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Synthesis, crystal structures and solid state reactions of zinc(II) cyclobutane-1,1′-dicarboxylates containing 1,2-bis(pyrid-4-yl)ethylene

Ivan E. Ushakov,[a] Alexander S. Goloveshkin,[a] Ekaterina N. Zorina-Tikhonova,[b] Aleksandr S. Chistyakov,[b] Aleksei A. Sidorov,[b] Igor L. Eremenko,[a,b] Alexander D. Volodin[a] and Anna V. Vologzhanina*[a]

[a] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: vologzhanina@mail.ru*

[b] *N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation*

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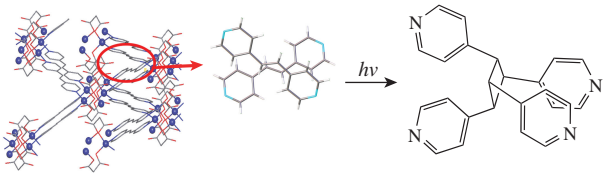
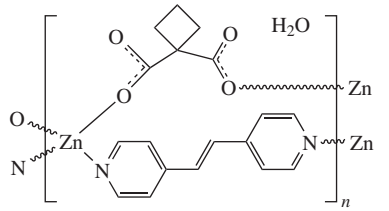
Synthesis and response towards heating and UV irradiation of two novel zinc(II) cyclobutane-1,1′-dicarboxylate complexes were examined using X-ray diffraction, FT-IR and ^{1}H NMR spectroscopy. One of the complexes underwent a photo-initiated solid state transformation of 1,2-bis(pyrid-4-yl)ethylene into 1,2,3,4-tetrakis(pyrid-4-yl)cyclobutane. A preliminary dehydration of this solid decreases the conversion rate of photoreaction.

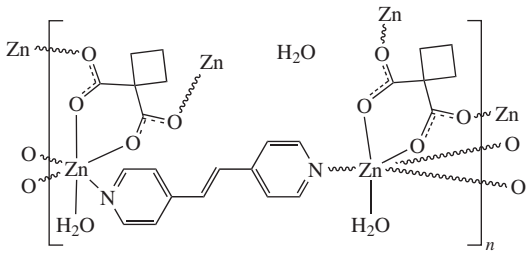


[Zn(bpe)(cbdc)]·H_2O

Topotactic photoinitiated reactions in solids are highly sensitive to the mutual disposition of reactive moieties in a crystal.[1,2] While their intramolecular photoreactivity (photochromism, linkage isomerism, spin-crossover, *etc.*) depends mainly on the molecular composition and conformation,[3,4] much efforts have been made to immobilize light-sensitive molecules for an intermolecular solid state photoreaction *via* intermolecular interactions including H-bonds,[5] coordination bonds,[6] or in molecular cavities.[7] Typically, a photoinitiated [2+2] cycloaddition reaction proceeds in crystals containing nearly coplanar and collinear olefins with the distance d < 4.2 Å between C=C bonds.[1] We have recently found that zinc(II) complexes containing substituted malonates and 1,2-bis-(pyrid-4-yl)ethylene (bpe) are promising for an investigation of solid state homo[8] and heterocycloaddition[9] reactions. Here, we report the synthesis, crystal structures of novel zinc(II) cyclobutane-1,1′-dicarboxylates (cbdc) containing bpe, and their response towards heating and UV irradiation.



1



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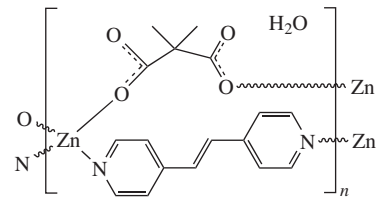

3

According to our previous data, the interaction of zinc(II) acetate with malonic acid in the presence of bpe or other N,N′-donor ligand favors a formation of coordination polymers with a 3D architecture.[8] A mixture of $\{[Zn(bpe)(cbdc)]\cdot H_2O\}_n$ **1** and $[Zn_2(H_2O)_2(bpe)(cbdc)_2]_n$ **2** was synthesized *via* a similar procedure. According to powder XRD data, the ratio between two phases was 0.88 : 0.12 (Online Supplementary Materials). Pure complex **1** can be obtained from zinc(II) nitrate instead of its acetate. Both **1** and **2** were characterized by the single crystal X-ray diffraction.† Figure 1 shows asymmetric units of these complexes. The anions in **1** act as bridge bidentate ligands, Zn^{II} atoms establish ZnN_2O_2 coordination polyhedra (Figures 2 and 3). The [Zn(cbdc)] units

† *Crystal data for* **1**. $C_{18}H_{18}N_2O_5Zn$, M = 407.71, monoclinic, space group $P2_1/c$; at 120 K: a = 8.5212(2), b = 10.5292(3) and c = 21.8613(5) Å, β = 117.551(1)°, V = 1739.00(8) Å^3, Z = 4, d_{calc} = 1.557 g cm^{-3}, μ(MoKα) = 1.444 mm^{-1}, F(000) = 840. There were 101799 reflections measured, and 16391 independent reflections (R_{int} = 0.0840) were used in a further refinement. The refinement converged to wR_2 = 0.089 and GOF = = 1.039 for all the independent reflections [R_1 = 0.046 was calculated against F^2 for 9104 observed reflections with $I > 2\sigma(I)$].

Crystal data for **2**. $C_{24}H_{26}N_2O_{10}Zn_2$, M = 633.21, monoclinic, space group $P2_1/c$; at 120 K: a = 7.2295(9), b = 23.080(3) and c = 10.6360(12) Å, β = 135.423(3)°, V = 1245.6(3) Å^3, Z = 2, d_{calc} = 1.688 g cm^{-3}, μ(MoKα) = = 1.987 mm^{-1}, F(000) = 648. There were 18177 reflections measured, and 4406 independent reflections (R_{int} = 0.0371) were used in a further refinement. The refinement converged to wR_2 = 0.071 and GOF = 1.042 for all the independent reflections [R_1 = 0.030 was calculated against F^2 for 3702 observed reflections with $I > 2\sigma(I)$].

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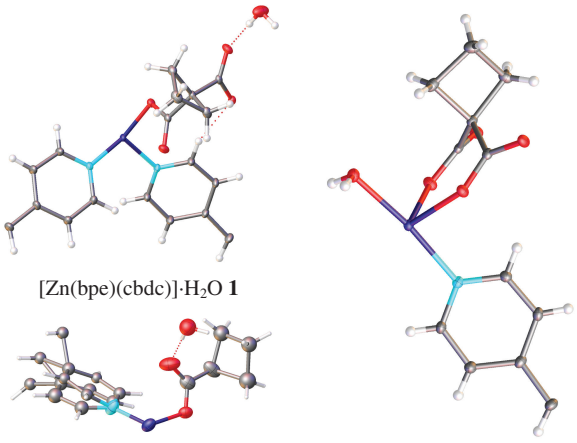

Figure 1 Asymmetric units of the obtained complexes, represented as thermal ellipsoids (at the probability levels of 70, 70 and 30 for **1**, **2** and **4**, respectively). Asymmetric units contain half of bpe (**1**, **2**, **4**) and half of the anion (**4**). For complex **4**, all the positions of disordered fragments are depicted. Colour code: Zn – dark blue, N – blue, O – red, C – gray, H – white.

form parallel chains, and the chains are connected by bridge interweaved bpe ligands into a framework (see Figure 2). Since both ligands are the bridge between two metal atoms, this framework can be described as a three-periodic uninodal 4-*c* net with **zst** topology in terms of RCSR (Reticular Chemistry Structure Resource) notation.[10] Water molecules occupy pores of this framework and participate in the formation of O–H···O bonds. The intercentroid distance between two bpe molecules in complex **1** is 4.28 Å, and the angle between olefin moieties is 29° (see other descriptors for bpe dimers in Online Supplementary Materials). Nevertheless, a rtct-stereoisomer of 1,2,3,4-tetrakis(pyrid-4-yl)-cyclobutane (tpcb) could be expected as a product of the cycloaddition reaction in solid **1**. In the case of **2**, Zn^{II} atom adopts an octahedral geometry of a $ZnNO_5$ coordination polyhedron with a water molecule and a nitrogen atom of bpe at the axial positions and oxygen atoms of bridge-chelate tetradentate anions at the equatorial one. The anions connect metal atoms to layered [Zn(cbdc)] units. The layers are further connected by parallel bpe molecules to form a framework coordination polymer (see Figure 2). The topology of this framework is **ins**, and half of zinc(II) malonates bearing N,N′-containing ligands belong to this family. In this

Crystal data for **4**. $C_{18}H_{16.5}N_2O_{4.25}Zn$, M = 394.20, orthorhombic, space group *Pnna*; at 120 K: a = 8.7964(4), b = 10.2838(3) and c = 19.4326(7) Å, V = 1757.9(1) Å^3, Z = 4, d_{calc} = 1.489 g cm^{-3}, μ(MoKα) = 2.175 mm^{-1}, F(000) = 810. There were 12365 reflections measured, and 1740 independent reflections (R_{int} = 0.0558) were used in a further refinement. The refinement converged to wR_2 = 0.230 and GOF = 1.221 for all the independent reflections [R_1 = 0.122 for 1376 observed reflections with $I > 2\sigma(I)$].

The measurements were performed using a Bruker Apex 2 CCD diffractometer operating with a graphite-monochromated MoKα radiation (λ = = 0.71073 Å). The structures were solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL[13] and OLEX2[14] software using full-matrix least-squares procedures based on F^2. A number of DFIX instructions was used to fix the geometry of disordered cyclobutane rings, as well as ISOR and EADP instructions were applied to the equivalent carbon atoms of disordered pyridine rings in the crystal of **4**. Free refinement of bpe : tpcb ratio gives 0.48(3) : 0.52(5) values, thus, occupancies of the disordered CH moiety were at the last stage fixed at the values of 0.5 (bpe), 0.25 (half of tpcb), and 0.25 (half of tpcb). The hydrogen atom positions were fixed geometrically at the calculated distances and allowed them to ride on the parent atoms.

CCDC 1902332, 1902334 and 1902335 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

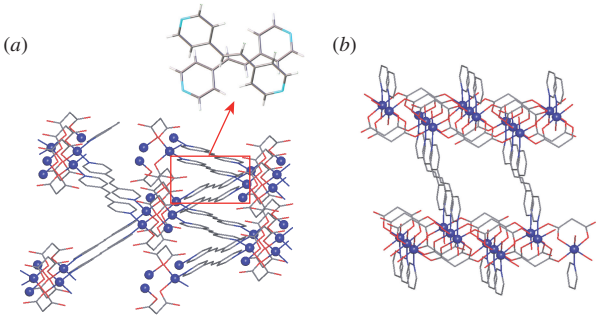

Figure 2 Fragments of crystal packing in complexes (*a*) **1** and (*b*) **2**. Solvent molecules, hydrogens and $(CH_2)_3$ moieties of cbdc are omitted. Colour code: Zn – dark blue, N – blue, O – red, C – gray, H – white.

complex, the cyclobutyl groups separate bpe molecules, which prevents any photoreaction occurrence.

Although olefin moieties of bpe molecules in **1** are slightly beyond the Schmidt criteria for a photocycloaddition reaction to occur, its isostructural 2,2′-dimethylmalonate-containing analogue, [Zn(bpe)(Me_2mal)]·H_2O **3**, is photoreactive.[8] On air, a single crystal of **3** irradiated for 8 h was transformed into orthorhombic [Zn(bpe)(Me_2mal)]$_2$[Zn_2(tpcb)(Me_2mal)$_2$]·H_2O **5** that contains the rtct-isomer of tpcb. Solid **1** irradiated for 8 h (Xe laser, λ = 365 nm, 200 W source used at 40% of the full intensity) also underwent the [2+2] cycloaddition according to the single-crystal and powder XRD data (see Online Supplementary Materials). ^{1}H NMR data of this phase revealed that complex **1** is photosensitive, since 64% of bpe in this complex reacted to afford tpcb (Figure 4), while in the case of **3**, the photoconversion was only 30% (^{1}H NMR data).[8] Only the rtct-isomer of tpcb was observed in ^{1}H NMR spectra of irradiated complexes **1** and **3**.

We have also succeeded in obtaining a crystal structure of the tpcb-containing complex (single-crystal XRD), although the quality

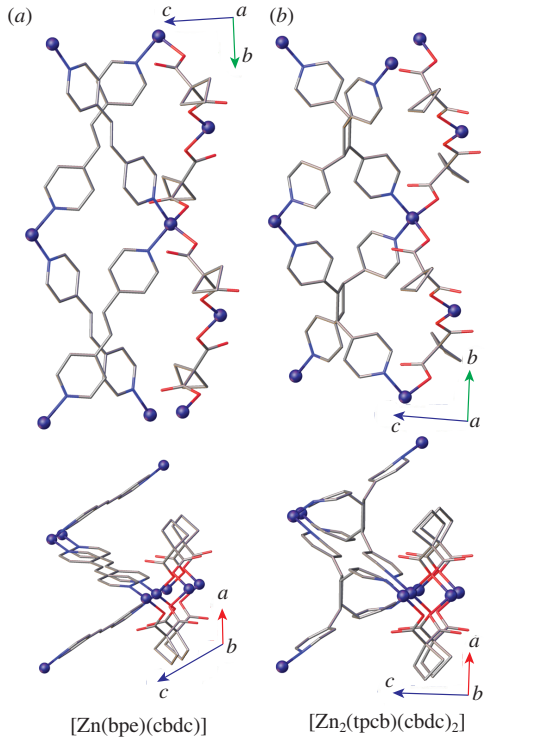

Figure 3 Fragments of crystal packing of (*a*) [Zn(bpe)(cbdc)]·H_2O **1** and (*b*) hypothetical coordination polymer [Zn_2(tpcb)(cbdc)$_2$], where one of two positions of disordered tpcb and cbdc ligands is shown. Water molecules and hydrogen atoms are omitted. Colour code: Zn – dark blue, N – blue, O – red, C – gray.

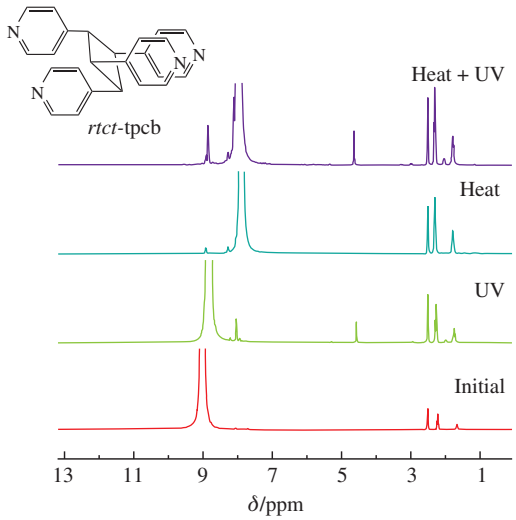

Figure 4 ^{1}H NMR spectra of complex **1** (300 MHz, 25 °C, TMS) dissolved in DMSO-d_6 with one drop of HNO_3 added.

of single crystal was poor due to its partial dehydration. The complex was found to be isostructural with Me_2mal-containing analogue. In complex **4**, Zn^{II} atom also adopts a tetrahedral geometry, and the anion acts as a bridge bidentate ligand with the cyclobutane ring disordered by symmetry over two sites. Thus, [Zn(cbdc)] chains keep parallel packing (see Figure 3). Residual density peaks indicate that the pyridine rings are equally disordered over two sites and are connected *via* either the HC=CH moiety to bpe or cyclobutane to tpcb. The conversion rate of bpe into tpcb was estimated from the free refinement of partially occupied positions of H(C) atoms in the 4-Py-CH moiety (see Figure 1) as 50% to afford $[Zn(bpe)(cbdc)]_2$-$[Zn_2(tpcb)(cbdc)_2]\cdot H_2O$ **4**. The tpcb acts as a bridge tetradentate ligand connecting parallel [Zn(cbdc)] chains. In this case, both Zn^{II} and tpcb act as 4-connected nodes of a three-periodic net, thus, the topology of this architecture is different that of complex [Zn(bpe)(cbdc)] **1**.

Finally, we attested if a dehydration before the irradiation can affect the conversion rate of [2+2] cycloaddition as was previously observed for some other complexes.[11,12] Another portions of solid isostructural complexes **1** and **3** were heated on air at 120 °C until the constant weights and then additionally irradiated for 8 h. Powder X-ray diffraction of dehydrated samples **1** and **3** indicates that the samples possess the unit cell parameters similar to those of initial complexes **1** and **3** (monoclinic, Figures S9 and S13, Online Supplementary Materials). After the irradiation, the dehydrated samples were converted to the orthorhombic phase with unit cell parameters similar to those of **4** and **5** (Figure S11). According to the ^{1}H NMR data, the preliminary dehydration also decreases the conversion of bpe into tpcb from 64 to 50%, and from 30 to 10% for complexes **1** and **3**, respectively.

In summary, the two novel zinc(II) coordination polymers containing cbdc anion and bpe were synthesized and characterized. One of them is isostructural with the previously reported photosensitive dimethylmalonate-containing analogue, and also undergoes the solid state [2+2] cycloaddition. The UV irradiation of $\{[Zn(bpe)An]\cdot H_2O\}_n$ resulted in the bpe → tpcb photoreaction in the yields of 30 and 64% for An = Me_2mal and cbdc, respectively (^{1}H NMR monitoring). The ^{1}H NMR data indicate that only the rtct-isomer of tpcb was obtained in that reaction. We have found that the dehydration of complexes **1** and **3** deactivates them towards an irradiation and decreases the conversion rate of [2+2] cycloaddition reaction.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.11.012.

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