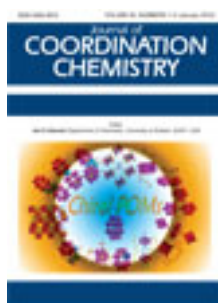


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Syntheses, crystal structures, and properties of silver(I) complexes with oxazoline-containing bidentate ligand

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Three new silver(I) complexes, $[\text{Ag}_2(\text{L})_3](\text{BF}_4)_2$ (**1**), $[\text{Ag}_2(\text{L})_3](\text{PF}_6)_2$ (**2**), and $[\text{Ag}_2(\text{L})(\text{CF}_3\text{COO})_2]$ (**3**), have been synthesized by reactions of 1,4-bis(2-oxazoliny)benzene (L) with the corresponding silver(I) salt. The complexes were characterized by elemental analysis, IR, electrospray mass spectrometry, thermogravimetric analyses, powder X-ray diffraction, and single-crystal X-ray diffraction. The crystal structure analyses reveal that **1** and **2** crystallize in the same monoclinic space group $P2_1/c$ and have the same 2-D layer structure, in which the counteranions BF_4^- and PF_6^- do not coordinate with silver(I). For **3**, CF_3COO^- are auxiliary linkers to connect silver(I)'s to give 1-D chains which are further connected by L to form a 2-D layer structure. The results revealed that the nature of counteranions have impact on the structure of complexes.

Keywords: Silver(I) complex; 1,4-Bis(2-oxazoliny)benzene; Metal–organic framework; Electrospray mass spectrometry

1. Introduction

Construction of metal–organic frameworks (MOFs) through assembly of metal salts with ligands has been a hot research field, due to intriguing structures (cage, honeycomb, herringbone, catenane [1–4]) and potential applications in catalysis, non-linear optics, gas storage, and magnetism [5–8]. However, supramolecular assembly is not well-understood since many factors influence the assembly process, such as pH of the reaction, the nature of metal ions, counterions, reaction medium, and temperature [9–12]. Therefore, design and synthesis of MOFs is still a formidable task and effort is required to understand the assembly process.

Ligands containing imidazole, pyridine, and carboxylate are used to construct MOFs [13]. Oxazoliny-containing ligands are not so common in construction of MOFs in spite of the value of oxazoline in catalysis and molecular recognition [14]. In previous

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work, a series of oxazoline-containing ligands were synthesized, and assembly of the ligands with Ag(I), Cu(I) and Cu(II) salts were systematically investigated [15]. To further study the coordination of oxazolanyl ligands and examine the effect of counteranions, we carried out the reactions of 1,4-*bis*(2-oxazolanyl)benzene (L) with different silver salts under the same reaction conditions [16]. Three new coordination polymers, $[\text{Ag}_2(\text{L})_3](\text{BF}_4)_2$ (**1**), $[\text{Ag}_2(\text{L})_3](\text{PF}_6)_2$ (**2**), and $[\text{Ag}_2(\text{L})(\text{CF}_3\text{COO})_2]$ (**3**), were obtained. Herein we report the syntheses, crystal structure, and properties of the complexes.

2. Experimental

2.1. Materials and methods

All materials were obtained from commercial suppliers and used without purification. The ligand was synthesized according to the procedures reported for other 2-oxazolanyl compounds [15]. Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240C Elemental Analyzer at the analysis center of Nanjing University. FT-IR spectra were measured as KBr pellets on a Bruker Vector22 FT-IR spectrophotometer from 400 to 4000 cm^{-1} . Thermogravimetric analyses (TGA) were performed on a simultaneous SDT 2960 thermal analyzer under nitrogen with a heating rate of $10^\circ\text{C min}^{-1}$. Electrospray mass spectrometry (ES-MS) measurements of the complexes were performed on an LCQ System (Finnegan MAT, USA) using methanol as mobile phase. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer using $\text{Cu-K}\alpha$ radiation (1.5418 \AA), and the X-ray tube was operated at 40 kV and 40 mA. The data were collected in the 2θ range of $5.00\text{--}50.00^\circ$ with a step size of 0.02° .

2.2. Syntheses of complexes

2.2.1. Preparation of $[\text{Ag}_2(\text{L})_3](\text{BF}_4)_2$ (1**).** At room temperature, a methanol solution (3 mL) of L (6.5 mg, 0.03 mmol) was added slowly with constant stirring to a methanol solution (5 mL) of AgBF_4 (5.8 mg, 0.03 mmol) and white precipitate appeared. Then a few drops of acetonitrile were added to the mixture. After 5 min stirring, the mixture was filtered and clear filtrate was obtained. After 1 week, colorless crystals were obtained by slow diffusion of diethyl ether into the filtrate. Yield: 66%. Anal. Calcd for $\text{C}_{18}\text{H}_{18}\text{AgBF}_4\text{N}_3\text{O}_3$ (%): C, 41.65; H, 3.50; N, 8.10. Found (%): C, 41.74; H, 3.56; N, 8.02. IR (KBr pellet, cm^{-1}): 3048 (w), 2983 (w), 2935 (w), 2877 (w), 1643 (vs), 1514 (w), 1479 (w), 1412 (m), 1365 (s), 1323 (m), 1257 (s), 1082 (vs), 1041 (vs), 941 (s), 870 (w), 688 (s), 521 (w).

2.2.2. Preparation of $[\text{Ag}_2(\text{L})_3](\text{PF}_6)_2$ (2**).** Complex **2** was prepared in a similar way to that used for **1**, except that AgPF_6 was used instead of AgBF_4 . Yield 56%. Anal. Calcd for $\text{C}_{18}\text{H}_{18}\text{AgF}_6\text{N}_3\text{O}_3\text{P}$ (%): C, 37.46; H, 3.14; N, 7.28. Found (%): C, 37.41; H, 3.06; N, 7.22. IR (KBr pellet, cm^{-1}): 3048 (w), 2983 (w), 2939 (w), 2877 (w), 1643 (vs), 1514

(w), 1408 (m), 1365 (m), 1325 (w), 1255 (s), 1082 (s), 1018 (m), 941 (m), 843 (vs), 688 (s), 560 (m).

2.2.3. Preparation of [Ag₂(L)(CF₃COO)₂] (3). Complex **3** was prepared in a similar way to that used for **1**, except that AgCF₃COO was used instead of AgBF₄. Yield 45%. Anal. Calcd for C₈H₆AgF₃NO₃ (%): C, 29.21; H, 1.84; N, 4.26. Found (%): C, 29.27; H, 1.92; N, 4.21. IR (KBr pellet, cm⁻¹): 2992 (w), 1683 (vs), 1635 (vs), 1509 (w), 1406 (m), 1367 (m), 1327 (w), 1257 (m), 1209 (vs), 1135 (s), 1097 (m), 937 (m), 839 (m), 804 (m), 725 (m), 688 (m).

2.3. X-ray crystallography

The X-ray diffraction data of the complexes were collected on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. The diffraction data were integrated using *SAINTE* [17], which was also used for intensity corrections for Lorentz and polarization effects. Semi-empirical absorption correction was applied using *SADABS* [18]. The structures were solved by direct methods and all non-hydrogen atoms were refined anisotropically on F^2 by full-matrix least-squares using the *SHELXL-97* crystallographic software package [19]. Hydrogen atoms were generated geometrically. Details of the crystal parameters, data collection, and refinements for **1–3** are summarized in table 1; selected bond lengths and angles are listed in table 2.

Table 1. Crystal data and structure refinements for **1–3**.

Compound	1	2	3
Empirical formula	C ₁₈ H ₁₈ AgBF ₄ N ₃ O ₃	C ₁₈ H ₁₈ AgF ₆ N ₃ O ₃ P	C ₈ H ₆ AgF ₃ NO ₃
Formula weight	519.03	577.19	329.01
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>
Unit cell dimensions (Å, °)			
<i>a</i>	10.2733(18)	9.8773(9)	21.306(5)
<i>b</i>	13.615(2)	14.0702(13)	5.8782(15)
<i>c</i>	14.512(3)	15.1690(14)	16.714(4)
β	102.807(3)	96.4080(10)	111.798(3)
Volume (Å ³), <i>Z</i>	1979.3(6), 4	2094.9(3), 4	1943.6(8), 8
Calculated density (g cm ⁻³)	1.742	1.830	2.249
Absorption coefficient (mm ⁻¹)	1.081	1.118	2.110
<i>F</i> (000)	1036	1148	1272
Reflections collected	9628	10,472	4552
Independent reflection	3485	3706	1699
<i>R</i> _{int}	0.0402	0.0446	0.1121
Parameters refined	271	283	127
Goodness-of-fit on F^2	1.176	1.185	0.983
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (<i>I</i> > 2 σ (<i>I</i>))	0.1041, 0.2759	0.0333, 0.0944	0.0564, 0.1632
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (all data)	0.1081, 0.2788	0.0385, 0.0973	0.0601, 0.1693

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR_2 = \frac{\sum w(|F_o|^2 - |F_c|^2)}{\sum w(F_o)^2}^{1/2}$$

Table 2. Selected bond lengths (Å) and angles (°) for **1–3**.

Complex 1			
Ag(1)–N(1)	2.161(9)	Ag(1)–N(2)	2.172(9)
Ag(1)–N(3)	2.455(10)		
N(1)–Ag(1)–N(2)	158.3(3)	N(1)–Ag(1)–N(3)	105.0(3)
N(2)–Ag(1)–N(3)	95.6(3)		
Complex 2			
Ag(1)–N(1)#1	2.469(3)	Ag(1)–N(2)	2.179(3)
Ag(1)–N(3)	2.160(3)		
N(1)#1–Ag(1)–N(2)	92.89(11)	N(1)#1–Ag(1)–N(3)	111.04(10)
N(2)–Ag(1)–N(3)	156.07(11)		
Complex 3			
Ag(1)–N(1)	2.217(5)	Ag(1)–O(1)	2.264(4)
Ag(1)–O(2)	2.419(5)	Ag(1)–O(1)#2	2.570(4)
N(1)–Ag(1)–O(1)	138.14(18)	N(1)–Ag(1)–O(2)	106.9(2)
O(1)–Ag(1)–O(2)	96.14(17)	O(1)–Ag(1)–O(1)#2	104.53(12)
O(2)–Ag(1)–O(1)#2	104.71(16)	N(1)–Ag(1)–O(1)#2	102.69(18)

Symmetry codes for **2–3**: #1: $-x, 0.5 + y, 1.5 - z$; #2: $0.5 - x, 0.5 + y, 0.5 - z$.

3. Results and discussion

3.1. Structural description

3.1.1. Crystal structures of [Ag₂(L)₃](BF₄)₂ (1**) and [Ag₂(L)₃](PF₆)₂ (**2**).** X-ray crystallographic analysis reveals that **1** and **2** are isostructural. Although the bond lengths and bond angles are not identical (as listed in table 2), the coordination of L to Ag(I) and the framework structures of **1** and **2** are the same and similar to the previously reported Ag(I) complexes with AsF₆[−] and SbF₆[−] anions [20], thus only the structure of **1** is described here as an example. Complex **1** crystallizes in monoclinic space group *P2₁/c* (table 1), and the asymmetric unit consists of one Ag(I), one and half L, and a non-coordinated tetrafluoroborate. As shown in figure 1(a), each Ag(I) is triangularly coordinated by three nitrogen atoms from three different ligands, with slightly distorted T-shape geometry. The N–Ag–N bond angles vary from 95.6(3) to 158.3(3)° and the Ag–N bond distances range from 2.161(9) to 2.455(10) Å for **1** (the corresponding values are 92.89(11) to 156.07(11)° and 2.160(3) to 2.469(3) Å for **2** as listed in table 2). Each L uses two oxazoline groups to connect two Ag(I)'s to give a 2-D layer structure (figure 1b). The 2-D networks are further linked through hydrogen-bonding interactions to produce a 3-D structure (figure 1c). The hydrogen-bonding data are summarized in table S1. Similar 2-D network structure has been observed in the previously reported complex [Ag₂(L)₃](ClO₄)₂ (**4**), in which the perchlorate anions also do not participate in coordination [16].

3.1.2. Structure of [Ag₂(L)(CF₃COO)₂] (3**).** To further investigate the influence of counteranion on the structure, the reaction of L with AgCOOCF₃ instead of AgBF₄ was performed under the same reaction conditions; **3** with different structure was obtained. Complex **3** crystallizes in monoclinic space group *C2/c* (table 1). Unlike **1** and **2** where counteranions do not coordinate, in **3**, trifluoroacetates are auxiliary linkers. There are one Ag(I), half L, and one trifluoroacetate in the repeat unit of **3**. Each Ag(I)

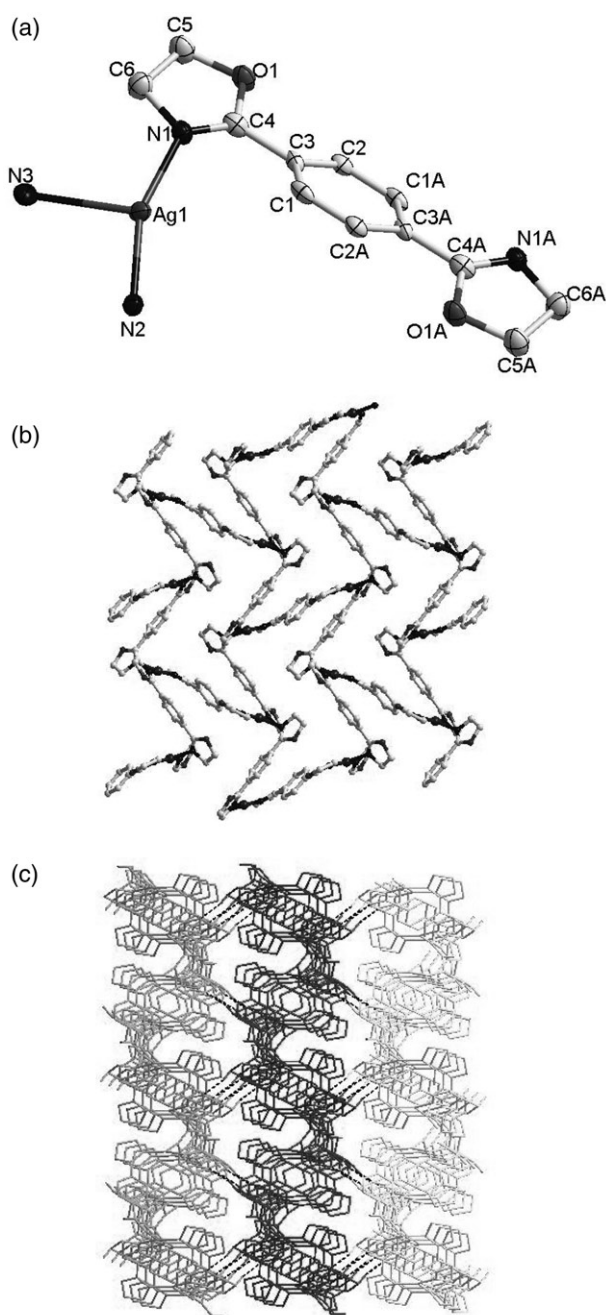


Figure 1. (a) ORTEP drawing showing the coordination environment around Ag(I) at 30% probability level. Hydrogen atoms and tetrafluoroborates were omitted for clarity. (b) The 2-D network of **1**. (c) The 3-D structures of **1** through hydrogen-bonding interactions indicated by dashed lines.

is coordinated by one nitrogen atom from L and three oxygen atoms from three different trifluoroacetates with distorted tetrahedral geometry (figure 2a). The bond distances and bond angles around Ag(I) range from 2.214(5) to 2.569(4) Å and 96.34(16) to 138.24(17)° (table 2). Ag–O bond lengths are significantly longer than

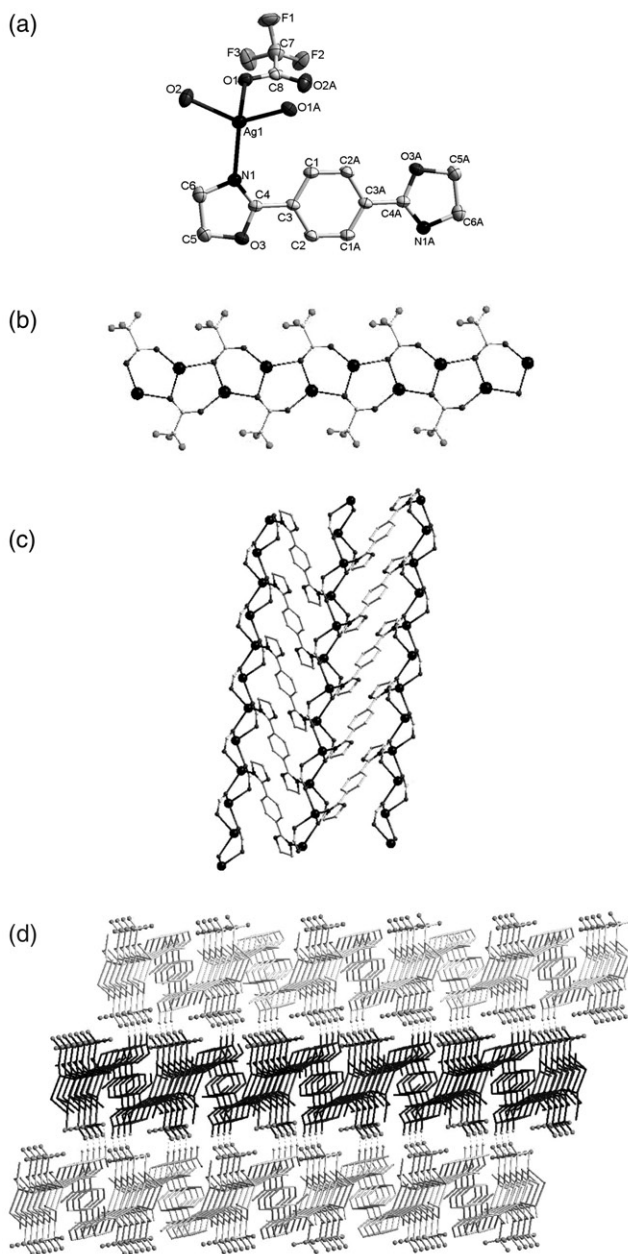


Figure 2. (a) The coordination environment of Ag(I) in **3** with ellipsoids drawn at the 30% probability level. The hydrogen atoms were omitted for clarity. (b) The 1-D wavy chain of **3**. (c) The 2-D wavelike network of **3**. (d) The 3-D structure of **3** linked by hydrogen bonds between adjacent layers.

Ag–N indicating weak coordination of trifluoroacetate, similar to previously reported complexes [21]. In **3**, each trifluoroacetate serves as a three connected node, using O1 to coordinate with two Ag(I) and O2 to coordinate with one Ag(I), generating an infinite 1-D silver-carboxylate chain (figure 2b) as observed in previously reported Ag(I) complexes [22]. Adjacent 1-D chains are further linked to give a polymeric 2-D network through N–Ag coordination bonds (figure 2c). The 2-D layer structures are further joined to form a 3-D structure through C5–H5A...F3 hydrogen bonds with C5...F3 distance of 3.354(10) Å (figure 2d, table S1).

The structural difference of **1–3** is that in **1** and **2** the counteranions do not take part in coordination, while in **3** trifluoroacetate coordinate to Ag(I) as linkers, consistent with higher coordination ability of CF_3COO^- than BF_4^- and PF_6^- [23]. The results imply that non-coordinating counteranions do not influence the structure of complexes (**1**, **2**, and **4**); however, coordinating counteranions can have great effect on the structures (**3** and **5**). Furthermore, it is interesting to note that $[\text{Ag}_2(\text{L})(\text{CH}_3\text{COO})_2]$ (**5**) with acetate rather than the trifluoroacetate in **3** crystallizes in triclinic *P*-1 space group and has a different 2-D network structure [16]. The coordination modes of the carboxylate group of CF_3COO^- in **3** and CH_3COO^- in **5** are the same, however, the 1-D chain structures of the $\text{Ag}(\text{CF}_3\text{COO})$ in **3** (figure 2b) and $\text{Ag}(\text{CH}_3\text{COO})$ in **5** are different [16], implying the subtle influence of the counteranions as auxiliary linkers.

3.2. PXRD, IR, and TGA

To confirm that the crystal structure is representative of the bulk sample, PXRD measurements were carried out for **1–3** at room temperature. The experimental and simulated patterns of the corresponding complex are shown in figure S1. Diffraction peaks of simulated and experimental patterns match well, indicating pure phase of **1–3**.

In IR spectra of **1–3**, a very strong band at 1643 cm^{-1} is from L since a similar band was also found in the IR spectrum of L, while very strong bands at 1082 cm^{-1} for **1**, 843 cm^{-1} for **2**, and 1683 and 1209 cm^{-1} for **3** correspond to vibrations of BF_4^- , PF_6^- , and CF_3COO^- , respectively, confirming the existence of the anions in the complexes.

The thermal stabilities of **1–3** were studied by thermal analysis under nitrogen. The TGA curves of **1–3** are given in figure 3. TGA data show that **1–3** are thermally stable to *ca* 244°C , 268°C , and 252°C , respectively, since no weight losses were observed before these temperatures. The results indicate that there are no solvent molecules in **1–3**, in agreement with the results of the crystal structures described above. Continuous weight losses were found from *ca* 244°C , 268°C , and 252°C for **1–3**, respectively, due to decomposition of the complexes.

3.3. Electrospray mass spectra of **1–3**

ES-MS is a powerful technique for investigation of complexes [24]. In the present case, we utilize this technique to characterize **1–3** and observed mono-, di-, tri-, and tetra-nuclear cationic species under ES-MS conditions. The spectral data are summarized in table 3. As a typical example, the ES mass spectrum of **3** in acetonitrile solution is shown in figure 4(a) and gives a clear picture of the different species. All the assignments were confirmed by good agreement between the observed and calculated isotopic distributions. Figure 4(b) shows a typical example for comparison between the

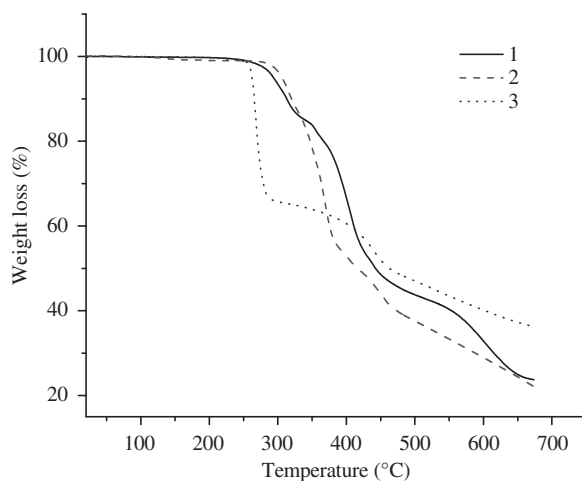


Figure 3. TGA curves of 1–3.

Table 3. ES mass spectral data for 1–3.

<i>m/z</i>	Assignment
1	
217.07	[HL] ⁺
364.24	[Ag(L)(CH ₃ CN)] ⁺
539.16	[Ag(L) ₂] ⁺
1144.92	[Ag ₃ (L) ₃ (BF ₄) ₂] ⁺
2	
217.07	[HL] ⁺
323.05	[Ag(L)] ⁺
364.24	[Ag(L)(CH ₃ CN)] ⁺
539.16	[Ag(L) ₂] ⁺
792.92	[Ag ₂ (L) ₂ (PF ₆)] ⁺
1261.07	[Ag ₃ (L) ₃ (PF ₆) ₂] ⁺
3	
217.07	[HL] ⁺
364.24	[Ag(L)(CH ₃ CN)] ⁺
539.16	[Ag(L) ₂] ⁺
761.04	[Ag ₂ (L) ₂ (CF ₃ COO)] ⁺
793.08	[Ag ₂ (L) ₂ (CF ₃ COO)(CH ₃ OH)] ⁺
980.90	[Ag ₃ (L) ₂ (CF ₃ COO) ₂] ⁺
1202.82	[Ag ₄ (L) ₂ (CF ₃ COO) ₃] ⁺
1263.08	[Ag ₃ (L) ₃ (CF ₃ COO) ₂ (CH ₃ OH) ₂] ⁺

experimental and calculated isotopic distributions for the peak at $m/z=1263.08$, corresponding to the tri-nuclear species $[\text{Ag}_3(\text{L})_3(\text{CF}_3\text{COO})_2(\text{CH}_3\text{OH})_2]^+$.

4. Conclusion

Through assembly of oxazoline-containing ligand L and varied silver(I) salts, three new MOFs with 2-D layer structures were obtained. In **1** and **2**, the counteranions do not

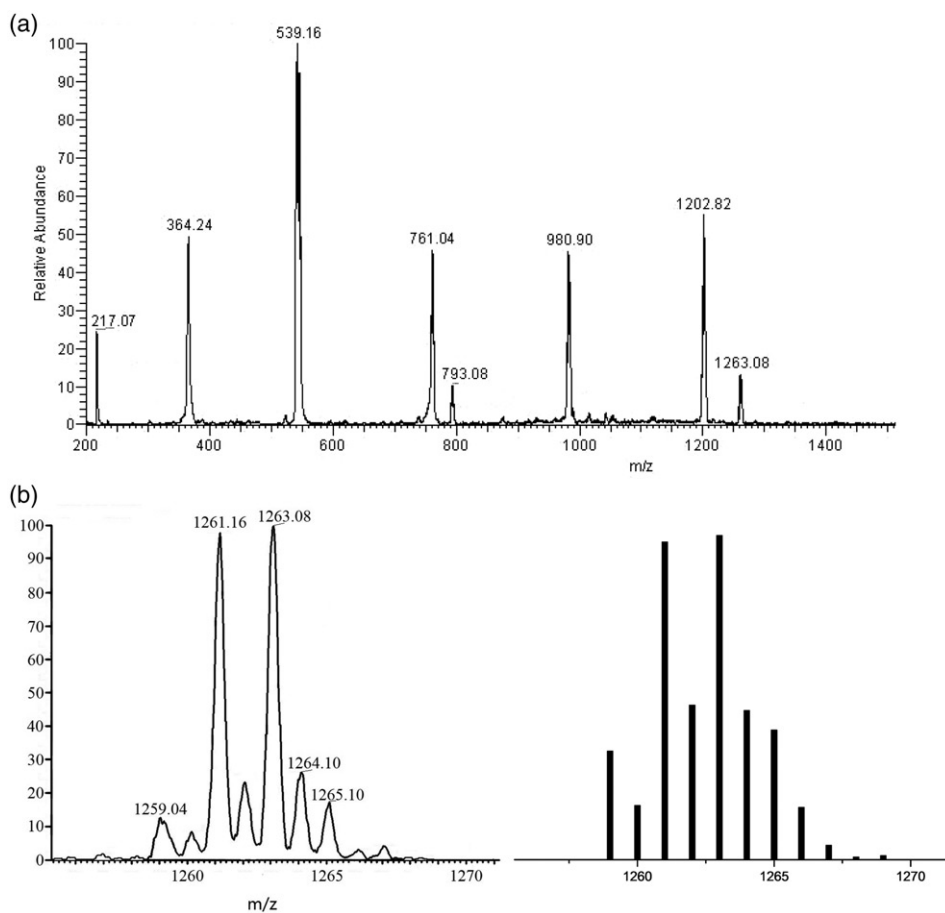


Figure 4. (a) The ES mass spectrum of **3** in acetonitrile. (b) The observed (traces) and calculated (bars) isotopic distributions for the peak at $m/z = 1263.08$.

take part in coordination, while in **3** the trifluoroacetates are auxiliary linkers. This work further proves the impact of counteranions on the structure of complexes and the coordination versatility of oxazoline-containing ligands in construction of MOFs.

Supplementary material

Crystallographic data for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos CCDC-849479 (**1**), 849480 (**2**), and 849481 (**3**). Copies of the data can be obtained at <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223336033; E-mail: deposit@ccdc.cam.ac.uk).

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