Synthesis and Crystal Structures of Copper(II), Zinc(II), Lead(II) and Cadmium(II) Tetrazole-5-carboxylate Complexes Generated *via in situ* Hydrolysis Reaction

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Four metal complexes, namely $[Cu_2(ttzCOO)_2(H_2O)_4]\cdot 4H_2O$ (**1**), $[Zn_2(ttzCOO)_2(H_2O)_6]\cdot 2H_2O$ (**2**), $[Pb(ttzCOO)(H_2O)_2]_n$ (**3**), and $\{[Cd(ttzCOO)(H_2O)]\cdot 1/2H_2O\}_n$ (**4**), where $ttzCOO^{2-}$ = tetrazole-5-carboxylate dianion, have been prepared by the reaction of the sodium salt of 1*H*-tetrazole-5-carboxylic acid ethyl ester in aqueous methanolic solution at room temperature with $CuCl_2$, ZnI_2, $Pb(NO_3)_2$, or $Cd(NO_3)_2$, respectively. The compounds were characterized by elemental analysis, IR spectroscopy, TG-DSC analysis and single-crystal X-ray diffraction. While **1** and **2** are structurally similar dinuclear complexes, **3** and **4** exhibit a 1D chain structure and a 3D polymeric framework, respectively.

Key words: Tetrazole-5-carboxylate, Complex, *in situ* Synthesis, Structure

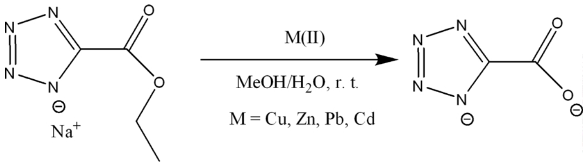
Introduction

Tetrazoles have found a wide range of applications, *e. g.* in coordination chemistry as a type of versatile ligand [1], in medicinal chemistry as a metabolically stable surrogate for carboxylic acid groups [2], and in materials science as high-energy substances [3]. When the 5-position of tetrazole is modified by a coordinative group such as pyridyl, pyrimidyl, tetrazolyl *etc*., it has been shown that the coordination patterns of tetrazolato ligands become more diverse and much more useful in construction of metal-organic frameworks [4 – 9]. Tetrazole-5-carboxylic acid, uniting the coordination features of tetrazole and carboxylate, is one of the C^5-functionalized tetrazoles we are interested in. Recently, Klapötke and co-workers prepared some alkaline earth and transition metal complexes of tetrazole-5-carboxylate, which can be used as thermally and physically stable colorants for pyrotechnic compositions [10]. In this paper, we describe a facile method to synthesize metal complexes with dianionic tetrazole-5-carboxylate ($ttzCOO^{2-}$) ligands, involving an *in-situ* hydrolysis of the commercially available 1*H*-tetrazole-5-carboxylic acid ethyl ester sodium salt to the corresponding carboxylate ligand in the presence of Cu(II), Zn(II), Pb(II), and Cd(II) ions. Crystal structures of the four complexes are also reported here.

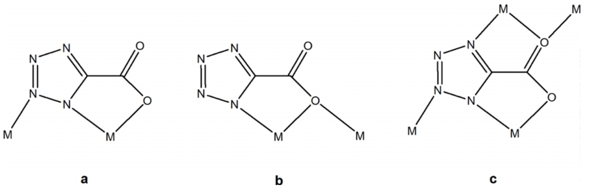
Results and Discussion

Synthesis

All the four complexes reported here were prepared by the reaction of 1*H*-tetrazole-5-carboxylic acid ethyl ester sodium salt with the corresponding divalent metal salts in aqueous methanolic solution at room temperature. Obviously, the dianionic ligand found in the products is generated *in situ* by metal-promoted hydrolysis of the ethyl ester (Scheme 1). Compared with the literature method [10], our one-pot synthesis of metal tetrazole-5-carboxylates is more convenient. The metals we used successfully were transition metals (Cu^{II}, Zn^{II}, Cd^{II}) or a main group metal (Pb^{II}), which suggests that the method described here can be generalized to cover a wide range of divalent or higher-valent metals.



Scheme 1.



Scheme 2.

Crystal structures

The dicopper complex **1** crystallizes in the monoclinic space group $C2/c$, and the asymmetric unit consists of one crystallographically independent Cu(II) atom, one ttzCOO^{2-} ligand, and four water molecules. Complex **1** is a dinuclear complex, in which ttzCOO^{2-} serves as a tridentate ligand in a μ_2–O,N^1:N^2 fashion (Scheme 2a). This complex is identical with the Cu(II) complex prepared by Klapötke [10]. We notice the cell at 298 K reported here is slightly larger than that measured at 200 K.

The centrosymmetric dizinc complex **2** crystallizes in the triclinic space group $P\bar{1}$ and structurally resembles **1** (Fig. 1). However, unlike the Cu(II) atom in **1**, the zinc(II) atom has a much more regular octahedral coordination geometry, obviously resulting from the absence of a Jahn-Teller effect for the d^{10} configuration. Extensive hydrogen bonds are present in the crystal structure of **2**, involving the water molecules, carboxy O atoms and tetrazolyl N atoms.

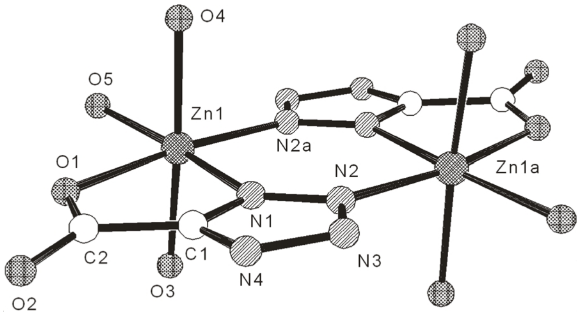


Fig. 1. Ball-and-stick diagram of **2** (lattice water molecules are not shown). Symmetry code: a $-x$, $-y$, $-z$. Selected bond lengths (Å) and angles (deg): Zn1–O5 2.049(3), Zn1–O3 2.081(3), Zn1–O4 2.097(3), Zn1–N2a 2.119(3), Zn1–N1 2.148(3), Zn1–O1 2.167(2), Zn1···Zn1a 4.176; O5–Zn1–O3 88.18(11), O5–Zn1–O4 87.61(12), O3–Zn1–O4 175.78(12), O5–Zn1–N2a 94.25(11), O3–Zn1–N2a 90.41(11), O4–Zn1–N2a 90.24(12), O5–Zn1–N1 169.26(11), O3–Zn1–N1 95.44(12), O4–Zn1–N1 88.64(12), N2a–Zn1–N1 95.83(11), O5–Zn1–O1 94.23(10), O3–Zn1–O1 87.67(11), O4–Zn1–O1 92.30(11), N2a–Zn1–O1 171.24(10), N1–Zn1–O1 75.86(10).

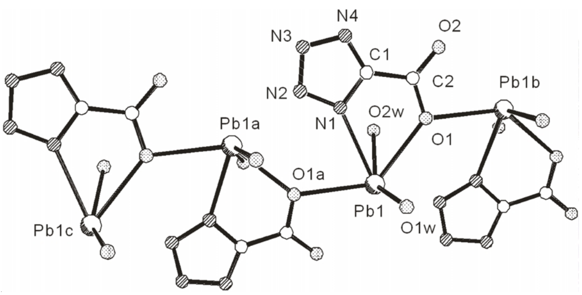


Fig. 2. Ball-and-stick diagram of a fragment of the coordination polymer of **3** with atom labels, showing the coordination geometry around the Pb atom and the coordination mode of the ttzCOO^{2-} ligand. Symmetry codes: a $x-0.5$, $-y+0.5$, $z-0.5$; b $x+0.5$, $-y+0.5$, $z+0.5$; c $x+1$, y, $z-1$. Selected bond lengths (Å) and angles (deg): Pb1–O1w 2.485(15), Pb1–O1a 2.540(16), Pb1–N1 2.554(14), Pb1–O1 2.563(15), Pb1–O2w 2.669(15); O1w–Pb1–O1a 97.1(7), O1w–Pb1–N1 109.2(5), O1a–Pb1–N1 72.3(5), O1w–Pb1–O1 93.4(7), O1a–Pb1–O1 135.2(3), N1–Pb1–O1 63.2(5), O1w–Pb1–O2w 148.9(5), O1a–Pb1–O2w 104.0(6), N1–Pb1–O2w 57.7(5), O1–Pb1–O2w 55.6(6).

The 1D lead(II) complex **3** crystallizes in the monoclinic space group Cc, the asymmetric unit consisting of one Pb(II) atom, one ttzCOO^{2-} ligand and two water molecules. As shown in Fig. 2, the Pb(II) atom is bound to one tetrazolyl N atom, two carboxy O atoms (O1,O1A) and two water molecules, forming an irregular NO$_4$ coordination geometry. The geometry of the Pb(II) atom can be regarded as a ψ-octahedron with the lone pair occupying one coordination site. The ligand ttzCOO^{2-} in this complex serves as a bidentate ligand in a μ_2–N^1,O:O fashion (Scheme 2b), the Pb···Pb distance bridged by one carboxy O atom being 4.711 Å. Hydrogen bonds involving water molecules and tetrazolyl N atoms and π-π stacking between the tetrazole rings might contribute to the formation of the crystal structure of **3**.

The 3D cadmium(II) complex **4** crystallizes in the orthorhombic space group $Fdd2$, and the asymmetric unit consists of two crystallographically independent Cd(II) ions residing on crystallographic two-fold axes, one ligand, one aqua ligand and half of an interstitial water molecule. As shown in Fig. 3a, the Cd1 atom is bound to four tetrazolyl N atoms (Cd–N = 2.300, 2.308 Å) and two (possibly four) carboxy O atoms (Cd–O = 2.627, 2.777 Å), forming an irregular coordination geometry; the Cd2 atom is coordinated by two tetrazolyl N atoms, two carboxy O atoms and two aqua ligands in a quasi-trigonal prismatic geometry. Five of the six possible donating atoms of

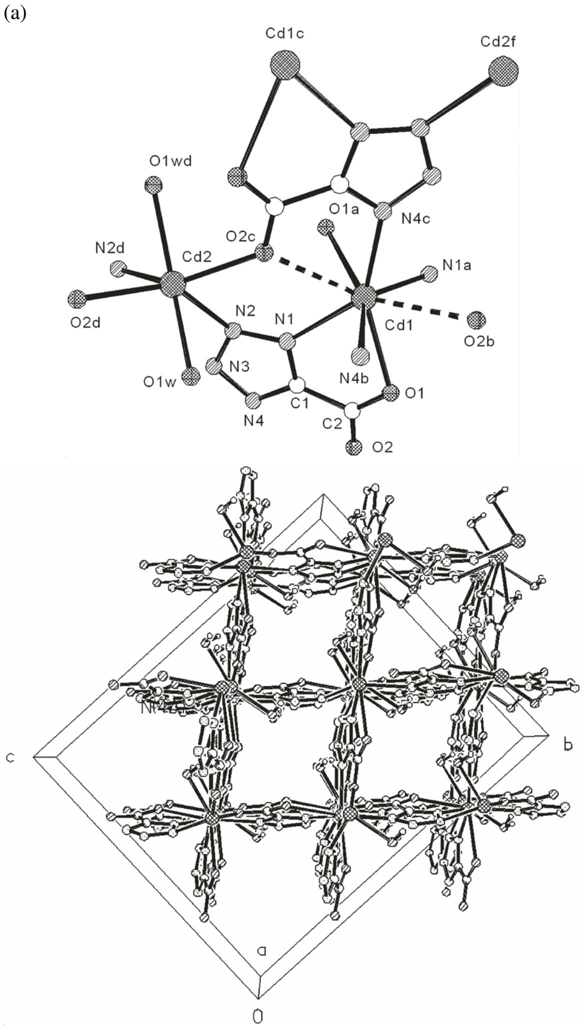


Fig. 3. (a) Ball-and-stick diagram of a fragment of **4** with atom labels, showing the coordination geometries around Cd1 and Cd2 atoms and the coordination mode of the ttzCOO^{2-} ligand. Symmetry codes: a $-x+0.5$, $-y+0.5$, z; b $x-0.25$, $-y+0.25$, $z-0.25$; c $-x+0.75$, $y+0.25$, $z-0.25$; d $-x+1.5$, $-y+0.5$, z; f $-x+0.75$, $y+0.25$, $-z+0.75$. Selected bond lengths (Å): Cd1–N1 2.300(8), Cd1–N4b 2.308(9), Cd1–O1a 2.627(7), Cd1–O2b 2.777(8), Cd2–O1w 2.290(7), Cd2–O2c 2.312(7), Cd2–N2 2.396(9), Cd1···Cd2 4.428. (b) The packing diagram of **4** as viewed along the crystallographic *a* axis (interstitial water molecules are not shown).

ttzCOO^{2-} are utilized to bind the Cd(II) atoms in a μ_4-$O,N^1{:}N^2{:}N^4,O'{:}O'$ fashion (Scheme 2c), which is different from the patterns in **1**, **2** and **3**. Nearly square-prismatic channels (5.9 × 5.9 Å^2) are formed along the *a* axis, in which interstitial water molecules are located (Fig. 3b). Strong hydrogen bonds involving an aqua ligand (as a donor), a tetrazolyl N atom and carboxy O atoms (as acceptors) may further stabilize the 3D structure (O1w···N3$^{\mathrm{i}}$ = 2.933 Å; O1w···O1$^{\mathrm{ii}}$ = 2.941 Å; O1w···O2$^{\mathrm{ii}}$ = 3.023 Å; symmetry codes: i $x-1/4$, $-y+1/4$, $z-1/4$; ii $x+3/4$, $-y+1/4$, $z-1/4$). The interstitial water molecules are attached *via* hydrogen bonding to carboxy O atoms (O2w···O1 = 2.856 Å).

The TG/DSC curves of **4** (in air) show a mass loss of 8.7 % in the range 140–205 °C with an endothermic signal at 200 °C corresponding to the dehydration process. From an onset of 280 °C, the dehydrated sample experienced a two-step thermal decomposition with mass losses of 28.7 % and 10.4 % and exothermic signals at 332 °C and 523 °C, respectively. The final residue at 540 °C accounts for 52.2 % of the total mass, which may be CdO, based on the calculated residual mass percentage of 51.1 %.

Conclusion

In summary, we have successfully prepared four complexes with tetrazole-5-carboxylate ligands involving *in situ* ligand formation from sodium ethyl 1*H*-tertazole-5-carboxylate. As demonstrated by the X-ray work of others and us, this ligand, uniting the coordination features of both tetrazole and carboxylate, displays versatile coordination modes upon binding to metals, and therefore can find use in the construction of metal-organic frameworks with potential practical applications.

Experimental Section

The IR spectra were recorded on a Nicolet Nexus 470-FTIR instrument from KBr pellets in the range of 400–4000 cm^{-1}. The CHN microanalyses were carried out on a Flash EA 1112 elemental microanalyzer. Thermogravimetry and differential scanning calorimetry were measured on a Netzsch STA 409 PC/PG system in flowing air at a scanning rate of 10 °C min^{-1}. 1*H*-Tetrazole-5-carboxylic acid ethyl ester sodium salt (97 %) was purchased from Alfa Aesar and used without further purification and other chemicals were also from commercial sources.

*[Cu$_2$(ttzCOO)$_2$(H$_2$O)$_4$]·4H$_2$O (**1**)*

A solution of CuCl$_2$·2H$_2$O (0.2 mmol, 34 mg) in CH$_3$OH (2 mL) was mixed with 2 mL of an aqueous solution of 1*H*-tetrazole-5-carboxylic acid ethyl ester sodium salt (0.1 mmol, 16 mg). The resulting mixture was allowed to evaporate for two weeks to yield blue crystals of **1**, suitable for X-ray work. Yield: 80 % (based on the ligand). –

Table 1. Crystal data and structure refinement parameters for **1** – **4**.

	1	**2**	**3**	**4**
Formula	$C_4H_{16}Cu_2N_8O_{12}$	$C_4H_{16}N_8O_{12}Zn_2$	$C_2H_4N_4O_4Pb$	$C_2H_3CdN_4O_{3.5}$
M_r	495.33	499.03	355.28	251.48
Crystal size, mm^3	$0.31 \times 0.18 \times 0.09$	$0.22 \times 0.12 \times 0.06$	$0.12 \times 0.07 \times 0.05$	$0.14 \times 0.13 \times 0.13$
Crystal system	monoclinic	triclinic	monoclinic	orthorhombic
Space group	$C2/c$	$P\bar{1}$	Cc	$Fdd2$
a, Å	15.5281(19)	7.1571(11)	8.489(2)	8.8306(11)
b, Å	6.4627(8)	7.7527(11)	12.776(4)	15.2742(18)
c, Å	17.781(2)	8.7813(13)	6.702(2)	18.113(2)
α, deg	90	97.108(2)	90	90
β, deg	114.346(2)	112.674(2)	111.025(4)	90
γ, deg	90	108.619(2)	90	90
V, Å^3	1625.7(4)	408.73(10)	678.5(3)	2443.1(5)
Z	4	1	4	16
T, K	298(2)	298(2)	298(2)	298(2)
D_{calcd}, g cm^{-3}	2.02	2.03	3.48	2.74
μ, mm^{-1}	2.7	3.0	24.8	3.5
$F(000)$, e	1000	252	632	1904
hkl range	$-20 \le h \le 20$, $-8 \le k \le 8$, $-23 \le l \le 22$	$-5 \le h \le 8$, , $-9 \le k \le 7$, $-10 \le l \le 10$	$-10 \le h \le 10$, $-16 \le k \le 16$, $-8 \le l \le 8$	$-11 \le h \le 10$, $-19 \le k \le 19$, $-23 \le l \le 17$
Refl. collected	5849	2261	2497	3926
Refl. unique / R_{int}	1836 / 0.0190	1578 / 0.0212	1416 / 0.0504	1276 / 0.0438
Param. refined	146	118	102	97
Final $R1/wR2$ [$I \ge 2\sigma(I)$]	0.0243 / 0.0630	0.0385 / 0.0930	0.0427 / 0.1168	0.0617 / 0.1568
Final $R1/wR2$ (all data)	0.0304 / 0.0653	0.0478 / 0.0965	0.0433 / 0.1173	0.0650 / 0.1594
GoF (F^2)	1.052	1.000	1.122	1.134
Flack param.	–	–	0.29(4)	−0.08(13)
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	0.45 / −0.27	0.73 / −0.70	2.58 / −3.52	2.27 / −1.58

$C_4H_{16}Cu_2N_8O_{12}$ (495.33): calcd. C 9.70, H 3.26, N 22.62; found C 9.80, H 3.21, N 22.46. – IR (KBr pellet): ν = 3376 s, 1664 s, 1489 s, 1429 s, 1319 s, 1230 s, 1193 m, 1091 m, 845 s, 674 s cm^{-1}.

*[Zn$_2$(ttzCOO)$_2$(H$_2$O)$_6$]·2H$_2$O (**2**)*

This compound was prepared by a procedure analogous to that used for **1**, using ZnI_2 instead of $CuCl_2$. Yield: 75 %.

*[Pb(ttzCOO)(H$_2$O)$_2$]$_n$ (**3**)*

This compound was prepared by a procedure analogous to that used for **1**, using $Pb(NO_3)_2$ instead of $CuCl_2$. Yield: 75 % (based on the ligand). – $C_2H_4PbN_4O_4$ (355.28): calcd. C 6.76, H 1.13, N 15.77; found C 6.56, H 0.98, N 15.61. – IR (KBr pellet): ν = 3182 s, 1568 s, 1489 s, 1379 s, 1316 s, 1191 m, 1075 m, 825 s, 673 s cm^{-1}.

*{[Cd(ttzCOO)(H$_2$O)]·1/2H$_2$O}$_n$ (**4**)*

The compound was prepared by a procedure analogous to that used for **1**, using $Cd(NO_3)_2$ instead of $CuCl_2$. Yield: 45 % (based on the ligand). – $C_2H_3CdN_4O_{3.5}$ (251.48): calcd. C 9.55, H 1.20, N 22.28; found C 9.65, H 1.10, N 22.44. – IR (KBr, pellet): ν = 3276 s, 1613 s, 1506 s, 1432 s, 1346 s, 1217 m, 1174 m, 820 s, 681 s cm^{-1}.

X-Ray structure determination

Diffraction data for the four complexes were collected on a Siemens SMART 1K CCD diffractometer with graphite-monochromated MoK_α radiation, and multi-scan absorption corrections were applied. The structures were solved by Direct Methods and refined by full-matrix least-squares on F^2 using the programs SHELXS-97 and SHELXL-97, respectively [11]. All non-hydrogen atoms were refined with anisotropic displacement parameters; the water H atoms were either located from difference Fourier maps or calculated by the program HYDROGEN [12]. For **1**, the second H atom can not be added properly to O1w, therefore the presence of a coordinated hydroxide ion instead of water ligand cannot be fully excluded. Crystal data as well as details of data collection and refinements for the complexes are summarized in Table 1.

CCDC 782461–782464 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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