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Crystal structure of Cr (III) complex containing nitrilotriacetic acid and 4, 4'-bipyridine

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Abstract: The title compound $(C_{10}H_9N_2)[Cr(C_6H_7NO_6)_2](C_{10}H_8N_2)\cdot 2H_2O$ or (4,4′-bipyH)[Cr(ntaH)$_2$](4,4′-bipy)·2H$_2$O (ntaH$_3$ is nitrilotriacetic acid) was synthesized by reaction of $Cr(NO_3)_3\cdot 9H_2O$ with 4,4′-bipyridine, and nitrilotriacetic acid with 4:2:1 molar ratio in aqueous solution. The crystal structure of this complex was identified using X-ray crystallography. The unit cell parameters are as follows:
a = 9.8501(3) Å, ***b*** = 13.157(2) Å, ***c*** = 26.842(4) Å, ***β*** = 104.807(7)°.
The final ***R*** value is 0.041 for 7747 independent reflections. The title compound crystallized in monoclinic system and belongs to ***P***2$_1$/c space group. The central Cr^{III} atom is coordinated by two tridentaid (ntaH$_2$) ligands and the resulted CrO4N2 set can be described as distorted octahedral geometry. The asymmetric unit contains two half of anionic complex, one 4, 4′-bipyridiniom ion, $(4, 4'\text{-bipyH})^+$, one neutral 4, 4′-bipyridine molecule and two non-coordinated water molecules. Intramolecular hydrogen bonds, π-π [centroid –centroid distances of 3.674 Å], C-H…π, O-H…π and N-H…π stacking interactions [with distance of 3.714, 3.736 and 3.270 Å respectively], connect the various components into a supramolecular structures.

Keywords: *Cr (III) complex; 4, 4′-bipyridine; nitrilotriacetic acid; crystal structure; hydrogen bonding; π–π and C═O···π stacking interactions.*

Introduction

The preparation and characterization of self-assembling systems have been considered by chemists in recent years. Intramolecular interactions play an important role in the formation of stable and structurally well-defined supramolecular structures [1]. Much of the investigations on reviewed compounds focused on the concept of supramolecular systems, co-crystallization, stereochemically active lone pairs, coordination polyhedron and mainly on various interactions involve including van der Waals, ion pairing, hydrogen bondings, face to face π-π stackings and edge to face C-H···π, C-O···π, N-H···π, S-O···π, Ti···π and Hg-Cl···π interactions. The mentioned interactions are the most commonly used strategies in the extension of supramolecular structures. Research has shown that hydrogen bonding plays the key role in preparation of self-assembled compounds. There is a very close relationship between hydrogen bonding and formation of proton transfer compounds [2]. In complexes thus obtained, the ion pairs act as ligand or counter ion, partially or totally. The anionic fragment of the ion pair is usually, not always, coordinated to metallic ion and lies in the ligand domain, and the counter ion remains in the periphery domain [3]. It is well known that 4,4'-bipyridine is an excellent candidate for the construction of three-dimensional network motifs. It can act as coordinating or bridging ligand [4] or as proton acceptor agent for metal complexes [5-9]

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or in proton transfer compound [10]. Herein we report the synthesis and X-ray crystal structure of the title compound.

Preparation and experiments

The proton transfer ion pair was prepared by refluxing 4, 4′-bipy (312mg, 2mmol) and nitrilotriacetic acid (191mg, 1mmol) in water (10ml) for about 30 minutes. A violet solution of $Cr(NO_3)_3.9H_2O$ (200mg, 4mmol) in water (5ml) was added to above solution and reflux for 1 hour. Cubic dark violet crystals of the title compound suitable for X-ray analysis were obtained by slow evaporation after two weeks at room temperature.

The X-ray data was collected on a Bruker SMART diffractometer (MoKα -radiation) at 296 K. The crystal data and experimental parameters are given in Table 1. The crystal was solved by direct methods (SHELXS-97) and a refinement was carried out with full-matrix least-squares methods based on F^2 with SHELXL-97 [11].

Results and discussion

The title compound, (4,4′-bipyH)[Cr(ntaH)$_2$](4,4′-bipy)·2H$_2$O, crystallized in the monoclinic system, space group $P2_1/c$ with four molecules in the unit cell. Crystallographic data of this compound are given in Table 1. The final atomic coordinates of non-hydrogen atoms are listed in Table 2. Selected bond lengths and angles are given in Table 3 and hydrogen bond geometries are given in Table 4. According to the crystal structure of the title compound, the asymmetric unit consists of two half of the anionic component, $[Cr(ntaH)_2]^-$, one cationic component $(4,4'\text{-bipyH})^+$, one neutral 4,4′-bipyridine molecule and two non-coordinated water molecules (Fig. 1). In anionic component each Cr (III) atom is six coordinated by two $(ntaH)^{2-}$ groups which act as tridentate ligand through one N atom and two O atoms (Fig. 2). The N2-Cr1-O8, O7-Cr1-O8 and N2-Cr1- O7 angles are 95.03, 89.12 and 82.34°, respectively. Therefore, the Cr (III) atom has a distorted octahedral coordination environment.

Table 1. Crystal data and structure refinement of the title compound.

Empirical formula = $C_{32}H_{35}CrN_6O_{14}$	
Formula weight = 3118.64	
Wavelength = 0.71073 Å	
Crystal system = Monoclinic	T = 296(2) K
Space group = $\boldsymbol{P}2_1/c$	Z = 4
$\boldsymbol{a}$ = 9.8501(3) Å	
$\boldsymbol{b}$ = 13.157(2) Å	β= 104.807(7)°
$\boldsymbol{c}$ = 26.842(4) Å	
V = 3363.1(8) Å^3	
Density (calculated) = 1.540 Mg/m^3	
Absorption coefficient = 0.421 mm-1	
F(000) = 1620	
Crystal size = 0.29 x 0.19 x 0.13 mm^3	-12<=$\boldsymbol{h}$<=12
Theta range for data collection = 1.57 to 27.61°.	-17<=$\boldsymbol{k}$<=16
Reflections collected = 74813	-34<=$\boldsymbol{l}$<=34
Independent reflections = 7747 [$\boldsymbol{R}$(int) = 0.041]	
Absorption correction = Semi-empirical from equivalents	
Max. and min. transmission = 0.9473 and 0.8876	
Refinement method = Full-matrix least-squares on F^2	
Data / restraints / parameters = 7747 / 0 / 481	
Goodness-of-fit on F^2 = 1.035	
Final $\boldsymbol{R}$ indices [I>2sigma(I)]	$\boldsymbol{R}_1$ = 0.041, w$\boldsymbol{R}_2$ = 0.107
$\boldsymbol{R}$ indices (all data)	$\boldsymbol{R}_1$ = 0.075, w$\boldsymbol{R}_2$ = 0.126
Largest diff. peak and hole 0.458 and -0.299 e.Å^{-3}	

Table 2. Atomic coordinate ($\times 10^4$) & equivalent isotropic displacement parameters ($Å2\times 10^3$) for non hydrogen atoms.

Atom	x	y	z	U(eq)
Cr1	5000	-5000	0	15(1)
Cr2	0	0	0	17(1)
O1	848(2)	1104(1)	453(1)	36(1)
O1S	4430(2)	-7627(2)	-1265(1)	68(1)
O2	918(2)	-961(1)	531(1)	36(1)
O2S	-341(2)	-7696(1)	-1380(1)	42(1)
O3	2610(2)	-136(1)	-1471(1)	35(1)
O4	4159(2)	-86(1)	-698(1)	30(1)
O5	2666(2)	2157(1)	655(1)	27(1)
O6	2719(2)	-1997(1)	795(1)	28(1)
O7	5998(2)	-5872(1)	569(1)	26(1)
O8	5795(2)	-3818(1)	402(1)	29(1)
O9	7555(2)	-5246(1)	-1476(1)	33(1)
O10	9131(2)	-5077(1)	-713(1)	30(1)
O11	7705(1)	-7024(1)	784(1)	23(1)
O12	7760(2)	-2962(1)	714(1)	29(1)
N1	1919(2)	-42(1)	-196(1)	17(1)
N2	6915(2)	-5067(1)	-197(1)	16(1)
N3	2848(2)	-2615(1)	-2193(1)	22(1)
N4	10044(2)	-2729(1)	-2177(1)	21(1)
N5	-5292(2)	-57(1)	-1899(1)	21(1)
N6	363(2)	-267(1)	-3089(1)	21(1)
C1	2670(2)	910(2)	21(1)	23(1)
C2	2653(2)	-977(2)	56(1)	24(1)
C3	1661(2)	-85(2)	-764(1)	25(1)
C4	2964(2)	-102(2)	-964(1)	24(1)
C5	2041(2)	1439(2)	414(1)	20(1)
C6	2086(2)	-1348(2)	499(1)	21(1)
C7	7577(2)	-6037(2)	32(1)	21(1)
C8	7742(2)	-4157(2)	47(1)	23(1)
C9	6643(2)	-5068(2)	-764(1)	23(1)
C10	7935(2)	-5133(2)	-973(1)	22(1)
C11	7083(2)	-6350(2)	503(1)	17(1)
C12	7083(2)	-3607(2)	423(1)	21(1)
C13	3264(2)	-2567(2)	-2632(1)	23(1)
C14	4667(2)	-2597(2)	-2647(1)	21(1)
C15	5713(2)	-2670(2)	-2186(1)	18(1)
C16	7235(2)	-2705(2)	-2181(1)	18(1)
C17	7661(2)	-2824(2)	-2640(1)	22(1)
C18	9072(2)	-2825(2)	-2625(1)	23(1)
C19	9685(2)	-2632(2)	-1729(1)	23(1)
C20	8283(2)	-2612(2)	-1721(1)	20(1)
C21	5279(2)	-2707(2)	-1729(1)	20(1)
C22	3859(2)	-2679(2)	-1749(1)	24(1)
C23	574(2)	-317(2)	-2579(1)	24(1)
C24	-491(2)	-246(2)	-2331(1)	21(1)
C25	-1875(2)	-136(1)	-2619(1)	17(1)
C26	-3052(2)	-91(1)	-2368(1)	16(1)
C27	-2829(2)	15(2)	-1835(1)	23(1)
C28	-3961(2)	19(2)	-1618(1)	24(1)
C29	-5512(2)	-142(2)	-2408(1)	22(1)
C30	-4441(2)	-173(2)	-2656(1)	20(1)
C31	-2093(2)	-83(2)	-3154(1)	23(1)
C32	-963(2)	-147(2)	-3368(1)	25(1)

Table 3. Selected bond distances (Å), and bond angels (°)

O(1)-Cr(2)	1.9415(15)	O(7)-Cr(1)	1.9611(14)
O(2)-Cr(2)	1.9454(15)	O(8)-Cr(1)	1.9406(15)
N(1)-Cr(2)	2.0879(17)	N(2)-Cr(1)	2.0869(16)
O(8)#1-Cr(1)-O(8)	180.00(8)	O(1)-Cr(2)-O(2)#	291.01(8)
O(8)#1-Cr(1)-O(7)	90.88(7)	O(1)-Cr(2)-O(1)#2	180.00(10)
O(7)-Cr(1)-O(7)#1	180.00(9)	O(1)-Cr(2)-N(1)#2	95.40(6)
O(8)#1-Cr(1)-N(2)	95.02(6)	O(2)#2-Cr(2)-N(1)#2	83.45(6)
O(7)-Cr(1)-N(2)	82.34(6)	O(1)-Cr(2)-N(1)	84.60(6)
N(2)-Cr(1)-N(2)#1	180.00(8)	O(2)#2-Cr(2)-N(1)	96.55(6)
O(2)#2-Cr(2)-O(2)	180.00(10)	N(1)#2-Cr(2)-N(1)	180.00(8)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y-1,-z #2 -x,-y,-z

Table 4. Hydrogen bond geometry (Å , °) D-H...A d(D-H) d(H...A) d(D...A) <(DHA)

O(1S)-H(1)...O(6)#1	0.85	1.97	2.813(2)	168.7
O(1S)-H(2)...O(12)#1	0.85	2.19	3.012(2)	162.8
O(1S)-H(2)...O(8)#1	0.85	2.36	3.047(2)	137.8
O(2S)-H(3)...O(2)#3	0.85	2.30	3.050(2)	147.7
O(2S)-H(3)...O(6)#3	0.85	2.37	3.159(2)	155.5
O(2S)-H(4)...O(12)#1	0.85	2.01	2.844(2)	168.5
O(3)-H(3C)...N(5)#4	0.85	1.77	2.611(2)	173.0
O(9)-H(9C)...N(6)#5	0.85	1.76	2.607(2)	172.0
N(4)-H(4C)...N(3)#4	0.85	1.93	2.777(2)	175.3

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y-1,-z #2 -x,-y,-z #3 -x,-y-1,-z
#4 x+1,y,z #5 -x+1,y-1/2,-z-1/2

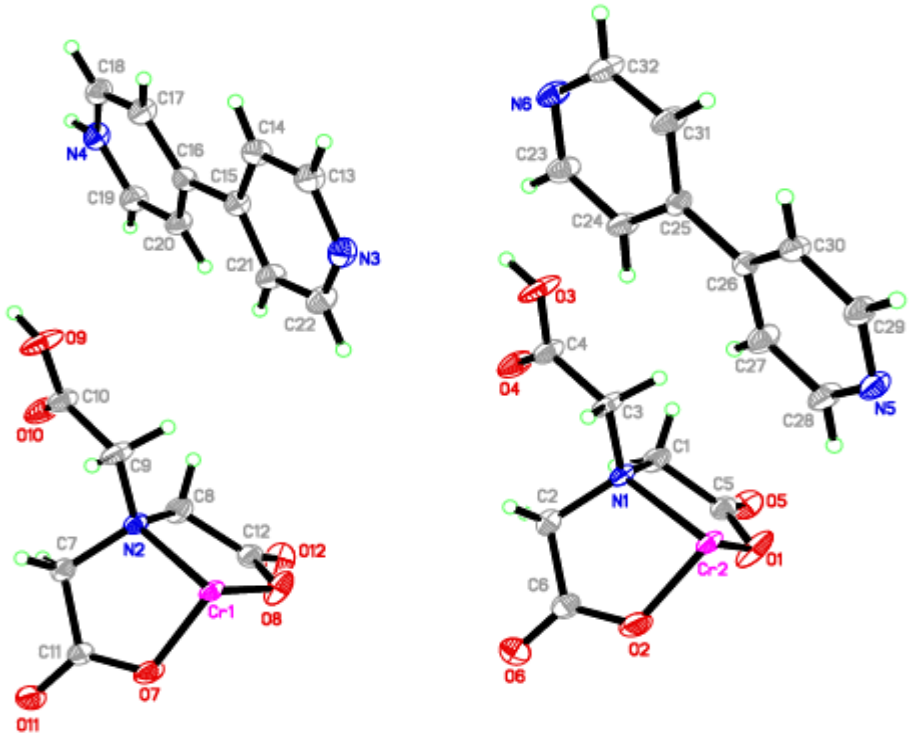

Fig. 1 A drawing of asymmetric unit of the title compound, water molecules are omitted for clarity. Displacement ellipsoids are drawn at 50% probability level.

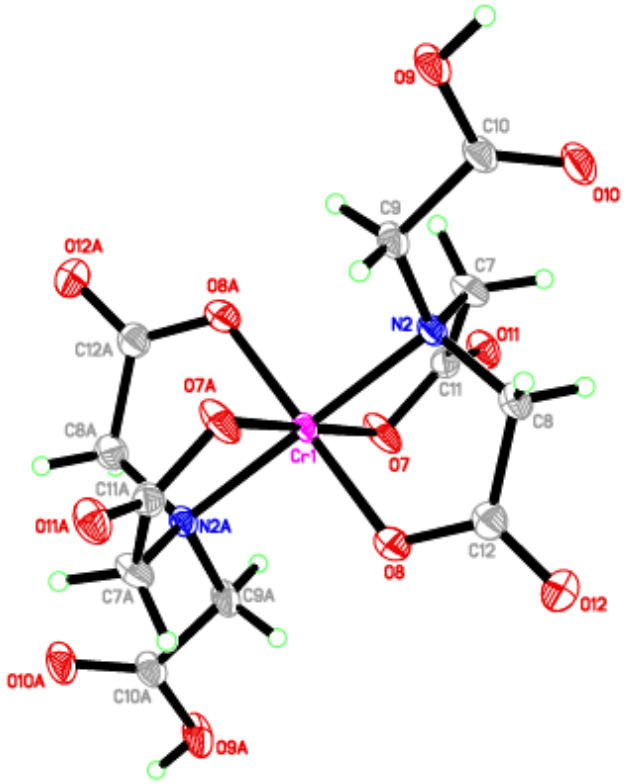

Fig. 2 Coordination environment around the Cr(III), displacement ellipsoids are drawn at 50% probability level.

OH…π stacking interactions between OH groups of carboxylate fragments and aromatic rings of 4,4′-bipy with distance of 3.862 Å for O3-H3…Cg and 3.736 Å for O9H9…Cg are observed in the title compound. Also, a considerable centrosymmetric C-H…π Stacking interactions between CH groups of 4, 4′-bipy and aromatic rings with distance of 3.714 Å for C29-H29…Cg and N-H…π stacking interactions between NH group of (4, 4′-bipyH)$^+$ cation and aromatic rings with distance of 3.270 Å for N4-H4…Cg and π-π interactions with distance of 3.674 Å are presented in this structure (Fig. 3).

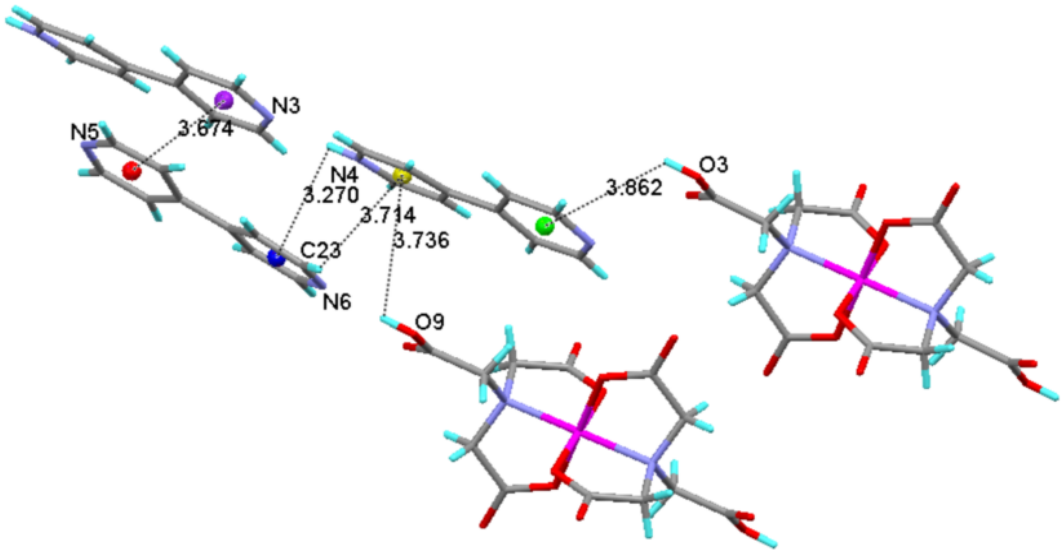

Fig. 3 C═O···π stacking interactions between C═O group of carboxylate groups with aromatic rings of 4,4′-bipyridine units. C-H···π and N-H···π stacking interactions between CH and NH groups of 4, 4′-bipyridine and aromatic rings. π-π Interactions between aromatic rings of 4,4′-bipyridine.

The presence of O-H…O, N-H…O and C-H…O hydrogen bonds (Table 4), with D…A distances ranging from 2.607 to 3.159 Å between (4, 4′-bipyH)$^{+}$ and [Cr(ntaH)$_2$]$^{-}$ fragments and uncoordinated water molecules is another feature of the title compound. The free carboxylate group of [Cr (ntaH)$_2$]$^{-}$ fragments is connected to the 4,4′-bipy units through two O3-H3…N5 and O9-H9…N6 hydrogen bonds to form linear chains (Fig. 4). Also, uncoordinated water molecules play a bridging role and bridging together the [Cr(ntaH)$_2$]$^{-}$ units by two O1S-H1…O6 and O1S-H2…O12 H-bonds (Fig. 5). In crystal structure of the title complex, the spaces between layers of (ntaH)$^{2-}$ anions are filled with (4,4′-bipyH)$^{+}$ cations and water molecules (Fig. 6). The unit cell packing of the title compound is shown in Fig. 7.

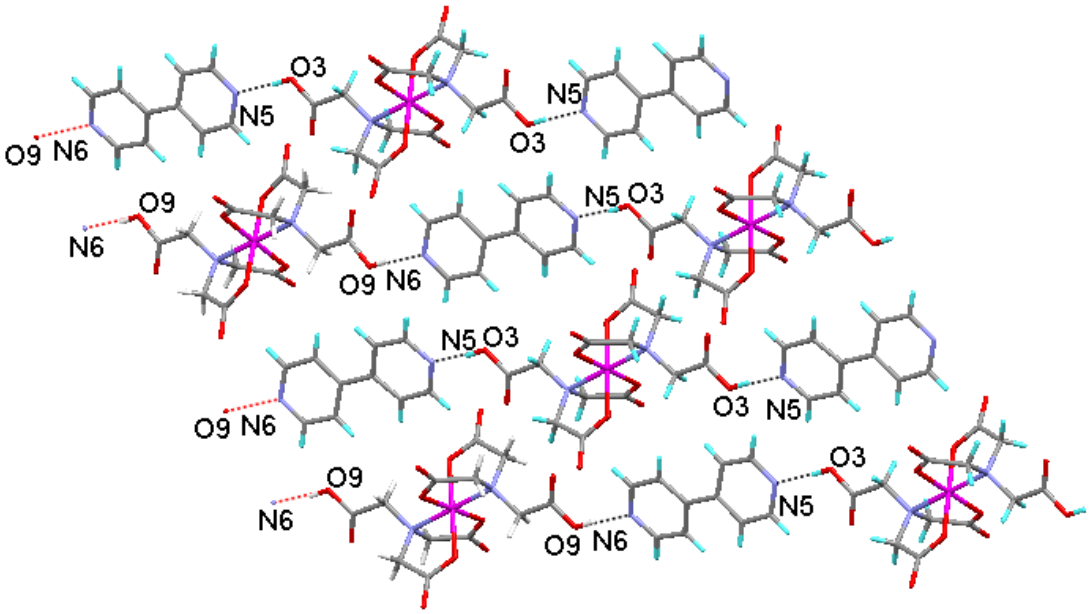

Fig. 4 O3-H3…N5 and O9-H9…N6 H-bonds between 4,4′-bipyridine fragments and free carboxylate group of [Cr(ntaH)2]- units.

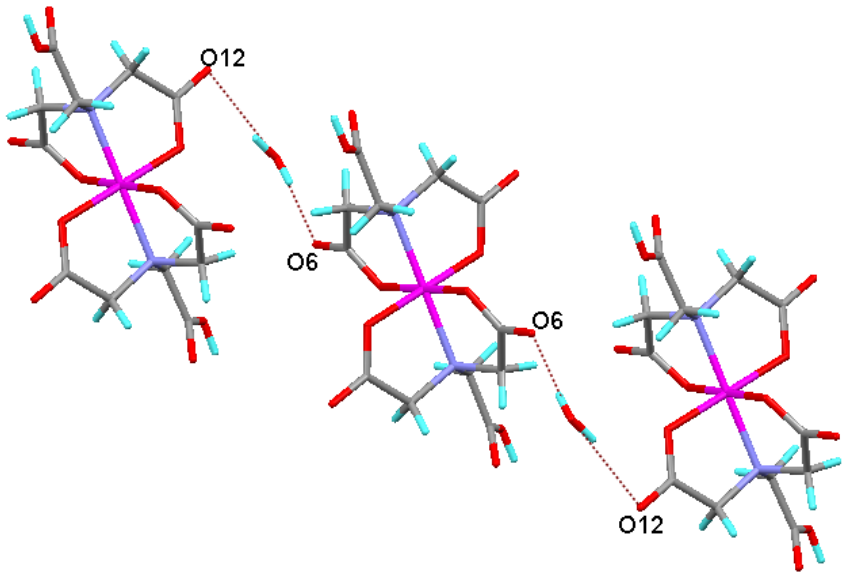

Fig. 5 O1S-H1…O6 and O1S-H2…O12 H-bonds between water molecules and carboxylate group of [Cr(ntaH)2]- units.

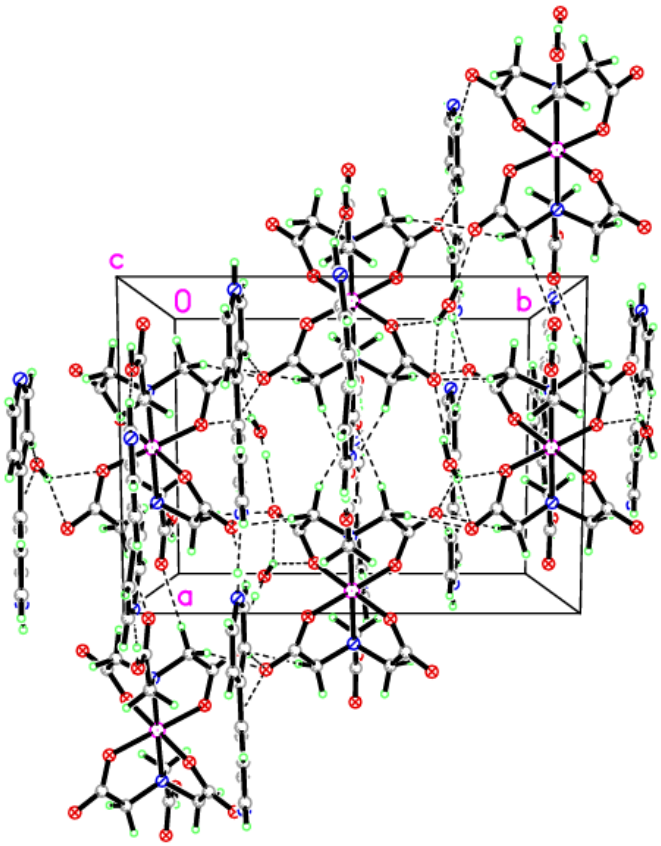

Fig. 6 Packing structure of title compound, dashed lines indicate hydrogen bonds.

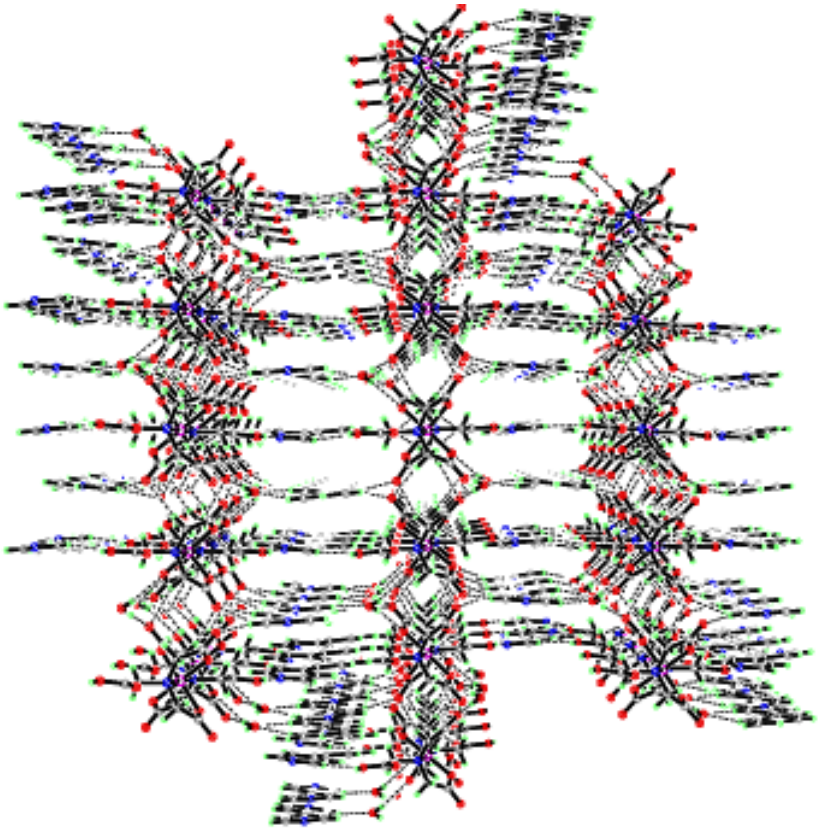

Fig. 7 Unit cell packing of the title compound viewed along a axis. Hydrogen bonds are shown as dashed lines.

References

[1] Venkataramanan B., Saifudin M.A., Jagadese V., Suresh V., *"Self assembly of methacrylamides assisted by an interplay of N-H…O, C-H…O, C-H…π and π-π intractions",* CrystEngComm, (2004), 6(49), 284.

[2] Aghabozorg H., Manteghi F., Sheshmani S., *"A Brief Review on Structural Concepts of Novel Supramolecular Proton Transfer Compounds and Their Metal Complexes",* J. Iran. Chem. Soc., (2008), 5(2), 184.

[3] Desiraju G.R., *"Crystal Design: Structure and Function",* J. Wiley & Sons Ltd., New York, (2003), p. 8.

[4] Chiang P. H., Hsu S. C., Lin C. H., *"Poly [bis (μ2-4,4'-bipyridine)bis(3-nitrobenzoato)cobalt(II)] "*, Acta Cryst., (2009). E65, m1302-m1303.

[5] Soleimannejad J., Aghabozorg H., Hooshmand S., *"4-(4-Pyridyl)pyrid bis(pyridine-2,6-dicarboxylato)chromium(III)tetrahydrate",* Acta Cryst., (2008). E64, m564–m565.

[6] Soleimannejad J., Gharamaleki J.A., Aghabozorg H., Mohammadzadeh Y., Golenjia A., *"4,4'-Bipyridinium bis(μ-4-oxo-1,4-dihydropyridine-2,6-dicarboxylato) bis[aquahydroxidoantimonate(III)] dihydrate ",* Acta Cryst., (2010), E66, m467–m468.

[7] Soleimannejad J., Aghabozorg H., Mohammadzadeh Y., Golenjia A., Gharamaleki J. A, Adams H., *"Bis (4, 4'-bipyridinium) di-μ-hydroxido bis[dihydroxido (pyridine-2,6-dicarboxylato) antimonate(III,V)] octahydrate",* Acta Cryst., (2008). E64, m387–m388.

[8] Soleimannejad J., Aghabozorg H., Hooshmand S., Adams H., *"4, 4'-Bipyridinediium triaquabis (pyridine-2, 6-dicarboxylato) strontium (II) trihydrate",* Acta Cryst., (2007), E63, m3089-m3090

[9] Özyürek C., Sendil K., Günes T., Dilek N., Arslan N.B., *"4,4'-Bipyridinium μ-oxo-bis(fluorodioxochromate)",* Acta Cryst., (2006). E62, m2191-m2193.

[10] Soleimannejad J., Aghabozorg H., Morsali A., Hemmati F., Manteghi F., *"4,4'-Bipyridinium bis(2-carboxypyridine-3-carboaxylato)",* Acta cryst., (2009), E65, m153.

[11] Sheldrick G. M., SHELXTL v. 5.10, Structure Determination Software Suite, Bruker AXS, Madison, Wisconsin, USA. (1998).