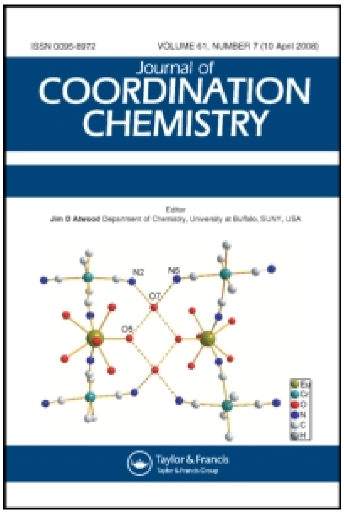

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Metal-organic frameworks constructed with 1,2,4-triazol-1-ylacrylic acid ligand: syntheses and crystal structures

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Metal–organic frameworks constructed with 1,2,4-triazol-1-ylacrylic acid ligand: syntheses and crystal structures

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Synthesis of a triazole-based N,O ligand, 1,2,4-triazol-1-yl)acrylate (ta) is described. The coordination of this new ligand is studied by the reaction of K[ta] (**3**) with zinc(II), manganese(II), cobalt(II), iron(II), and magnesium(II). The ligand favors the formation of metal–organic frameworks (MOFs) apart from magnesium(II). Single-crystal X-ray diffraction analyses reveal MOF structures for $[Mn(ta)_2]_n$ (**4**), $[Fe(ta)_2]_n$ (**5**), $[Co(ta)_2(H_2O)_2]_n$ (**6**), and $[Zn(ta)_2]_n$ (**7**).

Keywords: Ligand design; Metal–organic frameworks; Triazole; N,O ligand

1. Introduction

Ligands bearing one to several triazole units were intensively studied due to their interesting coordination properties for coordination polymers and metal–organic frameworks (MOFs) [1]. The resulting triazole-based coordination polymers showed potential applications in luminescence, catalysis, adsorption, non-linear optics, and magnetism [2–6]. Carboxylate substituted aromatic carbocycles and heterocycles were especially used in the synthesis of microporous materials for gas storage, ion exchange, and catalysis [7]. Recently, mixed-ligand frameworks constructed by carboxylates and triazole-based ligands have been reported [8]. However, coordination polymers formed through ligands bearing triazole and carboxylate functionalities remain rare. Fan and coworkers [9] investigated the coordination of 1H-1,2,4-triazol-1-acetic acid (Htaa) toward copper(II). Very recently, the ligand 1H-[1,2,3-triazole-4,5-dicarboxylic acid was used by Shi *et al.* [10] for the synthesis of some rare earth metal coordination polymers. The tridentate ligand *bis*(1,2,4-triazol-1-yl)acetic acid (btza) bearing two triazole units

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and a carboxylate and its coordination toward transition metals was recently studied by Batten *et al.* [11]. Here, we report the synthesis of 1,2,4-triazol-1-ylacrylate (ta) and its coordination toward transition metals of the first row.

2. Experimental

2.1. *General remarks*

All syntheses were performed under aerobic conditions, unless noted. All chemicals were used as purchased. Reported yields refer to analytically pure substances and were not optimized. ^{1}H- and ^{13}C{^{1}H}-NMR spectra: Bruker DPX 300 AVANCE, δ values relative to the residual solvent signal. IR spectra: Varian Excalibur FTS-3500 FT-IR spectrometer, CaF_2 cuvette ($d = 0.2$ mm) or KBr matrix. Mass spectra: Jeol JMS-700 using FD technique. Elemental analysis: Elemental Analyser Euro EA 3000 Euro Vector instrument. X-ray structure determination: Bruker–Nonius Kappa. For thermogravimetric measurements, the instrument STD 2960 Simultaneous DSC-TGA (TA Instruments) was used. About 15 mg of sample was heated in an air flow of 100 mL min^{-1} at 3 K min^{-1} to 500°C.

2.2. *Synthesis of methyl 1,2,4-triazol-1-ylacrylate (2)*

Under nitrogen atmosphere, a Schlenk flask was charged with NaH (60% suspension in mineral oil, 1.19 g, 29.8 mmol) and THF (30 mL), and 1H-1,2,4-triazole (4.11 g, 59.5 mmol) was added with stirring. After 1 h, methyl propiolate (2.65 mL, 2.50 g, 29.8 mmol) was added by syringe and the mixture was heated to reflux for 20 h. All the following procedures were carried out under aerobic conditions. The solvent was removed in vacuum and the residue was extracted with CH_2Cl_2 (250 mL); the extracts were filtered through a plug of celite. The solvent was removed and the residue was recrystallized from toluene, yielding colorless crystals (4.13 g, 27.9 mmol, 94%). m.p. 155°C; ^{1}H-NMR ($CDCl_3$): $\delta = 3.81$(s, 3H, CH_3), 6.59(d, $^3J_{H,H} = 13.7$ Hz, 1H, $CH_{acryl,\alpha}$), 8.01(d, $^3J_{H,H} = 14.0$ Hz, 1H, $CH_{acryl,\beta}$), 8.06(s, 1H, $CH_{5\text{-tz}}$), 8.34 (s, 1H, $CH_{3\text{-tz}}$) ppm; ^{13}C{^{1}H}-NMR ($CDCl_3$): $\delta = 52.2$(CH_3), 110.1($CH_{acryl,\alpha}$), 135.3($CH_{acryl,\beta}$), 144.7 ($CH_{5\text{-tz}}$), 153.8 ($CH_{3\text{-tz}}$), 166.2(CO_2) ppm; IR (CH_2Cl_2): $\tilde{\nu} = 1725$(s), 1665 (s, CO_2^-), 1511(w, C=N), 1303(m), 1199 (m) cm^{-1}. IR (KBr): $\tilde{\nu} = 3114$(w), 1713(s), 1664(s, $\nu_{as}(CO_2^-)$), 1518(m, ν(C=N)), 1369(m), 1341(w), 1312(m), 1266(m), 1193(s), 1170(m), 1137(m), 997(m), 966(w), 952(w), 861(w), 803(w), 701(w), 670(m), 642(w), and 518(w) cm^{-1}. FD MS (acetone): m/z (%) = 153 (100) [M^+]; Anal. Calcd for $C_6H_7N_3O_2$ (%): C, 47.06; H, 4.61; and N, 27.44. Found (%): C, 46.99; H, 4.66; and N, 27.54.

2.3. *Synthesis of potassium 1,2,4-triazol-1-ylacrylate K[ta] (3)*

To a solution of **2** (3.00 g, 19.6 mmol) in H_2O (50 mL), KOH (0.88 g, 15.7 mmol) was added and the mixture was stirred for 24 h. The mixture was washed with CH_2Cl_2 (3 × 50 mL) to remove excess **2** and the water phase was dried in vacuum to yield an off white powder (2.42 g, 13.7 mmol, 87%). m.p. 221°C (dec.); ^{1}H-NMR

(D_2O): $\delta = 6.54$(d, $^3J_{H,H} = 14.1$ Hz, 1H, $CH_{acryl,\alpha}$), 7.86(d, $^3J_{H,H} = 14.0$ Hz, 1H, $CH_{acryl,\beta}$), 8.18(s, 1H, CH_{5-tz}), and 8.76(s, 1H, CH_{3-tz}) ppm; $^{13}C\{^1H\}$-NMR (10% MeOH-d4/D_2O): $\delta = 117.7$($CH_{acryl,\alpha}$), 133.4($CH_{acryl,\beta}$), 146.2(CH_{5-tz}), 153.3(CH_{3-tz}), and 174.0(CO_2) ppm; IR (KBr): $\tilde{\nu} = 3485$(m), 3249(sh), 3133(w), 1668(s, $\nu_{as}(CO_2{}^-)$), 1579(s, $\nu(C=N)$), 1520(m), 1433(w), 1375(s), 1353(m), 1269(m), 1224(m), 1143(m), 1006(w), 994(m), 865(w), 671(m), 644(w), and 539(w) cm^{-1}. Anal. Calcd for $C_5H_4KN_3O_2$ (%): C, 33.89; H, 2.28; and N, 23.71. Found (%): C, 33.59; H, 2.27; and N, 23.69.

2.4. *Synthesis of [Mn(ta)$_2$]$_n$ (4)*

A test tube was charged with **3** (177 mg, 1.00 mmol), $MnSO_4 \times H_2O$ (84.0 mg, 0.50 mmol), and H_2O (20 mL). Colorless crystals of **4** were obtained by slow evaporation of the solvent at 70°C within 8 days (132 mg, 0.399 mmol, 80%). m.p.: 351°C (dec.); IR (KBr): $\tilde{\nu} = 3104$(w), 1666(s, $\nu_{as}(CO_2{}^-)$), 1561(s, $\nu(C=N)$), 1456(w), 1399(s), 1382(m), 1362(m), 1294(w), 1269(w), 1227(w), 1133(w), 997(m), 976(w), 951(w), 927(w), 864(w), 701(m), 673(m), 640(w), and 549(w) cm^{-1}; Anal. Calcd for $C_{10}H_8MnN_6O_4$ (%): C, 36.27; H, 2.44; and N, 25.38. Found (%): C, 36.42; H, 2.24; and N, 25.48.

2.5. *Synthesis of [Fe(ta)$_2$]$_n$ (5)*

A test tube was charged with **3** (200 mg, 1.13 mmol) and $FeSO_4 \times 7H_2O$ (117 mg, 0.421 mmol). The test tube was fitted into a Schlenk flask and H_2O (15 mL) was added under nitrogen. Bright orange crystals of **5** formed by slow evaporation of the solvent at 70°C under reduced pressure within 8 days (82 mg, 0.247 mmol, 59%). m.p.: 302°C (dec.); IR (KBr): $\tilde{\nu} = 3435$(br), 3126(w), 3104(w), 1666(s, $\nu_{as}(CO_2{}^-)$), 1558(s, $\nu(C=N)$), 1453(w), 1395(s), 1362(m), 1293(w), 1269(m), 1228(m), 1190(w), 1134(m), 998(m), 951(w), 930(w), 862(w), 745(w), 700(m), 674(m), 639(w), and 551(w) cm^{-1}; Anal. Calcd for $C_{10}H_8FeN_6O_4$ (%): C, 36.17; H, 2.43; and N, 25.31. Found (%): C, 35.93; H, 2.37; and N, 25.39.

2.6. *Synthesis of [Co(ta)$_2$(H$_2$O)$_2$]$_n$ (6)*

A test tube was charged with **3** (150 mg, 0.847 mmol), $CoSO_4 \times 7H_2O$ (119 mg, 0.423 mmol), and H_2O (10 mL). Pink crystals of **6** were deposited by slow evaporation of the solvent at 70°C within 6 days (132 mg, 0.356 mmol, 84%). m.p.: 205°C (dec.); IR (KBr): $\tilde{\nu} = 3348$(m), 3109(m), 3042(sh), 1675(s, $\nu_{as}(CO_2^-)$), 1662(sh), 1560(s, $\nu(C=N)$), 1534(s), 1452(m), 1398(s), 1385(s), 1360(m), 1296(m), 1271(w), 1227(w), 11945(w), 1136(m), 1002(m), 990(w), 935(m), 901(w), 858(w), 734(w), 698(m), 670(m), 645(w), and 534(w) cm^{-1}; Anal. Calcd for $C_{10}H_{12}CoN_6O_6$ (%): C, 32.36; H, 3.26; and N, 22.64. Found (%): C, 32.26; H, 3.29; and N, 22.75.

2.7. *Synthesis of [Zn(ta)$_2$]$_n$ (7)*

A test tube was charged with **3** (177 mg, 1.00 mmol), $ZnSO_4 \times 7H_2O$ (143.0 mg, 0.50 mmol), and H_2O (10 mL). Upon slow evaporation of the solvent at 70°C colorless crystals of **7** were produced over 10 days (119 mg, 0.348 mmol, 70%). m.p.: 301°C (dec.); IR (KBr): $\tilde{\nu} = 3448$(w), 3123(m), 1667(s, $\nu_{as}(CO_2^-)$), 1656(s, $\nu_{as}(CO_2^-)$), 1592(s, $\nu(C=N)$), 1583(s, $\nu(C=N)$), 1533(m), 1524(w), 1448(w), 1387(s), 1360(m), 1299(w), 1291(w), 1273(m), 1267(m), 1226(w), 1218(w), 1194(m), 1184(w), 1134(m), 1126(m), 990(m), 958(w), 952(w), 898(w), 867(w), 819(w), 747(w), 715(m), 670(m), 667(m), 647(w), 642(w), and 549(w) cm^{-1}; Anal. Calcd for $C_{10}H_8ZnN_6O_4$ (%): C, 35.16; H, 2.36; and N, 24.60. Found (%): C, 35.25; H, 2.27; and N, 24.64.

2.8. *Synthesis of [Mg(H$_2$O)$_6$](ta)$_2$ (8)*

A test tube was charged with K[ta] (500 mg, 2.82 mmol) and a solution of $MgSO_4 \times 7H_2O$ (350 mg, 1.41 mmol) in water (10 mL) was added. The test tube was stored at 70°C for 1 day and subsequently cooled to 4°C for 7 days. The colorless crystals that formed during cooling were collected and dried in air (248 mg, 0.607 mmol, 43%). m.p.: 101°C (dec.); IR (KBr): $\tilde{\nu} = 3506$(s), 3394(s), 3204(s), 3124(s), 3023(sh), 2518(w), 2455(w), 2408(w), 2382(w), 1669(s, $\nu_{as}(CO_2^-)$), 1560(s, $\nu(C=N)$), 1519(s), 1442(m), 1378(s), 1354(s), 1290(m), 1269(m), 1226(m), 1187(m), 1136(m), 997(m), 979(w), 958(m), 904(w), 873(m), 828(m), 750(m), 693(s), 640(m), 547(m), 462(w), and 403(w) cm^{-1}; Anal. Calcd for $C_{10}H_{20}MgN_6O_{10}$ (%): C, 29.57; H, 4.93; and N, 20.57. Found (%): C, 29.18; H, 4.93; and N, 20.45.

2.9. *X-ray structure determinations*

Single crystals of **4**, **6**, **7**, and **8** were mounted with perfluorinated ether or Paratone N on a glass fiber. A Bruker–Nonius Kappa CCD diffractometer and a STOE IPDS 2T diffractometer were used for data collection (graphite monochromator, Mo-Kα radiation, $\lambda = 0.71073$ Å). The structures were solved by using direct methods and refined with full-matrix least-squares against F^2 {SHELX-97} [12]. A weighting scheme was applied in the last steps of the refinement with $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [2F_c^2 + \max(F_o^2, 0)]/3$. The OH protons in **6** and **8** were found and refined free. All the other hydrogens were included in their calculated positions and refined in a riding model. All details and parameters of the measurements are summarized in tables 1 and 2. The structures were visualized with Diamond 2.1e [13].

3. Results and discussion

The ligand salt potassium 1,2,4-triazol-1-ylacrylate K[ta] (**3**) is easily available in multigram scale. Analogous to the synthesis of methyl *bis*(1,2,4-triazol-1-yl)propionate, which was first reported by Díez-Barra and coworkers [14], we gained methyl 1,2,4-triazol-1-ylacrylate (**2**) by reacting 1H-1,2,4-triazole (**1**) with sodium hydride, followed by the addition of methyl propiolate. Saponification of **2** in the presence of a deficit of KOH resulted in the potassium salt K[ta] (**3**) (scheme 1). Remaining ester **2**

Table 1. Details of the structure determination for **4** and **6**.

	4 (CCDC-771286)	**6** (CCDC-771288)
Empirical formula	$C_{10}H_8MnN_6O_4$	$C_5H_6Co_{0.50}N_3O_3$
Formula weight	331.16	185.59
Temperature (K)	150	150
Crystal color/habit	Colorless prism	Pink prism
Crystal system	Orthorhombic	Monoclinic
Space group	*F2dd*	*P2₁/n*
Unit cell dimensions (Å, °)		
a	11.3027(4)	9.6572(4)
b	14.7218(11)	6.6740(2)
c	15.2213(10)	11.6097(3)
α	90.00	90.00
β	90.00	112.264(2)
γ	90.00	90.00
Volume (Å^3), *Z*	2532.8(3), 8	692.48(4), 4
Calculated density (g cm^{-3})	1.737	1.780
Absorption coefficient (Mo-Kα) (mm^{-1})	1.070	1.284
F(000)	1336	378
Crystal size (mm^3)	$0.16 \times 0.16 \times 0.14$	$0.18 \times 0.16 \times 0.14$
θ range for data collection (°)	3.85–29.00	3.59–29.52
Limiting indices	$-15 \le h \le 15$; $-20 \le k \le 17$; $-20 \le l \le 20$	$-13 \le h \le 13$; $-9 \le k \le 9$; $-16 \le l \le 16$
Reflections collected	11,604	25,573
Independent reflections	1687	1937
Observed reflections ($I > 2\sigma(I)$)	1605	1794
Parameter	97	112
Weight parameter *a, b*	0.0198, 0.6023	0.0256, 0.3996
R_1 (observed)	0.0186	0.0193
R_1 (overall)	0.0213	0.0223
wR_2 (observed)	0.0404	0.0526
wR_2 (overall)	0.0410	0.0543
Largest difference peak and hole (e Å^{-3})	0.230 and −0.195	0.465 and −3.32

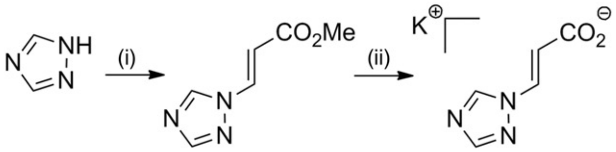
may easily be recovered by extracting the crude reaction product with CH_2Cl_2, yielding **3** in the form of a white powder.

The ligand was characterized by routine spectroscopic methods. The formation of **3** is clearly indicated by the ^{1}H-NMR spectrum. The loss of the methyl singlet, observed at 3.81 ppm in the ^{1}H-NMR spectrum of **2**, indicates complete saponification. The two singlets of triazole protons appear at 8.18 and 8.76 ppm. The olefinic protons attached to the α and β carbon atoms of the carboxylate give two doublets at 6.54 ppm ($CH_{acryl,\alpha}$) and 7.86 ppm ($CH_{acryl,\beta}$).

The ligand offers four donors to bind metal centers, two nitrogens – N2 and N4 of the triazole aromatic ring – and two oxygens of the carboxylate (figure 1). Thus, we expected this ligand to offer a variety of coordination modes, depending on the employed metal ions. Initial experiments demonstrated the coordinating properties of **3** with first row transition metals M^{2+} (M = Mn, Fe, Co, Zn) by reacting **3** with transition metal sulfates at 70°C in aqueous solutions. Depending on the solubility of the resulting coordination polymer, crystals formed from the reaction solutions within several days by slow evaporation of the water solutions. Since a monoanionic

Table 2. Details of the structure determination for **7** and **8**.

	7 (CCDC-771289)	**8** (CCDC-771290)
Empirical formula	$C_{10}H_8N_6O_4Zn$	$C_{10}H_{20}MgN_6O_{10}$
Formula weight	341.59	408.63
Temperature (K)	100(2)	150
Crystal color/habit	Colorless block	Colorless block
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	7.1423(14)	6.8041(4)
b	9.659(2)	7.5250(5)
c	9.9751(19)	9.6571(5)
α	61.515(14)	72.404(4)
β	81.469(16)	76.679(5)
γ	72.789(15)	64.297(4)
Volume (Å^3), Z	577.7(2), 2	421.84(4), 2
Calculated density (g cm^{-3})	1.964	1.609
Absorption coefficient (Mo-Kα) (mm^{-1})	2.156	0.174
F(000)	344	214
Crystal size (mm^3)	$0.2 \times 0.2 \times 0.2$	$0.39 \times 0.25 \times 0.15$
θ range for data collection (°)	2.32–25.54	3.35–29.00
Limiting indices	$-8 \le h \le 8$; $-11 \le k \le 11$; $-12 \le l \le 12$	$-9 \le h \le 9$; $-10 \le k \le 10$; $-13 \le l \le 13$
Reflections collected	7432	12,084
Independent reflections	2159	2235
Observed reflections ($I > 2\sigma(I)$)	1840	1999
Parameter	190	164
Weight parameter a, b	0.0621, 0.0000	0.0397, 0.1299
R_1 (observed)	0.0581	0.0260
R_1 (overall)	0.046	0.0304
wR_2 (observed)	0.1152	0.0707
wR_2 (overall)	0.1112	0.0732
Largest difference peak and hole (e Å^{-3})	1.661 and −1.197	0.429 and −0.213



Scheme 1. Synthesis of K[ta]: (i) 1. NaH, THF, 0°C, 2. $HC{\equiv}CCO_2Me$, reflux; (ii) KOH, H_2O, room temperature.

ligand 1,2,4-triazol-1-ylacrylate is employed, binary coordination polymers without incorporated counter ions should be obtained.

The reaction of **3** with manganese(II) sulfate and ferrous sulfate led to frameworks of composition $[Mn(ta)_2]_n$ (**4**) and $[Fe(ta)_2]_n$ (**5**). IR spectra (KBr) show characteristic signals at $\tilde{\nu} = 1666$ (for **4** and **5**), $\tilde{\nu} = 1561$ (**4**), and $\tilde{\nu} = 1558$ cm^{-1} (**5**), respectively, that are assigned to asymmetric carboxylate vibration and $\nu(C{=}N)$ of the triazole (table 3). This indicates only one coordination mode present in the MOF, for the carboxylate functionality as well as for the triazole donor. The almost identical values in $[Mn(ta)_2]$ (**4**) and $[Fe(ta)_2]$ (**5**) support the assumption of **4** and **5** to be isostructural. Meanwhile, reacting K[ta] with $ZnSO_4$ results in a coordination polymer of composition

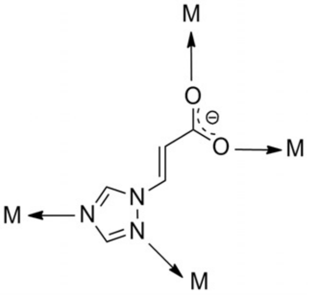


Figure 1. Possible binding sites of the ligand ta.

Table 3. Selected IR signals (cm^{-1}) of K[ta] and the coordination polymers **4**–**7** and ligand.

Compound	$\nu_{as}(CO_2^-)$	$\nu(C=N)$
K[ta] (**3**)	1668	1579
$[Mn(ta)_2]_n$ (**4**)	1666	1561
$[Fe(ta)_2]_n$ (**5**)	1666	1558
$[Co(ta)_2(H_2O)_2]_n$ (**6**)	1675	1560
$[Zn(ta)_2]_n$ (**7**)	1667, 1656	1592, 1583
$[Mg(H_2O)_6](ta)_2$ (**8**)	1667	1560

$[Zn(ta)_2]_n$ (**7**). The IR spectrum shows two bands for the asymmetric carboxylate vibration at 1667 and 1656 cm^{-1} and two for the triazole $\nu(C=N)$ at 1592 and 1583 cm^{-1}, suggesting the ligand occupies two different coordination modes within the polymer. Finally, the structures of **6** synthesized by employing $CoSO_4$ incorporate some water molecules. The composition of the polymer is $[Co(ta)_2(OH_2)_2]_n$ according to elemental analysis. The IR spectrum shows one signal for carboxylate and one for the triazole group. Thus, again only one coordination mode of the ligand seems to be present in the coordination polymer (table 3).

Sulfates are commonly non-coordinating counter ions under the conditions described here in these coordination polymer formation reactions [15]. However, the chlorido ligand is well known to coordinate to metal centers in analogous reactions employing neutral triazole-based *N*,*N*-ligands. Thus, we reacted **3** with the corresponding first row transition metal chlorides to check if any formation of heteroleptic coordination polymers occurs. Interestingly, no incorporation of chlorides in the networks was observed. Resulting crystals, characterized by IR spectrometry and elemental analysis, were identical in composition to the corresponding coordination polymers gained employing the transition metal sulfates.

4. MOF structures

The representative nature of the molecular structures obtained by single-crystal X-ray structure determinations was, in all cases, verified by a positive match of the corresponding X-ray powder diffractogram of a microcrystalline sample with the diffractogram simulated from the CIF data of the coordination polymers **4**, **6**, and **7**.

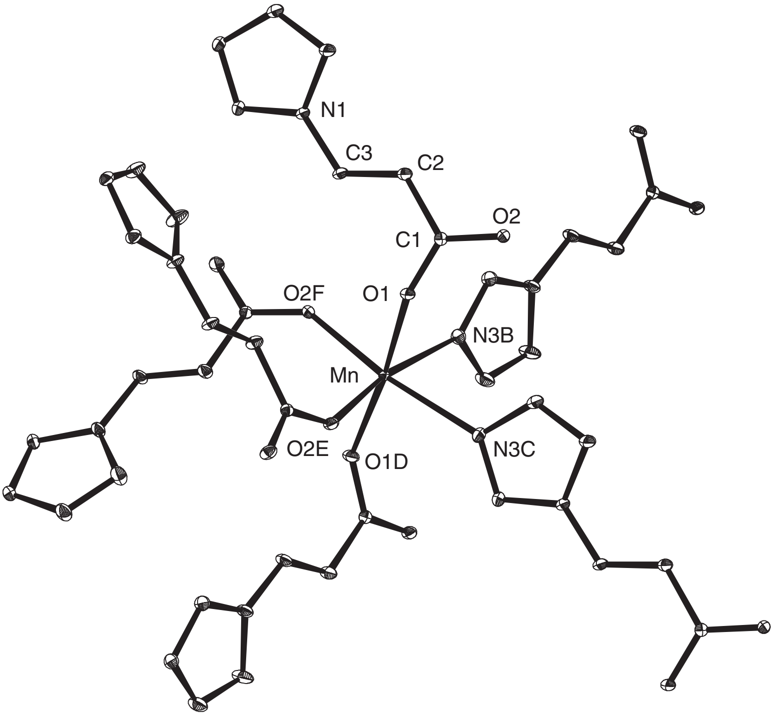


Figure 2. Coordination environment in the molecular structures of $[Mn(ta)_2]_n$ (**4**). Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): C1–O2, 1.2603(15); C1–O1, 1.2669(15); C1–C2, 1.4851(17); Mn–O1, 2.1333(8); Mn–O2, 2.1503(9); Mn–N3, 2.3000(11); O2–C1–O1, 122.98(11); O1–Mn–O1D, 174.52(6); O1–Mn–O2E, 88.64(3); O1–Mn–O2F, 87.96(3); O2E–Mn–O2F, 103.17(5); O1–Mn–N3B, 92.12(4); O1–Mn–N3C, 92.03(4); O2F–Mn–N3C, 169.10(4); O2F–Mn–N3B, 87.72(4); O1D–Mn–N3C, 92.12(4); and N3B–Mn–N3C, 81.39(6).

4.1. *$[Mn(ta)_2]_n$ (4) and $[Fe(ta)_2]_n$ (5)*

Reaction of K[ta] with Mn^{2+} results in the formation of a 3-D MOF. According to single-crystal X-ray structure determination, the metal centers are surrounded by six independent (1,2,4-triazol-1-yl)acrylate ions. The ligand binds in a μ_3-ta-κN4 : O1 : O2 mode (figures 2–4). The octahedral metal centers are coordinated by two nitrogen donors N4 in *cis* position. The four remaining coordination sites are occupied by oxygens of four different carboxylate donors. The ligand features a conjugated double bond system, resulting in a nearly flat conformation with torsion angles of O2–C1–C2–C3 = −176.29(13)°, O1–C1–C2–C3 = 5.4(2)°, C1–C2–C3–N1 = −176.46 (12)°, C2–C3–N1–C5 = −175.48(13)°, and C2–C3–N1–N2 = 8.2(2)° in $[Mn(ta)_2]_n$ (**4**). Cutouts of the network structure are given in figures 3 and 4, in which two different views are shown.

The view of the 3-D framework, shown in figure 4, reveals small channel-like gaps. The metal–metal distances were determined as Mn–Mn = 6.00 Å (μ_2–O1 : O2 bridged), 9.28 Å (μ_2–N4 : O1), and 9.99 Å (μ_2–N4 : O2); Fe–Fe = 5.91 Å (μ_2–O1 : O2 bridged), 9.22 Å (μ_2–N4 : O1), and 9.89 Å (μ_2–N4 : O2).

An analogous reaction of K[ta] with Fe^{2+} results in the formation of $[Fe(ta)_2]_n$ (**5**). Almost identical X-ray powder diffraction data compared to $[Mn(ta)_2]_n$ (**4**) suggest an

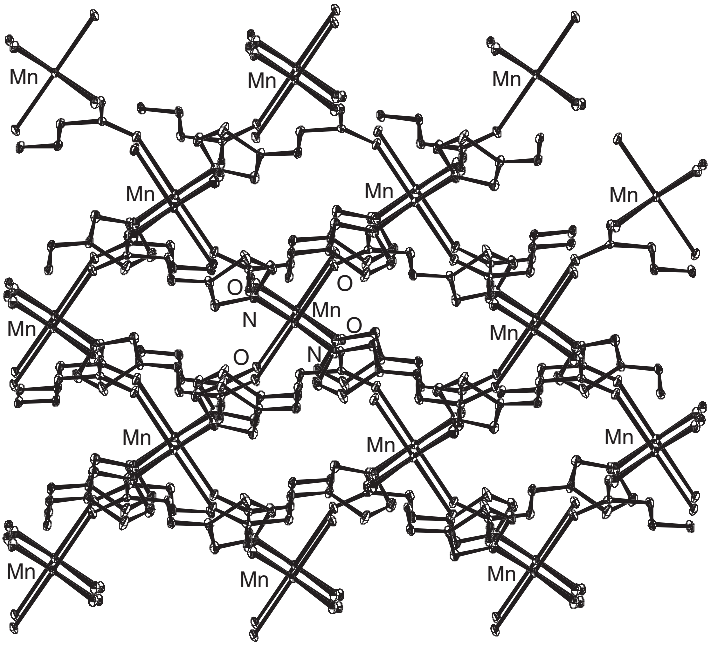


Figure 3. The 3-D framework in the molecular structure of $[Mn(ta)_2]_n$.

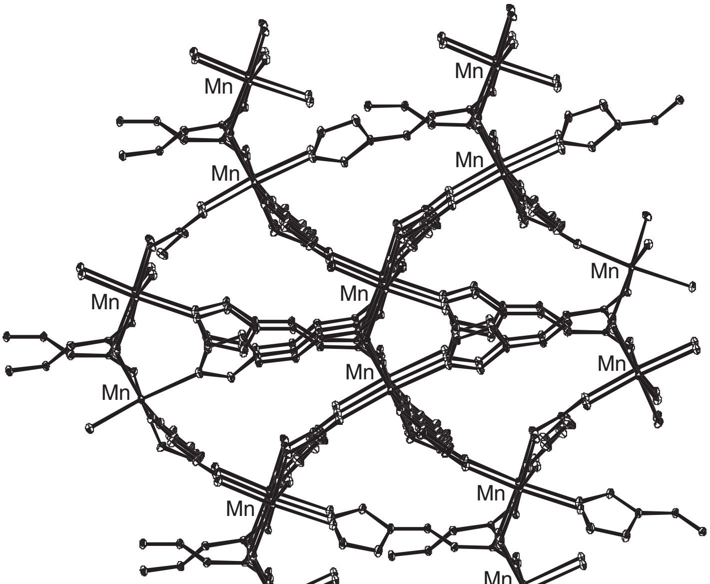


Figure 4. Side views on the 3-D framework in the molecular structure of **4**, revealing the channel-like structure of the holes within the structure.

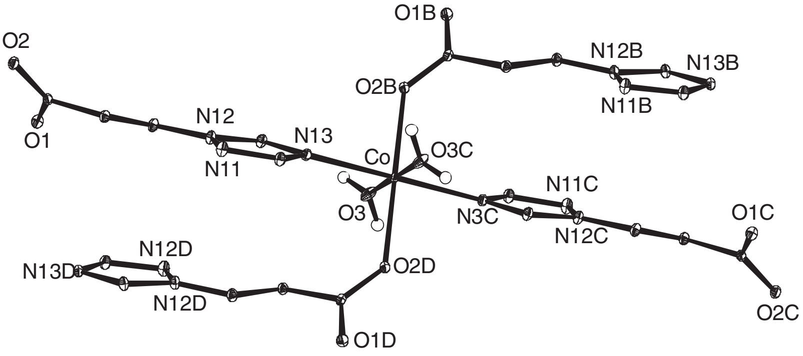


Figure 5. Coordination environment in the molecular structure of $[Co(ta)_2(H_2O)_2]_n$ (**6**). Thermal ellipsoids are drawn at the 50% probability level.

isostructural 3-D metal–organic framework structure. This is also backed by the elemental analysis and rather similar IR data (see above).

4.2. *$[Co(ta)_2(H_2O)_2]_n$ (6)*

Reacting cobalt sulfate with K[ta] afforded a 2-D coordination polymer. The metal center is coordinated by four independent 1,2,4-triazol-1-ylacrylate ions. Two additional water molecules occupy axial coordination sites. The ligand coordinates in a μ_2-ta-κN4 : O mode (figures 5 and 6). The nitrogen donors N4 of the triazolyl rings are *trans*, as are the carboxylate groups.

A view on the network structure of $[Co(ta)_2(H_2O)_2]_n$ is given in figure 6. The alignment of metal centers and ligands affords coordination polymer sheets with the coordinated water intercalating between the sheets. The network structure is stabilized by inter-sheet hydrogen bonds [inter-planar hydrogen bond length (Å): O1 $\cdots$ H 1.912(1)]. Generally, the structure is rather compact, leaving no larger holes within the network.

4.3. *$[Zn(ta)_2]_n$ (7)*

Coordination of 1,2,4-triazol-1-ylacrylate K[ta] (**3**) toward zinc(II) sulfate afforded 1-D double-strand coordination polymer chains. The zinc(II) is coordinated by four independent ligands (figure 7), three binding through the carboxylate functionality and one through N4 of the triazole group. As supported by the IR spectrum, two different coordination modes of the ta-ligand are present in the structure. Half bind in the μ_2-ta-κN4 : O mode, also observed in **6**, resulting in linear chains of zinc centers; **7** reveals a second, for the ligand, unique coordination mode. The second half of the ligands are bound in a μ_2-ta-κO1 : O2 fashion, fusing two single strings to the double strand while leaving one triazole ring non-coordinating. Hence, small Zn–Zn distances of 4.06 Å (μ_2-O1 : O2 bridged) for the adjacent zinc centers within the double strand can be observed. The *d*(Zn–Zn) along the single strand was determined as 9.65 Å (μ_2-N4 : O bridged).

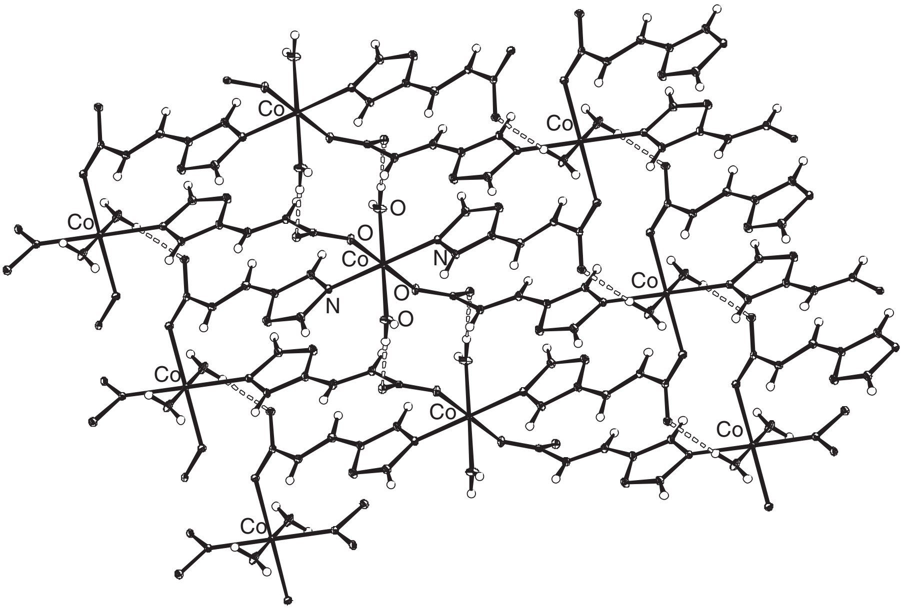


Figure 6. Top view on the 2-D network in **6**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): C1–O2, 1.2578(13); C1–O1, 1.2644(13); C1–C2, 1.5013(14); Co–O2, 2.0862(8); Co–N13, 2.1375(9); and O2–C1–O1, 123.61(11). Intraplanar hydrogen bond length (Å): O1 ··· H 1.969(1).

Dangling non-coordinating triazole groups from different double-strand arrays interdigitate through π–π stacking like a zipper, building up the 3-D network (figure 8). The sheets of "zipped" coordination polymer double strands then interlace into a tight network structure, without larger spaces between chains.

All the above-described structures contain M^{2+} metal centers of first row transition metals. However, the different geometrical preferences of the metals determine the variant final topologies. Hence, we focused on an investigation of the metal-directed assembly of MOFs employing alkaline earth metals.

4.4. *[Mg(H$_2$O)$_6$](ta)$_2$ (8)*

Whereas the 1,2,4-triazol-1-ylacrylate coordinates to transition metals, a simple salt exchange occurs by reacting k[ta] with $Mg(SO_4)_2 \times 6H_2O$. In the mononuclear magnesium complex, the metal center is coordinated by six water ligands, bearing 1,2,4-triazol-1-ylacrylate anion as counter ions. The asymmetric unit contains one ta-moiety and half a $[Mg(H_2O)_6]^{2+}$ ion. Each hydrogen of coordinated water is part of a hydrogen bridge (figure 9).

According to the thermogravimetric measurements, most coordination polymers described in this report are stable at 200°C (figure 10). In the case of $[Co(ta)_2(H_2O)_2]_n$ (**6**), a weight loss of approximately 10% occurs between 150°C and 225°C due to the loss of two coordinated water molecules.

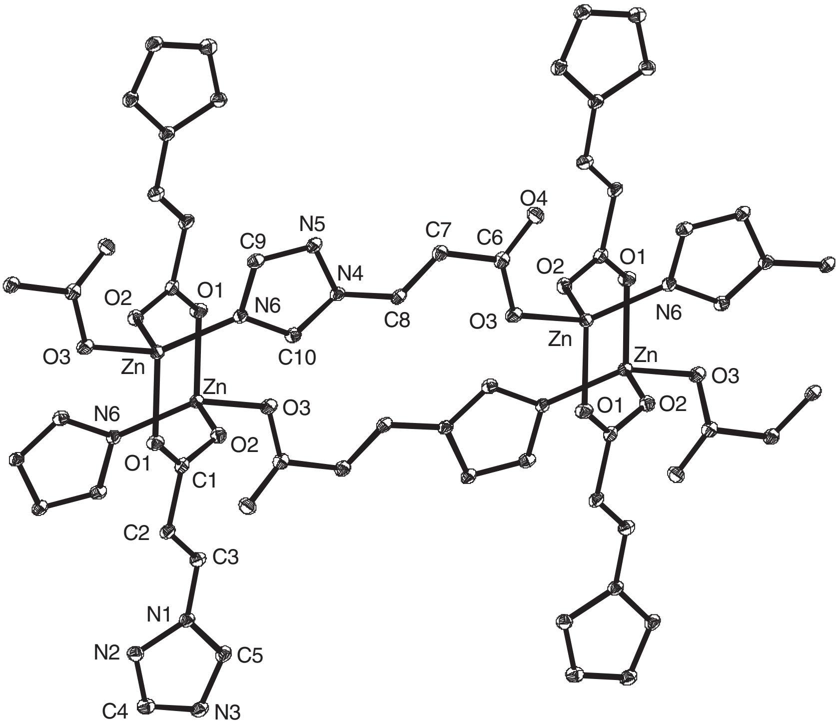


Figure 7. Coordination environment of the metal centers and ligand in the molecular structure of $[Zn(ta)_2]_n$ (**7**). Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): C1–O2, 1.262(5); C1–O1, 1.269(5); C1–C2, 1.487(6); C2–C3, 1.337(6); C3–N1, 1.392(6); Zn–O1, 1.982(3); Zn–O2, 2.018(3); Zn–O3, 1.921(3); Zn–N6, 1.985(4); O1–Zn–O2, 103.95(13); O1–Zn–O3, 96.87(13); O2–Zn–O3, 107.95(13); O1–Zn–N6, 115.47(14); O2–Zn–N6, 101.87(14); and O3–Zn–N6, 128.54(11).

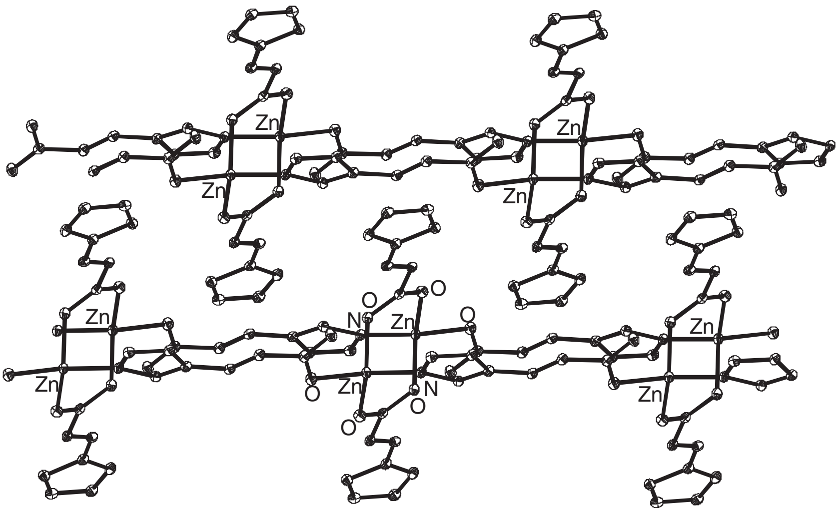


Figure 8. A cut-out of two "zipped" coordination polymer strings of **7**.

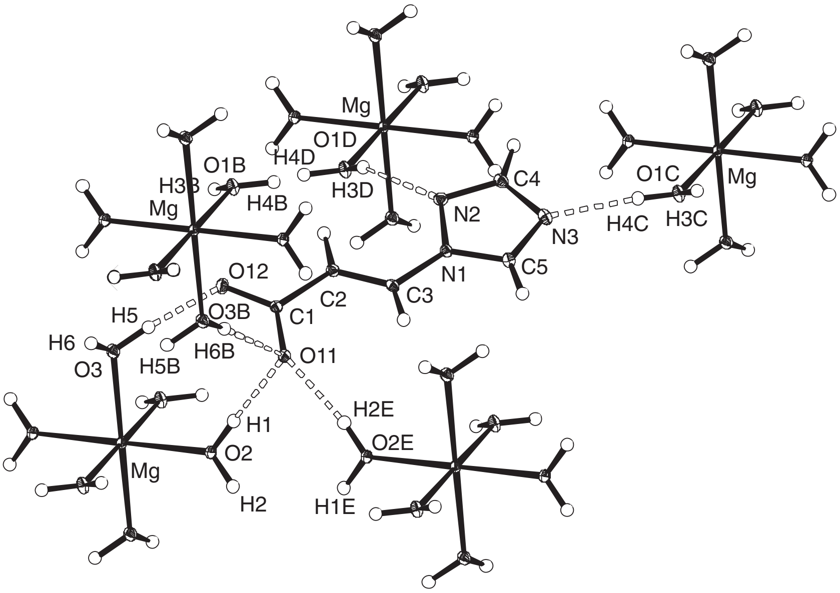


Figure 9. Molecular structure of $[Mg(OH_2)_6](ta)_2$ (**8**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen bond lengths (Å): O11 ··· H1, 1.860(3); O11 ··· H2E, 1.869(7); O11 ··· H6B, 2.094(8); O12 ··· H5, 1.761(2); N2 ··· H3D, 2.455(5); and N3 ··· H4C, 1.968(3).

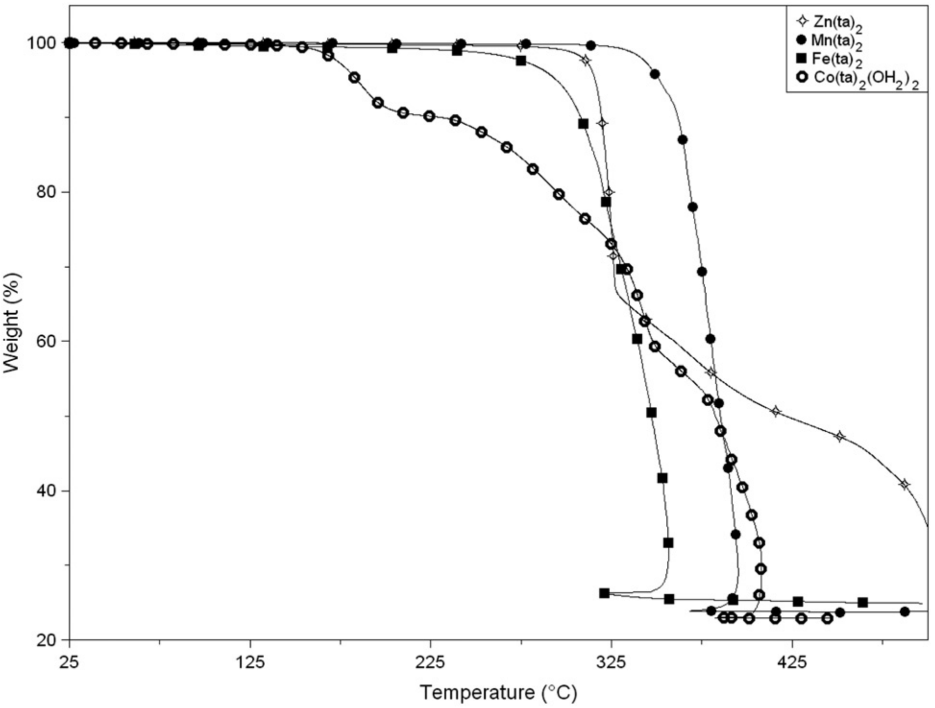


Figure 10. TGA measurements of **4–7**.

5. Conclusions

The 1,2,4-triazol-1-ylacrylate ligand ta with the two carboxylate O-donors and the two triazole N-donors (in position 2 and 4) offers four potential binding sites to transition metals. If three of these donors take part in coordination, MOFs are formed, as represented by the coordination polymers $[Mn(ta)_2]_n$ (**4**) and $[Fe(ta)_2]_n$ (**5**). The syntheses although performed in water, afford water-free MOFs and are rather simple and reproducible processes. A water-free coordination polymer built by interdigitating polymer double strands is observed for $[Zn(ta)_2]_n$ (**7**), in which half of the ta ligands are coordinated only *via* the carboxylate O-donors in a κ^2-O,O′ coordination mode. On the other hand, κ^2-N,O coordination of the ta ligand is observed for $[Co(ta)_2(H_2O)_2]_n$ (**6**) in which two water molecules occupy two *trans* positions of the octahedral cobalt. All MOFs discussed here show rather compact structures as indicated by a calculated density of $1.737\,\mathrm{g\,cm^{-3}}$ in the case of $[Mn(ta)_2]_n$ (**4**). Thus, future projects will focus on the syntheses of similar network structures, which form larger cavities.

Supplementary material

CCDC-771286 (for **4**), CCDC-771288 (for **6**), CCDC-771289 (for **7**), and CCDC-771290 (for **8**) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Dta centre *via* www.ccdc.cam.ac.uk/datarequest/cif.

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