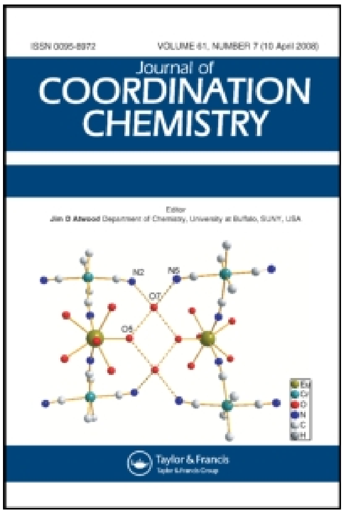

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Synthesis and characterization of one-dimensional coordination polymers, $[M(sac)_2(\mu\text{-pyz})(H_2O)_2]$<i>_n [M=Zn^{II}, Cd^{II}, pyz = pyrazine, and sac = saccharinate]

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Synthesis and characterization of one-dimensional coordination polymers, $[M(sac)_2(\mu\text{–}pyz)(H_2O)_2]_n$ $[M = Zn^{II}, Cd^{II}$, pyz = pyrazine, and sac = saccharinate]

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Two new coordination polymers, $[M(sac)_2(\mu\text{–}pyz)(H_2O)_2]_n$ $[M{=}Zn^{II}$(**1**), Cd^{II}(**2**), pyz = pyrazine, and sac = saccharinate], have been prepared and characterized by elemental analysis, FTIR spectroscopy, thermal analysis and single crystal X-ray diffraction. Both complexes are isomorphous and crystallize in the triclinic $P\bar{1}$ space group. The metal(II) ions are octahedrally coordinated by two sac, two aqua and two pyz ligands. The sac ligands are N-coordinated, while the pyz ligands are bridges between the metal centers, leading to one-dimensional linear chains. Intra-chain M–M separations in **1** and **2** are 7.218 and 7.498 Å, respectively. The individual chains are linked by strong OW–H ⋯ O(sac) hydrogen bonds into two–dimensional layers, which are further assembled into three–dimensional supramolecular networks by aromatic π(sac) ⋯ π(sac) stackings interactions.

Keywords: Saccharinate; Pyrazine; Coordination polymer; One-dimensional chain; Crystal structure

1. Introduction

Coordination polymers have been studied because of their attractive network structures and potential applications as functional materials in catalysis, conductivity, magnetism, optical behaviors, etc. [1–10].

Saccharinate (sac) is the anion of the artificial sweetener saccharin (also named *o*–benzosulfimide) and has attracted attention in coordination chemistry [11]. The negatively charged imino nitrogen and the carbonyl and sulfonyl oxygens,

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readily coordinate various metal ions, exhibiting different coordination modes from monodentate (through the *N*– or the carbonyl *O*–atom), to bridge forming. In addition to its polyfunctional ligand character, the donor sites in sac also act as hydrogen bond acceptors to generate supramolecular networks.

We have prepared and characterized a number of metal-sac complexes during the last decade [11]. In this work, we synthesized two new coordination polymers assembled from pyrazine (pyz), and zinc(II)- and cadmium(II)-saccharinates, since it is well documented that pyz is a rod-like bifunctional ligand usually acting as a bridge between the metal centers [12–15]. The present paper reports preparations, crystal structures, spectral and thermal properties of $[Zn(sac)_2(\mu\text{–}pyz)(H_2O)_2]_n$ (**1**) and $[Cd(sac)_2(\mu\text{–}pyz)(H_2O)_2]_n$ (**2**).

2. Experimental

2.1. *Materials and measurements*

All reagents were commercially available and used without further purification. The starting complex $[M(sac)_2(H_2O)_4]\cdot 2H_2O$, where M is Zn^{II}, or Cd^{II}, was prepared according to literature methods [16, 17]. Elemental analyses (C, H and N) were carried out on an Elementar Vario EL elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} using a Mattson 100 FTIR spectrophotometer. Thermal analysis curves (TG and DTA) were obtained using a Rigaku TG8110 thermal analyzer in a static air atmosphere at a heating rate of 10°C min^{-1}.

2.2. *Synthesis of 1 and 2*

Pyrazine (0.16 g, 2.0 mmol) was added drop–wise to a solution of $[Zn(sac)_2(H_2O)_4]\cdot 2H_2O$ (0.54 g, 1 mmol) in a aqueous solution of MeOH (30 cm^3, $H_2O : MeOH = 6 : 1$) and the reaction mixture was stirred for 15 min at room temperature. The resulting solution was allowed to stand at room temperature and X–ray quality crystals were formed after a few days. Yield 80% (Found: C, 39.4, H, 3.0, N, 10.5; $C_{18}H_{16}N_4O_8S_2Zn$ Calcd: C 39.6, H 2.9, N 10.3%).

The preparation method for **2** was the same as described for **1**, but $[Zn(sac)_2(H_2O)_4]\cdot 2H_2O$ was replaced by $[Cd(sac)_2(H_2O)_4]\cdot 2H_2O$. Yield 90% (Found: C, 36.3, H, 3.0, N, 9.7; $C_{18}H_{16}N_4O_8S_2Cd$ Calcd: C 36.5, H 2.7, N 9.5%).

2.3. *X-ray structure determination*

Intensity data for the complexes were collected using a STOE IPDS 2 diffractometer at 293 K. The structure was solved and refined using SHELXS-97 and SHELXL-97 [18]. All non-hydrogen atoms were found on the difference Fourier map and refined anisotropically. All CH hydrogen atoms were included using a riding model, while

Table 1. Crystallographic data for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{18}H_{16}N_4O_8S_2Zn$	$C_{18}H_{16}N_4O_8S_2Cd$
M_r	545.84	592.87
T(K)	293(2)	293(2)
Radiation, λ (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	7.2184(8)	7.4980(6)
b	7.6601(10)	7.7578(7)
c	10.6297(14)	10.5603(9)
α	106.400(10)	104.016(7)
β	95.799(10)	96.294(6)
γ	108.614(9)	110.306(7)
V (Å^3)	522.40(11)	546.14(9)
Z	1	1
D_c (g cm^{-3})	1.735	1.803
μ (mm^{-1})	1.432	1.245
F(000)	278	296
Crystal size (mm^3)	0.50 × 0.38 × 0.24	0.29 × 0.24 × 0.15
θ range (°)	3.05/26.00	2.03/27.87
Index range (h, k, l)	−8/8, −9/9, −13/13	−9/9, −10/10, −13/13
Reflections collected	11216	9432
Independent reflections (R_{int})	1729 (0.0870)	2589 (0.0740)
Absorption correction	numerical	numerical
Min. and max. transmissions	0.526 and 0.734	0.510 and 0.843
Data/restraints/parameters	1729/159	2589/163
Goodness–of–fit on F^2	1.041	1.076
R indices [$I > 2\sigma(I)$]	0.0322	0.0337
R indices (all data)	0.0345	0.0350
wR indices (all data)	0.0873	0.0857
Largest diff. peak and hole (e Å^{-3})	0.348 and −0.612	1.759 and −0.916

water hydrogen atoms are refined freely. The details of data collection, refinement and crystallographic data are summarized in table 1.

3. Results and discussion

3.1. *Synthesis*

Complexes **1** and **2** were obtained in yields over 80% by the reaction of $[M(sac)_2(H_2O)_4] \cdot 2H_2O$, ($M{=}Zn^{II}$, and Cd^{II}) with pyz in solution at room temperature. The analytical data (C, H, and N) are consistent with the expected formulations of these complexes and confirmed by single crystal X-ray analysis. Both complexes are non-hygroscopic and stable in air at room temperature. These complexes are slightly soluble in water, but highly soluble in warm water.

3.2. *IR spectra*

Complexes **1** and **2** show a number of strong absorption bands in the frequency range 3360 and 3550 cm^{-1}, assigned to the ν(OH) vibrations of the aqua ligands. Several weak bands between 3016 and 3153 cm^{-1} are attributed to the aromatic ν(CH). The carbonyl group of the *N*-coordinated sac ligand is characterized by very strong bands at 1636 and 1656 cm^{-1}. Two sharp split bands at ca. 1290 and 1260 cm^{-1} correspond to the asymmetric stretching vibrations of the sulfonyl group, while the symmetric stretching vibrations of SO_2 appear at 1165 cm^{-1}. The bands centered at 1460, 1120 and 1055 cm^{-1} are assignable to pyz.

3.3. *Description of the crystal structures*

Since complexes **1** and **2** are isomorphous and crystallizes in the triclinic crystal system $P\bar{1}$, only the figures corresponding to **1** are presented in figures 1–3. Selected bond distances and angles for both complexes are listed in table 2. The coordination geometry around the zinc(II) ion is shown in figure 1. The zinc(II) and cadmium(II) ions are six–coordinate with two aqua, two sac and two pyz ligands forming a distorted MN_4O_2 core. The structure of both complexes consists of linear chains with alternating [M(sac)$_2$(H$_2$O)$_2$] units and bridging pyz ligands, extending along the crystallographic *a* axis (see figure 2 for **1**).

Intra-chain M–M separations in **1** and **2** are 7.218 and 7.498 Å, respectively. The sac behaves as a monodentate ligand through the negatively charged imino N atom. M–N$_{\mathrm{sac}}$ bond distances are 2.208(2) and 2.326(2) Å in **1** and **2**, respectively, and are almost identical to the corresponding distances in the starting complexes, *viz.* 2.200(4) Å in [Zn(sac)$_2$(H$_2$O)$_4$] · 2H$_2$O and 2.323 Å in [Cd(sac)$_2$(H$_2$O)$_4$] · 2H$_2$O [17]. The Zn–N$_{\mathrm{pyz}}$ bond distance of 2.214(2) Å is slightly shorter than that observed in [Zn(pyz)$_2$(H$_2$O)$_4$] · pht (pht = 1,2-benzenedicarboxylate) [19], while the Cd–N$_{\mathrm{pyz}}$

Table 2. Selected bond lengths (Å), angles (°), and the hydrogen bonding geometry for **1** and **2**.$^{\mathrm{a}}$

	1		**2**	
M1–N1	2.208(2)		2.326(2)	
M1–N2	2.214(2)		2.367(2)	
M1–OW1	2.081(2)		2.310(2)	
M1–M1$^{\mathrm{i(a,\ b)}}$	7.218		7.498	
N1–M1–N2	92.05(7)		87.40(8)	
N1–M1–OW1	86.37(8)		94.96(8)	
N2–M1–OW1	87.42(6)		86.38(7)	
N1–M1–N2$^{\mathrm{i(a,\ b)}}$	87.95(7)		92.60(8)	
N1–M1–OW1$^{\mathrm{i(a,\ b)}}$	93.63(8)		85.04(8)	
N2 –M1– OW1$^{\mathrm{i(a,\ b)}}$	92.58(6)		93.62(7)	
Hydrogen bonds D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
1				
O1W–H1W···O1	0.84(5)	1.78(5)	2.589(3)	161(4)
O1W–H2W···O3$^{\mathrm{ii}}$	0.80(4)	2.08(4)	2.778(2)	146(4)
O1W–H2W···O3$^{\mathrm{i}}$	0.80(4)	2.62(4)	3.142(3)	125(3)
2				
O1W–H1W···O3$^{\mathrm{ib}}$	0.81(4)	1.84(2)	2.650(4)	169(5)
O1W–H2W···O2$^{\mathrm{iii}}$	0.81(4)	2.02(3)	2.779(3)	155(5)

Symmetry operations: ($^{\mathrm{ia}}$) $1-x$, $1-y$, $1-z$ for **1**, and ($^{\mathrm{ib}}$) $-x$, $-y$, $-z$ for **2**; ($^{\mathrm{ii}}$) x, $1+y$, z; ($^{\mathrm{iii}}$) $-x$, $-1-y$, $-z$.

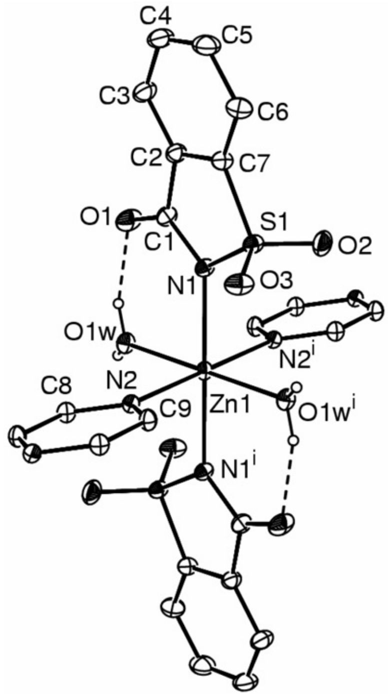

Figure 1. The building block and coordination environment of Zn^{II} in **1** with the atom labeling scheme. Symmetry code (i) = $1-x$, $1-y$, $1-z$. All the C–H hydrogen atoms are omitted for clarity.

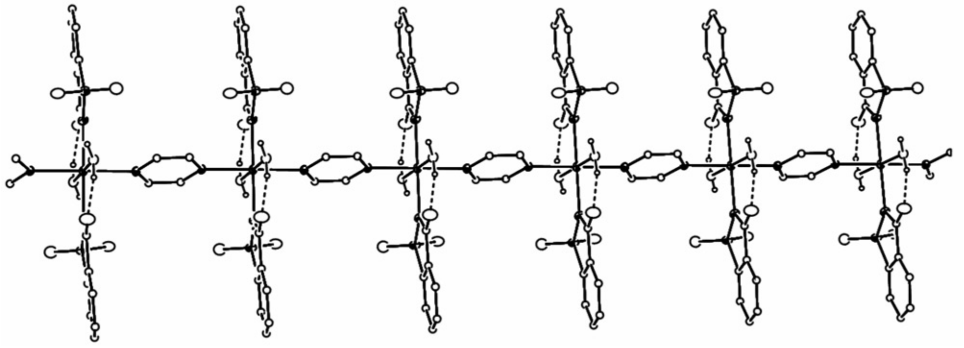

Figure 2. One-dimensional linear chain of **1**.

bond distance of 2.367(2) Å is similar to those of pyz complexes of cadmium(II) halides [20].

As shown in figure 3, in the solid state, linear polymeric chains are oriented parallel and interact by strong OW–HW $\cdots$ O hydrogen bonding through their water hydrogens and sulfonyl groups to construct two-dimensional layers, extending along the *bc* plane. This results in interchain M–M separations of 7.660 Å in **1** and 7.758 Å in **2**. The parallel oriented layers are further assembled into three-dimensional

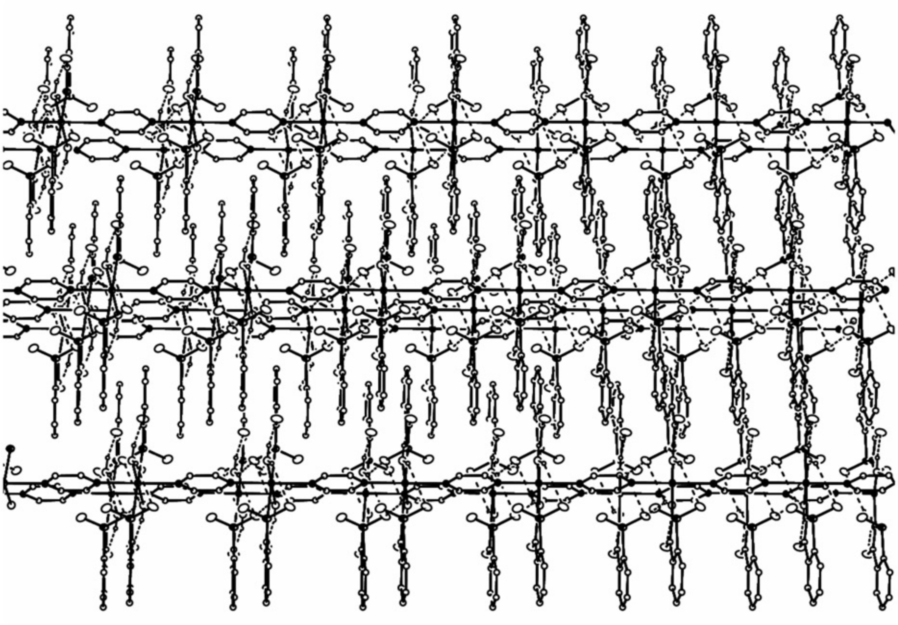

Figure 3. Packing of chains in **1**, viewed down the *b* axis, *via* hydrogen bonds and aromatic π–π stacking interactions.

networks by aromatic $\pi \cdots \pi$ stacking interactions between the planar phenyl rings of the sac ligands. The distance between the centroids of the phenyl rings is in the range 3.72–3.96 Å.

3.4. *Thermal behavior*

Thermal decomposition curves (DTA and TG) of **1** and **2** are illustrated in figure 4. Complex **1** undergoes five-step decomposition. The first two steps between 100–307°C correspond to dehydration and depyrazination, which are accompanied by endothermic DTA peaks at 153, 189 and 216°C. The mass loss value of 20.9% is in good agreement with the calculated mass loss value of a pyz and two H_2O molecules. The intermediate zinc(II) saccharinate is stable to 383°C and then decomposes in two stages: an endothermic one in the range 383–483°C and a highly exothermic one in the range 383–613°C, similar to $[Zn(sac)_2(H_2O)_4] \cdot 2H_2O$ [21]. The decomposition of **1** is complete at 613°C and the total experimental mass value of 84.4% agrees well with the calculated value of 85.1%, assuming that the remaining residue is ZnO.

Complex **2** shows step-wise decomposition (figure 4) with endothermic dehydration in the first step between 160 and 150°C with a mass loss of 6.0% (Calcd 6.1%). The intermediate formed at the end of the first step is assumed to be $[Cd(sac)_2(\mu\text{–}pyz)]$, which decomposes endothermically in the range 221–261°C to $Cd(sac)_2$. The observed mass loss 13.3% for depyrazination agrees well with the calculate value of 13.5%. The decomposition of $Cd(sac)_2$ takes place in two steps in the range 361–627°C with an

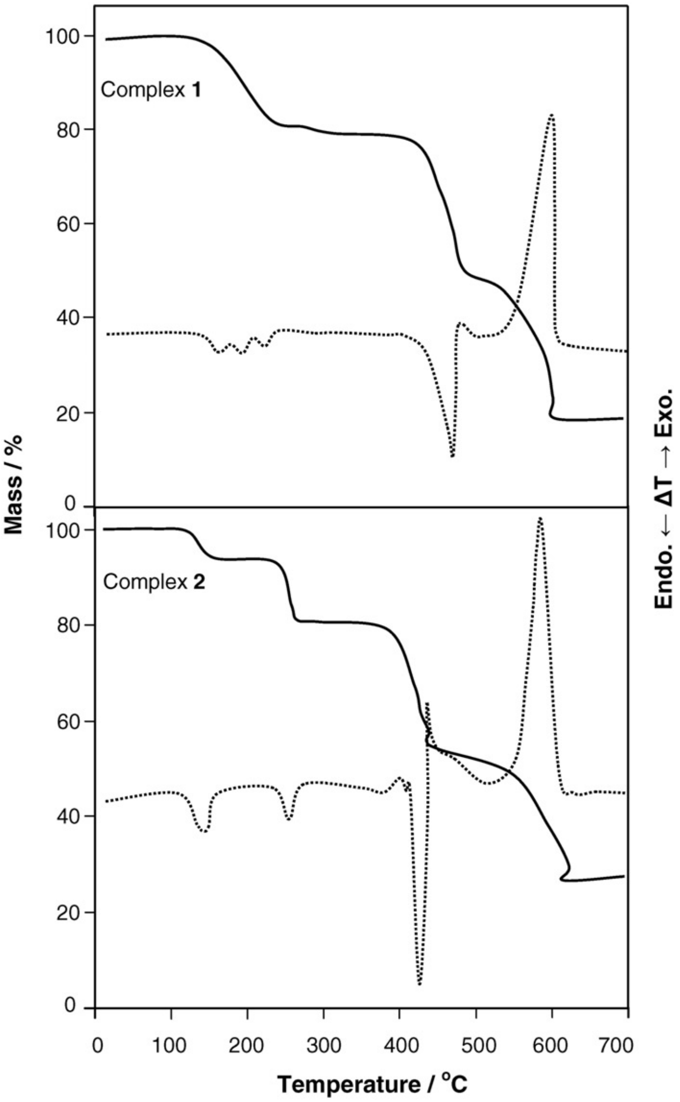

Figure 4. DTA and TG curves of **1** and **2**.

endothermic peak at 421°C and an exothermic peak at 600°C. Total mass loss of 77.8% (Calcd 78.3%) suggests formation of CaO as the end product.

Supplementary material

Crystallographic data for the structures reported in the article have been deposited at the CCDC as supplementary data, CCDC Nos. 658920 (**1**) and 658921 (**2**). Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Email: deposit@ccdc.cam.ac.uk.

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