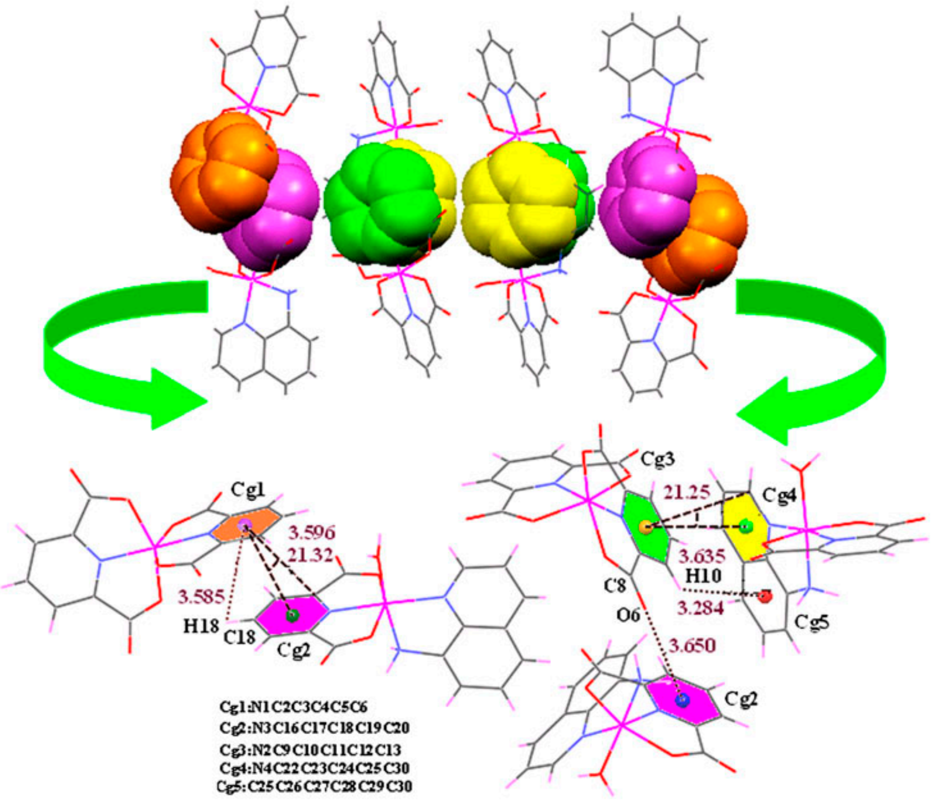


Figure 4. Partial view of the crystal packing of **1** with indication of the C–O···π, C–H···π, and π–π stacking interaction.

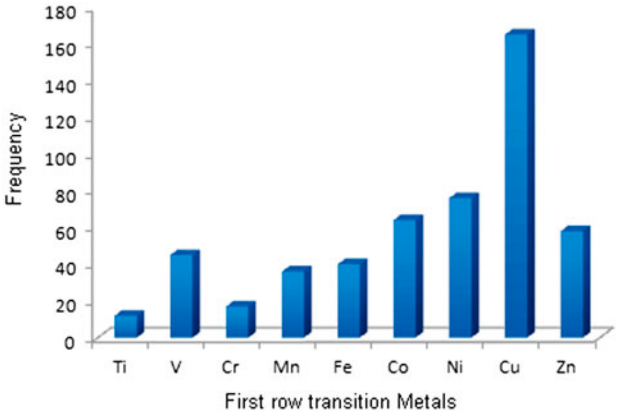


Figure 5. Frequency of coordination compounds containing (py-2, 6-dc)$^{2-}$ as a ligand.

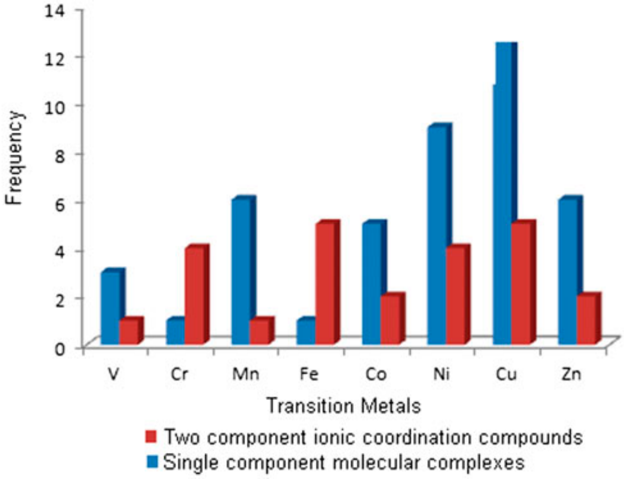


Figure 6. Comparison of frequency of coordination compounds containing (py-2, 6-dc)$^{2-}$ in the forms of two and one components.

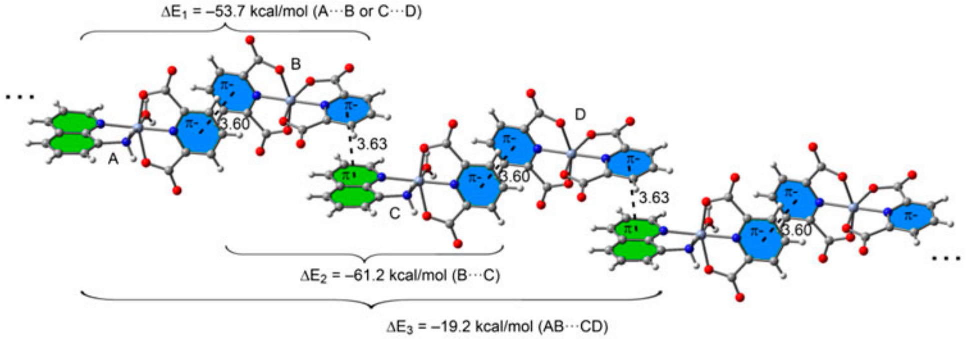


Figure 7. Polymeric chain dominated by π–π interactions. The energies have been computed at the BP86-D3/def2-TZVP level of theory. Distances in Å.

(py-2,6-dc)$^{2-}$ dianionic ligands (complex A···B) would be repulsive without the presence of the Cr(III) metal centers. In an effort to evaluate the interaction minimizing the contribution of the electrostatic forces, we have computed a tetrameric model (see figure 7), and we have evaluated the stacking interaction considering that the A···B and D···C dimers have been previously formed. Using this procedure, the interaction energy is reduced to $\Delta E_3 = -19.2$ kcal/mol. This binding energy is very large compared to conventional π–π interaction (e.g. benzene dimer) due to the donor–acceptor nature of the interaction and confirms the importance of this type of π-stacking interaction upon the crystal packing of **1**.

4. Conclusion

We report the synthesis and X-ray characterization of the first mixed-ligand coordination compound involving 8-aq and (py-2,6-dc)$^{2-}$ ligands, [Cr(py-2,6-dc)(8-aq)(H_2O)]

$[Cr(py\text{-}2,6\text{-}dc)_2]\cdot 2H_2O$ (**1**). Also, the incorporation of neutral N-donor co-ligands in these systems usually facilitates the supramolecular interactions and thus provides a possibility of constructing unusual supramolecular architectures. As expected, conventional non-covalent interactions (hydrogen bonds and C–H···*π*) between the 8-aq and $(py\text{-}2,6\text{-}dc)^{2-}$ ligands have a prominent influence on the assembly of the low-dimensional entities into a high-dimensional supramolecular network. More importantly, electrostatically assisted *π*–*π* stacking interactions are very important in the solid state of **1** and energetically very favored as demonstrated by means of DFT calculations.

Supplementary material

CCDC 1052407 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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References

[1] B. Bhattacharya, R. Dey, D.K. Maity, D. Ghoshal. *CrystEngComm.*, **15**, 9457 (2013).
[2] (a) Z.C. Hu, B.J. Deibert, J. Li. Chem. Soc. Rev., **43**, 5815 (2014); (b) J.C. Ahern, A. Shilabin, K.M. Henline, R.D. Pike, H.H. Patterson. Dalton Trans., **43**, 12044 (2014).
[3] S.F. Liu, A. Motta, A.R. Mouat, M. Delferro, T.J. Marks. *J. Am. Chem. Soc.*, **136**, 10460 (2014).
[4] M.H. Zeng, Z. Yin, Y.X. Tan, W.X. Zhang, Y.P. He, M. Kurmoo. *J. Am. Chem. Soc.*, **136**, 4680 (2014).
[5] F. Yin, J. Chen, Y. Liang, Y. Zou, J. Yinzhi, J. Xie. *J. Solid State Chem.*, **225**, 310 (2015).
[6] M. Mirzaei, H. Eshtiagh-Hosseini, M. Mohammadi Abadeh, M. Chahkandi, A. Frontera, A. Hassanpoor. *CrystEngComm.*, **15**, 1404 (2013).
[7] H. Eshtiagh-Hosseini, M. Mirzaei, M. Biabani, V. Lippolis, M. Chahkandi, C. Bazzicalupid. *CrystEngComm.*, **15**, 6752 (2013).
[8] H.R. Khavasi, B. Mir Mohammad Sadegh. *Inorg. Chem.*, **49**, 5356 (2010).
[9] P. Yang, J.J. Wu, H.Y. Zhou, B.H. Ye. *Cryst. Growth Des.*, **12**, 99 (2012).

[10] J.S. Hu, X.Q. Yao, M.D. Zhang, L. Qin, Y.Z. Li, Z.J. Guo, H.G. Zheng, Z.L. Xue. *Cryst. Growth Des.*, **12**, 3426 (2012).

[11] H.M. He, F.X. Sun, J.T. Jia, Z. Bian, N. Zhao, X.P. Qiu, L.X. Gao, G.S. Zhu. *Cryst. Growth Des.*, **14**, 4258 (2014).

[12] H.-W. Kuai, X.-C. Cheng, X.-H. Zhu. *Polyhedron*, **50**, 390 (2013).

[13] Z.X. Li, T.L. Hu, H. Ma, Y.F. Zeng, C.J. Li, M.L. Tong, X.H. Bu. *Cryst. Growth Des.*, **10**, 1138 (2010).

[14] Y. Gong, T. Wu, P.G. Jiang, J.H. Lin, Y.X. Yang. *Inorg. Chem.*, **52**, 777 (2013).

[15] H. Eshtiagh-Hosseini, M. Mirzaei, A. Mousavinezhad, M. Necas, J.T. Mague. *Acta Crystallogr.*, **E68**, m71 (2012).

[16] (a) H. Eshtiagh-Hosseini, A. Hassanpoor, N. Alfi, M. Mirzaei, K.M. Fromm, A. Shokrollahi, F. Gschwind, E. Karami. *J. Coord. Chem.*, **63**, 3175 (2010); (b) M. Mirzaei, H. Eshtiagh-Hosseini, V. Lippolis, H. Aghabozorg, D. Kordestani, A. Shokrollahi, R. Aghaei, A.J. Blake. *Inorg. Chim. Acta*, **370**, 141 (2011); (c) M. Mirzaei, H. Eshtiagh-Hosseini, A. Hassanpoor, T. Szymańska-Buzar, J.T. Mague, M. Korabik, A. Kochel. *Inorg. Chim. Acta*, **391**, 232 (2012).

[17] (a) H. Eshtiagh-Hosseini, H. Aghabozorg, M. Mirzaei, M.M. Amini, Y.-G. Chen, A. Shokrollahi, R. Aghaei. *J. Mol. Struct.*, **973**, 180 (2010); (b) H. Eshtiagh-Hosseini, Z. Yousefi, M. Shafiee, M. Mirzaei. *J. Coord. Chem.*, **63**, 3187 (2010); (c) M. Mirzaei, H. Aghabozorg, H. Eshtiagh-Hosseini. *J. Iran Chem. Soc.*, **8**, 580 (2011); (d) H. Eshtiagh-Hosseini, M. Mirzaei, N. Alfi. *Review on Proton Transfer Metal Complexes*, 1st Edn, Lambert Academic Publishing GmbH & Co. KG. (2012).

[18] (a) J. Hu, Z. Zhao, D. Zhao, S. Chen, J. Zhao, H. Zhao. *Z. Anorg Allg. Chem.*, **639**, 821 (2013); (b) X.-L. Wang, L.-L. Hou, J.-W. Zhang, C.-H. Gong, G.-C. Liu. *Inorg. Chim. Acta*, **405**, 58 (2013); (c) J. Wei, D. Zhang, Q. Yang, S. Chen, S. Gao. *Inorg. Chem. Commun.*, **30**, 13 (2013); (d) R.-Q. Zou, X.-H. Bu, M. Du, Y.-X. Sui. *J. Mol. Struct.*, **707**, 11 (2004); (e) K.J. Akerman, C. Venter, L.A. Hunter, M.P. Akerman. *J. Mol. Struct.*, **1091**, 74 (2015); (f) M. Mirzaei, H. Eshtiagh-Hosseini, Z. Bolouri, Z. Rahmati, A. Esmaeilzadeh, A. Hassanpoor, A. Bauza, P. Ballester, M. Barceló-Oliver, J.T. Mague, B. Notash, A. Frontera. *Cryst. Growth Des.*, **15**, 1351 (2015).

[19] G.M. Sheldrick. *SADABS*, University of Göttingen, Germany (2008).

[20] G.M. Sheldrick. SHELXS and SHELXL, *Acta Crystallogr.*, **A64**, 112 (2008).

[21] (a) L.K. Das, R.M. Kadam, A. Bauzá, A. Frontera, A. Ghosh. *Inorg. Chem.*, **51**, 12407 (2012); (b) M. Mitra, P. Manna, A. Bauzá, P. Ballester, S. Kumar Seth, S.R. Choudhury, A. Frontera, S. Mukhopadhyay. *J. Phys. Chem. B*, **118**, 14713 (2014); (c) S. Saha, A. Sasmal, C.R. Choudhury, G. Pilet, A. Bauzá, A. Frontera, S. Chakraborty, S. Mitra. *Inorg. Chim. Acta*, **425**, 211 (2015); (d) A. Bauzá, A. Terrón, M. Barceló-Oliver, A. García-Raso, A. Frontera. *Inorg. Chim. Acta* (2015) doi:10.1016/j.ica.2015.04.028. (e) D. Sadhukhan, M. Maiti, G. Pilet, A. Bauzá, A. Frontera, S. Mitra. *Eur. J. Inorg. Chem.*, **11**, 1958 (2015); (f) P. Chakraborty, S. Purkait, S. Mondal, A. Bauzá, A. Frontera, C. Massera, D. Das. *CrystEngComm.*, **17**, 4680 (2015); (g) A. Bauzá, A. Frontera. *Chem. Phys. Lett.*, **633**, 282 (2015); (h) A. Bauzá, A. Frontera. *Angew. Chem. Int. Ed.*, **54**, 7340 (2015).

[22] R. Ahlrichs, M. Bär, M. Hacer, H. Horn, C. Kömel. *Chem. Phys. Lett.*, **162**, 165 (1989).

[23] S. Grimme, J. Antony, S. Ehrlich, H. Krieg. *J. Chem. Phys.*, **132**, 154104 (2010).

[24] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B*, 5th Edn, Wiley, New York (1997).

[25] M. Ranjbar, H. Aghabozorg, A. Moghimi, A. Yanovsky. *Z. Kristallogr-New Cryst. Struct.*, **216**, 626 (2001).

[26] K. Wieghardt, U. Quilitzsch, J. Weiss. *Inorg. Chim. Acta*, **89**, L43 (1984).

[27] Z. Aghajani, H. Aghabozorg, E. Sadr-Khanlou, A. Shokrollahi, S. Derki, M. Shamsipur. *J. Iran. Chem. Soc.*, **6**, 373 (2009).

[28] A.C. González-Barö, R. Pis-Diez, O.E. Piro, B.S. Parajón-Costa. *Polyhedron*, **27**, 502 (2008).

[29] H. Aghabozorg, Z. Derikvand, M.M. Olmstead, J. Attar Gharamaleki. *Acta Crystallogr.*, **E64**, m1234 (2008).

[30] C.C. Ou, W.J. Borowski, J.A. Potenza, H.J. Schugar. *Acta Crystallogr. B*, **33**, 3246 (1977).

[31] U. Casellato, R. Graziani, R.P. Bonomo, A.J. Di Bilio. *J. Chem. Soc., Dalton Trans.*, 23 (1991).

[32] Y. Dai, W. Shi, X.-J. Zhu, B. Zhao, P. Cheng. *Inorg. Chim. Acta*, **359**, 3353 (2006).

[33] M. Tabatabaee, B.-M. Kukovec, M. Kazeroonizadeh. *Polyhedron*, **30**, 1114 (2011).

[34] M. Rafizadeh, V. Amani, B. Neumuller. *Z. Anorg. Allg. Chem.*, **632**, 2190 (2006).

[35] W. Furst, P. Gouzerh, Y. Jeannin. *J. Coord. Chem.*, **8**, 237 (1979).

[36] D. Braga, C. Bazzi, L. Maini, F. Grepioni. *CrystEngComm.*, **1**, 15 (1999).

[37] J. Soleimannejad, H. Aghabozorg, S. Hooshmand. *Acta Crystallogr.*, **E64**, m564 (2008).

[38] N.M. Halim, V. Abramov, I. Pantenburg, G. Meyer. *Z. Naturforsch., B: Chem. Sci.*, **66**, 685 (2011).

[39] H. Eshtiagh-Hosseini, Z. Yousefi, M. Mirzaei, Y.-G. Chen, S.A. Beyramabadi, A. Shokrollahi, R. Aghaei. *J. Mol. Struct.*, **973**, 1 (2010).