

Synthesis and crystal structures of four transition metal complexes with 1,4,5,6-tetrahydro-6-oxo-3-pyridazinecarboxylic acid

Xiaoge Bao^a, Xiuqing Zhang^{a,c}, Qing Yu^{a*}, Hedong Bian^{a,b} and Hong Liang^{b*}

^aCollege of Chemistry and Chemical Engineering, Guangxi Normal University, Guilin 541004, P. R. China

^bKey Laboratory for Chemistry and Molecular Engineering of Medicinal Resources, Ministry of Education of China, Guangxi Normal University, Guilin, Guangxi 541004, P. R. China

^cCollege of Chemistry and Bioengineering, Guilin University of Technology, Guilin 541004, P. R. China

Four transition metal complexes [Zn(topca)₂(H₂O)₂], [Zn(topca)₂(H₂O)₂·2H₂O], [Ni(topca)₂(H₂O)₂·2H₂O] and [Cd(topca)₂(H₂O)₂], (Htopca = 1,4,5,6-tetrahydro-6-oxo-3-pyridazinecarboxylic acid), have been synthesised and their X-ray structures determined. The complexes are isomorphous, and the metal centres are six-coordinated with two pyridazinyl N atoms, two carboxyl O atoms from two ligands and two water molecules.

Keywords: crystal structures, 1,4,5,6-tetrahydro-6-oxo-3-pyridazinecarboxylic acid, transition metal, thermal analyses

Recently, studies on the synthesis of metal–organic frameworks from transition metals and organic ligands have received much attention in coordination chemistry because of their interesting molecular topologies and their potential applications in catalysis, molecular selection, non-linear optics, ion exchange and microelectronics.^{1–5} Nitrogen heterocycles substituted in the 3-position with carboxylic acid groups are frequently used as ligands in coordination chemistry with a variety of metals.^{6–8} Many complexes with pyridazine-3-carboxylate and water ligands have been obtained. In these complexes, the metal:ligand ratio is normally 1:2,^{9–11} and the *trans*-coordination mode is frequently found. However, other structures and stoichiometries are possible.¹² In order to explore the different coordination modes of pyridazine carboxylic acid with metals, we have synthesised a series of new complexes using 1,4,5,6-tetrahydro-6-oxo-3-pyridazine carboxylic acid as ligand precursor.

Experimental

1,4,5,6-Tetrahydro-6-oxo-3-pyridazinecarboxylic acid was prepared according to ref.13. All reagents and other solvents were of reagent-grade quality from commercial sources and were used as received.

IR spectra were taken on a Perkin-Elmer Spectrum One FT-IR spectrometer in the 4000–400 cm⁻¹ region as KBr pellets. TG-DTA was carried out in N₂ with 5 °C/min heating in the temperature range of 30–300 °C and 10 °C/min in the range of 300–900 °C. Elemental analyses for C, H and N atoms were carried out on a Model 2400 II Perkin-Elmer elemental analyser.

[Zn(topca)₂(H₂O)₂] (1): A solution of ZnCl₂·2H₂O (0.0863 g, 0.5 mmol) in water (10 mL) was slowly added to a solution of Htopca (0.1420 g, 1.0 mmol) in ethanol (7 mL) under stirring at room temperature. The mixture was sealed in a 25 mL Teflon-lined stainless steel vessel and heated under autogenous pressure at 90 °C for 6 days, and then slowly cooled to room temperature. The colourless crystals obtained were filtered off, washed with ethanol and dried in air. Yield: 36% on the basis of Htopca. Anal. Calcd for C₁₀H₁₄N₄O₈Zn: C, 31.30; H, 3.69; N, 14.61. Found: C, 31.25; H, 3.63; N, 14.65%. IR data (KBr, cm⁻¹): 3259(br), 2925(m), 1702(s), 1664(ms), 1400(m), 1291(m), 1225(m), 1168(ms), 832(w).

[Zn(topca)₂(H₂O)₂·2H₂O] (2): Htopca (0.1420 g, 1.0 mmol) in water (5 mL) was added to an aqueous solution (10 mL) containing ZnCl₂·2H₂O (0.0861 g, 0.5 mmol). The mixture was refluxed for 2 h and then filtered. The colourless single crystals were obtained by slow evaporation of the filtrate at room temperature. Yield: 75% on the basis of Htopca. Anal. Calcd for C₁₀H₁₈N₄O₁₀Zn: C, 28.62; H, 4.33; N, 13.35. Found: C, 28.57; H, 4.26; N, 13.38%. IR data (KBr, cm⁻¹): 3424(m), 3246(br), 1686(s), 1650(m), 1616(ms), 1397(m), 1319(m), 1225(m), 1166(m), 845(w), 747(w), 648(w).

[Ni(topca)₂(H₂O)₂·2H₂O] (3): Prepared by a similar procedure as described for (2), with ZnCl₂·2H₂O replaced by Ni(OAc)₂·4H₂O

(0.1245 g, 0.5 mmol). Green block-shaped crystals of (3) were obtained. Yield: 78% on the basis of Htopca. Anal. Calcd for C₁₀H₁₈N₄NiO₁₀: C, 29.06; H, 4.36; N, 13.56. Found: C, 29.01; H, 4.30; N, 13.63%. IR data (KBr, cm⁻¹): 3422(br), 3257(m), 1686(s), 1651(m), 1400(m).

[Cd(topca)₂(H₂O)₂] (4): Complex (4) was prepared by a similar procedure as described for (2), with ZnCl₂·2H₂O replaced by CdCl₂·2.5H₂O (0.1142 g, 0.5 mmol). Colourless block-shaped crystals of (4) were obtained. Yield: 73% on the basis of Htopca. Anal. Calcd for C₁₀H₁₂CdN₄O₈: C, 27.80; H, 2.80; N, 13.06. Found: C, 27.58; H, 2.76; N, 13.10%. IR data (KBr, cm⁻¹): 3398(br), 3259(m), 1703(s), 1649(m), 1397(m).

Determination of the unit cell and data collection were performed with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) on a Bruker SMART CCD diffractometer equipped with a graphite monochromator. The structures were solved by direct methods, successive Fourier difference synthesis and refined by full matrix least squares based on F^2 using the SHELXTL-97 program package.^{14,15} In all cases, all non-hydrogen atoms were assigned anisotropic thermal parameters. The organic hydrogen atoms were generated geometrically; the hydrogen atoms of the water molecules were located from difference maps and refined with isotropic temperature factors. Crystallographic data are summarised in Table 1. Selected bond lengths and angles are listed in Table 2. CCDC Nos. 636069 (1), 636070 (2), 777738 (3) and 777739 (4). The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or E-mail: deposit@ccdc.cam.ac.uk).

Result and discussion

The X-ray structures analysis revealed that the main structural features of complexes (1), (2), (3), and (4) are similar, except that there are two H₂O molecules in every unit of (2) and (3). Therefore the structural features of the four complexes will be described by that of complex (1). The molecular structure of complex (1) is shown in Fig. 1.

Complex (1) possesses crystallographic C_i symmetry. The two topca ions play the role of bidentate ligands coordinating via a pyridazine N atom and one O atom of the deprotonated carboxylic acid function. Two axial water O atoms complete a distorted octahedron around the Zn^{II} ion. This mode of coordination of 1,4,5,6-tetrahydro-6-oxo-3-pyridazinecarboxylic acid is similar to that found in the complex [Co(topca)₂(H₂O)₂·2H₂O].¹⁶ The Zn–O(carboxylic), Zn–O(water), and Zn–N distances (Table 2) are closely equivalent to distances observed in other monomeric Zn^{II} complexes with pyridazine-3-carboxylate.^{10,11} The M^{II} ion forms a relatively planar five-membered chelate ring M1/O1/C1/C2/N1 with a closed N–M–O angle of 77.69(7)°, 78.66(7)°, 79.8(2)°, 71.79(9)° for (1), (2), (3) and (4), respectively. The mean deviation from planarity is 0.0065 Å, 0.0198 Å, 0.0191 Å, 0.0069 Å for (1), (2), (3) and (4), respectively.

* Correspondent. E-mail: gxnuchem312@yahoo.com.cn

Table 1 Crystal data and structure refinement for complexes (1)–(4)

Complex	(1)	(2)	(3)	(4)
Empirical formula	C ₁₀ H ₁₄ N ₄ O ₈ Zn	C ₁₀ H ₁₈ N ₄ O ₁₀ Zn	C ₁₀ H ₁₈ N ₄ NiO ₁₀	C ₁₀ H ₁₄ CdN ₄ O ₈
Formula weight	383.62	419.65	412.99	430.84
Temperature (K)	298(2)	294(2)	298(2)	294(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>n</i>
<i>a</i> (Å)	4.851(2)	5.598(3)	5.549(2)	4.7663(8)
<i>b</i> (Å)	23.366(9)	18.054(10)	17.828(4)	24.087(4)
<i>c</i> (Å)	6.423(3)	7.999(5)	7.869(2)	6.4647(12)
β (°)	108.836(5)	105.401(8)	105.493(3)	108.035(2)
Volume (Å ³)	689.0(5)	779.4(7)	750.1(4)	705.7(2)
<i>Z</i>	2	2	2	2
Calculated density (Mg/m ³)	1.849	1.788	1.829	2.017
Absorption coefficient (mm ⁻¹)	1.835	1.640	1.360	1.599
<i>F</i> (000)	392	432	428	424
Crystal size (mm ³)	0.54 × 0.50 × 0.30	0.22 × 0.20 × 0.16	0.43 × 0.13 × 0.09	0.28 × 0.16 × 0.14
θ range for data collection (deg)	1.74 ≤ θ ≤ 25.01	2.26 ≤ θ ≤ 26.25	2.28 ≤ θ ≤ 25.01	3.38 ≤ θ ≤ 25.02
Limiting indices	−5 ≤ <i>h</i> ≤ 5 −27 ≤ <i>k</i> ≤ 27 −7 ≤ <i>l</i> ≤ 5	−6 ≤ <i>h</i> ≤ 6 −14 ≤ <i>k</i> ≤ 22 −9 ≤ <i>l</i> ≤ 8	−6 ≤ <i>h</i> ≤ 6 −21 ≤ <i>k</i> ≤ 21 −9 ≤ <i>l</i> ≤ 8	−5 ≤ <i>h</i> ≤ 5 −28 ≤ <i>k</i> ≤ 18 −7 ≤ <i>l</i> ≤ 7
Reflections collected / unique	3433 / 1211 [<i>R</i> _{int} = 0.0541]	4259 / 1568 [<i>R</i> _{int} = 0.0323]	3527 / 1276 [<i>R</i> _{int} = 0.0846]	3542 / 1244 [<i>R</i> _{int} = 0.0293]
Completeness to θ	25.01 (99.9%)	26.25 (99.7%)	25.01 (96.6%)	25.02 (99.9%)
Max. and min. transmission	0.6090 and 0.4373	–	0.8874 and 0.5925	1.000000 and 0.763259
Data / restraints / parameters	1211 / 3 / 106	1568 / 0 / 119	1276 / 2 / 115	1244 / 3 / 114
Goodness-of-fit on <i>F</i> ²	0.999	0.951	1.060	1.183
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ¹ = 0.0327 <i>wR</i> ² = 0.0897	<i>R</i> ¹ = 0.0289 <i>wR</i> ² = 0.0682	<i>R</i> ¹ = 0.0818 <i>wR</i> ² = 0.1781	<i>R</i> ¹ = 0.0305 <i>wR</i> ² = 0.0682
<i>R</i> indices (all data)	<i>R</i> ¹ = 0.0370 <i>wR</i> ² = 0.0926	<i>R</i> ¹ = 0.0427 <i>wR</i> ² = 0.0759	<i>R</i> ¹ = 0.1188 <i>wR</i> ² = 0.1932	<i>R</i> ¹ = 0.0348 <i>wR</i> ² = 0.0698
Largest diff. peak and hole (eÅ ⁻³)	0.309 and −0.622	0.316 and −0.337	1.079 and −0.731	0.575 and −0.658

Table 2 Selected bond distances and angles for complex (1)–(4)

(1)					
Zn(1)–O(1)	2.0496(18)	Zn(1)–N(1)	2.152(2)	Zn(1)–O(4)	2.1589(19)
O(1)–Zn(1)–N(1)	77.69(7)	O(1)–Zn(1)–N(1A)	102.31(7)	O(1)–Zn(1)–O(4A)	89.94(8)
N(1)–Zn(1)–O(4A)	93.00(8)	O(1)–Zn(1)–O(4)	90.06(8)	N(1)–Zn(1)–O(4)	87.00(8)
(2)					
Zn(1)–O(1)	2.0420(18)	Zn(1)–O(1)	2.118(2)	Zn(1)–O(4)	2.1964(18)
O(1)–Zn(1)–N(1)	78.66(7)	O(1)–Zn(1)–N(1)	101.34(7)	O(1)–Zn(1)–O(4A)	88.65(7)
N(1)–Zn(1)–O(4A)	91.64(8)	N(1)–Zn(1)–O(4A)	91.35(7)	N(1)–Zn(1)–O(4)	88.36(8)
(3)					
Ni1–O1	2.018(5)	Ni1–N1	2.026(6)	Ni1–O4	2.093(5)
O1–Ni1–N1A	100.2(2)	O1A–Ni1–O4	88.8(2)	N1–Ni1–O4	88.9(2)
O1–Ni1–N1	79.8(2)	N1A–Ni1–O4	91.1(2)	O1–Ni1–O4	91.2(2)
(4)					
Cd1–N1	2.334(3)	Cd1–O4	2.338(3)	Cd1–O1	2.235(2)
O1–Cd1–N1A	108.21(9)	O1A–Cd1–O4	90.47(9)	N1–Cd1–O4	85.64(10)
O1–Cd1–O4	89.53(9)	N1A–Cd1–O4	94.36(10)	O1–Cd1–N1	71.79(9)

Symmetry code: for (1) A = −*x*, −*y*, −*z*; (2) A = −*x*, 1−*y*, −*z*; (3) A = −*x*+1, −*y*+1, −*z*+1; (4) A = −*x*+1, −*y*, −*z*+1.

The crystal cohesion is assured by hydrogen bonding involving the coordinated water molecules, the uncoordinated hetero-ring N2 atom and the methylene C4 atom (Table 3). The coordinated water molecule, O4, links the molecules *via* two donor hydrogen bonds with carboxylate O atoms O1 and O2, and accepts a hydrogen bond from the non-coordinated pyridazinyl N2 atom. There is hydrogen bonding between the methylene C4 atom and the carbonyl O3 atom. The crystal forms a tight two-dimensional layer structure.

The TG-DTA curve of (1) exhibits two steps of weight loss. The first weight loss was observed in the temperature range 130–190 °C and involves liberation of two coordinated water molecules (Found: 9.31%, Calcd 9.39%) with an endothermic peak at 170 °C. The second weight loss occurs from 190 to

850 °C due to the decomposition of two topca ligands (Found: 76.60%, Calcd 73.57%). The remaining weight of 19.80% corresponds to the percentage (21.22%) of the Zn and O components, indicating that the final product is ZnO. For the complex (2), the TG-DTA curve exhibits three weight loss stages. The first weight loss of 13.38% occurred over the temperature range 90–130 °C, corresponding to the removal of two lattice water molecules and one coordinated water molecule (Calcd 12.88%). The second weight loss of 3.82% between 140 and 155 °C is consistent with the removal of the remaining coordinated water molecule (Calcd 4.29%). Further decomposition finished at 850 °C, and the remaining weight was 19.15% (Calcd 18.59%), this indicates that the final product was ZnO.

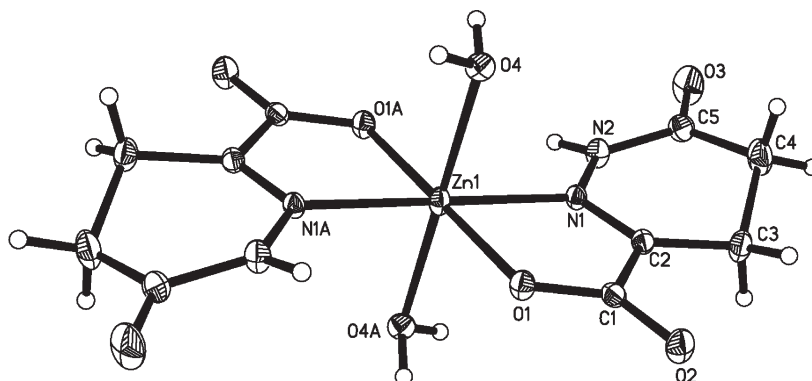


Fig. 1 The molecular structure of complex (1) at 30% thermal ellipsoids.

Table 3 Selected hydrogen-bond geometry (Å, °) for complex (1)–(4)

	D-H...A	d(D-H)	d(H...A)	d(D...A)	∠(DHA)	
(1)	O(4)–H(1)···O(1) ⁱ	0.85	1.89	2.6691	152	i = -1/2-x, 1/2+y, 1/2-z;
	N(2)–H(2)···O(4) ⁱⁱ	0.86	2.08	2.9285	169	ii = 1+x, y, z; iii = x, y, -1+z;
	O(4)–H(3)···O(2) ⁱⁱⁱ	0.85	1.85	2.6525	157	iv = -1+x, y, z.
	C(4)–H(4A)···O(3) ^{iv}	0.97	2.45	3.3298	151	
(2)	O(4)–H(4C)···O(5) ⁱ	0.89	1.84	2.7184	171	i = x, y, z-1; ii = x-1, y, z-1;
	O(4)–H(4D)···O(3) ⁱⁱ	0.89	1.86	2.7520	173	iii = x+1, y, z+1; iv = x+1/2,
	O(5)–H(5A)···O(2) ⁱⁱⁱ	0.82	2.04	2.8622	176	-y+3/2, z+1/2; v = -x+1, -y+1,
	O(5)–H(5B)···O(2) ^{iv}	0.91	1.96	2.8436	162	-z.
	N(2)–H(2A)···O(4) ^v	0.86	2.16	2.9946	163	
(3)	N2–H2···O4 ⁱ	0.860	2.187	3.005	158.79	i: -x+2, -y+1, -z+1; ii: x-1, y,
	O4–H6···O5	0.850	1.885	2.694	158.43	z-1; iii: x+1/2, -y+3/2, z-1/2;
	O4–H7···O3 ⁱⁱ	0.850	1.923	2.727	157.34	iv: x+1, y, z.
	O5–H8···O2 ⁱⁱⁱ	0.850	2.141	2.817	136.25	
	O5–H9···O2 ^{iv}	0.850	2.017	2.851	166.80	
(4)	O4–H1···O1 ⁱ	0.850	1.852	2.661	158.36	i: -x+2, -y, -z+1; ii: x, y, z+1.
	N2–H2···O4 ⁱⁱ	0.861	2.079	2.841	176.47	iii: x, y, -1+z. iv: 1+x, y, z.
	O4–H3···O2 ⁱⁱⁱ	0.851	1.809	2.639	164.43	
	C4–H4···O3 ^{iv}	0.970	2.439	3.331	152.64	

Conclusions

In summary, a series of transition metal complexes with 1,4,5,6-tetrahydro-6-oxo-3-pyridazine carboxylic acid were synthesised and characterised by X-ray diffraction. In the complexes, the metal atom is six-coordinated with an N₂O₄ environment and possesses crystallographic C_i symmetry.

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