J. Iran. Chem. Soc., Vol. 8, No. 3, September 2011, pp. 762-774.

JOURNAL OF THE
Iranian
Chemical Society

Hydrothermal Synthesis, X-Ray Crystallography, TGA and SEM Analyses and Solution Studies of a Novel Nano-Sized 1D Zinc(II) Coordination Polymer

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(Received 4 August 2010, Accepted 4 December 2010)

A novel coordination polymer of zinc(II) atom, $[(pipzH_2)[Zn(pyzdc)_2].6H_2O]_n$ (**1**) (H_2pyzdc and pipz are pyrazine-2,3-dicarboxylic acid and piperazine, respectively), was successfully synthesized under hydrothermal conditions and structurally characterized by means of elemental analysis, FTIR, TGA and SEM. Polymer **1** was further structurally characterized by single crystal X-ray diffraction consisting of 1D-polymeric units. The crystal structure of the title polymer consisted of polymeric Zn complex anions and discrete piperazindiium cations. The Zn cation, located on the inversion center, was N,O-chelated by two $(pyzdc)^{2-}$ anions in the basal plane, and was further coordinated by two carboxyl O atoms from the adjacent pyzdc anions in the axial directions with a longer Zn-O bond distance of 2.1746(15) Å, forming a distorted ZnN_2O_4 coordination geometry. The pyzdc anions bridged the Zn cations to the one-dimensional polymeric chains running along the crystalographic *b* axis. The $(pipzH_2)^{2+}$ linked with the complex chains *via* kinds of hydrogen bonds. The polymer **1** crystallized in the monoclinic space group $P2_1/n$ with Z = 2. The cell parameters of the title polymer were a = 6.5318(16) Å, b = 17.492(4) Å, c = 10.688(3) Å and β = 100.841(4)°. The polymer **1** bears ion-pairing interactions, O-H···O, N-H···O, and C-H···O hydrogen bonds as main factors in the formation of its 1D supramolecular architecture. Obtained results from TGA showed that the title polymer was thermally quite stable, and so its framework possessed remarkable thermal stability up to 700 °C. The SEM analysis verified that layers present in **1** were formed in Nano-sized particle. The protonation constants of acridine (Acr), H_2pyzdc, and pipz as the building blocks of the proton transfer systems including pyzdc-Acr in mixed 20% dioxane-80% water (V/V) solvent and pyzdc-pipz in aqueous solvent, and the corresponding stability constants of these systems were determined by potentiometric study. The stoichiometry and stability of complexation of these systems with Zn^{2+} ion were investigated by potentiometric pH titration method. The stoichiometry of the most complex species in the solution was compared with the corresponding crystalline metal ion complexes.

Keywords: Acridine, Piperazine, Proton transfer methodology, Water cluster, Nano-sized, SEM

INTRODUCTION

The field of metal-organic polymers with pyridine-dicarboxylate is rapidly expanding due to their potential applications and intriguing structural features. A large number of multidimensional coordination polymers containing ligands bearing *ab initio* HF and various DFT calculations have been recently prepared and characterized [1-4]. Even so, the prediction and synthesis of the solid-state architectures still remain a long-term challenge for the chemists [5]. On the other hand, the development of supramolecular assembled chemistry has opened up the possibility to rationally design

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*Corresponding author. E-mail: heshtiagh@ferdowsi.um.ac.ir and prepare supramolecular architectures [6]. Meanwhile, many investigations indicate that the combination of metal coordination and supramolecular interaction (in particular hydrogen bonding and π-π stacking) are powerful forces for supramolecular structural assembly in crystal engineering [7].

By comparison, H_2pyzdc is a multifunctional ligand containing two types of coordinating atoms (N and O), which can potentially afford various coordination modes tending to bind metal ions and diverse molecular building blocks forming extended networks. Kitagawa *et al.* have reported the preparation and structures of a series of 1D pillared layer porous cadmium coordination networks based on H_2pyzdc and pillar ligands. These coordination polymers possess interesting selective guest adsorption properties [8]. H_2pyzdc is therefore regarded as an excellent candidate for the construction of these categories of coordination polymers [9], so that recently many of its complexes containing Cu(II), Cd(II), Ln(III), Ag(I), Mn(II), *etc.* are reported [10]. However, by comparison, zinc(II) coordination chemistry has not been extensively explored so far [11]; specially, few efforts have been made to investigate the assembly of metal-organic coordination polymers induced by the external factors, such as high temperature and pressure in hydrothermal conditions governing the crystallization process and the stability of the overall crystals. Our interest lies in the d^{10} metal-based H_2pyzdc for the self-assemblies of metal-organic coordinations and supramolecular architectures under different reaction conditions. Prompted by the above-mentioned points and due to our interest in the syntheses of metal-organic polymers [1], and to give birth to a variety of hydrogen-bonded frameworks with fascinating structures, in this paper, we present the hydrothermal synthesis, X-ray structure characterization, thermal and SEM properties, and solution study of a novel 1D-zinc(II) coordination polymer, $[(pipzH_2)[Zn(pyzdc)_2].6H_2O]_n$ (**1**), for the first time.

EXPERIMENTAL

Chemicals and Apparatus

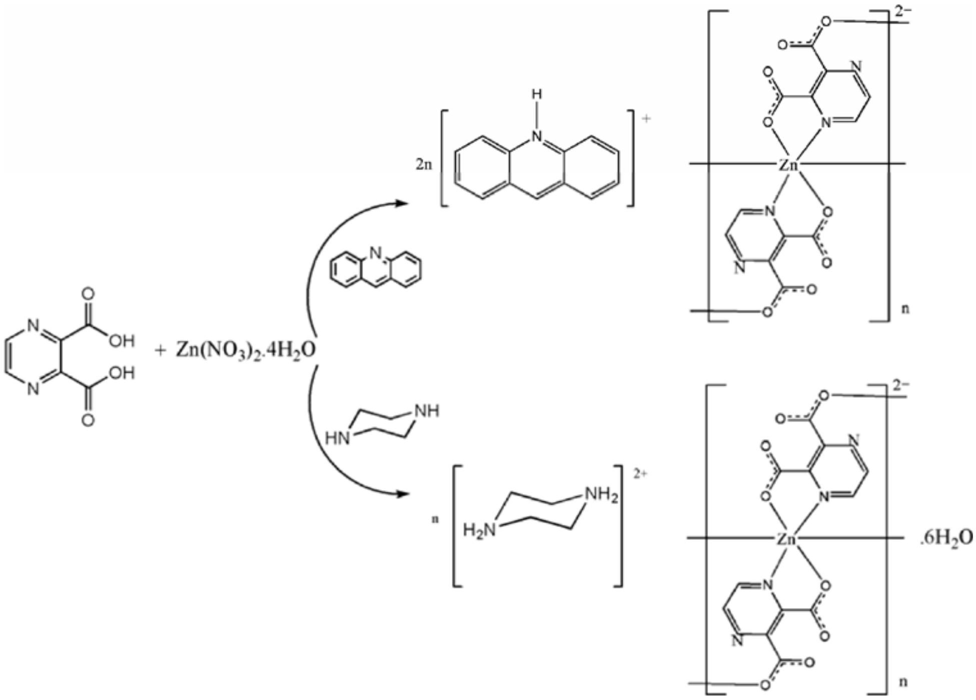
$Zn(NO_3)_2.4H_2O$, H_2pyzdc, pipz, Acr, and used solvents (analytical grade, Merck Chemicals) were used without further purification.

The FTIR spectra were recorded on a Bomem B-154 Fourier transform spectrometer using KBr discs. Elemental analyses were carried out on a Thermo Finnigan Flash-1112EA microanalyzer. The TGA runs were taken on a TGA-50/50H standard type thermal analysis system. The polymers **1** and $\{(AcrH)_2[Zn(pyzdc)_2]\}_n$ (**2**) (previously published in Acta Cryst Section E by our research group [12]) were heated up to 1000 °C in the atmosphere of nitrogen, at a heating rate of 10 K per min. The SEM images were taken on a Zeiss LEO 1450 VP, Germany. The X-ray structure analysis of prism colorless single crystals of **1** was carried out on a Bruker SMART diffractometer with an APEX II CCD area detector (Mo-Kα radiation, graphite monochromator, $\lambda = 0.71073$ Å). Diffracted data were corrected for absorption using the SADABS program. Some software including APEX II (data collection) and SAINT$^+$ (cell refinement and data reduction), SHELXTL (version 6.2, structure solution & refinement; molecular graphics and publication material) were used. Crystal and refinement data for **1** were: $Fw = 593.81$ g mol^{-1}, monoclinic, space group $P2_1/n$, $a = 6.5318(16)$ Å, $b = 17.492(4)$ Å, $c = 10.688(3)$ Å, $V = 1199.3(5)$ Å^3, $Z = 2$, $\mu = 1.106$ mm^{-1}, Final R indices $[I > 2\text{sigma}(I)]$ $R_1 = 0.0354$, $wR_2 = 0.0868$.

All potentiometric pH measurements were made on solutions in a 50 ml double-walled glass vessel using a Model 686 Metrohm Titroprocessor equipped with a combined glass-calomel electrode. The temperature was controlled at 25.0 ± 0.1 °C by circulating water through the jacket, from a constant-temperature bath (MLW thermostat). In the case of the mixed solvent the pH meter-electrode system was calibrated to read -log[H^+] in 20% dioxane-80% water (V/V) solvent.

Synthesis of $[(pipzH_2)[Zn(pyzdc)_2].6H_2O]_n$ (1)

The title compound was obtained by a similar method used for the preparation of **2**. The title polymer presented here was prepared as follows: Hydrothermal reactions of $Zn(NO_3)_2.4H_2O$ with H_2pyzdc, pipz, in aqueous solution in 1:3:3 molar ratios of Zn:H_2pyzdc:base, respectively, afforded a novel nano-sized layered pyrazinecarboxylate-based zinc(II) coordination polymer using proton transfer mechanism (Scheme 1). A mixture of H_2pyzdc (0.50 mmol, 90 mg), pipz (0.50 mmol, 100 mg), and $Zn(NO_3)_2.4H_2O$ (0.16 mmol, 40 mg) in distilled water (12 ml) was placed in a Teflon-lined stainless steel vessel, heated to 150 °C for 4 days, and then



Scheme 1. The path to synthesize polymers **1** and **2**

cooled to room temperature over 12 h. Prism colorless crystals of **1**, suited for the single crystal X-ray diffraction analyses, formed with a yield of approximate 55% (based on Zn) were obtained. Anal. Calcd. for **1**: C, 32.32; H, 4.70; N, 14.15. Found: C, 33.73; H, 3.93; N, 14.88%. FTIR (cm^{-1}): 3387(b), 3028(m), 2783(m), 2493(m), 2350(m), 1656(s), 1623(s), 1455(m), 1378(s), 1350(s), 1147(s), 1125(s).

RESULTS AND DISCUSSION

The SEM analysis on polymer **1** (Fig. 1) verified firstly that the title polymer bore polymeric layered structure and secondly that its layers formed as Nano-sized. Indeed, the obtained data from SEM were in good agreement with the single crystal X-ray results. Recently, Khanpour *et al*. reported a novel nano-sized 2D Zn(II) coordination polymer which was synthesized using a sonochemical irradiation [13]. They claimed that the thermal decomposition at air of their polymeric polymer in bulk size, produced by grinding its single crystals in air produced ZnO, as established by its powder XRD pattern but the particles were not nano-size. This demonstrates that the particles size of the coordination polymers is an important factor in the produced nanoscale materials from coordination polymers. So, as we see here, the size of our synthesized coordination polymer is suitable for the nano-size targets, hence, it is not needed to use sonochemical irradiation for obtaining nano-size polymer.

The data of single crystal X-ray structure determinations on the title polymer reveal that $(H_2O)_\infty$ clusters in the crystal structure of **1** form an infinite chain with 3:3 repeating ratio [14] (Fig. 2). Indeed, this water cluster helped to gather all species present in the crystalline network and so resulted in further stabilization of **1**. To examine the thermal stability of the two complexes, its TGA were carried out in nitrogen atmosphere from 20 to 1000 °C (Fig. 3). The TG curve for **1** shows the loss of six crystallization water molecules in the temperature range from 20 to 180 °C (found, 19.5%; calcd.: 18.20%). And then the further weight loss of 55% (calcd.: 56%) from 180 to 350 °C is ascribable to the loss of two $(pyzdc)^{2-}$ ligands. Another major weight loss occurred in the range 350-500 °C, which may correspond to the complete destruction of the crystalline network and formation of ZnO

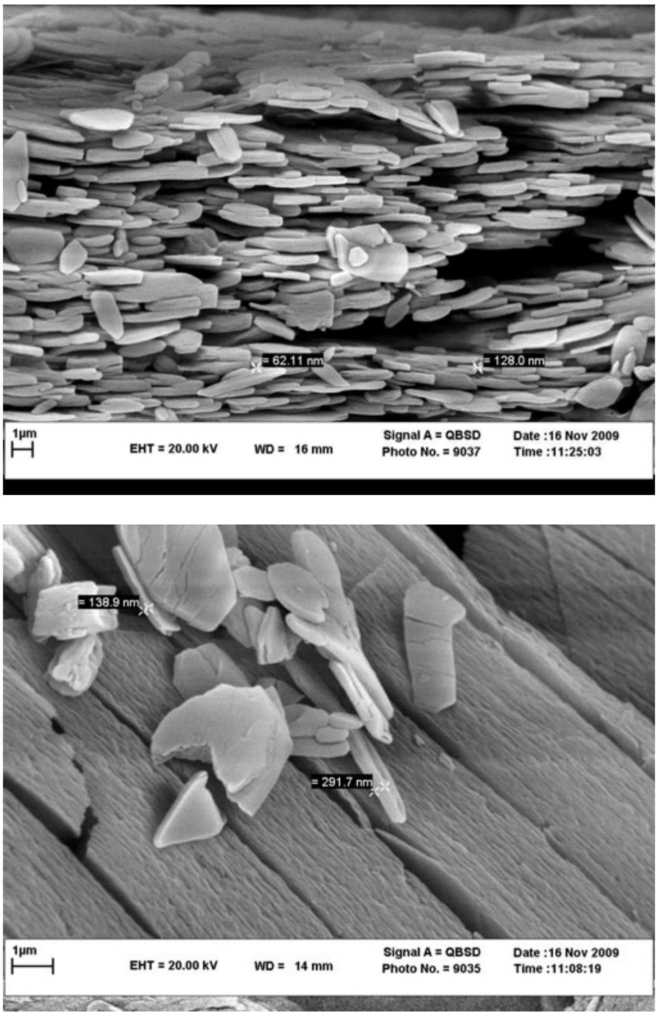


Fig. 1. SEM photograph of $[(pipzH_2)[Zn(pyzdc)_2].6H_2O]_n$ (**1**) in nano-layers form.

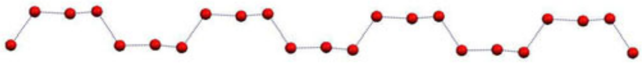


Fig. 2. Infinite chain with 3:3 repeating ratio of present $(H_2O)_\infty$ cluster in the crystalline network of polymer **1**.

particles. In general, an FTIR spectrum of the complexes **1** is complicated. But they have common characteristic absorptions, such as υH_2O absorption in the range of 3500-3100 cm^{-1} centered at 3387 cm^{-1} for **1**, which confirm the existence of water molecules in **1**. The presence of carboxylate COO^- group was reflected by FTIR spectrum in absorption bands of the asymmetric (υ_{as}) and symmetric (υ_s) stretching vibrations at 1611 and 1447, cm^{-1} for **1**. Moreover, the differences between the asymmetric and symmetric stretches of the carboxylate groups in **1**, $\Delta = 164$ cm^{-1}, suggest a bidentate binding of the carboxylate group to the znic(II) metal ion. However, $\upsilon_{as}COO^-$ absorption was submerged in the range of 1656-1500 cm^{-1} because of the presence of υCO, υCN and υCC absorptions in the same range.

To examine the thermal stability of anhydrated inorganic polymer **2**, and to compare it with the structure of **1**, its TGA was carried out in nitrogen atmosphere from 20 to 800 °C. The obtained results showed that the polymeric polymer went through three stages of weight loss. First, there was a 40% weight loss from 200 to 250 °C, which can be attributed to the loss of $(pyzdc)^{2-}$ moieties (calcd.: 44%). The second weight loss (55%) was in the range 250 to 330 °C, corresponding to the thermal decomposition and loss of acridine molecules (calcd.: 48%). The third weight loss occurred above 500 °C, corresponding to the thermal decomposition and complete destruction of the crystalline network of the title polymer. In general, an FTIR spectrum of **2** was complicated. But they had common characteristic absorptions, such as the absence of υH_2O absorption in the range of 3500-3100 cm^{-1} which proves that there were no crystallization water molecules for the title polymer. The presence of carboxylate COO^- group was reflected by FTIR spectrum in absorption bands of the asymmetric (υ_{as}) and symmetric (υ_s) stretching vibrations at 1635 and 1447 cm^{-1} for the title inorganic polymer. Moreover, the difference between the asymmetric and symmetric stretches of the carboxylate groups in the title polymer, $\Delta = 188$ cm^{-1}, suggests a bidentate binding of the carboxylate group to the zinc(II) atom. However, $\upsilon_{as}COO^-$ absorption submerged in the range of 1656-1500 cm^{-1} because of the presence of υCO, υCN and υCC absorptions in the same range.

X-Ray Crystallographic Study of 1

The crystallographic data of **1** are given in Table 1; the bond lengths and angles are shown in Table 2, and the hydrogen bond geometry is given in Table 3. The crystal and

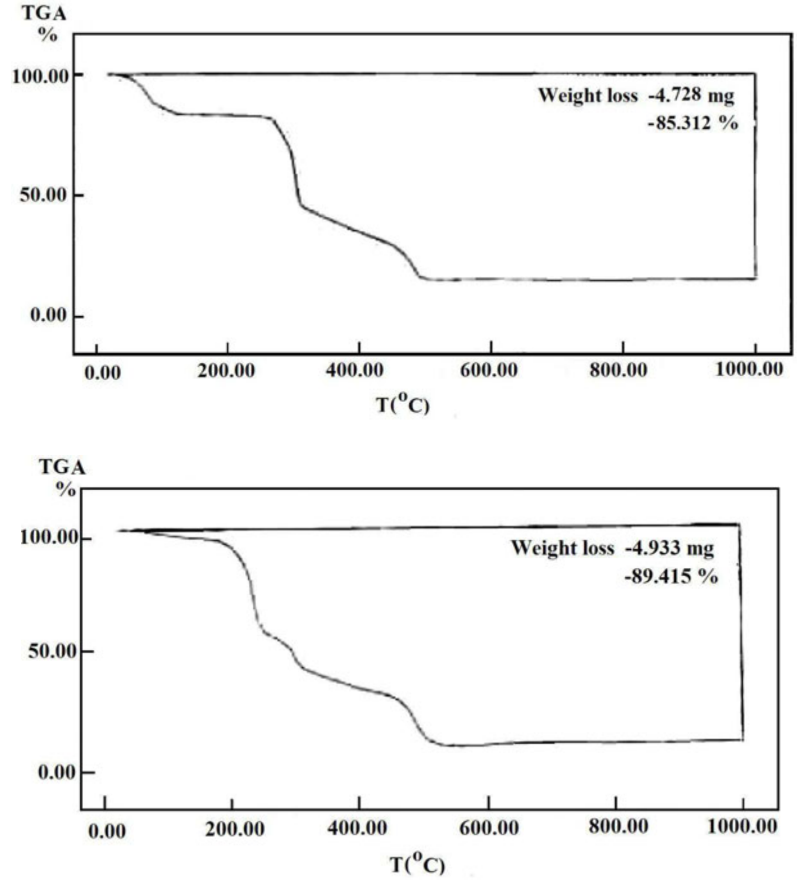


Fig. 3. TGA curves of polymer **1** (top) and **2** (bottom).

molecular structure, coordination environment around each zinc(II) atom, layered structure, and schematic representation of polmeric layers of the polymer are illustrated in Figs. 4, 5, 6 and 7, respectively. In the unit cell, the molecular structure of polymer **1** contains the $Zn(pyzdc)_2]^{2-}$ anion with protonated pipz organic moiety, and water molecules in a 1:1:6 molar ratio, respectively (Fig. 4). Figure 5 demonstrates that the Zn(II) ion in the $[Zn(pyzdc)_2]^{2-}$ is six-coordinated by the two N atoms and four O atoms of two pyzdc ligands, forming a distorted octahedral geometry. Nitrogen and oxygen atoms of pyzdc ligand in the equatorial plane which are bonded to Zn(II) ion form a fivemember chelate ring.

According to Table 2, the Zn-N and Zn-O distances lie in the range of 2.1046(17) Å and 2.0613(14)-2.1746(15) Å, respectively. This Zn-N bond distance is shorter than the corresponding values found in $\{[Zn(pyzdc).3H_2O].H_2O\}_n$ [2.191(3) Å] [15], $\{[Zn_2(pyzdc)_2.4H_2O].2.5H_2O\}_n$ [2.1401(15) Å] [15] and $\{[Zn(pyzdc)(phen).4H_2O]\}_n$ [2.112(5)-2.230(5) Å] [15]. The Zn-O bond distance of average 2.1180 Å is longer than the corresponding bond in $\{[Zn(pyzdc).3H_2O].H_2O\}_n$ [2.096 Å], [15], $\{[Zn_2(pyzdc)_2.4H_2O].2.5H_2O\}_n$ [2.100 Å] [15] and $\{[Zn(pyzdc)(phen).4H_2O]\}_n$ [2.071 Å] [15]. The C-N and C-C distances in the pyzdc ligands are normal. By devoting attention to Table 2, it could be concluded that in the anionic $[Zn(pyzdc)_2]^{2-}$ complex, the N-Zn-N bond angle does not deviate significantly from 180°, which is presumably due to the absence of steric constraints arising from the shape of the used ligand [N1-Zn-N1a = 180.00(9)°].

The intermolecular interactions between the cationic and anionic units in this complex consist of kinds of hydrogen bonding such as O-H···O, N-H···O, and C-H···O contacts. Six crystallizations of water molecules increase the number of

Table 1. Crystal Data and Structure Refinement for **1**

Empirical formula	$C_{16}H_{28}N_6O_{14}Zn$	
Formula weight	593.81	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P\,2_1/n$	
Unit cell dimensions	a = 6.5318(16) Å	α = 90°
	b = 17.492(4) Å	β = 100.841(4)°
	c = 10.688(3) Å	γ = 90°
Volume	1199.3(5) $Å^3$	
Z	2	
Density (calculated)	1.644 mg m^{-3}	
Absorption coefficient	1.106 mm^{-1}	
$F(000)$	616	
Crystal size	0.24 × 0.18 × 0.17 mm^3	
Theta range for data collection	2.26 to 27.00°	
Index ranges	$-8 \leq h \leq 8$, $-22 \leq k \leq 22$, $-13 \leq l \leq 13$	
Reflections collected	11319	
Independent reflections	2627 [R(int) = 0.0275]	
Obserevd reflections [I > 2sigma(I)]	2146	
Completeness to theta = 27.00°	100.0%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.833 and 0.781	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	2627/0/169	
Goodness-of-fit on F^2	1.003	
Final R indices [I > 2sigma(I)]	R_1 = 0.0354, wR_2 = 0.0868	
R indices (all data)	R_1 = 0.0444, wR_2 = 0.0915	
Largest diff. peak and hole	0.850 and -0.247 e.$Å^{-3}$	

Crystallographic data for the two structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC 748370 for **1**. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+ (1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk; e-mail for deposition: deposit@ccdc.cam.ac.uk).

hydrogen bonds in polymer **1**. The pyzdc ligands in **1** are essentially planar, with a slight deviation from planarity arising from the non-zero torsion angle between the carboxylate group and the ring [N1-C2-C7-O2 = 175.19(6)°, N1-C2-C7-O1 = -5.24(9)° and C3-C2-C7-O2 = -4.00(11)° and C3-C2-C7-O1 = 175.57(8)°]. These torsion angles indicate that the distortion of the pyzdc ligand is caused by coordination to the Zn(II) ion. This interesting feature of polymer **1** implies that these van der Waals interactions form the unique supramolecular network in the crystal structure whose organic

Table 2. Bond Lengths [Å] and Angles [°] for **1**

Zn(1)-O(1)#1	2.0613(14)
Zn(1)-O(1)	2.0613(14)
Zn(1)-N(1)	2.1046(17)
Zn(1)-N(1)#1	2.1046(17)
Zn(1)-O(4)#2	2.1746(15)
Zn(1)-O(4)#3	2.1746(15)
O(1)-C(7)	1.284(2)
O(2)-C(7)	1.230(3)
O(3)-C(8)	1.263(3)
O(4)-C(8)	1.246(3)
O(4)-Zn(1)#4	2.1746(15)
O(1)#1-Zn(1)-O(1)	180.00(7)
O(1)#1-Zn(1)-N(1)	99.86(6)
O(1)-Zn(1)-N(1)	80.14(6)
O(1)#1-Zn(1)-N(1)#1	80.14(6)
O(1)-Zn(1)-N(1)#1	99.86(6)
N(1)-Zn(1)-N(1)#1	180.00(9)
O(1)#1-Zn(1)-O(4)#2	85.96(6)
O(1)-Zn(1)-O(4)#2	94.04(6)
N(1)-Zn(1)-O(4)#2	93.09(6)
N(1)#1-Zn(1)-O(4)#2	86.91(6)
O(1)#1-Zn(1)-O(4)#3	94.04(6)
O(1)-Zn(1)-O(4)#3	85.96(6)
N(1)-Zn(1)-O(4)#3	86.91(6)
N(1)#1-Zn(1)-O(4)#3	93.09(6)
O(4)#2-Zn(1)-O(4)#3	180.0
C(7)-O(1)-Zn(1)	115.38(13)
C(8)-O(4)-Zn(1)#4	142.82(13)
O(2)-C(7)-O(1)	125.88(19)
O(4)-C(8)-O(3)	125.81(19)

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

cationic moieties and water molecules fill the spaces between these tape-like structures (Fig. 6). Indeed, the anionic tape-like polymer of **1** resulted in the formation of the above-mentioned suitable vacancies for decorating other species in the crystalline network (Fig. 7).

Potentiometric Equilibrium Measurements

The jacketed cell containing test solution was equipped with a magnetic stirrer and a tightly fitting cap, through which the electrode system and 10-ml capacity Metrohm piston burrete were inserted and sealed with clamps and O-rings. The atmospheric CO_2 was excluded from the titration cell with a purging steam of purified nitrogen gas. Known amounts of Acr, pyzdc and pipz ($2.00\text{-}3.00 \times 10^{-3}$ M), were titrated in the absence and presence of $1.00\text{-}1.5 \times 10^{-3}$ M Zn^{2+} ions. A standard carbonate-free NaOH solution (0.098 M) was used in all titrations. The ionic strength was adjusted to 0.1 M with $NaClO_4$. Before an experimental point (pH) was measured, sufficient time was allowed for the establishment of equilibrium.

Ligands' protonation constants and stability constants of proton transfer and their metal complexes were evaluated using the BEST program described by Martell and Motekaitis [16]. The value of autoprotolysis constants for the aqueous and mixed solvent system of 20% dioxane-80% water (V/V), $Ks = [H^+]\,[OH^-]$ were chosen to be $10^{-13.78}$ and $10^{-14.62}$, respectively, according to literature [16,17]. It was discovered that acridine and some of its derivatives were slightly soluble in acidic and insoluble in neutral or alkaline aqueous solution. These compounds are soluble in some organic solvents. Therefore, we decided to accomplish the potentiometric study of Acr in a minimum extent of dioxane [20% dioxane-80% water (V/V)].

In order to evaluate the stoichiometry and stability of Zn^{2+} complexes with $pipz^{2+}$ and $pyzdc^{2-}$ in aqueous solution, Acr^+ and $pyzdc^{2-}$ in a mixture of 20% dioxane-80% water (V/V), known concentrations of their fully protonated and 1:1 mixture in the absence and presence of the metal ions were titrated with a 0.098 M solution of NaOH at the temperature of 25 °C and an ionic strength of 0.1 M, maintained by $NaClO_4$. Titration continued before precipitation. The resulting pH profiles are shown in Figs. 8 and 9. It was found that H_2pyzdc has good interaction with metal ions, because the potentiometric titration curves were depressed considerably in the presence of the metal ions. The extent of depression obviously depends both on the stoichiometries of the resulting complexes and the ability of the metal ions to bind the ligand components.

The cumulative stability constants, β_{mlqh}, are defined by Eq. (1) (charges are omitted for simplicity).

Table 3. Hydrogen Bonds for **1** [Å and °].

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O(1W)-H(1)···O(2W)#6	0.83	1.81	2.629(3)	167
O(1W)-H(2)···N(4)#7	0.90	1.95	2.814(3)	162
O(2W)-H(3)···O(1)#2	0.91	1.94	2.832(2)	166
O(2W)-H(4)···O(3W)#4	0.84	1.89	2.724(3)	174
O(3W)-H(5)···O(3)#7	0.87	1.90	2.771(3)	174
O(3W)-H(6)···O(1W)#8	0.90	1.92	2.743(3)	152
N(9)-H(9A)···O(3)#3	0.91	1.85	2.752(2)	171
N(9)-H(9B)···O(1W)#9	0.89	1.88	2.746(3)	164

Symmetry transformations used to generate equivalent atoms: #2 -*x*, -*y*, -*z*+1 #3 *x*+1, *y*, *z* #4 *x*-1, *y*, *z* #6 *x*, *y*, *z* #7 *x*+1/2, -*y*+1/2, *z*+1/2 #8 *x*+1/2, -*y*+1/2, *z*-1/2 #9 *x*, *y*, *z*-1.

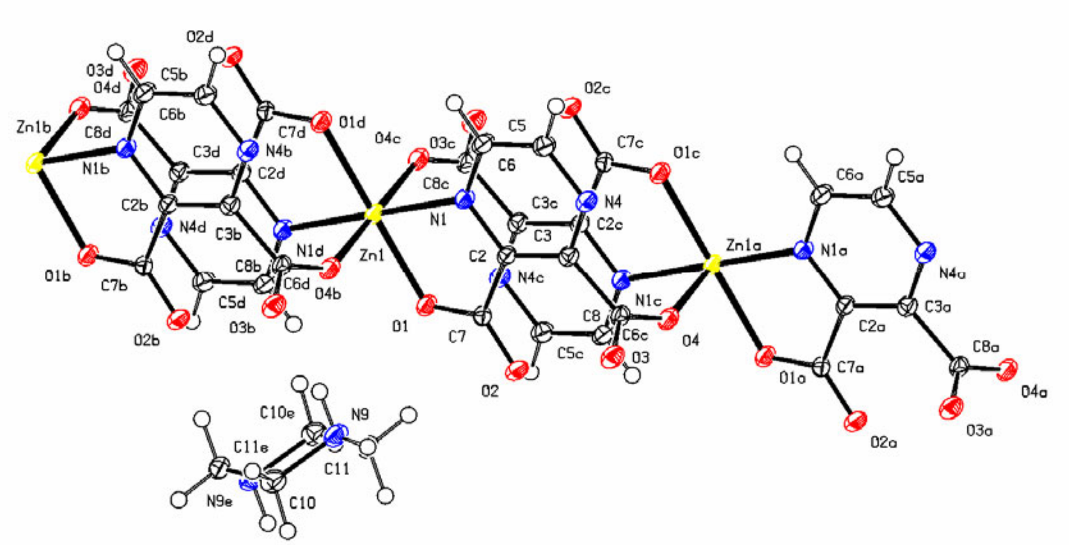


Fig. 4. The molecular and crystal structure of [(pipzH$_2$)[Zr(pyzdc)$_2$].6H$_2$O]$_n$, **1**, showing the atom-numbering scheme and displacement. Ellipsoids are at the 50% probability level. Water molecules are omitted for further clarity. Symmetry transformations used to generate equivalent atoms: -*x*+1, -*y*, -*z*+1; -*x*, -*y*, -*z*+1; *x*+1, *y*, *z*; *x*-1, *y*, *z*; -*x*+1, -*y*, -*z*.

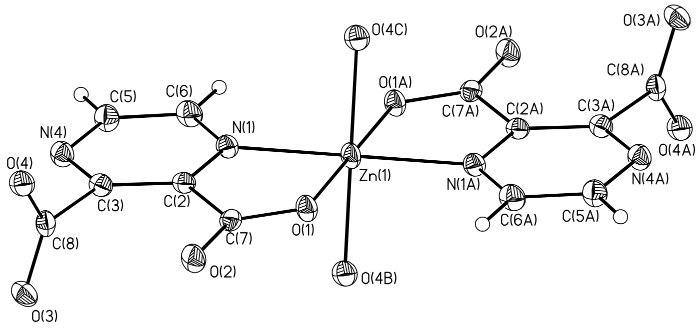


Fig. 5. Coordination environment around each zinc(II) atom as distorted octahedral in **1**, showing the atom- numbering scheme and displacement. Ellipsoids are at the 50% probability level. Symmetry transformations used to generate equivalent atoms: -*x*+1, -*y*, -*z*+1; -*x*, -*y*, -*z*+1; *x*+1, *y*, *z*; *x*-1, *y*, *z*; -*x*+1, -*y*,-*z*.

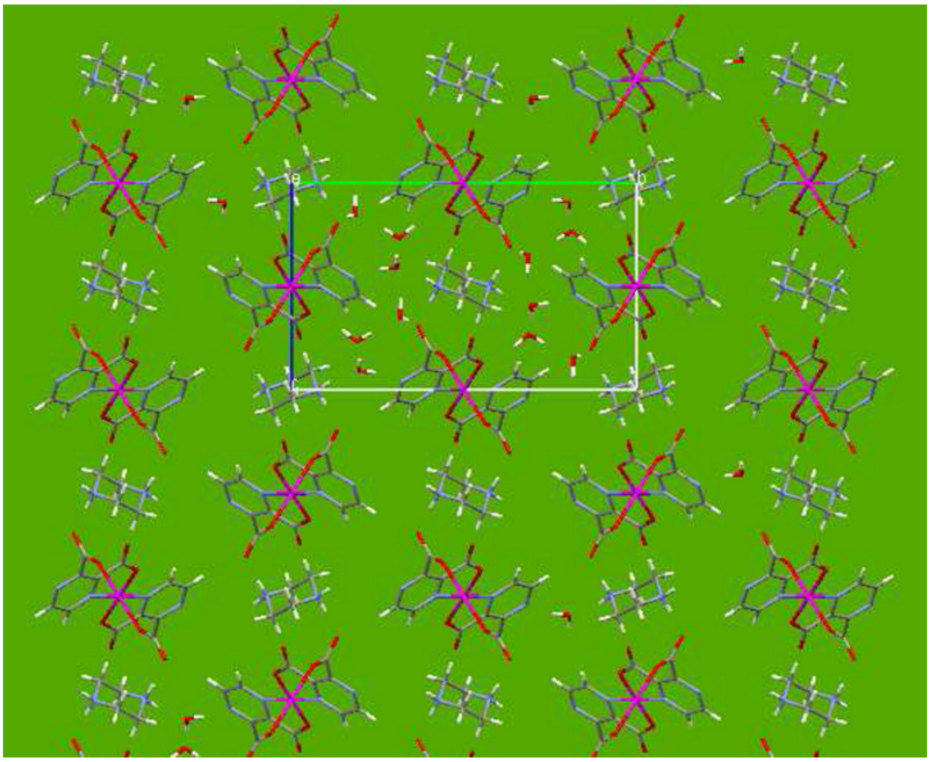


Fig. 6. The layered packing diagram of polymer **1**, the space between the two layers of $[Zn(pyzdc)_2]^{2-}$ fragments is filled with a layer of $(pipzH_2)^{2+}$ cations and water molecules.

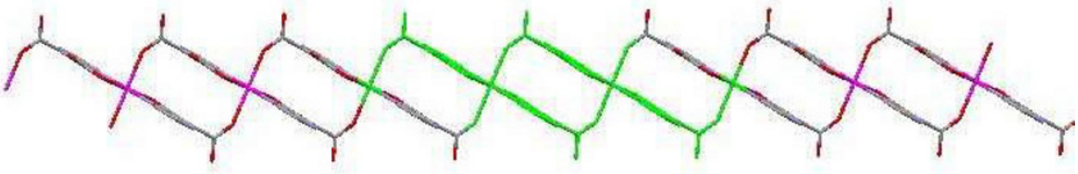


Fig. 7. Schematic representation of polymeric layers presence in the crystalline network of the title polymer.

$$mM + lL + qQ + hH \underset{\beta_{mlqh}}{\rightleftharpoons} M_mL_lQ_qH_h$$

$$\beta_{mlqh} = [M_mL_lQ_qH_h]/[M]^m[L]^l[Q]^q[H]^h \qquad (1)$$

where M is metal ion, L is pyzdc, Q is pipz or Acr and H is proton, and m, l, q, and h are the respective stoichiometric coefficients. Since the ligands' and complexes' 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 of 0.1 M and low ligand concentrations (in the order of 10^{-3} M).

The potentiometric pH titration profiles of H_2pyzdc, pipz and their 1:1 mixture in water and H_2pyzdc, Acr and their 1:1 mixture in 20% dioxane-80% water (V/V), in the presence of Zn^{2+} ions were fitted to the program BEST [18], and the resulting values for the most likely complexed species in aqueous and mixed solutions are listed in Tables 4 and 5, respectively. Sample species distribution diagrams for L + Q mixture in the presence of Zn^{2+} are shown in Figs. 10 and 11. It is obvious from Figs. 10 and 11 that the most abundant

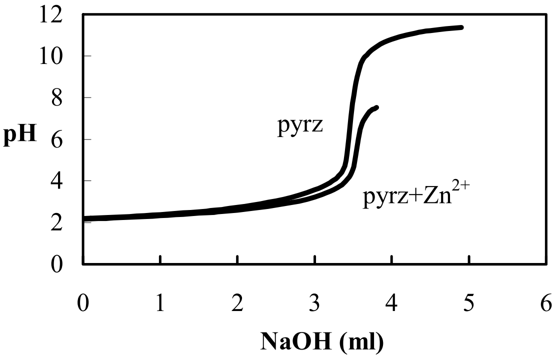


Fig. 8. Titration curve of (2.5 × 10^{-3} M) pyzdc in absence and presence of (1.25 × 10^{-3} M) Zn^{2+} with experimental conditions of 25 °C, I = 0.1 M $NaClO_4$ in aqueous solution.

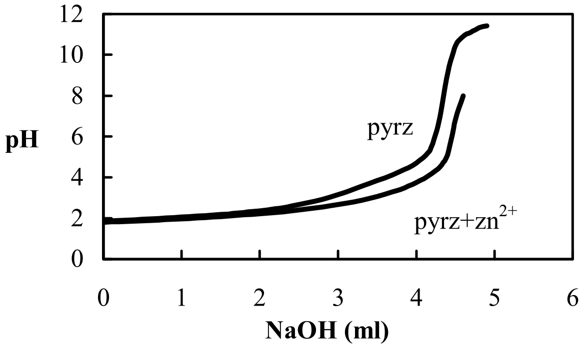


Fig. 9. Titration curve of (2.5 × 10^{-3} M) pyzdc in absence and presence of (1.25 × 10^{-3} M) Zn^{2+} with experimental conditions of 25 °C, I = 0.1 M $NaClO_4$ in 20% dioxane-80% water (V/V).

Table 4. Overall Stability Constants for $pyzdc^{2-}$ (L), pipz (Q), Zn^{2+} (M) Complexes at 25 °C and I = 0.1 M $NaClO_4$ in Aqueous Solution

H	M	L	Q	logβ	Max%	at pH
1	0	1	0	3.31	30.1	2.1
2	0	1	0	5.06	16.7	2.0
1	0	0	1	9.44	39.8	6.2
2	0	0	1	15.05	54.6	2.0-3.2
0	1	1	0	12.30	7.7	4.0
1	1	1	0	15.96	43.5	2.0
0	1	2	0	16.52	39.3	5.6
1	1	3	0	23.46	12.7	3.0
-2	1	3	0	4.72	4.3	11.3
1	0	1	1	10.95	0.4	6.2
2	0	1	1	16.32	0.2	3.7-5.4
-1	1	2	1	15.60	46.6	8.4-9.1

proton transfer species between pyzdc and pipz in aqueous solution are HLQ (5.6% at pH = 7.4) and H_2LQ (2.9% at pH = 4.7) and the most probable proton transfer species between pyzdc and Acr in the mixed solvent of 20% dioxane-80% water (V/V), are LQ (30.8% at pH > 7.0), HLQ (73.2% at pH= 3.6) and LQ_2 (38.6% at pH > 7.2). Tables 4 and 5 show that the overall stability constants of pyzdc differ in aqueous (3.31 and 5.06) and mixed organic-aqueous (4.01 and 5.49) media, because of the solvent effect [17]. This effect is observed in the overall stability constants of ML complexes, too. For example, logβ of ML_2 complexes in aqueous and mixed solvents are 16.52 and 12.57, respectively. Figures 12 and 13 and Tables 4 and 5, revealed the formation of a variety of ternary complexes between the Zn^{2+} ion and two proton transfer systems at different ranges of pH. The ML_2QOH complex (logβ = 15.60 max 46.6% at pH = 8.4-9.1) in aqueous solution and ML_2QOH (logβ = 12.12 max 37.7% at pH = 5.9), ML_2Q_2 (logβ = 20.04 max 7.6% at pH = 5.3), $ML_2Q_2(OH)_2$

Table 5. Overall Stability Constants for pyzdc^{2-} (L), Acr (Q), Zn^{2+} (M) Complexes at 25 °C and I = 0.1 M NaClO$_4$ in 20% Dioxane-80% Water (V/V)

H	M	L	Q	logβ	Max%	at pH
1	0	1	0	4.01	0.3	2.0
2	0	1	0	5.49	negligible	-
1	0	0	1	5.20	40.2	6.1
0	1	2	0	12.57	7.7	3.9
1	1	2	0	16.59	35.6	2.8
2	1	2	0	18.78	30	2.0
-1	1	2	0	6.58	negligible	-
0	1	3	0	16.84	negligible	-
-1	1	3	0	13.22	negligible	-
0	0	1	1	4.20	negligible	-
1	0	1	1	9.17	negligible	-
0	0	1	2	8.49	negligible	-
-1	1	2	1	12.12	37.7	5.9
0	1	2	2	20.04	7.6	5.3
-2	1	2	2	8.39	49.9	10.1-12.0
1	1	2	2	25.24	31.3	4.2

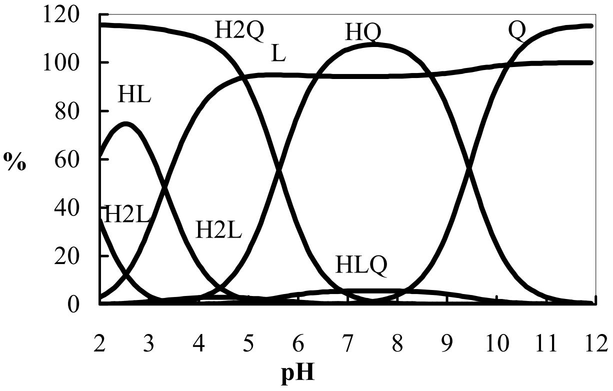


Fig. 10. Species distribution diagram of proton transfer interactions of pyzdc^{2-} (L) with pipz (Q) at 25 °C and ionic strength 0.1 M NaClO$_4$ in aqueous solution.

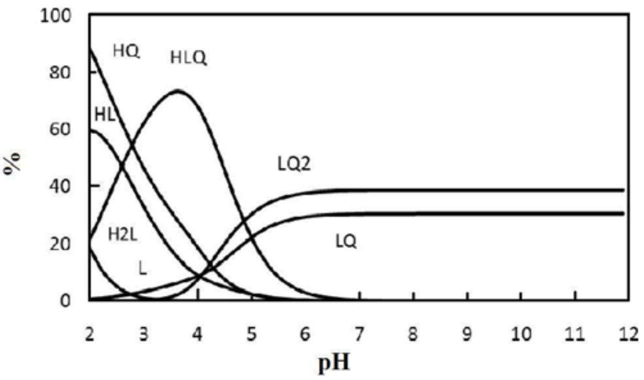


Fig. 11. Species distribution diagram of proton transfer interactions of pyzdc^{2-} (L) with Acr (Q) at 25 °C and ionic strength 0.1 M NaClO$_4$ in 20% dioxane-80% water (V/V).

(logβ = 8.31 max 49.9% at pH = 10.1-12.0) and HML$_2$Q$_2$ (logβ = 25.24 max 31.3% at pH = 4.2) in the mixed solvent 20% dioxane-80% water (V/V) were observed.

CONCLUSIONS

In summary, a novel nano-sized 1D-Zn(II) coordination polymer, polymer **1**, was synthesized under hydrothermal conditions without using sonochemical irradiation and structurally characterized by means of elemental analysis, FTIR, TGA, and SEM techniques. We have prepared a novel topological net with channel by using a flexible ligand. These findings are interesting not only for being a novel structure type but also for indicating the relationship between the

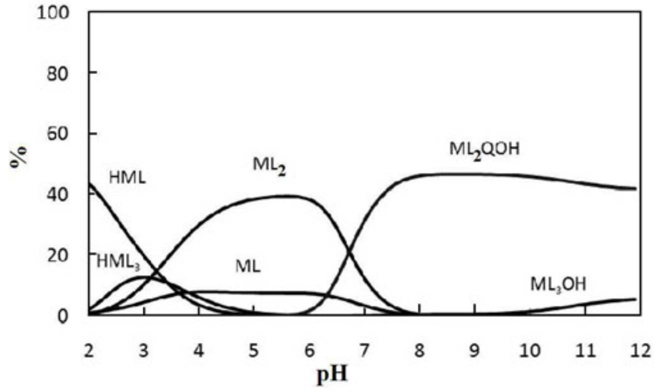


Fig. 12. Species distribution diagram for pyzdc^{2-} (L), pipz (Q), Zn^{2+} (M) at 25 °C and ionic strength 0.1 M $NaClO_4$ in aqueous solution.

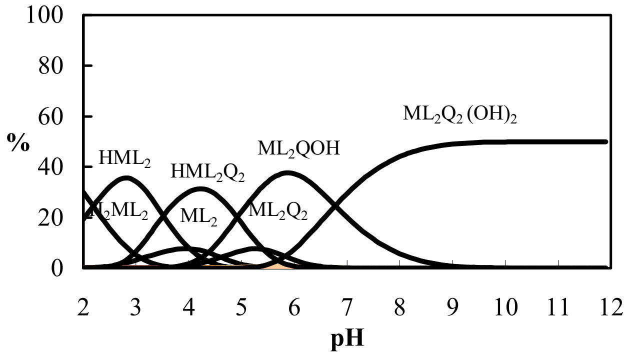


Fig. 13. Species distribution diagram for pyzdc^{2-} (L), Acr (Q), Zn^{2+} (M) at 25 °C and ionic strength 0.1 M $NaClO_4$ in 20% dioxane-80% water (V/V).

structure and property. Polymer **1** was structurally characterised by single crystal X-ray diffraction. The crystal structure of polymer **1** consists of a three-dimensional polymer and shows that the coordination number in the Zn(II) ions is six. We found that stability constant and distribution of the complexes are affected by the nature of the solvent. It is interesting to note that the stoichiometry of some of the most abundant ternary complexes, existing in aqueous solution ML_2QOH and 20% dioxane-80% water (V/V) solution ML_2QOH, ML_2Q_2, $ML_2Q_2(OH)_2$, and HML_2Q_2 were identical or very similar to those reported for the corresponding isolated complexes in the solid state. We are presently exploring other complexes with much more flexible polycarboxylate ligands and studying relationships between their coordinate modes and synthesized structures. Many aspects of these categories of coordination polymer such as their fluorescent measurement in the solid phase, biological activity test, and further study of the results obtained from SEM and/or TEM techniques in view of getting layered coordination polymer in Nano-size using sonochemical irradiation for comparing with the routine methods await investigation that we intend to pursue in the near future.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the help they received from the Central and Chemical Engineering Laboratories of Ferdowsi University of Mashhad for the measurement of TGA and SEM.

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