Syntheses and Crystal Structures of Two Silver (I) Complexes with Organic Carboxylic Acid and Bidentate N-donor Ligands

ARTICLE in CHINESE JOURNAL OF STRUCTURAL CHEMISTRY · JUNE 2011
Impact Factor: 0.51

2 AUTHORS:

Chong-Chen Wang
Beijing University of Civil Engineering and A...
44 PUBLICATIONS 387 CITATIONS

Peng Wang
Beijing University of Civil Engineering and A...
759 PUBLICATIONS 18,770 CITATIONS

Available from: Chong-Chen Wang
Retrieved on: 15 March 2016
Syntheses and Crystal Structures of Two Silver(I) Complexes with Organic Carboxylic Acid and Bidentate N-donor Ligands

WANG Chong-Chen a,b  WANG Peng a

a (Key Laboratory of Urban Stormwater System and Water Environment (Beijing University of Civil Engineering and Architecture), Ministry of Education, Beijing 100044, China)
b (School of Environment and Energy Engineering, Beijing University of Civil Engineering and Architecture, Beijing 100044, China)

ABSTRACT The title complexes \((\text{NH}_4)[\text{Ag(dpe)}(\text{H}_2\text{bpte})]\) (1) and \(\text{Ag}_2(\text{bpy})(\text{ox})\cdot7\text{H}_2\text{O}\) (2) were synthesized via slow evaporation at room temperature, and characterized by elemental analysis and infrared spectra. The crystal of 1 crystallizes in triclinic, space group \(P\overline{1}\) with \(a = 8.3959(7), b = 11.8088(12), c = 12.8175(13) \text{ Å}, \alpha = 85.507(2), \beta = 79.245(1), \gamma = 84.174(2)\), \(V = 1239.7(2) \text{ Å}^3\), \(Z = 2\), \(C_{28}\text{H}_{22}\text{AgN}_3\text{O}_8\), \(M_r = 636.36\), \(D_c = 1.705\ \text{g/cm}^3\), \(F(000) = 644\) and \(\mu(\text{Mo}\text{K}a) = 0.874\ \text{mm}^{-1}\). The final \(R = 0.0479\) and \(wR = 0.1426\) for 3632 observed reflections with \(I > 2\sigma(I)\) and \(R = 0.0559\) and \(wR = 0.1503\) for all data. The crystal of 2 crystallizes in orthorhombic, space group \(Pnna\) with \(a = 17.2291(17), b = 7.5289(6), c = 21.369(2), V = 2771.9(4) \text{ Å}^3\), \(Z = 4\), \(C_{22}\text{H}_{30}\text{Ag}_2\text{N}_4\text{O}_{11}\), \(M_r = 742.24\), \(D_c = 1.779\ \text{g/cm}^3\), \(F(000) = 1488\) and \(\mu(\text{Mo}\text{K}a) = 1.476\ \text{mm}^{-1}\). The final \(R = 0.0648\) and \(wR = 0.2058\) for 1996 observed reflections with \(I > 2\sigma(I)\) and \(R = 0.0769\) and \(wR = 0.2192\) for all data. X-ray diffraction reveals that in complexes 1 and 2, both 1,2-di(4-pyridyl)ethylene and 4,4'-bipyridine act as typical bidentate N-donor ligands to link two Ag centers. 3,3',4,4'-Biphenyltetracarboxylate and oxalate anions play the role of organic linkers and counter-ions to balance the cationic charge of Ag\(^{+}\). The rich hydrogen-bonding interactions and ligand-unsupported Ag···Ag interactions as well as π-π stacking interactions contribute to the construction of three-dimensional sandwich-like frameworks.

Keywords: silver complexes, 3,3',4,4'-biphenyltetracarboxylic acid, oxalic acid, 1,2-di(4-pyridyl)ethylene, 4,4'-bipyridine

1 INTRODUCTION

The design and assembly of Ag(I) coordination polymers have received more and more attention due to their intriguing structures and possible usages in hydrogen storage\(^{[1]}\), catalysis\(^{[2]}\), magnetism\(^{[3]}\), fluorescence\(^{[4]}\) and gas separation materials\(^{[5]}\). The construction of coordination polymers is highly influenced by the factors like coordination nature of metal ions, structural characteristic of poly-dentate organic ligands, metal-ligand ratio, and possible counter-ions\(^{[6]}\). The key to the construction of a-
sired framework is the selection of organic ligands, and in some cases, a subtle alteration of organic ligands could lead to different architectures, such as [Ag(bpp)][Ag₂(ppa)(ox)]NO₃[6] and [Ag₂(ppa)(ox)]·9H₂O[6] (bpp = 1,3-bis(pyridyl)propane, ppa = N-(4-pyridinylmethyl)-4-pyridinecarboxamide, ox = oxalate), [Ag(bpp)]₂(tdc)·8H₂O[7] and [Ag₂(bpp)(H₂O)]·6H₂O[8] (tdc = thiophene-2,5-dicarboxylate), and [Ag₂(bpp)(H₂O)]·6H₂O[9] (bpy = 4,4′-bipyridine, tdc = thiophene-2,5-dicarboxylate), [Ag(bpp)]₂(tdc)·8H₂O[7] and [Ag₂(bpp)(H₂O)]·6H₂O[8] (bpy = 4,4′-bipyridine, HA = hexanedioic acid, pdc = pyridine-3,5-dicarboxylic acid, bptc = 3,3′,4,4′-biphenyltetracarboxylic acid)[9]. Some complexes of silver(I) and bpy but different counterions have been reported, like Ag₂(bpy)₀.₅(dpa), Ag₂(bpy)₁.₅(dpa)(H₂O), Ag₂(bpy)₁.₅(Hdpa), α-[Ag(bpy)]·(Hdpa), β-[Ag(bpy)]·(Hdpa), [Ag(bpy)]₂·(dpa)·6H₂O, and [Ag(bpy)]₄·(dpa)·2(NO₃)·6H₂O (H₂dpa = 1,1′-biphenyl-2,2′-dicarboxylic acid, bpy = 4,4′-bipyridine)[10]. The alteration of different counterions resulted into different structures. A single 1D chain of {Ag₂(dpa)} exists in Ag₂(bpy)₀.₅(dpa), while one supramolecular chain of tetraneurial {Ag₂(dpa)(H₂O)}₂ subunits linked by Ag⋯Ag interactions and hydrogen bonding interactions is observed in Ag₂(bpy)₁.₅(dpa)(H₂O), and one 1D alternate chain of eight-membered {Ag₂(Hdpa)}₂ ring bridged by bpy is present in Ag₂(bpy)₁.₅(Hdpa). However, two different 1D supramolecular double chains of [Ag(bpy)(Hdpa)] are found in α-[Ag(bpy)]·(Hdpa) and β-[Ag(bpy)]·(Hdpa), which are sustained by the combination of weak Ag⋯O interactions, π–π stacking interactions, and argenticophilic interactions in α-[Ag(bpy)]·(Hdpa), while only by π–π stacking interactions in β-[Ag(bpy)]·(Hdpa). Compounds [Ag(bpy)]₂·(dpa)·6(H₂O) and [Ag(bpy)]₄·(dpa)·2(NO₃)·6(H₂O) are based upon 2D supramolecular substructures of [Ag(bpy)]₂·(dpa) and [{Ag(bpy)}₄·(dpa)·(H₂O)]₂· respectively.

Rigid 4,4′-bipyridine (4,4′-bpy) and flexible 1,2-di(4-pyridyl)ethylene (dpe) as typical and excellent pyridyl-donor bridging ligands have been used to construct many infinite frameworks[11–16]. Meanwhile, 3,3′,4,4′-biphenyltetracarboxylic acid (H₄bptc) and oxalic acid (ox) have been employed as exomultidentate ligands for the design and construction of novel coordination polymers owing to their thermal stability and symmetry[9, 17–21]. We are exploring the use of rigid 4,4′-bpy/flexible dpe, plus H₄bptc and ox, to generate silver coordination complexes. In this paper, we report the syntheses and crystal structures of two new coordination complexes assembled from AgNO₃ with these ligands, namely 1 and 2. The single-crystal diffraction results revealed that both complexes contain a fascinating sandwich-like framework, in which rich hydrogen-bonding interactions and ligand-unsupported Ag⋯Ag interactions contribute to the construction of three-dimensional crystal structures.

2 EXPERIMENTAL

2.1 Materials and general methods

All commercially available chemicals were of reagent grade, and used as received without further purification. C, N and H of the title complexes were performed by Elementar Vario EL-III, and O of the title complexes was performed by Flash EA1112. Infrared spectra in the region of 400–4000 cm⁻¹ were recorded on a PerkinElmer Spectrum 100 Fourier Transform infrared spectrophotometer.

2.2 Synthesis of the complexes

2.2.1 Synthesis of 1

An ammonia solution (25 mL) containing 0.0085 g AgNO₃ (0.05 mmol) and 0.017 g 3,3′,4,4′-biphenyltetracarboxylic acid (0.05 mmol, H₄bptc) was added dropwise to an alcohol solution (25 mL) of 0.0078 g 1,2-di(4-pyridyl)ethylene (0.05 mmol, dpe). The clear mixture was stirred for a few minutes and then allowed to evaporate at room temperature slowly. Block-like colorless crystals of 1 appeared after several weeks. Anal. Calcd. for C₂₉H₂₂AgN₃O₈ (%): C, 52.85; H, 3.48; N, 6.60; O, 20.11. Found (%): C, 53.11; H, 3.51; N, 6.49; O, 20.34. IR (KBr)/cm⁻¹: 3435, 3202, 1695, 1601, 1578, 1499, 1423, 1358, 1191, 1110, 1010, 972, 851, 828, 790, 710, 676, 643, 619, 549.
2.2.2 Synthesis of 2

An ammonia solution (25 mL) containing 0.0085 g AgNO₃ (0.05 mmol) and 0.005 g oxalic acid (0.05 mmol, H₂ox) was added dropwise to an alcohol solution (25 mL) of 0.0078 g 4,4΄-bipyridine (0.05 mmol, bpy). The clear mixture was stirred for ca. 30 minutes and then allowed to evaporate at room temperature slowly. Block-like colorless crystals of 2 appeared after four weeks. Anal. Calcd. for C_{22}H_{30}Ag_{2}N_{4}O_{11} (%): C, 35.58; H, 4.04; N, 7.54. Found (%): C, 36.21; H, 4.16; N, 7.35. IR (KBr)/cm⁻¹: 3439, 1643, 1598, 1532, 1487, 1411, 1311, 1220, 1073, 995, 810, 779, 617, 507.

2.3 Structure determination

Two suitable crystals (0.48 mm × 0.41 mm × 0.40 mm for 1 and 0.40 mm × 0.30 mm × 0.12 mm for 2) were selected for X-ray diffraction. Diffraction intensities for complexes 1 and 2 were recorded with a Bruker CCD area detector diffractometer equipped with a graphite-monochromatized MoKα radiation (λ = 0.71073 Å) using a φ-ω mode at 298(2) and 296(2) K, respectively. A total of 6376 reflections for 1 were collected in the range of 1.62<θ<25.01°, of which 4248 were unique (Rint = 0.0243) and 3632 were observed (I > 2σ(I)); while out of the 12333 total reflections for 2 in the 2.869<θ<27.834° region, 2453 were unique with Rint = 0.134 and 2002 were observed (I > 2σ(I)). Semi-empirical absorption corrections were applied using the SADABS program[22]. The structures were solved by direct methods and refined by full-matrix least-squares on F² using the SHELXS-97 and SHELXL-97 programs, respectively[23, 24]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of organic ligands were added according to theoretical models, and those of water molecules and ammonia ions were found by difference Fourier maps. For 1, the final R = 0.0479, wR = 0.1426 (w = 1/[(σ²(Fo²) + (0.907P)² + 1.9023P)], where P = (Fo² + 2Fc²)/3, S = 1.077, (Δρ)max = 1.453 and (Δρ)min = −0.793 e/Å³. For 2, the final R = 0.0648, wR = 0.2058 (w = 1/[(σ²(Fo²) + (0.1197P)² + 15.3351P)], where P = (Fo² + 2Fc²)/3, S = 1.014, (Δρ)max = 1.00 and (Δρ)min = −1.05 e/Å³. The selected bond distances and bond angles for complexes 1 and 2 are listed in Table 1.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Dist. (Å)</th>
<th>Bond</th>
<th>Dist. (Å)</th>
<th>Bond</th>
<th>Dist. (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(1)-N(2)</td>
<td>2.189(4)</td>
<td>Ag(1)-N(1)</td>
<td>2.196(4)</td>
<td>Ag(1)-O(1)</td>
<td>2.567(3)</td>
</tr>
<tr>
<td>Angle</td>
<td>(°)</td>
<td>Angle</td>
<td>(°)</td>
<td>Angle</td>
<td>(°)</td>
</tr>
<tr>
<td>N(2)-Ag(1)-N(1)</td>
<td>170.51(14)</td>
<td>N(2)-Ag(1)-O(1)</td>
<td>98.73(14)</td>
<td>N(1)-Ag(1)-O(1)</td>
<td>88.82(13)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond</th>
<th>Dist. (Å)</th>
<th>Bond</th>
<th>Dist. (Å)</th>
<th>Bond</th>
<th>Dist. (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(1)-N(2)</td>
<td>2.162(7)</td>
<td>Ag(1)-N(1)</td>
<td>2.178(8)</td>
<td>Ag(1)-O(1)</td>
<td>2.607(11)</td>
</tr>
<tr>
<td>Angle</td>
<td>(°)</td>
<td>Angle</td>
<td>(°)</td>
<td>Angle</td>
<td>(°)</td>
</tr>
<tr>
<td>N(2)-Ag(1)-N(1)</td>
<td>172.7(4)</td>
<td>N(1)-Ag(1)-O(2)</td>
<td>91.55(2)</td>
<td>N(2)-Ag(1)-O(1)</td>
<td>105.71(3)</td>
</tr>
</tbody>
</table>

3 RESULTS AND DISCUSSION

3.1 IR spectrum

In the IR spectrum of complex 1, a strong and broad absorption at 3435 m⁻¹ is assigned to the stretching vibration of hydroxyl, showing the presence of lattice water molecules. The asymmetric and symmetric vibrations of carboxylate group in the complex appear at about 1601 and 1423 cm⁻¹, respectively. Observed from the IR spectrum of complex 2, a strong band at 3439 m⁻¹ results from the stretching vibration of hydroxyl, indicating the existence of lattice water molecules. The sharp bands at 1598 and 1411 m⁻¹ are attributed to the asymmetric and symmetric vibrations of carboxylate group, respectively.

3.2 Structure description of complex 1

The crystallographic analysis reveals that the
asymmetric unit of complex 1 consists of one Ag atom, one dpe ligand, one H$_2$bptc$^{2-}$ ligand and one discrete ammonia cation. The coordination environment around the Ag(I) center is illustrated in Fig. 1. Each Ag(I), in a T-shaped coordination geometry, is coordinated by two nitrogen atoms from two different dpe ligands (Ag–N 2.189(4) Å and 2.196(4) Å; N–Ag–N 170.51(14)o) and one oxygen from the H$_2$bptc$^{2-}$ ligand (Ag–O 2.567(3) Å, N(2)–Ag(1)–O(1) 98.73(14)o, N(1)–Ag(1)–O(1) 88.82(13)o), comparable to the reported Ag(I) complexes [6–9]. The dpe acts as a typical bidentate ligand to link two different Ag(I) atoms via two nitrogen atoms on the pyridyl rings. The H$_2$bptc$^{2-}$ serves as a monodentate ligand to link one Ag(I) atom through one oxygen atom of one COO group attached on the benzene ring, forming anionic [Ag(dpe)(H$_2$bptc)]$^{-}$. The role of bptc ligand in complex 1 is much different from that in [Ag$_4$(bpy)$_4$(bptc)$_4$]·14H$_2$O[9], in which the completely deprotonated bptc$^{4-}$ ions only balance the charge of cationic [Ag$_4$(bpy)$_4$]$^{4+}$ chains but do not participate in coordination with the Ag$^{4+}$ atoms. In complex 1, the discrete cationic NH$_4$$^{+}$ plays the role of counterions to balance the anionic [Ag(dpe)(H$_2$bptc)]$^{-}$.

In complex 1, the H$_2$bptc$^{2-}$ anions coordinate and bridge the adjacent Ag$^{4+}$ centers to form double chains, thus reducing the effective positive charge in each Ag$^{4+}$, and further allowing the cations to approach more closely so as to form Ag···Ag interactions with the distances of 3.3935(6) Å, which is comparable to those (2.970(2)–3.422(3) Å) found in other Ag$^{4+}$ coordination polymers with pyridyl-donor ligands[6–10]. The above-stated ligand-unsupported Ag···Ag interactions further strengthen the double cationic chains. Furthermore, there are $\pi$-$\pi$ stacking interactions between adjacent double chains: Cg(1)–Cg(1)* = 3.874(3) Å and Cg(2)–Cg(2)* = 4.229(3) Å (Cg(1) is the centroid of aromatic ring N(1), C(17), C(18), C(19), C(20), C(21), and Cg(1)* the centroid symmetric aromatic ring; Cg(2) is the centroid of aromatic ring N(2), C(22), C(23), C(24)a, C(25)a, C(26), and Cg(2)* the centroid symmetric aromatic ring), giving rise to a two-dimensional network, as depicted in Fig. 2(a).

In complex 1, the anionic layers are constructed between H$_2$bptc$^{2-}$ anions and NH$_4$$^{+}$ cations by hydrogen-bonding interactions, which may play the role in the orientation of H$_2$bptc$^{2-}$ ions in the crystal, as listed in Table 2. The adjacent [Ag(dpe)]$^{n+}$ chains joined by Ag···Ag interactions to build cationic 2-D layers. The anionic and cationic layers are stacked in an A···B···A mode via electrostatic interactions and intermolecular hydrogen bonds to construct a three-dimensional sandwich-like framework, as shown in Fig. 2(b).

3.3 Structure description of complex 2

The crystal structure reveals that Ag$_4$(bpy)(ox)$_7$H$_2$O is made up of an infinite 2-D [Ag$_4$(bpy)(ox)] network formed by cationic [Ag$_4$(bpy)]$_{2n+}$ chains, ox$^{2-}$ ligands, and H$_2$O molecules. In the [Ag$_4$(bpy)]$_{2n+}$ chains, the Ag$^{4+}$(1) in a T-shaped coordination geometry is coordinated by two nitrogen atoms from two different bpy ligands (Ag–N 2.162(7) and 2.178(8) Å; N–Ag–N 172.7(4)o) and one weakly
coordinated oxygen atom from the ox$^{2-}$ ligands (Ag–O 2.607(11) Å, N–Ag–O 91.551(2)$^\circ$ and 105.711(3)$^\circ$), as expected for complex 1 and the previously reported similar Ag complexes (Fig. 3 and Table 2).

Fig. 2. (a) 2-D layer formed via Ag···Ag and π–π stacking interactions between the cationic [Ag(dpe)]$^{n+}$ chains in the crystal of (1); (b) Packing view of 1 along the $a$-axis framework linked via rich hydrogen-bonding and π–π stacking interactions

Fig. 3. Asymmetric unit of 2 and coordination environments of
Table 2. Hydrogen Bond Lengths (Å) and Bond Angles (°) for Complexes 1 and 2

<table>
<thead>
<tr>
<th>D–H⋅⋅⋅A</th>
<th>d(D–H)</th>
<th>d(H⋅⋅⋅A)</th>
<th>d(D⋅⋅⋅A)</th>
<th>∠DHA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(3)–H(3A)⋅⋅⋅O(2)</td>
<td>0.90</td>
<td>2.23</td>
<td>2.896(6)</td>
<td>130</td>
</tr>
<tr>
<td>N(3)–H(3A)⋅⋅⋅O(5)i</td>
<td>0.90</td>
<td>2.29</td>
<td>2.938(6)</td>
<td>129</td>
</tr>
<tr>
<td>N(3)–H(3B)⋅⋅⋅O(5)v</td>
<td>0.90</td>
<td>2.29</td>
<td>2.879(6)</td>
<td>123</td>
</tr>
<tr>
<td>N(3)–H(3C)⋅⋅⋅O(3)vii</td>
<td>0.90</td>
<td>1.98</td>
<td>2.879(6)</td>
<td>175</td>
</tr>
<tr>
<td>N(3)–H(3D)⋅⋅⋅O(4)vii</td>
<td>0.90</td>
<td>1.90</td>
<td>2.798(6)</td>
<td>175</td>
</tr>
<tr>
<td>O(3)–H(3)⋅⋅⋅O(7)i</td>
<td>0.82</td>
<td>1.98</td>
<td>2.433(5)</td>
<td>163</td>
</tr>
<tr>
<td>O(6)–H(6)⋅⋅⋅O(2)vii</td>
<td>0.82</td>
<td>1.90</td>
<td>2.486(5)</td>
<td>174</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(3)–H(3A)⋅⋅⋅O(2)iv</td>
<td>0.85</td>
<td>2.16</td>
<td>2.768(14)</td>
<td>128</td>
</tr>
<tr>
<td>O(3)–H(3C)⋅⋅⋅O(3)v</td>
<td>0.85</td>
<td>1.94</td>
<td>2.762(14)</td>
<td>169</td>
</tr>
<tr>
<td>O(3)–H(3D)⋅⋅⋅O(3)vii</td>
<td>0.85</td>
<td>1.97</td>
<td>2.808(11)</td>
<td>168</td>
</tr>
<tr>
<td>O(5)–H(5C)⋅⋅⋅O1viii</td>
<td>0.85</td>
<td>1.87</td>
<td>2.708(16)</td>
<td>169</td>
</tr>
<tr>
<td>O(5)–H(5D)⋅⋅⋅O(4)vii</td>
<td>0.85</td>
<td>1.90</td>
<td>2.842(15)</td>
<td>169</td>
</tr>
<tr>
<td>O(6)–H(6C)⋅⋅⋅O(5)ix</td>
<td>0.85</td>
<td>1.90</td>
<td>2.758(14)</td>
<td>178</td>
</tr>
<tr>
<td>O(6)–H(6D)⋅⋅⋅O(6)i</td>
<td>0.85</td>
<td>1.85</td>
<td>2.704(4)</td>
<td>177</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) x−1, y+1, z; (ii) x, y+1, z; (iii) x+1, y, z; (iv) −x+1, −y+1, −z+2; (v) −x+1, −y+1, −z+2; (vi) x, y, −z+1; (vii) −x+1, −y+1, −z+2; (viii) x, y+1, z; (ix) −x+1/2, −y+1, z for 1 and (i) −x+1/2, −y, z; (ii) x+1/2, y, −z; (iii) x, −y+1/2, −z; (iv) −x+3/2, −y+1, z; (v) x, −y+1/2, −z; (vi) −x+3/2, −y+1, z; (vii) x, y+1, z; (viii) x, y+1, z for 2.

In complex 2, bpy acts as a typical bidentate ligand, linking two Ag atoms via nitrogen atoms from two pyridyl rings. Completely deprotonated ox2- acts as both counter-ions, balancing the cationic charge of AgI and bidentate ligands and joining the Ag(1) atom via O(1) and O(1A) from two different COO− groups attached on the same ox2- ligands, as illustrated in Fig. 3 and Table 2.

In complex 2, as illustrated in Fig. 4(d), anionic layers are constructed between oxalate anions and aqua molecules by hydrogen-bonding interactions, as listed in Table 2. The adjacent [Ag2(bpy)]2n+∞ chains are joined by Ag···Ag interactions (3.4772(10) Å), Ag···N interactions (3.5763(83) Å and 4.2440(83) Å) and π-π stacking interactions (Cg(1)–Cg(2) = 3.726(6) Å, where Cg(1) is the centroid of aromatic ring N(1)–C(3)–C(4)–C(5)–C(6)–C(7) and Cg(2) the centroid of aromatic ring N(2)–C(8)–C(9)–C(10)–C(11)–C(12)) to build cationic layers, as shown in Fig. 4(a). The anionic and cationic layers are stacked in an A···B···A mode via oxalate as a ridge ligand into a 3D sandwich-like framework. Furthermore, lattice water molecules of complex 2 are situated among the 3D framework and stabilized by hydrogen bonding interactions (Fig. 4(c)).

The crystal structure of complex 2 can also be described as the neutral sheets built from cationic [Ag2(bpy)]2n+∞ chains and ox2- bridging ligands via oxygen atoms (Fig. 4(b)) and stacked by weak Ag···Ag interactions (Ag···Ag 3.4772(10) Å), weak Ag···N interactions (Ag···N 3.5763(83) Å and 4.2440(83) Å), and π-π stacking interactions to construct a 3-D framework. The lattice water molecules situated among the sheets further strengthen the sandwich-like structure.

4 CONCLUSION

Two silver complexes, (NH4)[Ag(dpe)(bptc)] 1 and Ag2(bpy)(ox)·7H2O 2, have been synthesized by slow evaporation at room temperature and characterized by single-crystal diffraction. In 1, the dpe acts as a typical bidentate ligand to link two different Ag(I) atoms and the H2bptc2- serves as a monodentate ligand to link one Ag(I) atom. And in 2, the ligand bpy is a typical ligand to join two different Ag...
(I) centers, while ox\textsuperscript{2–} ligands work as bis-mono-dentate linkers to coordinate with the corresponding Ag(I) atoms. The isolation of 1 and 2 implies that the utilization of different ligands can lead to new types of metal coordination compounds with fascinating architectures.

![Fig. 4. (a) 2-D cationic sheet formed by adjacent [Ag\textsubscript{2}(bpy)]\textsuperscript{2+}∞ chains via Ag···Ag, Ag···N and π–π interactions in 2; (b) 2-D network linked by ox\textsuperscript{2–} viewed along the c axis of complex 2 with the hydrogen bonds omitted for clarity; (c) Packing view of complex 2 along the c axis of the 3-D sandwich-like framework formed via rich hydrogen-bonding interactions (Both the position occupancy factor ratios of H(3C)/H(3D) and H(6D)/H(6B) are 0.50/0.50); (d) 2-D anionic sheet formed from ox\textsuperscript{2–} and lattice water molecules]

REFERENCES


(3) Figuerola, A.; Ribas, J.; Casanova, D.; Maestro, M.; Alvarez, S.; Diaz, C. Magnetic properties of cyano-bridged Ln\textsuperscript{3+}–M\textsuperscript{3+} complexes. Part I: trimuclear complexes (Ln\textsuperscript{3+} = La, Ce, Pr, Nd, Sm; M\textsuperscript{3+} = Fe, S, Co) with bpy as blocking ligand. Inorg. Chem. 2005, 44, 6949–6958.


WANG C. C. et al.: Syntheses and Crystal Structures of Two Silver(I) Complexes with Organic Carboxylic Acid and Bidentate N-donor Ligands

(11) Wang, C. C.; Yin, C. Crystal structure of catena-\((\text{trans-bis}(1-(4\text{-pyridyl})-2-(4\text{-pyridinio})\text{ethylene})\text{dodecaoxocyclotetravanadato(V)cobalt(II)})_2\), \(\text{Co(C}_3\text{H}_6\text{O}_2\text{)}(\text{V}_4\text{O}_{12})_2\). \textit{Z. Kristallogr. NCS} \textbf{2008}, \textit{223}, 13–15.


(17) Wang, C. C. Crystal structure of catena-tetraaquabis(\(\mu_4\)-pyridine-3,5-dicarboxylato)-\(\mu_2\)-oxalato-dicerium(III) dihydrate, \(\text{Ce}_2(\text{H}_2\text{O})_4(\text{C}_8\text{H}_7\text{NO}_4\text{)}_2(\text{C}_2\text{O}_4\text{)}·2\text{H}_2\text{O}\). \textit{Z. Kristallogr. NCS}. \textbf{2007}, \textit{222}, 351–352.


(22) Sheldrick, G. M. \textit{SADABS}, \textit{Program for Empirical Absorption Correction of Area Detector Data}, University of Göttingen Germany \textit{1997}.
