

Chromium(III) and Calcium(II) Complexes Obtained from Dipicolinic Acid: Synthesis, Characterization, X-Ray Crystal Structure and Solution Studies

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The Cr(III) and Ca(II) complexes (dmpH)[Cr(pydc)₂].H₂O (**1**) and [Ca₂(pydc)₂(H₂O)₆].2pydcH₂ (**2**) were synthesized by reaction of 2,9-dimethyl-1,10-phenanthroline (dmp) and pyridine-2,6-dicarboxylic acid (pydcH₂) with Cr(NO₃)₃ and Ca(NO₃)₂, respectively, and characterized using IR spectroscopy, single crystal X-ray diffraction method and solution studies. The space group and crystal system of these two compounds are *P*2₁/*c* and monoclinic. The crystal dimensions are *a* = 9.785(3) Å, *b* = 25.671(4) Å, *c* = 9.3402(16) Å, β = 90.790(17)° for (**1**) and *a* = 9.1319(4) Å, *b* = 14.8430(8) Å, *c* = 12.2449(7) Å, β = 98.227(5)° for (**2**). In complex (**1**), a water molecule presents in the crystal packing, linking the anionic and cationic fragments together by hydrogen bonding and thus increases the stabilization of crystal lattices. In complex (**2**), the coordinated water molecules relate each dimer to adjacent dimers forming infinite molecular ribbons by strong hydrogen bondings. Hydrogen bonding and ion pairing play an important role in stabilizing these crystals. The complexation reactions of pydc, dmp and pydc+dmp with Cr³⁺ and Ca²⁺ ions in aqueous solution were investigated by potentiometric pH titrations and the equilibrium constants for all major complexes formed were evaluated.

Keywords: Pyridine-2,6-dicarboxylic acid, 2,9-Dimethyl-1,10-phenanthroline, Chromium(III) and calcium(II) complexes, Crystal structures, Hydrogen bonding, Solution study

INTRODUCTION

A self-assembly process involves the noncovalent interactions between two or more molecular subunits, mostly organics, forming a noncovalent supramolecular arrangement whose novel structure and properties are determined by the nature and positioning of the components involved [1]. Coordinative frameworks imply the involvement of metals in extended assemblies. The purpose of involving metals may be

purely structural, *e.g.*, providing linkages or controlling network connectivity. Many different types of interactions are involved, including different degrees of strength and directionality depending on their distances and angles [2], such as hydrogen bonding, ion pairing, hydrophobic or hydrophilic, host-guest, π - π stacking and donor-acceptor interactions. Various studies confirm the hydrogen bonding as the most influential. Since some of the organic systems have the ability for metal ion complexation and forming hydrogen bonding, it is of interest to coordinate them to metal ions and have an inorganic self-assembled system. Our vast studies in

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construction of several metal-organic frameworks from noncovalent systems reveal that providing suitable conditions for the transfer of acidic protons to appropriate bases will result in increasing intermolecular interactions and stabilizing the resulting system. Furthermore carboxylic acids are tentative for coordination to metal centers by different coordinative modes. The metal carboxylate complexes are vastly studied [3-12], clearly indicating the fact that compounds with multiple carboxylic acid groups are good targets for supramolecular architectures and coordination polymers [4-7].

In continuation of our research, here we wish to report a study of the complexation behavior of chromium(III) and calcium(II) ions with pyridine-2,6-dicarboxylic acid-2,9-dimethyl-1,10-phenanthroline assembled system.

EXPEIMENTAL

Materials and Methods

Pyridine-2,6-dicarboxylic acid (pydcH₂) and 2,9-dimethyl-1,10-phenanthroline (dmp) were purchased from Merck and used as received. All other chemical used were of reagent grade from Merck and Fluka chemical companies and used without any further purification. Doubly distilled deionized water was used in the procedures when needed.

The IR spectra were recorded on a Perkin-Elmer 343 and 1720X spectrophotometer using KBr discs. The single-crystal X-ray diffraction experiments were carried out with a Bruker SMART 1000 CCD area detector, using graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$, φ - and ω -scans with a 0.5° step in ω , $2\theta < 54$) at 120 K. Low temperature of the crystals was maintained using a Cryostream open-flow N₂ gas cryostat (Cryosystems, Oxford). Reflection intensities were integrated using the SAINT software [13] and semiempirical method SADABS [14].

The structures were solved by direct method and refined by the full-matrix least-squares against F² in anisotropic (for non-hydrogen atoms) approximation. The H atom of water molecule and NH group of cationic moiety are located from Fourier difference maps and refined in isotropic approximation with constrained O(N)H distance which is equal 0.85(0.92) \AA . The hydrogen atoms of OH groups and water molecules were found in difference Fourier synthesis. The H(C) atom

positions were calculated. All hydrogen atoms were refined in isotropic approximation in riding model with the Uiso(H) parameters equal to 1.2 Ueq(Ci), for methyl groups equal to 1.5 Ueq(Cii), where U(Ci) and U(Cii) are respectively the equivalent thermal parameters of the carbon atoms to which corresponding H atoms are bonded.

Synthesis of Complexes

A solution of Cr(NO₃)₃·9H₂O (193 mg, 0.25 mmol) in water (2 ml) was added to the 20 ml of an aqueous solution of dmp (200 mg, 1 mmol) and pydcH₂ (162 mg, 1 mmol). The resulting precipitate was dissolved in DMSO. Red prismatic crystals of (dmpH)[Cr(pydc)₂].H₂O (**1**) were obtained after allowing the mixture to stand for a year at room temperature.

To a 10 ml of a stirring aqueous solution of dmp (104 mg, 0.5 mmol) and pydcH₂ (84 mg, 0.5 mmol) was added a 0.5 molar equivalent of Ca(NO₃)₂·4H₂O (73 mg, 0.25 mmol) at room temperature. A neutral calcium(II) complex [Ca₂(pydc)₂(H₂O)₆].2pydcH₂ (**2**) was isolated as colorless crystals. Slow evaporation of the solvent during two weeks resulted in product complexes. Recrystallization of resultants for several times leads to X-ray quality crystals.

IR Studies

The IR spectrum of complex (**1**) contained several indicative peaks such as N-H stretching frequency at 3521 cm⁻¹ and the stretching frequencies due to the aromatic rings at 3084 and 3055 cm⁻¹. The N-H bending frequency (in-the-plane) appears as a weak band at 1596 cm⁻¹ while the out-of-plane mode exists at 786 cm⁻¹. The ν_{COO} band appears at 1654 and 1662 cm⁻¹ belonging to the unsymmetrical coordination of both carboxylate oxygen atoms. The other ν_{COO} band appears at 1309 cm⁻¹ representing the stretching mode of C-O bond. Lattice water normally appears in the 3200-3550 cm⁻¹ (antisymmetric and symmetric OH stretching) and 1600-1630 cm⁻¹ regions (HOH bendings). The vibration frequencies depict the uncoordinative mode of water fragments.

The IR spectrum of complex (**2**) shows broad peaks in the range of 3452-3042 cm⁻¹ which could be related to the existence of O-H...O hydrogen bonding between water molecules and also to the N-H...O intramolecular hydrogen bonding in acid molecules. It must have been coupled by other indicative peaks such as N-H and O-H stretching frequencies

and the stretching frequencies due to the aromatic rings which originally fall within this region. The N-H bending frequency (in-the-plane) appears as a weak band at 1572 cm^{-1} while the out-of-plane mode exists at 768 cm^{-1} . The HOH bending of lattice water usually appears at nearly $1550\text{--}1600\text{ cm}^{-1}$ which could also be depicted in this spectrum.

In the middle of the stretching vibrations, there are two peaks at 1702 and 1621 cm^{-1} with about the same intensities, attributed to the C=O stretching frequencies. This IR results could be employed to distinguish the coordination modes of carboxylate groups. It can be concluded that there are two kinds of carboxylic groups. The band at 1702 cm^{-1} belongs to the fragment in which there is no proton transfer process and thus is uncoordinated. While the loss of proton and coordination to Ca(II) center is a result of appearance of 1621 cm^{-1} peak. In both cases, there are the other stretching vibrations for C-O. Well separated 1377 and 1271 cm^{-1} absorbances confirm the above-described phenomenon. Since hydrogen bonding is known to lower a carboxylate stretching frequency by $30\text{--}40\text{ cm}^{-1}$ [7], the transition at 1621 cm^{-1} can be assigned to the formation of strong hydrogen bonding interaction by carboxylate group.

Potentiometric pH Titrations

All potentiometric pH measurements were made on solutions in a 75-ml double-walled glass vessel using a Model 794 Metrohm Basic Titrino with a combined glass-calomel electrode which coupled with 10-ml capacity Metrohm automatic piston burette and the temperature was controlled at $25.0 \pm 0.1\text{ }^\circ\text{C}$ by circulating water through the jacket, from a constant-temperature bath (home made thermostat). The cell was equipped with a Model 728 Metrohm magnetic stirrer and a tightly fitting cap, through which the electrode system and tip of burette were inserted and sealed with clamps and O-rings. The atmospheric CO_2 was excluded from the titration cell with a purging stream of purified nitrogen gas. The concentrations of dmp and pydcH_2 were $2.0\text{--}2.5 \times 10^{-3}\text{ M}$, for the potentiometric pH titrations of pydcH_2 , dmp and $\text{pydcH}_2 + \text{dmp}$, in the absence and presence of $9.38 \times 10^{-4}\text{--}1.25 \times 10^{-3}\text{ M}$ of the metal ions. A standard carbonate-free NaOH solution (0.0983 M) was used in all titrations. The ionic strength was adjusted to 0.1 M with NaNO_3 . Sufficient time was allowed for the establishment of equilibrium before measuring an

experimental (pH) point. The protonation constants of reactants pydcH_2 and dmp and stability constants of the resulting proton transfer adduct and their metal complexes were evaluated using the program BEST described by Martell and Motekaitis [15]. The value of $K_w = [\text{H}^+][\text{OH}^-]$ used in the calculations was according to our previous works [16-19].

RESULTS AND DISCUSSION

Crystal Structure of $(\text{dmpH})[\text{Cr}(\text{pydc})_2]\cdot\text{H}_2\text{O}$ Complex

In order to ascertain the coordination environment and structural characteristics of $(\text{dmpH})[\text{Cr}(\text{pydc})_2]\cdot\text{H}_2\text{O}$ complex, crystals of suitable size for single crystal X-ray diffraction were prepared. A summary of crystallographic data, some important bond lengths, bond and torsion angles and hydrogen bonds are presented in Tables 1-4, respectively.

As it has been shown in Fig. 1a, central atom is coordinated by two nitrogen atoms of two pyridine units and four oxygen atoms (O(1), O(3), O(1'), O(3')) of two carboxylate groups. Therefore, pyridine-2,6-dicarboxylate acts as a tridentate ligand and the lattice is composed of anionic hexacoordinated complex, $[\text{Cr}(\text{pydc})_2]^-$ (with two $(\text{pydc})^{2-}$ **A1** and **A2**) $(\text{dmpH})^+$ counter ion (**C1**) and one lattice water. The $(\text{pydc})^{2-}$ frameworks **A1** and **A2** are both highly planar (average atom deviation from the mean plane: 0.007 and 0.003 \AA for **A1** and **A2**, respectively) and are almost perpendicular to each other (87.7°) (Fig. 1a).

The metal atom lies in a *pseudo*-octahedral environment with O(1), O(3), O(1') and O(3') atoms occupying equatorial positions (deviations of the atoms from the mean plane: O(1): 0.391 ; O(3): 0.386 ; O(1'): -0.385 ; O(3'): -0.393 ; Cr: 0.002 \AA). The N(1) and N(1') atoms lie in axial positions with an N(1)-Cr-N(1') angle of $177.25(7)^\circ$. The metal-nitrogen distances are nearly identical, and the same evidence has been observed for Cr-O distances (Table 2). The average C-O distance of coordinated carboxylate group ($1.301(3)\text{ \AA}$) is more than the value for free carboxylate groups (1.23 \AA), suggesting more constraints for coordinated group.

Selected bond and torsion angles are reported in Table 3. The O(1)-Cr-O(3) and O(1')-Cr-O(3') bond angles are $157.62(7)^\circ$ and $157.40(8)^\circ$, respectively. This shows that the four carboxylate groups of $(\text{pydc})^{2-}$ ligands are oriented in a

Table 1. The Summary of Crystallographic Data for Compounds **1** and **2**

	Compound 1	Compound 2
Empirical formula	C ₁₈ H ₂₆ N ₈ O ₁₁ Cr	C ₂₈ H ₂₈ Ca ₂ N ₄ O ₂₂
Formula weight	595.84	852.70
Temperature (K)	193(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group, unit cell	<i>P</i> 2 ₁ / <i>c</i> , <i>Z</i> = 4	<i>P</i> 2 ₁ / <i>c</i> , <i>Z</i> = 2
Unit cell dimensions	<i>a</i> = 9.785(3) Å <i>b</i> = 25.671(4) Å <i>c</i> = 9.3402(16) Å β = 90.790(17)°	<i>a</i> = 9.1319(4) Å <i>b</i> = 14.8430(8) Å <i>c</i> = 12.2449(7) Å β = 98.227(5)°
Reflections collected	4897	9035
Refinement method	Full-matrix least-square on F ²	Full-matrix least-square on F ²
Data/Restraints/Parameters	4497/0/343	3936/0/253
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0349 <i>wR</i> ₂ = 0.0869	<i>R</i> ₁ = 0.0318 <i>wR</i> ₂ = 0.0797
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0442 <i>wR</i> ₂ = 0.0959	<i>R</i> ₁ = 0.0419 <i>wR</i> ₂ = 0.0861

Table 2. Selected Bond Distances (Å) for Compounds **1** and **2**

	Compound 1	Compound 2		Compound 2
Cr1-N1	1.978(2)	Ca(1)-O(1)		2.4307(11)
Cr1-N1'	1.980(2)	Ca(1)-O(1) [- <i>x</i> +1, - <i>y</i> , - <i>z</i> +2]		2.4050(11)
Cr1-O1	1.9910(18)	Ca(1)-O(3)		2.4719(11)
Cr1-O3'	1.9904(18)	Ca(1)-N(1)		2.4632(12)
Cr1-O3	1.9980(19)	Ca(1)-O(1W)		2.3242(11)
Cr1-O1'	1.9991(17)	Ca(1)-O(2W)		2.3595(11)
		Ca(1)-O(3W)		2.4654(11)

flattened tetrahedral arrangement around central atom. The O(1)-Cr-O(3') and O(1')-Cr-O(3) angles and O(1)-Cr-O(3')-C(7') and O(1')-Cr-O(3)-C(7) torsion angles show that the carboxylato ligands, which coordinate to the metal center, are almost perpendicular to the corresponding pyridine frames.

The mean plane of the **C1** cation, (dmpH)⁺, (average atom deviation: 0.004 Å) is almost parallel to the **A1** pyridine frame of one complex (*x*, -*y*+1, *z*+1/2) and **A2** pyridine frame of another (*x*-1/2, *y*+1/2, *z*) [**C1**^**A1** = 9.61°, **C1**^**A2** = 7.88°].

The important characteristic of this compound is the infinite one dimensional chains based on [1-10] and [1-10] vectors. The crystal structure lattice of (**1**) is constructed *via* three kinds of interactions rather than ion pairing.

Figure 2a shows the main chain in this compound, in which two [Cr(pydc)₂] complexes and one (dmpH)⁺ counter cation are connected by C-H...O interactions. The graph set descriptor belong to this chain is C₃³(23). The parallel chains are related to each other by water linkage *via*

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Table 3. Selected Bond and Torsion Angles (°) Compounds **1** and **2**

Compound 1		Compound 2	
N1-Cr1-N1'	177.25(7)	O(1)-Ca(1)-O(1)#1	73.19(4)
N1-Cr1-O1	78.90(8)	O(1)-Ca(1)-N(1)	65.93(4)
N1-Cr1-O3	78.76(8)	O(1)-Ca(1)-O(2W)	89.83(4)
O1-Cr1-O3'	91.20(7)	O(1)-Ca(1)-O(3W)	87.03(4)
O1-Cr1-O3	157.62(7)	O(1W)-Ca(1)-O(1)#1	81.58(4)
O1-Cr1-O1'	92.73(5)	O(1W)-Ca(1)-O(3)	75.38(4)
O1'-Cr1-N1'	78.59(8)	O(1W)-Ca(1)-O(2W)	90.82(4)
O3-Cr1-O1'	92.43(7)	O(1W)-Ca(1)-O(3W)	87.00(4)
O3'-Cr1-O1'	157.40(8)	O(2W)-Ca(1)-O(1)#1	82.43(4)
O3'-Cr1-O3	92.35(5)	O(2W)-Ca(1)-O(3)	91.36(4)
O3'-Cr1-N1'	78.81(8)	O(2W)-Ca(1)-N(1)	96.95(4)
		O(2W)-Ca(1)-O(3W)	167.83(4)
O1'-Cr1-O3-C7	97.32(17)	O(3)-Ca(1)-O(3W)	99.65(4)
O1-Cr1-O3'-C7'	94.72(17)	O(3)-Ca(1)-N(1)	64.46(4)
		O(3W)-Ca(1)-O(1)#1	92.49(4)
		O(3W)-Ca(1)-N(1)	85.41(4)
		O(1)-Ca(1)-O(1)#1-Ca(1)#1	0.00(4)

#1: -x+1, -y, -z+2.

Table 4. Selected Hydrogen Bond for Compound **1**

D-H...A	D-H (Å)	D...A (Å)	D-H-A
N1A-H1AA...N2A	0.88	2.757(3)	104
N1A-H1AA...O1W#1	0.88	2.746(3)	156
O1W-H1WA...O2'#2	0.85	2.875(3)	160
O1W-H1WB...O4'	0.86	2.934(3)	154
C3'-H3'A...O2#3	0.95	3.186(3)	145
C5'-H5'A...O1'#4	0.95	3.212(3)	144
C3-H3A...O2'#5	0.95	3.193(3)	144
C3A-H3AA...O4'	0.95	3.076(3)	141
C14A-H14A...O2'	0.98	3.542(3)	176

#1: x, -y+1, z+1/2; #2: x-y+1/2, z; #3: x+1/2, -y-1/2, z+1/2; #4: x, -y, z+1/2;

#5: x-1/2, -y-1/2, z-1/2.

O1W-H1WA...O2'#2 and O1W-H1WB...O4' hydrogen bonds. The distance of chains is small enough to provide the π - π stacking interactions (Fig. 3). On the other hand, the crossing

chains are gathered by aid of N1A-H1AA...O1W#1 and C14-H14A...O2' interactions. Therefore, in the formation of this Cr(III) complex, ion pairing, metal-ligand coordination,

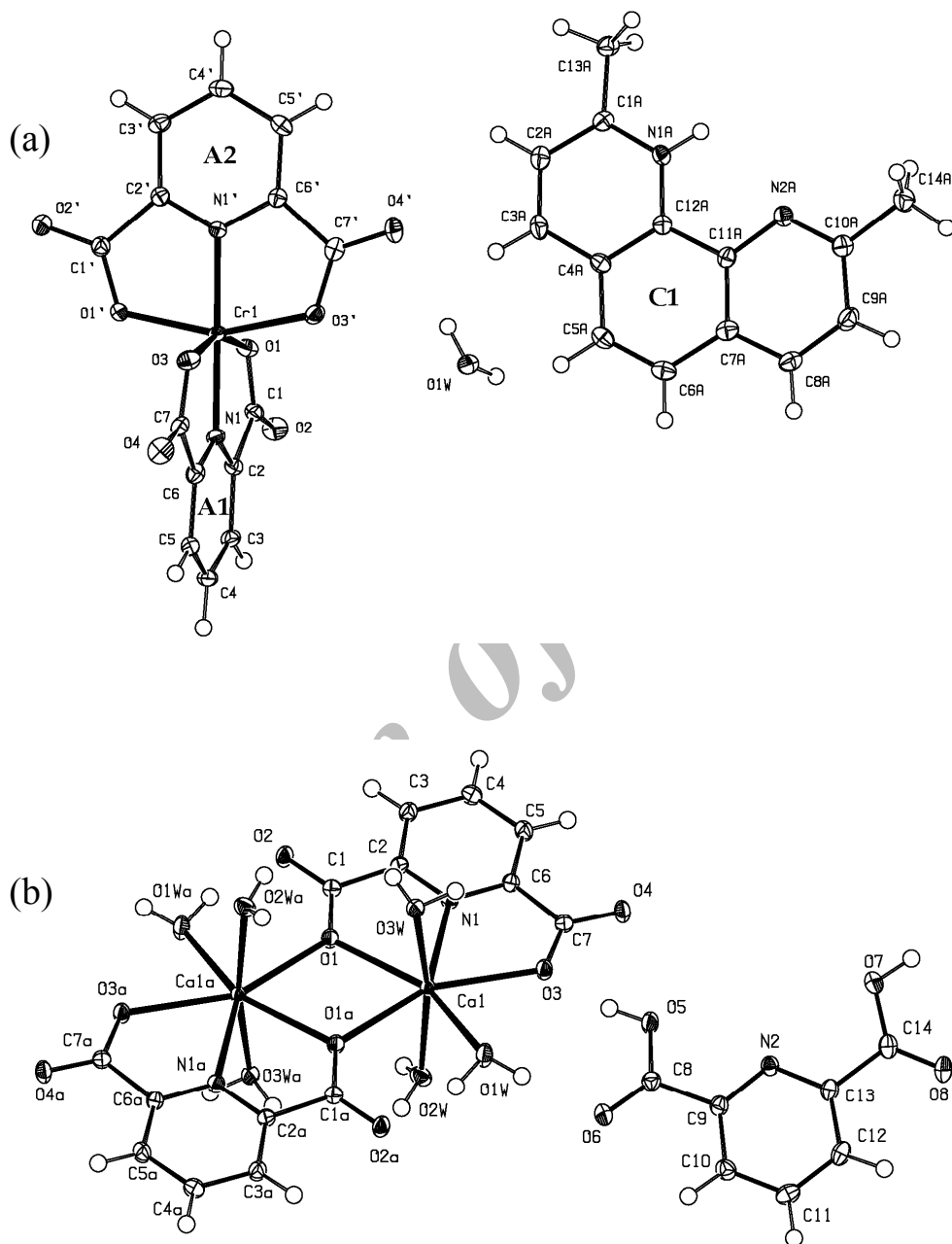


Fig. 1. The asymmetric unit of the title compounds, together with the atom-numbering scheme. (a) $(dmpH)[Cr(pydc)_2] \cdot H_2O$, (b) $[Ca_2(pydc)_2(H_2O)_6] \cdot 2pydcH_2$, (one $pydcH_2$ molecules is omitted for clarity).

hydrogen-bonding and π - π stacking interactions play important roles in the construction of its three-dimensional network. Figure 4a shows the resulting supramolecular network of this structure.

Crystal Structure of $[Ca_2(pydc)_2(H_2O)_6] \cdot 2(pydcH_2)$ Complex

$[Ca_2(pydc)_2(H_2O)_6] \cdot 2(pydcH_2)$ is a neutral colorless complex in which the proton transfer process between acid

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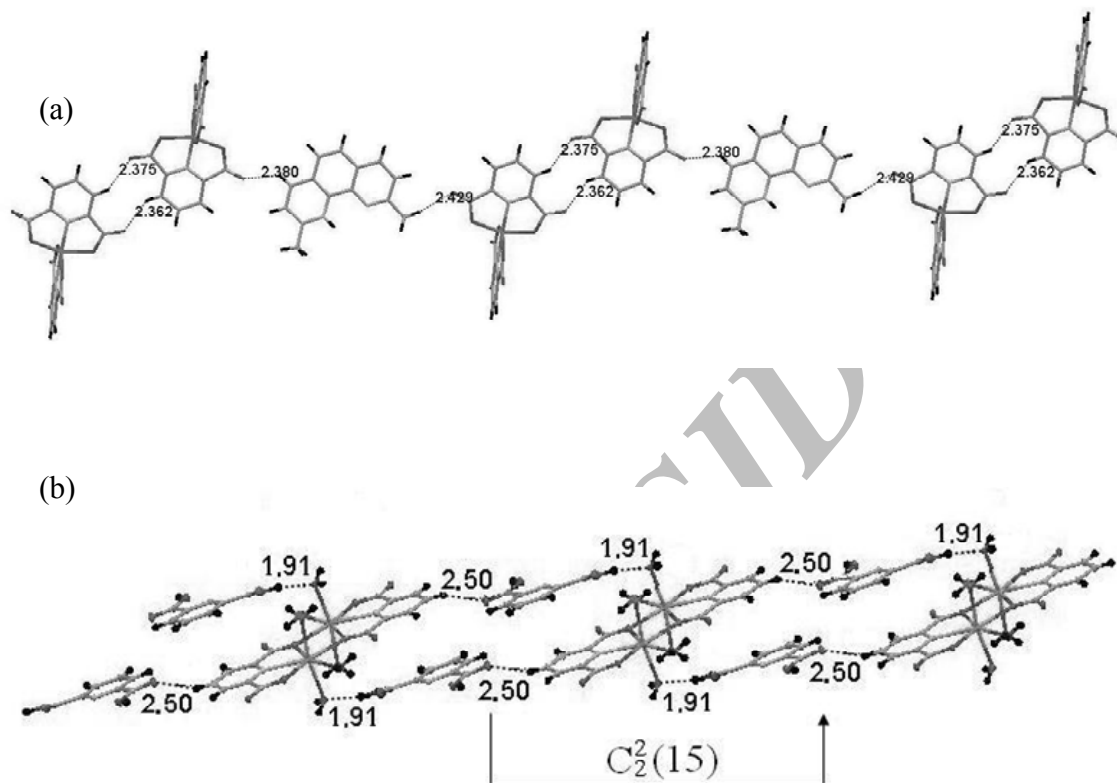


Fig. 2. The responsible chain in formation of crystals, (a) $(dmpH)[Cr(pydc)_2] \cdot H_2O$, (b) $[Ca_2(pydc)_2(H_2O)_6] \cdot 2pydcH_2$.

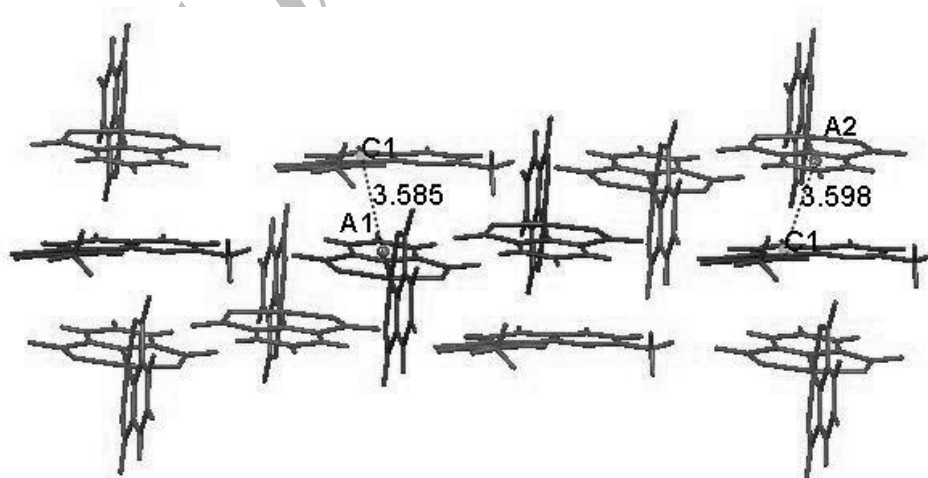


Fig. 3. The π - π stacking representation in $(dmpH)[Cr(pydc)_2] \cdot H_2O$.

and base units is dominated by coordination phenomenon. A summary of crystallographic data, some important bond lengths, bond and torsion angles and hydrogen bonds of this complex are presented in Tables 1, 2, 3 and 5, respectively.

An important feature of the complex crystal structure (Fig. 1b) is the presence of a four-membered planar Ca_2O_2 ring, linking two metal fragments in the nonionic complex. The bridging role of the carboxylic group of $(pydc)^{2-}$ leads to a

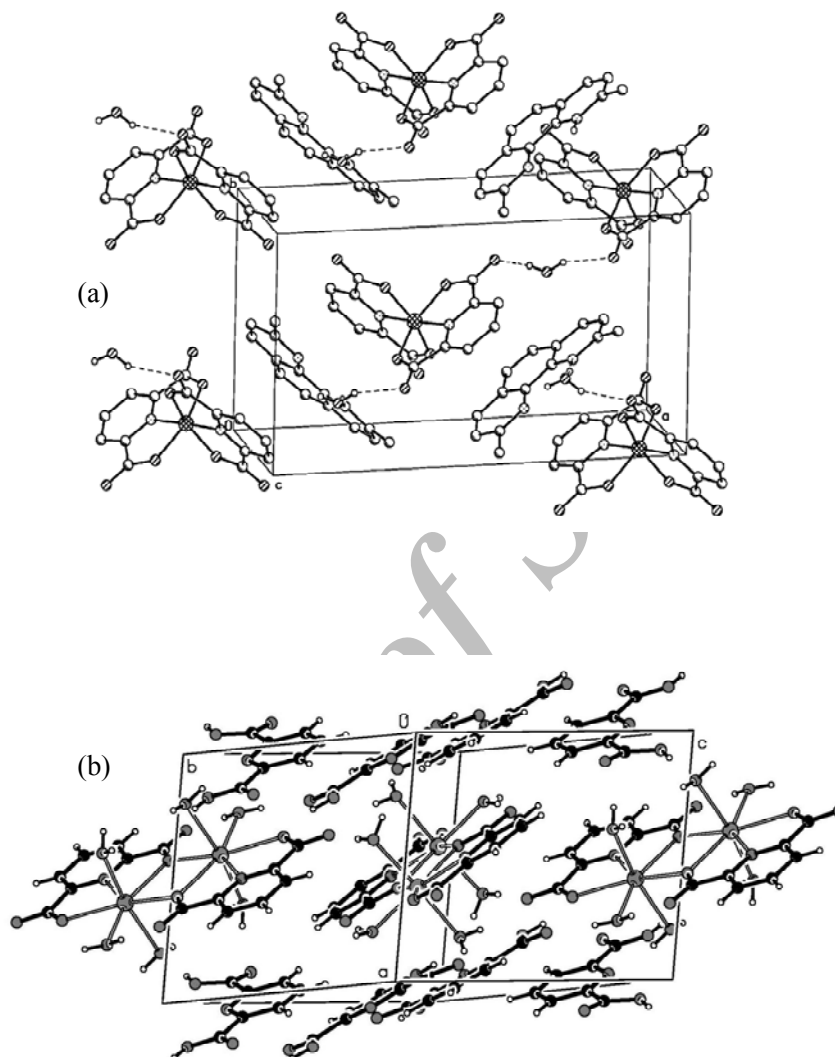


Fig. 4. Crystal packing diagram of (a): $(\text{dmpH})[\text{Cr}(\text{pydc})_2]\cdot\text{H}_2\text{O}$, (b): $[\text{Ca}_2(\text{pydc})_2(\text{H}_2\text{O})_6]\cdot 2\text{pydcH}_2$.

neutral complex which does not allow the Lewis base to stand along the metallic complex and, thus, is crystallized in the produced network. A similar behavior was already seen in a binuclear lead(II) complex [10].

Figure 1b shows the molecular structure of calcium(II) compound contained in a dimeric form consisting of two Ca(II), two ligand and six water molecules. The calcium centers are bridged by two oxygen atoms each donated by a different ligand molecule. Apart from the two bridging oxygen atoms, the Ca(II) is coordinated by an oxygen atom donated by the second carboxylic group of the ligand molecule, a heteroring nitrogen atom and three oxygen atoms of water

molecules; thus, the resulting coordination polyhedron is a distorted pentagonal bipyramid. Its equatorial plane is composed of three carboxylate oxygen atoms, one heteroring nitrogen and one water oxygen atom. Water oxygen atoms O2W and O3W with Ca1-O2W and Ca1-O3W bond distances of 2.360(1) and 2.465(1) Å, respectively, and a O2W-Ca1-O3W angle of 167.83(4)° constitute the vertices of the bipyramid.

The pyridine ring of the acid molecule is planar, with a maximum deviation of 0.007(1) Å from the mean plane, while the carboxylate oxygen atoms deviate from the mean plane from -0.368(1) Å (O7) to +0.196(1) Å (O8). The observed

Table 5. Selected Hydrogen Bond for Compound 2

D-H...A	D-H (Å)	D...A (Å)	D-H-A
O1W-H1WA...O2#1	0.90	2.6510(15)	161
O1W-H1WB...O6	0.88	2.7564(16)	175
O2W-H2WB...O4#2	0.79	2.6894(15)	169
O2W-H2WA...O8#3	0.88	2.7586(15)	169
O3W-H3WB...O4#4	0.81	2.9434(15)	167
O3W-H3WB...O5#5	0.81	2.8611(15)	109
O5-H5O...O3	0.89	2.5381(16)	162
O5-H5O...O4	0.89	2.9352(15)	104
O3W-H3WA...O5#6	0.90	2.8611(15)	111
O3W-H3WA...N2#7	0.90	2.9131(16)	168
O7-H7O...O3W#8	0.91	2.8022(15)	165
C4-H4A...O6#9	0.95	3.2358(19)	134
C11-H11A...O1W#10	0.95	3.4358(19)	147
C12-H12A...O2#11	0.95	3.1543(19)	130

#1: $-x+1, -y, -z+2$; #2: $-x+1, y-1/2, -z+3/2$; #3: $x-1, -y+1/2, z+1/2$; #4: $x, -y+1/2, z+1/2$; #5: $x, -y+1/2, z+1/2$; #6: $x, -y+1/2, z+1/2$; #7: $x, -y+1/2, z+1/2$; #8: $-x+2, y+1/2, -z+3/2$; #9: $-x+1, y+1/2, -z+3/2$; #10: $-x+2, -y, -z+1$; #11: $x+1, y, z-1$.

inter atomic distances and angles do not differ from those reported for the pyridine-2,6-dicarboxylic acid [11].

The stabilizing interactions existing in the crystal lattice are very strong intramolecular O-H...O and intermolecular O-H...O, O-H...N and C-H...O type hydrogen bonds. Both, bifurcated acceptor and donor type of hydrogen bonding interaction could be observed in this case. Each dimer is related to adjacent dimers by a pair of water molecules, forming infinite molecular ribbons by strong hydrogen bonds.

The interstitial acid molecules play an important role in the network of hydrogen bonds in which they act both as donors and acceptors. For example, a fairly short hydrogen bond of 2.538(2) Å links the carboxylate oxygen atom O5 of the acid molecule with coordinated carboxylate oxygen atom O3 of the adjacent dimer. The other hydrogen bond lengths are in the range from 2.6510(15) to 2.9434(15) Å. These bonds join the acid carboxylate oxygen atoms with the coordinated water molecules of the neighboring dimers. There are also C-H...O interactions relating the acid molecule and Ca(II) complex.

The water oxygen atoms which constitute the apices of the pentagonal bipyramid around the calcium(II) are interacting

with unbonded carboxylate oxygen atoms of the adjacent ligand molecules. Hydrogen atoms of coordinated water molecules participate in hydrogen bonded chains described by $C_2^2(15)$ graph set descriptors. Considering the location of water molecules, these chains are generated above and under the dimer complexes. Figure 2b represents the resulted chains.

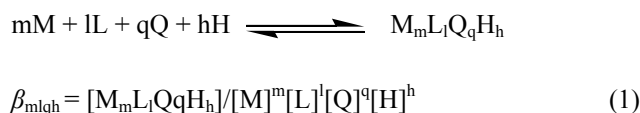
The ordered distribution of uncoordinated molecules of the ligand acid in the space between the dimers is interesting. This is illustrated in packing diagram of the resulting crystal in Fig. 4b. In construction of this crystal, which has an infinite three dimensional framework based on [100], [001] and [010] vectors, the intermolecular hydrogen bonding interactions play an essential role.

Summation of all above mentioned characteristics confirm the existence of a three dimensional supramolecule structure for $[Ca_2(pydc)_2(H_2O)_6] \cdot 2(pydcH_2)$ complex.

Solution Studies

We have previously reported the protonation constants of pydc, dmp species and the equilibrium constants for the proton transfer adduct formation between pydc and dmp in several

protonated forms in aqueous solution [16-18]. In order to determine the stoichiometry and stability of the Cr^{3+} and Ca^{2+} complexes with pydc-dmp proton transfer system in aqueous solution, in this work we obtained the equilibrium potentiometric $p\text{H}$ titration profiles of pydc, dmp and their 1:1 mixture in the absence and presence of the metal ions (Fig. 5). While no interaction was found between dmp and Ca^{2+} ion, in other cases, the corresponding titration curves depressed significantly in the presence of chromium(III) and calcium(II) ions. The cumulative stability constants for the resulting metal ion complexes, β_{mlqh} , are defined by Eq. (1) (charges are omitted for simplicity).



where M is Cr^{3+} or Ca^{2+} , L is pydc, Q is dmp and H is proton, and m, l, q and h are the respective stoichiometric coefficients. Since the ligand and complex activity coefficients are unknown, the β_{mlqh} values are defined in terms of concentrations. The errors are minimized by the use of a high constant ionic strength (0.1 M NaNO_3) and low ligand concentration (in the order of 10^{-3} M).

The cumulative stability constants were evaluated by fitting the corresponding $p\text{H}$ titration curves to the BEST program [15] and the resulting values for the most likely complexed species in aqueous solutions are included in Table 6. The corresponding species distribution diagrams for pydc, dmp and pydc-dmp in the presence of M^{n+} ions are shown in Figs. 6, 7 and 8, respectively.

As it is seen from Table 6 and Figs. 6 and 7, the most likely species in the case of pydc in the presence of Cr^{3+} and Ca^{2+} are: CrL , CrLH , CrLH_2 , CrL_2 , CrL_2H , CrL_2H_2 , CrLOH , CrL_2OH , CaL , CaL_2 , CaL_2H and CaL_2H_2 and for dmp are: CrQ , CrQH , CrQ_2 , CrQ_2H and $\text{CrQ}(\text{OH})_2$. From Table 6 and Fig. 8 it is readily seen that for the pydc-dmp-M systems, the most likely ternary species are: CrL_2Q , CrL_2QH , CrL_2QH_2 , CrL_2QH_3 , CaLQH and CaL_2QH . A comparison between the stoichiometry of the crystalline complex for the pydc-dmp- Cr^{3+} system and that of the most abundant species detected in aqueous solution (*i.e.*, CrL_2QH , CrL_2QH_2 and CrL_2QH_3) revealed that these complexed species existing in solution

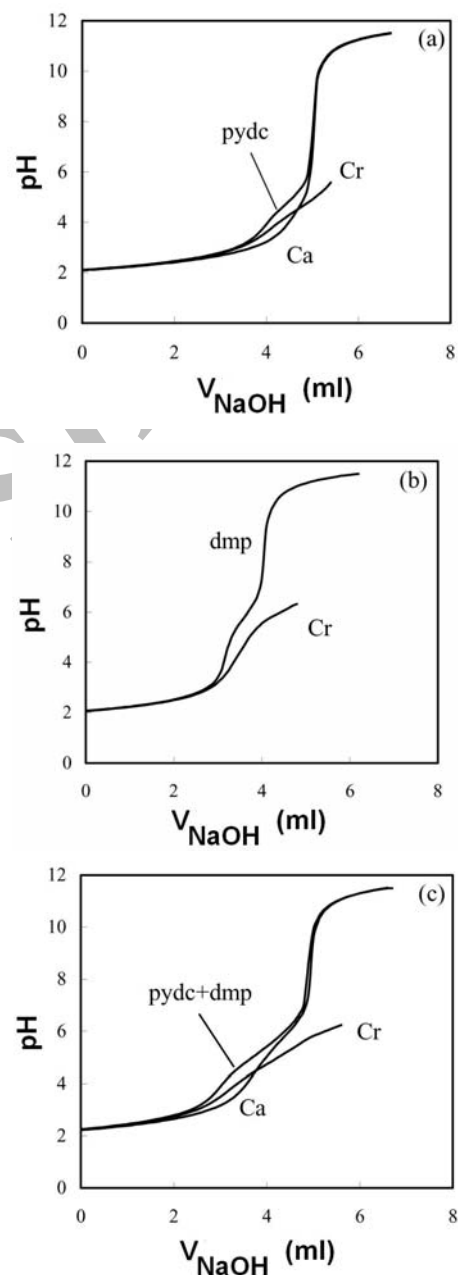


Fig. 5. Potentiometric titration curves for pydc, dmp and pydc+dmp in the absence and presence of Cr^{3+} and Ca^{2+} ions with NaOH 0.0983 M at 25°C and $\mu = 0.1$ M NaNO_3 .

possess a stoichiometry similar to that of the $(\text{dmpH})[\text{Cr}(\text{pydc})_2]\cdot\text{H}_2\text{O}$ complex, obtained in the solid state.

However, in the case of the pydc-dmp- Ca^{2+} system, the

Chromium(III) and Calcium(II) Complexes Obtained from Dipicolinic Acid

Table 6. Overall Stability Constants in dmp/pydc/Mⁿ⁺/Binary and Ternary System

System	m	l	q	h	logβ	Max %	at pH
Cr-dmp	1	0	1	0	10.49	62.4	4.9
	1	0	1	1	14.73	93.0	2.1
	1	0	2	0	13.93	24.8	5.6
	1	0	2	1	18.31	3.8	4.7
	1	0	1	-1	2.33	negligible	-
Cr-pydc	1	0	1	-2	-0.86	93.4	7.3
	1	1	0	0	4.66	9.0	4.6
	1	1	0	1	9.45	48.4	3.4
	1	1	0	2	12.24	86.2	2.0
	1	2	0	0	8.61	19.0	5.1
	1	2	0	1	13.64	38.6	4.4
	1	2	0	2	17.23	21.0	3.4
	1	1	0	-1	0.42	61.4	6.8
Ca-pydc	1	2	0	-1	3.32	38.0	8.1
	1	1	0	0	4.72	56.8	5.0
	1	1	0	2	6.13	negligible	-
	1	2	0	0	7.71	41.4	7.3
	1	2	0	1	12.64	33.0	4.0
Cr-dmp-pydc	1	2	0	2	15.43	14.8	2.7
	1	1	1	0	12.99	8.2	5.4
	1	1	1	2	21.16	2.2	3.0
	1	2	1	0	16.53	26.2	5.7
	1	2	1	1	21.54	15.6	4.9
	1	2	1	2	26.04	14.0	4.3
Ca-dmp-pydc	1	2	1	3	29.99	19.0	3.3
	1	1	1	1	13.99	50.8	4.1
	1	1	1	2	14.43	negligible	-
	1	2	1	1	17.30	31.8	5.9
	1	2	1	2	21.30	6.8	3.7
	1	2	2	2	21.35	negligible	-
	1	2	2	3	28.83	negligible	-
1	2	2	4	32.53	2.0	2.6	

most abundant species in aqueous solution include the following binary species: CaL, CaLH₂, CaL₂, CaL₂H and CaL₂H₂, where no ternary complex exists in solution. It is

interesting to note that the crystalline complex obtained from this system is [Ca₂(pydc)₂(H₂O)₆]-2(pydcH₂), which is also a binary complex.

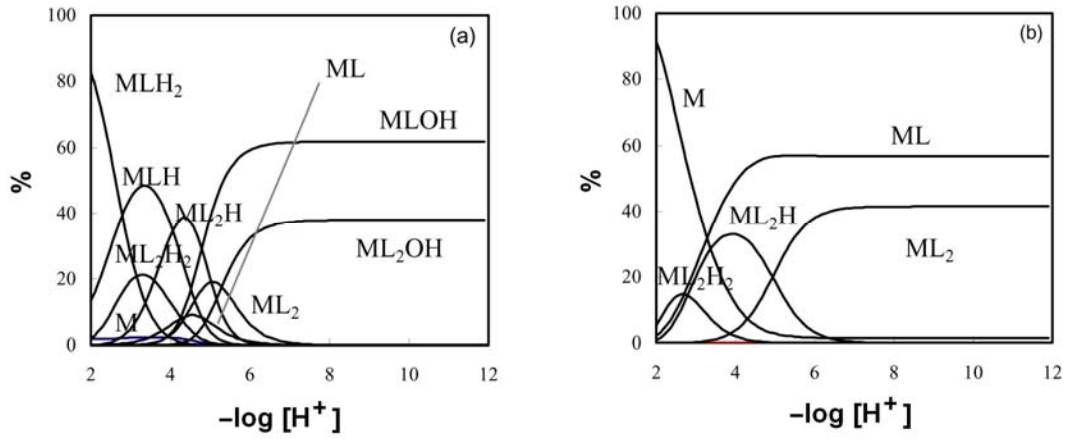


Fig. 6. Distribution diagrams of pydc(L)/M binary systems. M = Cr³⁺ (a) and Ca²⁺ (b).

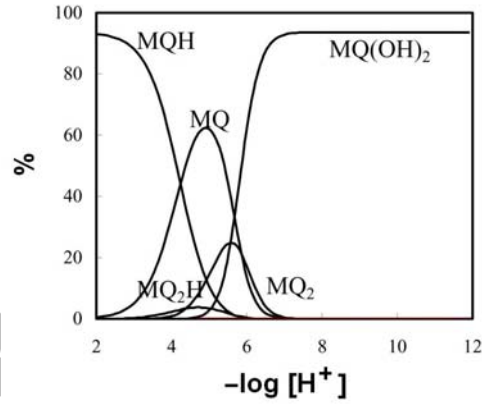


Fig. 7. Distribution diagrams of dmp(Q)/M binary systems. M = Cr³⁺.

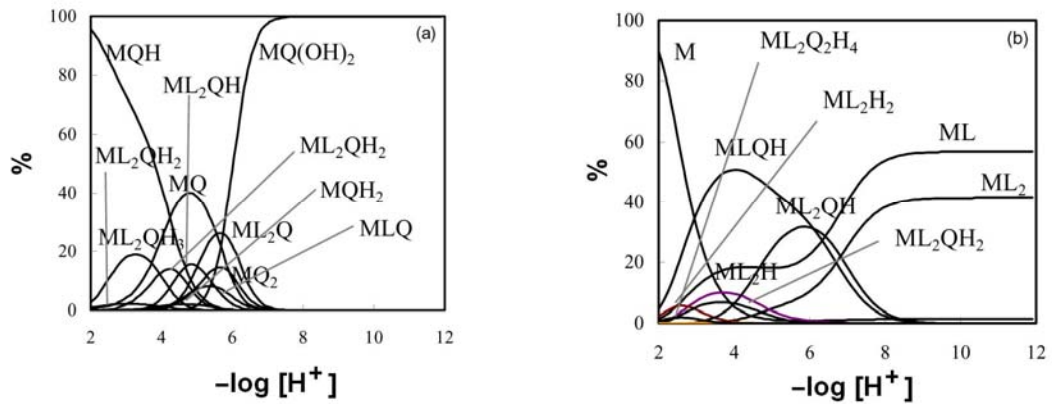


Fig. 8. Distribution diagrams of pydc(L)/dmp(Q)/M ternary systems. M = Cr³⁺ (a), Ca²⁺ (b).

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