Supporting Information

Silver(I) carboxylates: versatile inorganic analogs of carboxylic acids for supramolecular network formation.

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Experimental, Characterization and Crystallographic Data

Figure S1. View of **1** showing components of SBU and bridging mode of carboxylate ligand (30% probability ellipsoids).

Figure S2. View of **2** showing components of SBU and bridging mode of carboxylate ligand (30% probability ellipsoids).

Fig S3a. View of **3** showing components of SBU, bridging mode of carboxylate ligand and disordered CF_3 groups (30% probability ellipsoids).

Fig S3b. View of **3** showing extended silver carboxylate linkage that connects the layers built up from the SBU.

Full crystallographic data for compounds 1-3 in CIF format as a separate file.

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Crystal Syntheses and Characterization

Ag(CF₃COO)(DABCO) 1: Ag(CF₃COO) (28.0 mg, 0.127 mmol) in ethanol (4 mL) was added to DABCO (14.2 mg, 0.127 mmol) in ethanol (4 mL). White powder formed rapidly and was redissolved upon addition of 0.9M aqueous NH₃ (4 mL). Colorless crystals of **1** (13.5 mg, yield 32.0 %) resulted after 18 days. Partial decomposition (Ag(I) reduction) prevented satisfactory elemental and powder diffraction analysis. **Ag(CF₃COO)(TMP) 2*:** Ag(CF₃COO) (35.2 mg, 0.159 mmol) in ethanol (4 mL) was added to tetramethylpyrazine (TMP) (21.7 mg, 0.159 mmol) in toluene (4 mL). Colorless crystals of **2** (41.2 mg, yield 72.4 %) resulted after 7 days. Calcd: C, 33.64; H, 3.39; N, 7.85%; found: C, 33.73; H, 3.43 N, 7.57%. **Ag(CF₃COO)(pyraz) 3*:** Ag(CF₃COO) (34.0 mg, 0.154 mmol) in ethanol (4 mL) was added to pyrazine (12.2 mg, 0.153 mmol) in ethanol (6 mL). Colorless crystals of **3** (28.6 mg, yield 61.9 %) resulted after 11 days. Calcd: C, 23.94; H, 1.34; N, 9.31%; found: C, 24.07; H, 1.35 N, 9.11%. Crystals were grown by slow evaporation at ca. 22 °C. *Powder diffraction patterns (bulk samples) consistent with calculated patterns.

Crystal Data

1 Rectangular rods; M = 333.07, orthorhombic, Cmca, a = 12.5745(2), b = 12.3972(2), c = 14.2861(2) Å, U = 2227.04(6) Å³, Z = 8, $D_c = 1.987$ Mg m⁻³, T = 223(5) K; $R_1(F) = 0.037$, $wR_2(F^2) = 0.091$, $S(F^2) = 1.12$ for 1591 $F^2 > 2\sigma(F^2)$. **2** Hexagonal plates; M = 357.09, triclinic, P-1, a = 9.0587(2), b = 9.1231(2), c = 9.6097(2) Å, $\alpha = 117.553(1)$, $\beta = 116.433(1)$, $\gamma = 91.471$ (3) °, U = 603.07(2) Å³, Z = 2, $D_c = 1.966$ Mg m⁻³, T = 223(5) K; $R_1(F) = 0.021$, $wR_2(F^2) = 0.051$, $S(F^2) = 1.05$ for $2874 F^2 > 2\sigma(F^2)$. **3** Multifacetted blocks, M = 300.98, monoclinic, C2/c, a = 12.766(2), b = 10.141(2), c = 7.008(1) Å, $\beta = 102.030(3)$ °, U = 887.3(2) Å³, Z = 4, $D_c = 2.253$ Mg m⁻³, T = 296(2) K; $R_1(F) = 0.024$, $wR_2(F^2) = 0.072$, $S(F^2) = 1.41$ for $1215 F^2 > 2\sigma(F^2)$. CCDC nos.171148 - 171150.

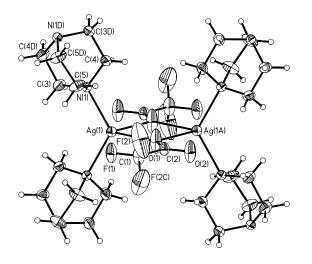


Fig S1. View of **1** showing components of SBU and bridging mode of carboxylate ligand (30% probability ellipsoids).

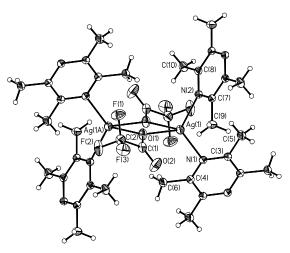


Fig S2. View of **2** showing components of SBU and bridging mode of carboxylate ligand (30% probability ellipsoids).

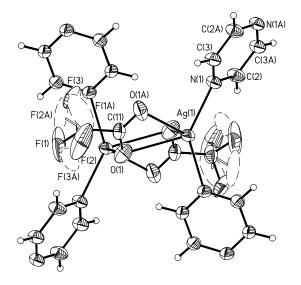


Fig S3a. View of **3** showing components of SBU, bridging mode of carboxylate ligand and disordered CF_3 groups (30% probability ellipsoids).

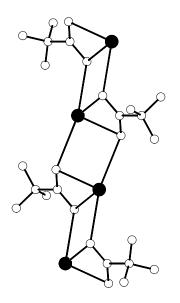


Fig S3b. View of **3** showing extended silver carboxylate linkage that connects the layers built up from the SBU.