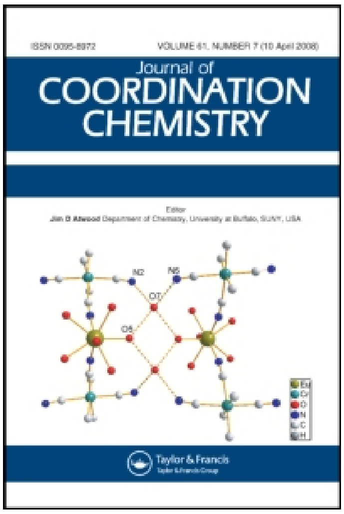

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Synthesis, X-ray crystal structure, thermal and solution studies of a centrosymmetric metal-organic polymer based on proton transfer methodology

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Synthesis, X-ray crystal structure, thermal and solution studies of a centrosymmetric metal–organic polymer based on proton transfer methodology

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A 3-D metal–organic coordination polymer based on pyrazine-2,3-dicarboxylic acid ($pzdcH_2$) formulated as $\{[Mn(pzdc)(H_2O)_2] \cdot 2H_2O\}_n$ (**1**), was obtained by the treatment of $MnCl_2 \cdot 6H_2O$ with $pzdcH_2$, 8-hydroxy quinoline (8-HQ), and 2-amino-4-methyl pyridine (ampy). In this study, we describe the synthesis, elemental analysis, IR spectroscopy, TG analysis, and single X-ray diffraction. The X-ray single crystal structure reveals that the chemical environment around each Mn(II) is a distorted octahedral by participating one nitrogen, five oxygens from three $(pzdc)^{2-}$ and two water molecules, O_5MnN. The centrosymmetric 1-D ladder-like structure of **1** is bridged by oxygens of $(pzdc)^{2-}$, and Mn–pzdc–Mn bonds are the rungs for our ladder structure. In the crystal structure, intermolecular O–H $\cdots$ O hydrogen bonds result in the formation of a supramolecular structure, effective for the stabilization of the structure. The thermal decomposition of **1** indicates that it is quite thermally stable. The protonation constants of ampy, 8-HQ and $pzdcH_2$ as the building blocks of proton transfer systems including $pzdcH_2$-ampy and $pzdcH_2$-8-HQ and the corresponding stability constants of these systems were determined by potentiometric study. The stoichiometry and stability constants of complexes of $pzdcH_2$-ampy and $pzdcH_2$-8-HQ with Mn^{2+} were investigated by this method in aqueous solution. The results obtained from solution study are comparable with the solid state results.

Keywords: Manganese; Pyrazine-2,3-dicarboxylic acid; Crystal structure; Coordination polymer; Solution studies

1. Introduction

A variety of factors can influence the self-assembly of coordination frameworks making desired topologies and specific properties a difficult challenge [1–5]. Construction of

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coordination polymers with new network motifs is of interest for the development of new functional materials and in the fundamental studies of crystal engineering and supramolecular chemistry [6–13]. Assembly of metal–organic frameworks (MOFs) is of interest as it may provide a new strategy for achieving solid functional material with application in molecular absorption/separation, magnetism, ion exchange, electric conductivity, catalysis, etc. [14, 15]. Self-assembly for coordination polymers is a useful method due to the following reasons: (1) a wide variety of frameworks can be realized from simple building blocks of metal, organic bridging ligand (such as dicarboxylic acid), and counter cation; (2) easy and rational modification of organic bridging ligand is possible; (3) interactions such as M–M bond and van der Waals interactions are available. Carboxylate groups present various coordination modes, leading to the formation of mononuclear, binuclear, and polymeric compounds. Recently, building blocks with heterocyclic acids, such as pyridine, pyrazole, and imidazole-carboxylic acids have been used in the construction of coordination polymers with 1-D-, 2-D-, and 3-D-networks [16–18]. There are numerous examples with suitable transition metal ions in which $(pzdc)^{2-}$ has played different coordination roles [19–22]. In this article, we report the synthesis and systematic structural behavior of a manganese compound.

2. Experimental

2.1. *Materials and physical measurements*

All reagents used in the syntheses were purchased commercially and used as received. Infrared spectrum ($4000–600\,\mathrm{cm^{-1}}$) was recorded on a Buck 500 scientific spectrometer using KBr disc. Elemental analysis was carried out with a Thermo Finnigan Flash-1112EA microanalyzer. The X-ray diffraction data were collected with a Bruker SMART CCD diffractometer. The thermogravimetric (TG) runs were taken on a TGA-50/50 H standard type thermal analysis system. The compound was heated to 1000°C in nitrogen at a heating rate of $10\,\mathrm{K\,min^{-1}}$. A Model 794 Metrohm Basic Titrino was attached to a combined glass-calomel electrode mounted in an air-protected, sealed, thermostated jacketed cell maintained at 25.0°C ± 0.1°C by circulating water, from a constant-temperature bath (Fisherbrand model FBH604, LAUDA, Germany) equipped with a stirrer and a 10,000 mL-capacity Metrohm piston buret. The pH meter-electrode system was calibrated to read $-\log\,[H^+]$.

2.2. *Potentiometric equilibrium measurements*

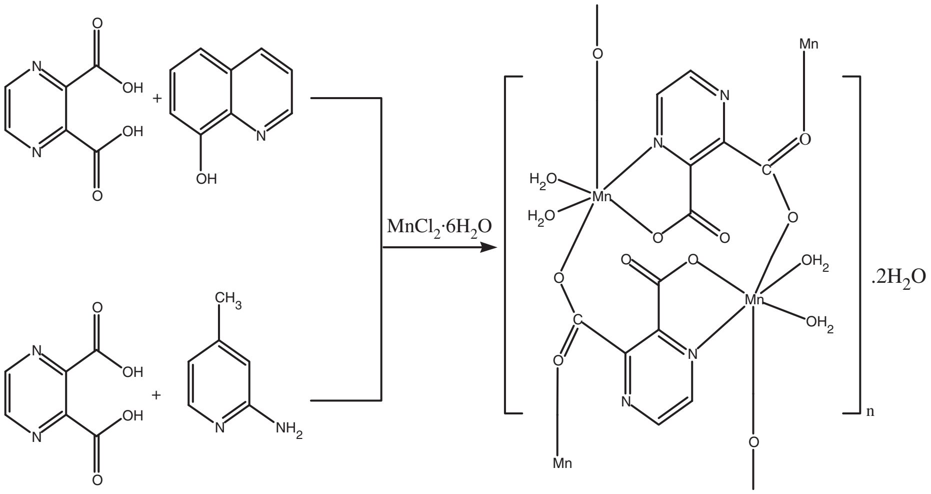
The details are described elsewhere [23–27]. The concentrations of ampy, 8-HQ and $pzdcH_2$ were $2.50 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$, for the potentiometric pH titrations of $pzdcH_2$, ampy, 8-HQ, $pzdcH_2$ + ampy and $pzdcH_2$ + 8-HQ, in the absence and presence of $1.25 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ Mn^{2+}. A standard carbonate-free NaOH solution ($0.1042\,\mathrm{mol\,L^{-1}}$) was used in all titrations. The ionic strength was adjusted to $0.1\,\mathrm{mol\,L^{-1}}$ with KNO_3. Before an experimental point (pH) was measured, sufficient time was allowed to establish equilibrium. Protonation constants of ligands and stability constants of proton transfer and their metal complexes were evaluated using the BEST program described by Martell and Motekaitis [28]. The value of $K_w = [H^+][OH^-]$ used in the calculations was according to our previous study [23–27].

2.3. *Preparation of 1*

A solution of pzdcH$_2$ (0.18 mmol and 0.03 g) and 8-HQ (0.33 mmol, 0.05 g) in water (10 mL) was refluxed for 1 h; then a solution of $MnCl_2 \cdot 6H_2O$ (0.06 mmol, 0.01 g) was added dropwise and refluxing was continued for 6 h at 60°C. The obtained lemon-yellow solution gave needle-like crystals of **1** after slow evaporation of solvent at room temperature. In a similar manner, a solution containing pzdcH$_2$ (0.24 mmol, 0.04 g), ampy (0.41 mmol, 0.05 g), and $MnCl_2 \cdot 6H_2O$ (0.07 mmol, 0.01 g) was applied to obtain **1** (scheme 1). Found: C, 24.9%; H, 3.3%; and N, 9.9%. $C_6H_{10}MnN_2O_{10}$, Calcd C, 24.6%; H, 3.4%; and N, 9.6%.

2.4. *Crystallographic data collection and structure determination*

Single crystal data were collected at 200(2) K on a STOE IPDS 2 diffractometer equipped with graphite-monochromated Mo-Kα radiation. The structure was solved using direct methods and successive Fourier difference synthesis (*SHELXS-97*) [29], and refined using full-matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (*SHELXL-97*) [29]. Hydrogens of C–H groups were placed in calculated positions and subsequently constraited to ride on their parent atoms, with C–H distances of 0.97 A (C–methyl) and the Uiso(H) values set at $1.5U_{eq}$(C–methyl). Hydrogens bonded to O or N were located in a difference map and their positional parameters were defined, with $U_{iso}(H) = 1.2U_{eq}(N)$ and $1.5U_{eq}(O)$. A summary of the crystallographic data is given in table 1.



Scheme 1. The synthesis of $\{[Mn(pzdc)(H_2O)_2] \cdot 2H_2O\}_n$.

Table 1. The summary of crystallographic data for **1**.

Empirical formula	$C_6H_{10}MnN_2O_8$
Formula weight	293.10
Temperature (K)	200(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2(1)/c$
Unit cell dimensions (Å, °)	
a	6.5433(13)
b	7.6704(15)
c	20.472(4)
α	90
β	92.93(3)
γ	90
Volume (Å^3), Z	1026.1(4), 4
Calculated density (mg m^{-3})	1.897
Absorption coefficient (mm^{-1})	1.323
F(000)	596
θ range for data collection (°)	1.99–30.54
Limiting indices	$-9 \le h \le 8$; $-10 \le k \le 10$; $-29 \le l \le 29$
Reflections collected	32,299
Independent reflection	3112 [R(int) = 0.0980]
Completeness to $\theta = 30.54$ (%)	99.1
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3112/0/186
Goodness-of-fit on F^2	1.144
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0509$, $wR_2 = 0.0980$
R indices (all data)	$R_1 = 0.0562$, $wR_2 = 0.0999$
Largest difference peak and hole (e Å^{-3})	0.501 and −0.632

3. Results and discussion

3.1. *Infrared spectrum*

The most diagnostic IR bands of $\{[Mn(pzdc)(H_2O)_2] \cdot 2H_2O\}_n$ correspond to the stretching vibration of carboxyl in the expected regions. The difference ($\Delta\nu$) between the asymmetric stretching vibration (ν_{asym}) and symmetric stretching vibration (ν_{sym}) of carboxylate reveals the coordination mode. Here, the $\Delta\nu$ value is 130 cm^{-1} suggesting bidentate binding of the carboxylate to manganese. The C≡N, C=C, and OCO stretching bands of free pzdcH$_2$ at 1753, 1715, and 1690 cm^{-1} were three bands from 1640 to 1594 cm^{-1} in **1**. The ν_{asym} OCO was at 1594 and ν_{sym} OCO at 1464 cm^{-1}. Another feature of the IR spectrum of **1** is a broad band centered at 3306 cm^{-1} due to the −OH stretching vibration of coordinated water and/or crystallization water. The spectroscopic data of **1** are in good agreement with X-ray diffraction results.

3.2. *Description of crystal and molecular structure*

Selected bond distances and angles together with intermolecular hydrogen-bond distances are listed in tables 2 and 3. Mn(II) is coordinated by one nitrogen and five oxygens in a distorted octahedral configuration. Each (pzdc)$^{2-}$ is coordinated by three Mn(II) centers through oxygen. Axial positions consist of oxygens of two (pzdc)$^{2-}$ which play bridging roles with bond distances of 2.2120(18) and 2.1567(18) Å

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

Mn1–O5	2.119(2)	O5–Mn1–O6	97.77(8)
Mn1–O6	2.1501(19)	O5–Mn1–O2	88.65(8)
Mn1–O2^{i}	2.1567(18)	O6–Mn1–O2^{i}	86.95(8)
Mn1–O4	2.1626(19)	O6–Mn1–O4	95.25(7)
Mn1–O1^{ii}	2.2120(18)	O5–Mn1–O4	166.62(8)
Mn1–N1	2.302(2)	O2^{i}–Mn1–O4	95.13(7)
Mn1^{ii}–O1	2.2120(18)	O5–Mn1–O1^{ii}	85.21(8)
Mn1^{i}–O2	2.1567(18)	O6–Mn1–O1^{ii}	79.36(8)
O2^{i}–Mn1–O1^{ii}	164.08(7)	O6–Mn1–N1	166.02(8)
O5–Mn1–N1	93.18(8)	O2^{i}–Mn1–N1	102.03(8)
O4–Mn1–O1^{ii}	94.19(7)	O4–Mn1–N1	73.49(7)
O1^{ii}–Mn1–N1	92.98(7)		

Symmetry transformations used to generate equivalent atoms: i: $-x, -y+2, -z+1$; ii: $-x+1, -y+2, -z+1$.

Table 3. Hydrogen bond geometry for **1** (Å, °).

D–H···A	D–H	H···A	D···A	D–H···A
O5–H5A···O8^{i}	0.832(17)	1.90(2)	2.707(3)	163(4)
O5–H5B···O3^{i}	0.80(4)	1.90(4)	2.687(3)	173(4)
O6–H6A···O8^{ii}	0.833(17)	1.846(17)	2.678(3)	177(3)
O7–H7A···N2^{iii}	0.829(17)	2.181(19)	2.985(3)	164(3)
O7–H7B···O1^{iv}	0.825(16)	2.036(19)	2.837(3)	164(3)

Symmetry codes: i: $x, y+1, z$; ii: $-x, y+1/2, -z+1/2$; iii: $-x+1, -y+2, -z+1$; iv: $x, -y+3/2, z-1/2$.

related to Mn1–O1 and Mn1–O2, respectively. This coordination behavior leads to the formation of a ladder-like structure (figure 1). Nitrogen and oxygen of one (pzdc)$^{2-}$ and two water molecules form the equatorial plane with bond distances of 2.302(2), 2.1626(19), 2.119(2), and 2.1501(19) Å related to Mn1–N1, Mn1–O4, Mn1–O5, and Mn1–O6, respectively. As can be seen in figure 2, the Mn–pzdc–Mn parts are rungs of the ladder which are alternately repeated in the crystalline network. The ladder structures are connected to each other *via* hydrogen bonds formed between water and carboxylic oxygen (figure 2). Intermolecular hydrogen bond interactions and Mn–pzdc–Mn covalent bonds have essential roles in the creation of the 3-D supramolecular structure of **1**. A comparison between four coordination compounds of manganese with different carboxylate ligand derivatives (table 4) has been done. Different electron densities of these ligands affect corresponding bond lengths [30–32]. "Water clusters," groups of water molecules held together by hydrogen bonds, have been the subject of a number of experimental and theoretical investigations because of their importance in understanding cloud and ice formation, solution chemistry, and a large number of biochemical processes. "Water clusters" play an important role in the stabilization of supramolecular systems both in solution and in the solid state and there is clearly a need for better understanding of how such aggregates influence the overall structure. Recently, Krygowski *et al.* [33] described the role of water as a "gluing factor" in organic/inorganic crystals because of its readiness to deform from an ideal polar hydrogen bond geometry. This hydrogen bonding interaction can result in the formation of diverse water/water contacts, $(H_2O)_n$. By considering the crystalline

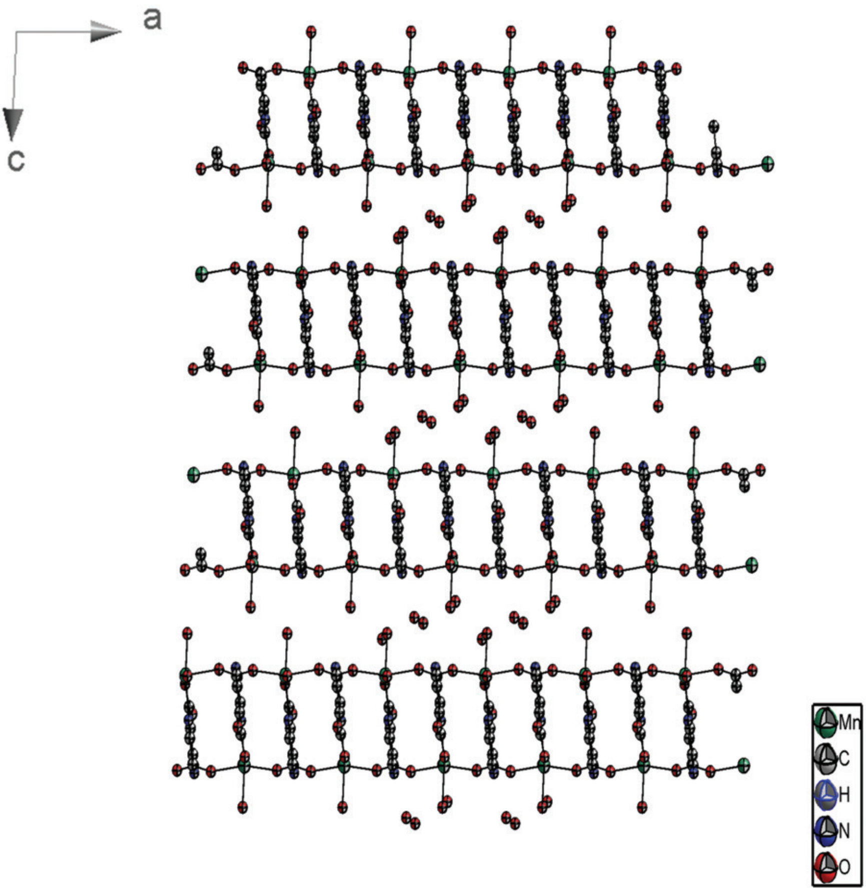


Figure 1. Stereo view of the ladder-like chain of **1**.

network of **1**, we found three types of $(H_2O)_n$ clusters with $n = 3$, 5, and 11. Hence, we have prepared a brief review about the formation of different $(H_2O)_n$ clusters among coordination and proton transfer compounds synthesized by our research group since 2000 [34].

3.3. *Solution studies*

In preliminary experiments, the fully protonated forms of pzdcH$_2$ (L), 8-HQ (Q′), and ampy (Q) were titrated with a standard NaOH aqueous solution in order to obtain some information about their protonation constants as building blocks of the pzdcH$_2$-8-HQ and pzdcH$_2$-ampy proton systems. The protonation constants of pzdcH$_2$ [35], 8-HQ and ampy were calculated by fitting the potentiometric pH data to the BEST program. The results, summarized in table 5, show that the resulting $\log \beta$ values are in satisfactory agreement with those reported for 8-HQ and ampy [36, 37]. Evaluation of equilibrium constants for the reactions of pzdc with 8-HQ and ampy in different protonation forms

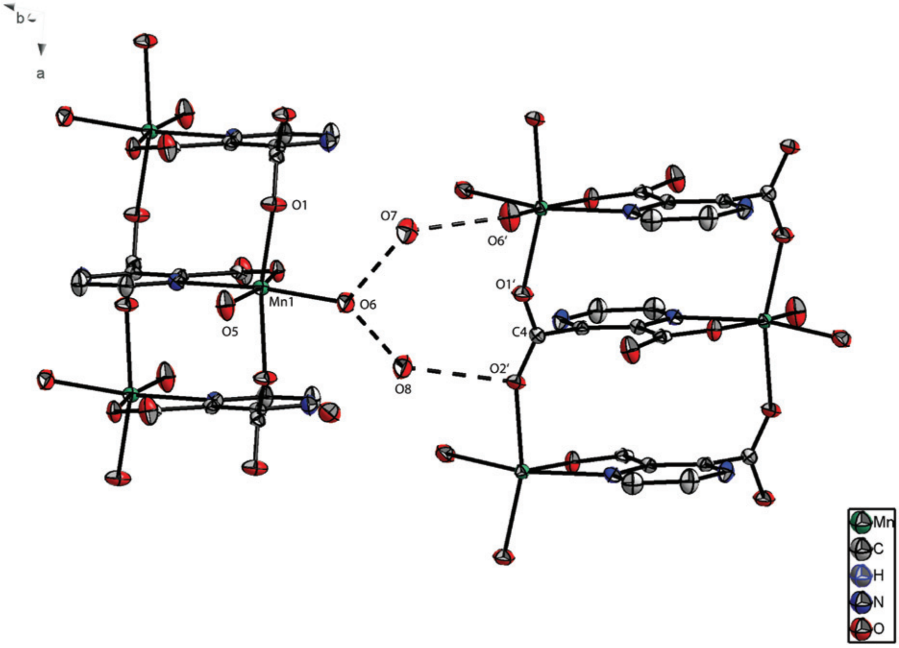


Figure 2. The hydrogen-bond existing between chains in **1**.

Table 4. Comparison between different Mn–O bond lengths. pbc, pdc(pydc), and phen are 3-pyrid-3-ylbenzoic acid, pyridine-2,6-dicarboxylate, and 1,10-phenanthroline, respectively (Å).

Compound	Mn–O1	Mn–O2	Mn–Ow1	Mn–Ow2
$\{[Mn(pzdc)(H_2O)_2]\cdot 2H_2O\}_n$	2.1626(19)	–	2.2808(17)	2.1501(19)
$[Mn(pbc)_2(H_2O)_2]_n$	2.157	2.157	2.194(16)	2.194(16)
$[Mn(pydc)_2(H_2O)_2]$	2.1982(15)	2.1982(15)	2.1331(15)	2.1331(15)
$[Mn(pdc)(phen)_2]\cdot CH_3OH$	2.2792(12)	2.2792(12)	–	–

was accomplished through comparison of calculated and experimental pH profiles, obtained with both pzdcH$_2$ and 8-HQ or pzdcH$_2$ and ampy present [23, 38, 39]. The results are shown in table 5. The corresponding species distribution diagrams for pzdcH$_2$-8-HQ and pzdcH$_2$-ampy are shown in figure 3. For pzdcH$_2$-8-HQ, the most abundant proton transfer species present at pH 7–7.5 (29.8%), 3.9–4.1 (7.4%) are 8-HQpzdcH ($\log K = 2.40$) and 8-HQpzdcH$_2$ ($\log K = 1.66$), and for pzdcH$_2$-ampy at: pH 2.4 (12.4%) is ampyHpzdcH ($\log K = 1.94$). Thus, the solution studies provide additional evidence for the association of 8-HQ + pzdcH$_2$ or ampy + pzdcH$_2$ supporting the evidence from the solid state studies. In order to determine the stoichiometry and stability of the metal ion complexes with pzdcH$_2$-8-HQ and pzdcH$_2$-ampy proton transfer systems in aqueous solution, potentiometric titration of each ligand in the presence of metal ion in a binary system must be carried out. 8-HQ and pzdcH$_2$ interact weakly with Mn^{2+} and ampy does not interact with it. The equilibrium potentiometric pH titration curves of pzdcH$_2$-ampy or pzdcH$_2$-8-HQ were obtained in the absence and presence of the Mn^{2+} ion. For these

Table 5. Overall and stepwise protonation constants for pzdcH$_2$, 8-HQ, and ampy, and recognition constants of interaction between pzdcH$_2$-8-HQ and pzdc-ampy at 25°C and $\mu = 0.1\,\mathrm{mol\,L^{-1}}$ KNO$_3$.

Stoichiometry								
8-HQ	PzdcH$_2$	ampy	h	$\log\beta$	Equilibrium quotient K	$\log K$	Max (%)	At pH
1	0	0	1	9.35	–	9.35	98.4	7.2
1	0	0	2	14.49	–	5.14	99.9	2.0
0	1	0	1	3.17	–	3.17	76.7	2.4
0	1	0	2	4.69	–	1.52	23.9	2.0
1	1	0	1	11.75	[8-HQpzdcH]/[8-HQH][pzdcH$_2$]	2.40	29.8	7–7.5
1	1	0	2	16.15	[8-HQpzdcH$_2$]/[8-HQH][pzdcH]	3.63	7.4	3.9–4.1
					[8-HQpzdcH$_2$]/[8-HQH$_2$][pzdcH$_2$]	1.66		
0	0	1	1	7.17	–	7.17	99.8	3.8–4.3
0	0	1	2	8.10	–	0.93	7.7	2.0
0	1	1	2	12.28	[ampypzdcH$_2$]/[ampyH][pzdcH]	1.94	12.4	2.4

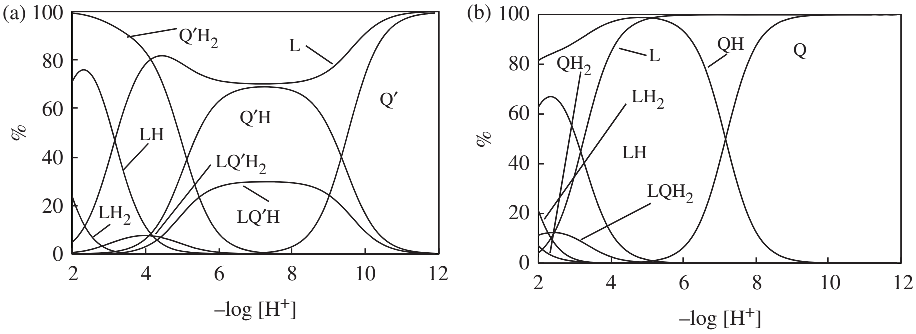


Figure 3. Distribution diagrams of proton transfer interaction of pzdcH2 (L) with 8-HQ (Q′) (a) and ampy (Q) (b).

systems, weak interactions with Mn^{2+} ion were observed. The cumulative stability constants of M$_m$L$_l$Q$_q$H$_h$, complexes β_{mlqh}, are defined in our previous publications [23]. M, L, Q, and H are metal ions, pzdcH$_2$ the second ligand and proton, respectively, and m, l, q, and h are the respective stoichiometric coefficients. The cumulative stability constants were evaluated by fitting the corresponding pH titration curves to the BEST program, and the resulting values for the most likely complexed species in aqueous solutions are included in tables 6 and 7. The corresponding species distribution diagrams for pzdcH$_2$, pzdcH$_2$-8-HQ, and pzdcH$_2$-ampy with Mn^{2+} ion are shown in figure 4(a)–(c). Obvious from figure 4(a) and table 6 for the pzdcH$_2$-Mn binary system, the most likely species are: MnL$_2$, MnL$_2$H, and MnLH$_{-1}$. The results for 8-HQ–Mn^{2+} are shown in table 6 with the most likely species: MnQ′H, MnQ′, MnQ′$_2$, and MnQ′$_2$H. From figure 4(a)–(c) and tables 6 and 7, the binary species including ML$_2$ and ML$_2$H, which are observed in solid state, are abundant in solution, although the ternary species are observed in some cases also.

3.4. *Thermogravimetric analysis studies*

Thermogravimetric analysis (TGA) for **1** was performed from 5°C to 1000°C (figure 5). The TG curve shows three steps of weight loss. At first step, **1** lost two coordinated

Table 6. Overall stability constants for 8Q/pzdc/Mn^{2+} binary and ternary systems at 25°C and $\mu = 0.1\,mol\,L^{-1}$ KNO_3.

System	*m*	*l*	*q*	*h*	log *β*	Max (%)	At pH
Mn–8-HQ	1	0	1	0	5.67	Negligible	<4.7
	1	0	1	1	12.60	47.0	>4.7
	1	0	2	0	10.62	Negligible	<4.7
	1	0	2	1	15.26	Negligible	<4.7
Mn–pzdcH$_2$	1	2	0	0	5.40	35.8	4.8–5
	1	2	0	1	8.67	17.6	3.0
	1	1	0	−1	−3.54	99.4	>8.9
Mn–pzdcH$_2$–8-HQ	1	1	1	0	7.77	Negligible	<4.2
	1	1	1	1	12.64	Negligible	<4.2
	1	1	1	2	20.28	40.2	3.5
	1	2	1	0	14.62	14.4	4.2
	1	2	1	1	18.83	1.8	4.2

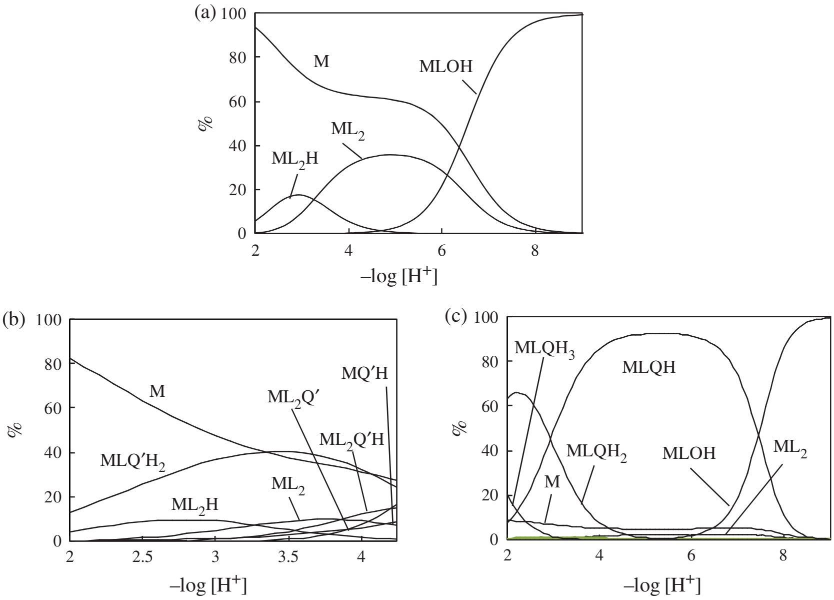


Figure 4. Distribution diagrams of pzdcH$_2$ (L)/Mn^{2+}: (a) binary system, pzdcH$_2$(L)/8-HQ (Q‘)/M = Mn^{2+} (b) and pzdcH$_2$(L)/ampy(Q)/M = Mn^{2+}, (c) ternary systems.

water molecules and two non-coordinated water molecules at 100°C (found: 18%, Calcd 19.6%); in the second step $(pzdc)^{2-}$ decomposed at 250°C (found: 23%, Calcd 30%). The final residue was MnO_2 with weight loss of 75% (Calcd 80.03%).

4. Conclusion

A metal–organic polymer, **1**, was obtained by the treatment of $MnCl_2 \cdot 6H_2O$ with H$_2$pzdc, 8-HQ and ampy. Treatment of both ligands with Mn(II) leads to the formation

Table 7. Overall stability constants for ampy/pzdc/Mn^{2+} ternary systems at 25°C and $\mu = 0.1\,mol\,L^{-1}$ KNO_3.

System	*m*	*l*	*q*	*h*	log *β*	Max (%)	At pH
Mn–pzdcH$_2$–ampy	1	1	1	1	14.24	92.4	5.1–5.6
	1	1	1	2	17.18	65.8	2.2
	1	1	1	3	18.70	20.4	2.0

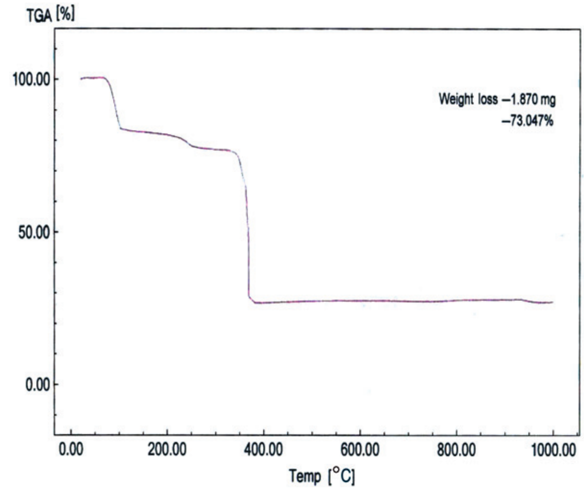


Figure 5. The TGA curve for **1**.

of the same products (scheme 1). The $(pzdc)^{2-}$ coordination leads to the formation of a 1-D ladder-like polymer. X-ray crystallography shows that two types of bonds, hydrogen bonding and covalent bonds effect formation of the 3-D supramolecular structure. The TG curve shows that **1** exhibits three steps of weight loss and is quite thermally stable. A comparison between the stoichiometry of the crystalline compound and that of the most abundant species detected in solution phase clearly reveals that the most abundant species existing in aqueous solution possesses a stoichiometry similar to that of the compounds obtained in the single crystal X-ray diffraction studies.

Supplementary material

CCDC no. 760088 for Mn(II) contains the supplementary crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0) 1223 336033; Email: deposit@ccdc.cam.ac.uk].

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