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Facile synthesis and structure elucidation of metal-organic frameworks with {ZnCa} and {Zn_2Ca} metal cores

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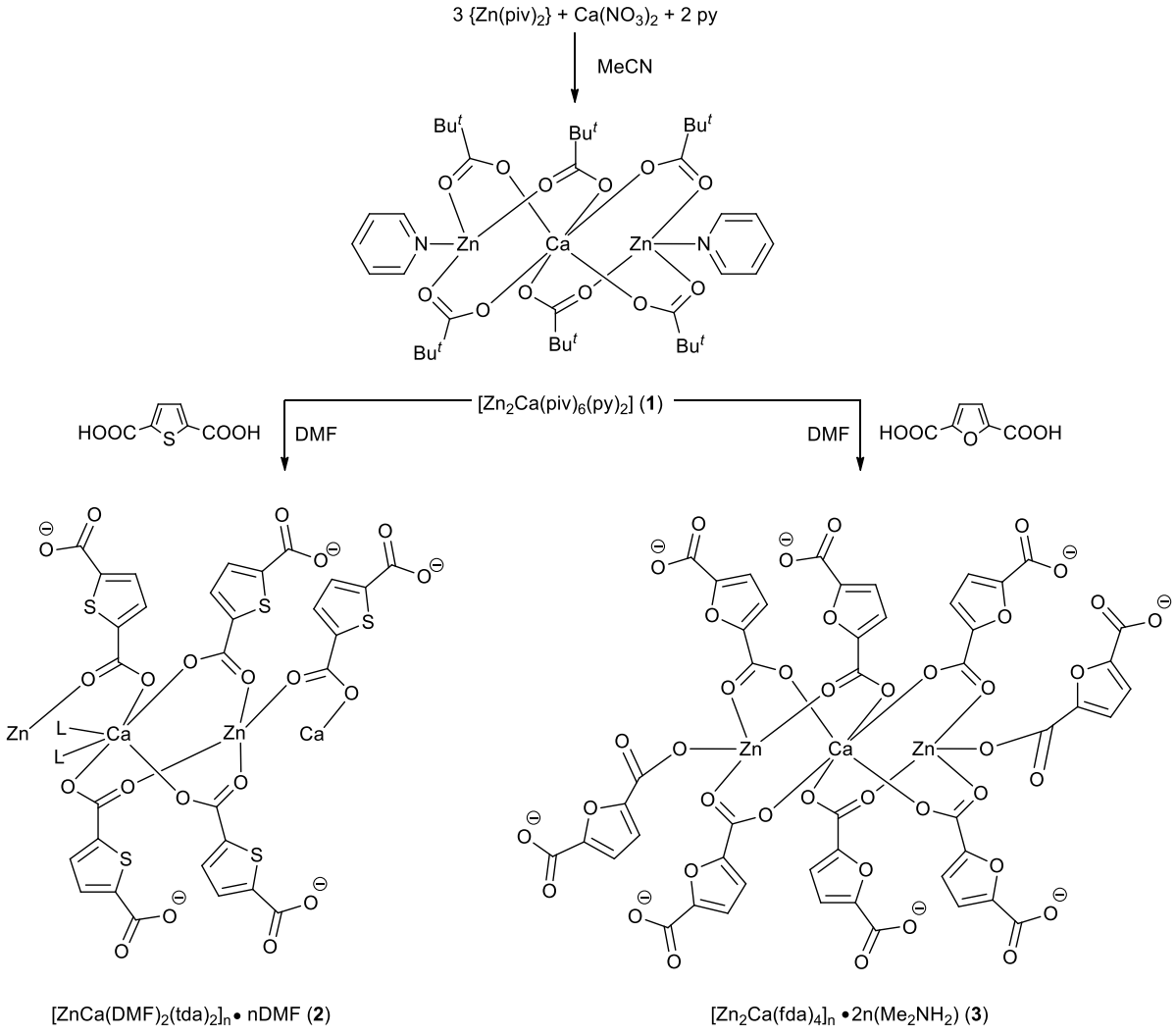
Contents

General considerations

All operations related to the synthesis of desirable complexes were conducted on air using commercially available acetonitrile, dimethylformamide (DMF) and reagents: pyridine (CarlRothGmbh+CoKG, 99%+) and $Ca(NO_3)_2 \cdot 4H_2O$ (CP, Chimmed). Zinc pivalate $[Zn(piv)_2]_n$ was synthesized according to the previously published procedure[S1].

IR spectra of compounds were recorded in the range of 400-4000 cm^{-1} on a spectrometer «Perkin Elmer Spectrum 65» equipped with the Quest ATR Accessory (Specac) by the method of attenuated total reflectance (ATR). The elemental analysis was performed on an automatic «EuroEA-3000» (EuroVektor) C,H,N,S-analyzer.

Synthesis



Scheme S1

Synthesis of [$Zn_2Ca(piv)_6(py)_2$] (1)

$Ca(NO_3)_2 \cdot 4H_2O$ (240 mg, 1 mmol) was added to a hot (ca. 75 °C) zinc pivalate (810 mg, 3 mmol) suspension in 35 ml of acetonitrile. After 15 minutes of vigorous stirring a solution of pyridine (160 mg, 2 mmol) in 10 ml of acetonitrile was added and reaction mixture became colorless. The obtained solution was kept at 75 °C and vigorous stirring 1.5 h and then stored at room temperature overnight. The colorless precipitate was filtered off and dried at ambient conditions. Single crystals suitable for X-ray diffraction were isolated from mother liquor in two days.

The yield was 580 mg (62% against $Ca(NO_3)_2 \cdot 4H_2O$). Found: C 51.65%; H 6.72%; N 3.01%. For $C_{40}H_{64}CaN_2O_{12}Zn_2$ calculated: C 51.34%; H 6.89%; N 2,99%.

IR (ATR, cm^{-1}): 2958 m, 2926 w, 2869 w, 1602 vs, 1575 vs, 1482 vs, 1449 s, 1407 vs, 1372 s, 1357 vs, 1226 vs, 1219 vs, 1155 w, 1072 m, 1044 m, 1016 w, 937 w, 895 m, 792 s, 755 s, 697 vs, 638 m, 613 s, 567 m.

Synthesis of [$ZnCa(DMF)_2(tda)_2]_n \cdot n(DMF)$ (2)

DMF (0.5 mL) and then a solution of $H_2(tda)$ (0.003 g, 0.0174 mmol) in DMF (0.3 mL) were added to [$Zn_2Ca(piv)_6(py)_2$] (0.0055 g, 0.0059 mmol) dissolved in DMF (0.1 mL). The resultant solution was fire-sealed in a glass ampoule, heated to 95 °C (5 °C / h), kept at 95 °C for 5 days, and then cooled to room temperature (5 °C / h). After that colorless single crystals of compound **2** were obtained.

The yield was 5.6 mg (87% against $H_2(tda)$). Found: C 38.09%; H 4.01%; N 6.69%. For $C_{21}H_{25}CaN_4O_{44}ZnS_2$ calculated: C 37.93%; H 3.79%; N 6.32%.

IR (ATR, cm^{-1}): 3462 w, 3117 w, 2929 m, 2869 w, 1650 s, 1608 s, 1595 s, 1571 s, 1508 m, 1482 w, 1440 m, 1403 m, 1356 s, 1342 s, 1259 m, 1998 m, 1556 m, 1160 w, 1110 m, 1017 m, 928 w, 865 m, 821 m, 815 m, 802 m, 793 s, 771 m, 726 s, 661 m, 655 m, 636 s, 625 s, 602 m, 585 m, 570 m, 495 s, 477 m.

Synthesis of [$Zn_2Ca(fda)_4]_n \cdot 2n(Me_2NH_2)$ (3)

DMF (0.5 mL) and then a solution of $H_2(fda)$ (0.0027 g, 0.0176 mmol) in DMF (0.3 mL) was added to [$Zn_2Ca(piv)_6(py)_2$] (0.0055 g, 0.0059 mmol) dissolved in DMF (0.1 mL). The resultant

solution was fire-sealed in a glass ampoule, heated to 95 °C (5 °C / h), kept at 95 °C for 5 days, and then cooled to room temperature (5 °C / h). After that colorless single crystals were obtained.

The yield was 5,4 mg (62% against H_2(fda)). Found: C 38.53%; H 2.99%; N 3.32%. For $C_{28}H_{24}CaN_2O_{20}Zn_2$ calculated: C 38.24%; H 2.75%; N 3.19%.

IR (ATR, cm^{-1}): 3432 w, 3117 w, 2932 m, 2884 w, 1635 s, 1608 s, 1595 s, 1571 s, 1508 m, 1478 w, 1448 w, 1399 m, 1356 s, 1342 s, 1302 s, 1257 m, 1224 m, 1998 m, 1161 w, 1114 m, 1017 m, 987 m, 928 w, 966 m, 849 m, 822 m, 815 m, 802 m, 791 s, 780 s, 659 m, 635 m, 625 s, 602 m, 585 m, 570 m, 495 s, 471 s.

Compound 1 structure description

The complex $[Zn_2Ca(piv)_6(py)_2]$ (**1**) crystallizes in P-1 space group. Metal cations are connected by six bridging pivalate anions forming linear metal core (the angle Zn…Ca…Zn 180°). Distortion of the CaO_6 and ZnO_3N coordination polyhedrons can be characterized by $S_Q(P)$ value, which measures the deviation of its shape from the ideal symmetry.[S2, S3] If the polyhedron corresponds to the case of ideal symmetry, $S_Q(P)$ is zero, while the largest theoretically possible deviation corresponds to $S_Q(P) = 100$ (this case not achievable in real structures). Calcium ions are characterized by an octahedral environment ($S_Q = 0.493$). Coordination polyhedrons of zinc ions are tetrahedrons ($S_Q = 1.335$). The compound **1** is isostructural with homometallic complex $[Zn_3(piv)_6(py)_2]$[S4]. Quite similar compounds with $\{Cd_2Ca\}$[S5] and $\{Co_2Ca\}$ metal cores[S6] were also described earlier.

Structural features of compounds 2 and 3

The structure of $[Zn_2Ca(fda)_4]_n \bullet 2n(Me_2NH_2)$ (**3**) contains two crystallographically different fda ligands. In the first case, the angle formed by carbon atoms of two carboxyl groups and the center of the furan ring (Cf) ∠C-Cf-C is 134,36°. The second furan ring is disordered over two positions, and ∠C-Cf-C varies in the range of 131,81–135,80°. The structure of $[ZnCa(DMF)_2(tda)_2]_n \bullet n$DMF (**2**) also contains two crystallographically different tda ligands. The angles formed by carbon atoms of two carboxyl groups and the center of the thiophene ring (Cf) ∠C-Cf-C are 151,81° and 152,66°. The angle in the thiophene ring is straighter and leads to a framework topology similar to one with linear linkers.

Main interatomic distances and angles for 1-3.

Table S1. Main interatomic distances and angles for **1-3**.

Complex/parameter	**1**	**2**	**3**
Interatomic distance	*d*/Å		
$Zn–O(R(COO)_2)$	1.795(18)–2.025(10)	1.942(2)–1.973(2)	1.954(3)–1.981(3)
$Zn–O(DMF)_2$	–	2.293(2), 2.369(2)	–
$Zn–O(Py)_2$	2.076(2)	–	–
$Ca–O(R(COO)_2$	2.274(7)–2.329(7)	2.281(2)–2.317(2)	2.338(3)–2.471(3)
Zn…Ca	3.812(1)	3.929(1), 5.734(1)	3.316(1)
Angle	ω/deg.		
Zn–Ca–Zn	180.00	141.02(2)	180.00

Additional figures

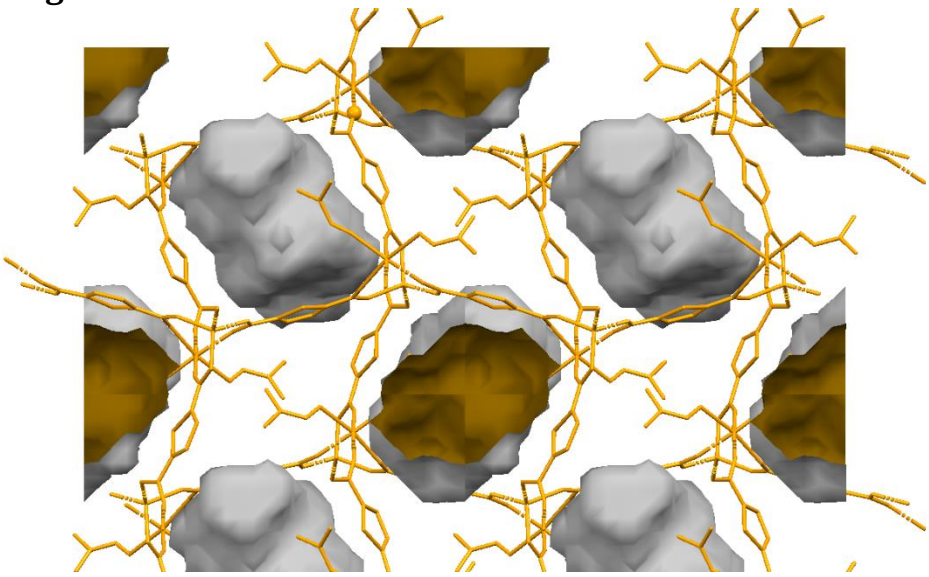


Figure S1. Calculated voids of MOF **2** (view along the axis *a*).

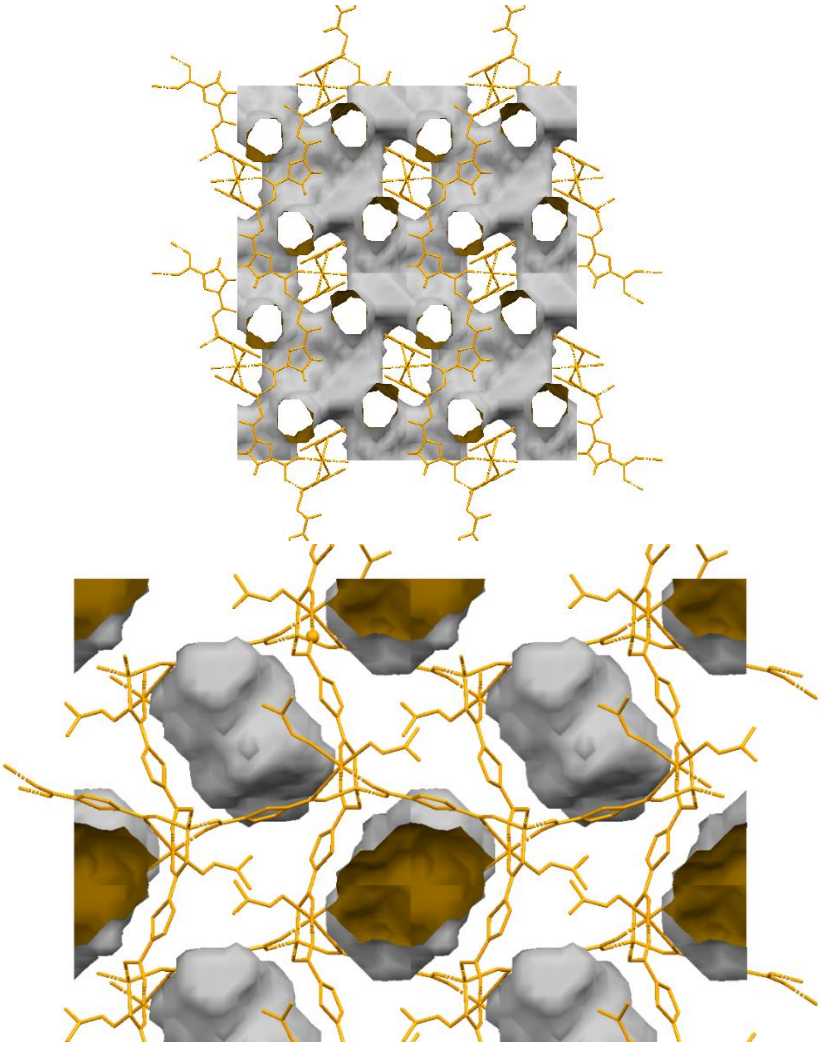


Figure S2. Calculated voids of MOF **3** (view along the axis *a* – top, view along the axis *c* - bottom).

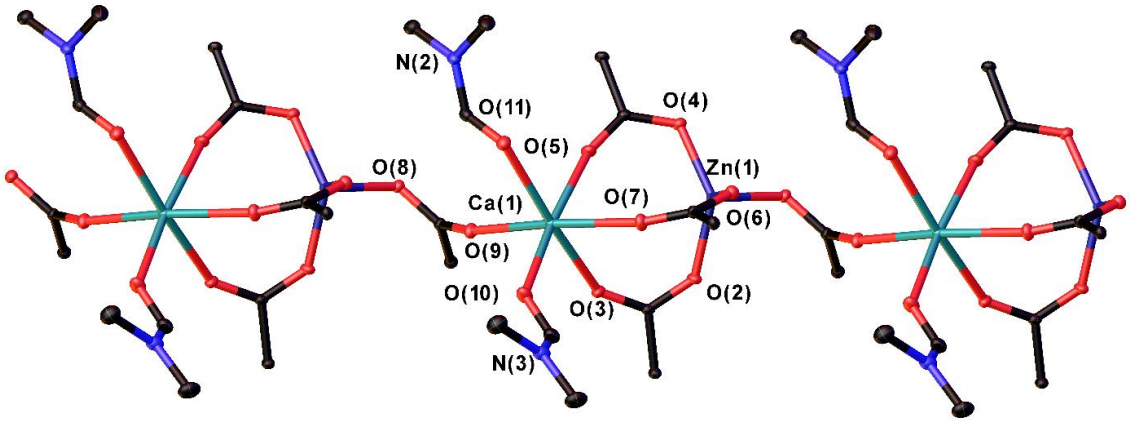


Figure S3. 1D chains of MOF **2**. Hydrogen atoms are omitted for clarity.

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