



Solid chemistry of the Zn^{II}/1,2,4-triazolate/anion system: Separation of 2D isorecticular layers tuned by the terminal counteranions X (X = Cl⁻, Br⁻, I⁻, SCN⁻)

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ABSTRACT

An array of 2D isorecticular layers, viz. [Zn(atrz)X]_∞ (**1**·X; X = Cl⁻, Br⁻, I⁻; atrz = 3-amino-1,2,4-triazole anion), [Zn₄(atzr)₄(SCN)₄·H₂O]_∞ (**1**·SCN·H₂O) and [Zn(trz)X]_∞ (**2**·X; X = Cl⁻, Br⁻, I⁻; trz = 1,2,4-triazole anion), have been hydrothermally synthesized and structurally characterized. Compounds **1**·X and **1**·SCN·H₂O are constructed from binuclear planar Zn₂(atzr)₂ subunits and exhibit (4,4) topological network when the subunits are simplified as four-connected nodes. Based on changing the terminal counteranions X (X = Cl⁻, Br⁻, I⁻, SCN⁻), the average interlayer separations of **1**·X and **1**·SCN·H₂O are enlarged, which equal to 5.851, 6.153, 6.651 and 8.292 Å, respectively. As a result, H₂O molecules reside in the spaces between two adjacent layers of **1**·SCN·H₂O. **2** and **1** are the isomorphous structures. In common with **1**, the interlayer separations of **2**·X are widened with increasing the ion radius. Solid-state luminescence properties and thermogravimetric analyses of **1** and **2** were investigated, respectively.

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1. Introduction

During the past decades, organic–inorganic hybrids derived from transitional metal ions and multifunctional bridging ligands have drawn great current interest due to their potential technological applications [1]. Using assembly strategy, prototypical organic–inorganic hybrid materials have been constructed from metal cluster nodes linked through polyfunctional carboxylates, polypyridyl ligands and organodiphosphonate ligands [2–14]. More recently, polyazaheteroaromatic organic ligands such as pyrazole, imidazole, triazole and tetrazole have been employed in the construction of organic–inorganic architectures [15–20].

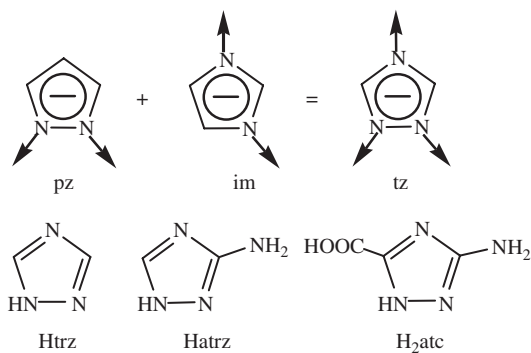
As the representative of simple organic ligands, in addition to affording different tether lengths, different charge-balance requirements and alternative functional group orientations, 1H-1,2,4-triazole (Htrz) unites the coordination geometries of both pyrazole and imidazole (see Scheme 1), and exhibits a strong and typical property of acting as bridging ligand among metal centers, which provides access to the design and syntheses of the molecular scale composites of inorganic and organic components [18,19,21]. Similarly, 3-amino-1H-1,2,4-triazole (Hatrz), one of

1,2,4-triazole derivatives, possesses all virtues of Htrz, and especially which could be employed as a asymmetrically substituted achiral ligand to build novel chiral compounds when N-ligating donor in the amino group attached to Hatrz participates in coordination. Li et al. [22] obtained a novel chiral cadmium coordination polymer, Cd(atrz)Cl, based on the unsymmetrical achiral atrz anion with an unprecedented μ₄-bridging mode.

The 2D isorecticular layers [Zn(μ₃-trz)Cl]_∞ were explored by Kröber via slow diffusion of methanol solution in an H-shape tube [23], which was the first entity of the isomeric structures [Zn(trz)X]_∞ (X = Cl⁻, Br⁻) [19,23]. Afterward, four similar 2D corrugated isorecticular networks [Cu(trz)]_∞, [Ag(trz)]_∞, Zn(dmtrz)Cl (dmtrz = 3,5-dimethyl-1,2,4-triazole anion), and Cd(datzr)I (datzr = 3,5-diamino-1,2,4-triazole anion) were reported by Zhang et al. [24] and Zhai et al. [25], respectively. As an extension of the above work, we expect the possible connection channels would be present in the whole crystalloid if the adjacent layers could be regularly overlapped face-to-face. Based on the considerations, zinc triazolate isorecticular layer frameworks, [Zn(atrz)X]_∞ (**1**·X; X = Cl⁻, Br⁻, I⁻; atrz = 3-amino-1,2,4-triazole anion), [Zn₄(atzr)₄(SCN)₄·H₂O]_∞ (**1**·SCN·H₂O) and [Zn(trz)X]_∞ (**2**·X; X = Cl⁻, Br⁻, I⁻; trz = 1,2,4-triazole anion) have been synthesized via a hydrothermal technique in the context. Structural analyses revealed that the average interlayer separations of the targets were enlarged by changing the terminal

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Scheme 1.

coordination counteranions X ($X = \text{Cl}^-$, Br^- , I^- , SCN^-). As expected, H_2O molecules reside in the spaces between two adjacent layers of $\mathbf{1} \cdot \text{SCN} \cdot \text{H}_2\text{O}$.

2. Experimental section

2.1. Materials and analytical methods

Commercially available reagents were used as received without further purification. Elemental analyses of C, H, N were performed on a Vario EL III analyzer. Infrared spectra were obtained from KBr pellets within the region $400\text{--}4000\text{ cm}^{-1}$ on a BEQ VZNDX 550 FTIR spectrometer. The powder X-ray diffraction (PXRD) was recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator. Thermogravimetric measurements were carried out from room temperature to 900°C for $\mathbf{1}$ and $\mathbf{2}$ on preweighed samples in hydrostatic air atmosphere using TA Instruments NETRZSCH STA 449C simultaneous TGA–DSC with a heating rate of $10^\circ\text{C min}^{-1}$. Fluorescence spectroscopy data were recorded on a model F-4500 fluorescence spectrophotometer.

2.2. Synthesis

2.2.1. Synthesis of $[\text{Zn}(\text{atrz})\text{Cl}]_\infty$ ($\mathbf{1} \cdot \text{Cl}$)

A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.119 g, 0.40 mmol), Hatrz (0.034 g, 0.40 mmol), NH_4Cl (0.021 g, 0.40 mmol) and H_2O (6 g, 333 mmol), was stirred until it was homogeneous, and then sealed in a 8 mL Teflon-lined stainless reactor, kept under autogenous pressure at 160°C for 72 h, followed by slow cooling down to room temperature by 5°C/h . Colorless rhombic crystals suitable for X-ray crystal analyses were isolated in 21% yield (based on Zn), which are stable in air and insoluble in water and common organic solvents. IR (KBr pellet, cm^{-1}): ν 3476 m, 3381 m, 3321 w, 3125 w, 1755 w, 1622 s, 1556 s, 1523 s, 1421 m, 1307 m, 1228 m, 1113 w, 1066 m, 1019 w, 879 m, 769 w, 742 m, 642 w, 486 m. Elemental analysis for $\mathbf{1} \cdot \text{Cl}$: $\text{C}_2\text{H}_3\text{N}_4\text{ZnCl}$ ($M_r = 183.90$). Calcd: H 1.64%, C 13.06%, N 30.46%. Found: H 1.51%, C 13.03%, N 30.54%.

2.2.2. Synthesis of $[\text{Zn}(\text{atrz})\text{Br}]_\infty$ ($\mathbf{1} \cdot \text{Br}$)

A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.089 g, 0.30 mmol), 3-amino-5-carboxyl-1,2,4-triazole (H_2atc) (0.055 g, 0.40 mmol), $(\text{Me})_4\text{NBr}$ (0.046 g, 0.30 mmol) and H_2O (6 g, 333 mmol), was stirred until it was homogeneous, and then sealed in a 8 mL Teflon-lined stainless reactor, kept under autogenous pressure at 160°C for 72 h, and then slowly cooled to room temperature at a rate of 5°C/h . Suitable colorless rhombic crystals, stable in air and insoluble in water and common organic solvents, were isolated in

32% yield (based on Zn). IR (KBr pellet, cm^{-1}): ν 3478 m, 3376 m, 3120 w, 1757 w, 1621 s, 1551 s, 1521 s, 1418 m, 1304 m, 1226 m, 1110 w, 1061 m, 1015 w, 879 m, 766 w, 740 m, 640 w, 484 m. Elemental analysis for $\mathbf{1} \cdot \text{Br}$: $\text{C}_2\text{H}_3\text{N}_4\text{ZnBr}$ ($M_r = 228.36$). Calcd: H 1.32%, C 10.52%, N 24.53%. Found: H 1.54%, C 10.56%, N 24.64%.

2.2.3. Synthesis of $[\text{Zn}(\text{atrz})\text{I}]_\infty$ ($\mathbf{1} \cdot \text{I}$)

Compound $\mathbf{1} \cdot \text{I}$ was prepared following the procedure described for compound $\mathbf{1} \cdot \text{Br}$, but KI was used instead of $(\text{Me})_4\text{NBr}$. Colorless rhombic crystals, stable in air and insoluble in water and common organic solvents, were isolated in 35% yield (based on Zn). IR (KBr pellet, cm^{-1}): ν 3473 m, 3362 m, 3113 w, 1760 w, 1622 s, 1548 s, 1519 s, 1416 m, 1299 m, 1223 m, 1105 w, 1056 m, 1013 w, 881 m, 765 w, 737 w, 637 w, 479 m. Elemental analysis for $\mathbf{1} \cdot \text{I}$: $\text{C}_2\text{H}_3\text{N}_4\text{ZnI}$ ($M_r = 275.35$). Calcd: H 1.10%, C 8.72%, N 20.35%. Found: H 1.09%, C 8.75%, N 20.46%.

2.2.4. Synthesis of $[\text{Zn}_4(\text{atrz})_4(\text{SCN})_4 \cdot \text{H}_2\text{O}]_\infty$ ($\mathbf{1} \cdot \text{SCN} \cdot \text{H}_2\text{O}$)

A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.089 g, 0.30 mmol), Hatrz (0.025 g, 0.30 mmol), NH_4SCN (0.023 g, 0.30 mmol) and H_2O (6 g, 333 mmol), was stirred until it was homogeneous, and then sealed in a 8 mL Teflon-lined stainless reactor, kept under autogenous pressure at 145°C for 72 h, followed by slow cooling down to room temperature at a rate of 5°C/h . Colorless and club-shaped crystals, stable in air and insoluble in water and common organic solvents, were isolated in 37% yield (based on Zn). IR (KBr pellet, cm^{-1}): ν 3455 m, 3364 m, 3118 w, 2081 s, 1630 s, 1558 s, 1524 m, 1422 m, 1305 m, 1228 m, 1116 w, 1066 m, 1018 w, 875 m, 770 w, 740 w, 643 w, 482 m. Elemental analysis for $\mathbf{1} \cdot \text{SCN} \cdot \text{H}_2\text{O}$: $\text{C}_{12}\text{H}_{11}\text{N}_{20}\text{S}_4\text{Zn}_4\text{O}$ ($M_r = 841.13$). Calcd: H 1.32%, C 17.14%, N 33.30%. Found: H 1.95%, C 16.40%, N 33.24%.

2.2.5. Synthesis of $[\text{Zn}(\text{trz})\text{Cl}]_\infty$ ($\mathbf{2} \cdot \text{Cl}$)

Compound $\mathbf{2} \cdot \text{Cl}$ was prepared following the procedure described for compound $\mathbf{1} \cdot \text{Cl}$, except that Htrz (0.028 g, 0.40 mmol) was used instead of Hatrz. Colorless rhombic crystals, stable in air and insoluble in water and common organic solvents, were isolated in 28% yield (based on Zn). IR (KBr pellet, cm^{-1}): ν 3111 m, 3042 w, 2945 w, 1529 s, 1331 w, 1303 s, 1218 w, 1177 s, 1097 s, 1045 m, 1007 s, 885 m, 659 s. Elemental analysis for $\mathbf{2} \cdot \text{Cl}$: $\text{C}_2\text{H}_2\text{N}_3\text{ZnCl}$ ($M_r = 168.89$). Calcd: H 1.19%, C 14.22%, N 24.88%. Found: H 1.37%, C 14.08%, N 24.56%.

2.2.6. Synthesis of $[\text{Zn}(\text{trz})\text{Br}]_\infty$ ($\mathbf{2} \cdot \text{Br}$)

Compound $\mathbf{2} \cdot \text{Br}$ was prepared following the procedure described for compound $\mathbf{2} \cdot \text{Cl}$, except that $(\text{Me})_4\text{NBr}$ (0.123 g, 0.80 mmol) was used instead of NH_4Cl . Colorless rhombic crystals, stable in air and insoluble in water and common organic solvents, were isolated in 33% yield (based on Zn). IR (KBr pellet, cm^{-1}): ν 3129 w, 3108 m, 3041 w, 2943 w, 1528 s, 1330 w, 1302 s, 1217 w, 1177 m, 1096 s, 1042 m, 1005 m, 902 w, 884 m, 658 s. Elemental analysis for $\mathbf{2} \cdot \text{Br}$: $\text{C}_2\text{H}_2\text{N}_3\text{ZnBr}$ ($M_r = 213.35$). Calcd: H 0.94%, C 11.26%, N 19.69%. Found: H 0.86%, C 11.28%, N 19.80%.

2.2.7. Synthesis of $[\text{Zn}(\text{trz})\text{I}]_\infty$ ($\mathbf{2} \cdot \text{I}$)

A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.119 g, 0.40 mmol), Htrz (0.028 g, 0.40 mmol), KI (0.083 g, 0.50 mmol) and H_2O (6 g, 333 mmol), was stirred until it was homogeneous, and then sealed in a 8 mL Teflon-lined stainless reactor, kept under autogenous pressure at 160°C for 72 h, and then slowly cooled to room temperature at a rate of 5°C/h . Colorless prism crystals, stable in air and insoluble in water and common organic solvents, were isolated in 23% yield (based on Zn). IR (KBr pellet, cm^{-1}): ν 3105 m, 3040 w, 2937 w, 1529 s, 1329 w, 1301 s, 1214 w, 1175 s,

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