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ARTICLE

Anion dependent silver(I) complexes of pyrazine mono-N-oxide

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Pyrazine mono-N-oxide shows a clear preference for coordination to silver(I) through the nitrogen atom. However, in some cases it acts as an N,O-bridging ligand to form 1D coordination polymers. The specific species formed is dependent on the nature of the counteranion. In general, the complexes formed have additional weak interactions that appear to control the crystal packing.

Introduction

Metallo-supramolecular chemistry¹ involves the use of combinations of bridging organic ligands with metal precursors to generate discrete assemblies or coordination polymers of varying dimensionality.² Silver(I) has proved popular as a metal in metallo-supramolecular synthesis because of its promiscuous coordination ability.³ Linear bridging N-heterocyclic ligands, such as pyrazine and 4,4'-bipyridine, have been extensively employed to prepare numerous coordination polymers⁴ and the coordination chemistry of silver with pyrazine derivatives has recently been reviewed.⁵

We are currently engaged in a study of the reactions of silver(I) salts with the N-oxides of bridging N-heterocyclic ligands. We began by studying the reactions of various silver salts with pyridine N-oxide, which has been extensively used as a ligand in coordination chemistry. Usually it binds through the oxygen to a single metal centre, but a search of the Cambridge Structural Database (CSD)⁶ revealed that there are thirty six structures which involve the oxygen bridging two metal centres (mainly copper, manganese and cadmium). However, we found⁷ that with silver salts pyridine N-oxide can bind to three metal centres through a single oxygen atom, in what we called a hyperdentate mode of coordination.⁷ In contrast, pyridine itself almost invariably binds to a single metal, although the CSD contains three examples of hyperdentate pyridine coordination, where the nitrogen atom bridges two metal centres.⁸

We now report the results of a study of reactions of pyrazine mono-N-oxide (Pzo) with various silver(I) salts. This ligand combines the coordination characteristics of both pyridine and pyridine N-oxide, along with the potential bridging nature of pyrazine. Surprisingly, there are only two reports⁹ of X-ray structures of metal complexes of this ligand in the CSD. We will show that Pzo can act as a bridging ligand, using both the N and O atoms for coordination, to generate 1D coordination polymers and as a monodentate N-donor to form discrete assemblies.

Results and discussion

Pyrazine mono-N-oxide (Pzo) was reacted with five different silver salts using a 1:2 ligand to metal ratio and crystals of complexes 1 – 5, suitable for X-ray analysis, were obtained by subsequent slow evaporation of the solutions (Scheme 1).

The silver perchlorate complex (1) crystallises in the monoclinic space group $P2_1/n$ with four molecules of Pzo, two silver atoms and two non-coordinated perchlorate anions in the asymmetric unit (Fig. 1). The two independent silver atoms are each three-coordinate, being bound to two pyrazine nitrogens and one oxygen atom of three different Pzo ligands. The

silver atoms have highly distorted trigonal geometries with angles ranging between $83.21(5)^\circ$ and $156.61(5)^\circ$. Two of the Pzo ligands are N-monodentate, whilst the other two display N,O-bridging coordination.

Scheme 1 Synthesis of complexes.

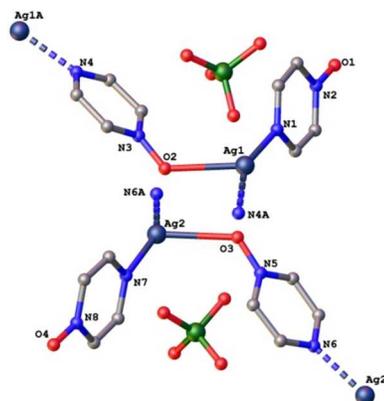
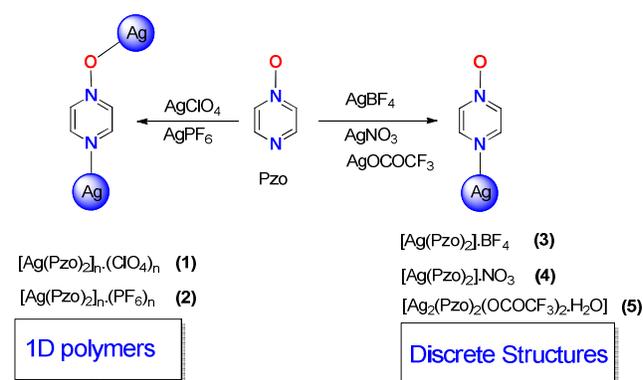


Fig. 1 The asymmetric unit of complex 1. Hydrogen atoms are excluded for clarity. Symmetry related atoms in the adjacent asymmetric unit are shown with dashed bonds. Selected bond lengths (Å) and bond angles ($^\circ$): N2-O1 = 1.2887(18), N3-O2 = 1.2975(18), N5-O3 = 1.3001(17), N8-O4 = 1.2816(18), N1-Ag1 = 2.1674(14), N4-Ag1ⁱ = 2.2036(14), N6-Ag2ⁱⁱ = 2.2014(14), N7-Ag2 = 2.1815(14), Ag1-O2 = 2.4416(12), Ag2-O3 = 2.4681(12), N1-Ag1-N4Aⁱⁱⁱ = 156.61(5), N1-Ag1-O2 = 118.58(5), N4Aⁱⁱⁱ-Ag1-O2 = 83.21(5), N7-Ag2-N6A^{iv} = 153.92(5), N7-Ag2-O3 = 112.68(5), N6A^{iv}-Ag2-O3 = 92.94(5). Symmetry codes: (i) $-\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $-\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $-\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (iv) $-\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.

The silver hexafluorophosphate complex (**2**) crystallises in the monoclinic space group $P2_1/c$, with two molecules of Pzo, a silver atom and a highly disordered hexafluorophosphate counteranion in the asymmetric unit (Fig. 2). Once again, one of the Pzo molecules is N-monodentate and the other is N,O-bridging and the three-coordinate silver has a highly distorted trigonal geometry, similar to that of complex **1**.

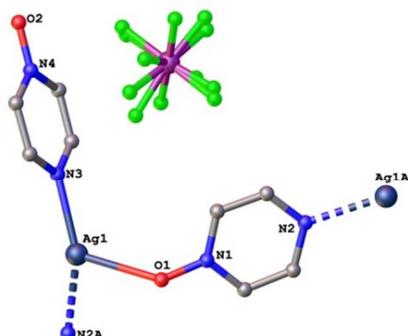


Fig. 2 The asymmetric unit of complex **2**. Hydrogen atoms are excluded for clarity. Symmetry related atoms in the adjacent asymmetric unit are shown with dashed bonds. Selected bond lengths (Å) and bond angles ($^\circ$): N1-O1 = 1.3024(18), N4-O2 = 1.282(2), N3-Ag1 = 2.1845(15), N2-Ag1Aⁱ = 2.2202(14), Ag1-O1 = 2.5014(13), N3-Ag1-N2Aⁱⁱ = 152.49(6), N3-Ag1-O1 = 117.31(5), N2Aⁱⁱ-Ag1-O1 = 88.70(5). Symmetry codes: (i) $-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (ii) $-x, \frac{1}{2}+y, \frac{1}{2}-z$.

Both of the complexes extend into 1D zigzag coordination polymers that propagate along the b -axis (Fig.3). The bridging Pzo ligands provide the links to the chains, whilst the monodentate ligands decorate the sides. Adjacent chains are held in place by weak inter-chain Ag-O interactions [Ag1-O3 = 2.860(1) Å and Ag2-O2 = 2.781(1) Å]. Complex **2** adopts a similar 1D polymeric structure. Thus, we have shown that Pzo can indeed act as a bridging ligand for the assembly of coordination polymers, albeit without the hyperdentecity seen with pyridine N-oxide.⁷

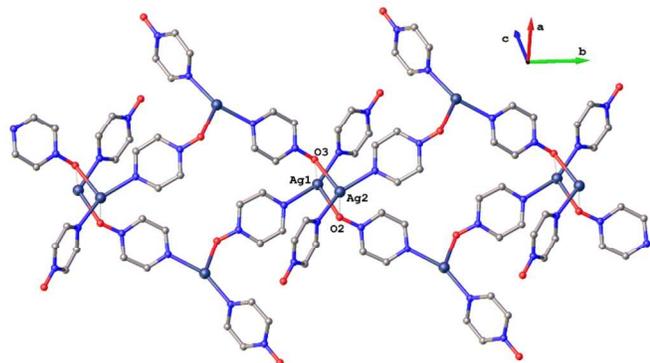


Fig. 3 Two of the 1D zigzag coordination polymers of complex **1**, held together by weak inter-chain Ag-O interactions. Hydrogen atoms are omitted for clarity.

In contrast to the structures of **1** and **2**, complexes **3-5** are all discrete assemblies. The silver tetrafluoroborate complex (**3**) crystallises in the monoclinic space group $P2_1/n$, with two molecules of Pzo, two independent silver atoms, both lying on crystallographic centres of inversion, and a tetrafluoroborate counteranion in the asymmetric unit (Fig. 4, top). The silver atoms are coordinated to two Pzo nitrogen atoms with strictly linear two-coordinate geometry. Although the complex is a discrete ML_2 species, there are numerous additional weak Ag \cdots O and CH \cdots F interactions that help to order the structure. For example, Ag2 makes weak contacts [2.808(1) Å

and 3.002(1) Å] with four non-coordinated oxygen atoms of adjacent Pzo ligands, which are within the sum of the van der Waals radii of silver and oxygen [3.24 Å].¹⁰ In turn, each of the oxygens make weak contacts with two silver atoms (Fig. 4, middle).

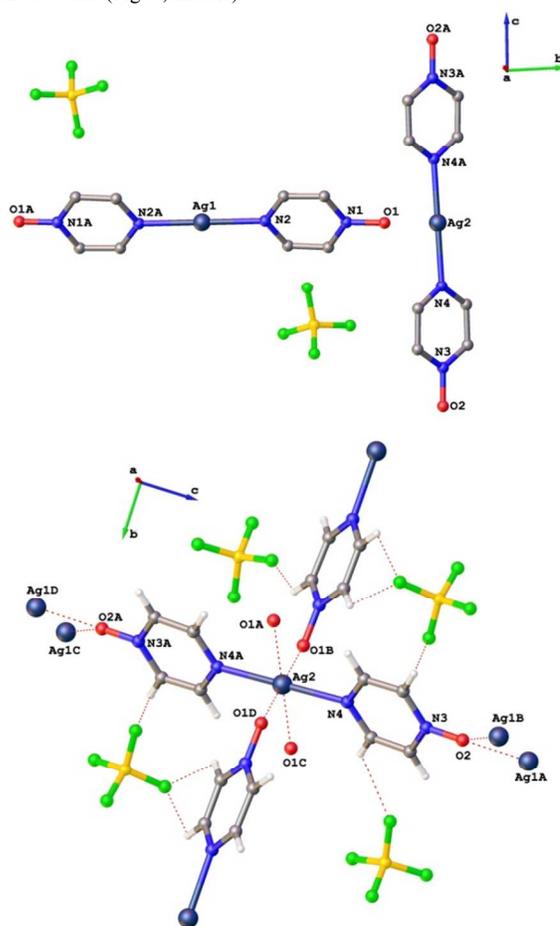


Fig. 4 (Top) The two independent units of complex **3**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): N1-O1 = 1.296(5), N3-O2 = 1.295(5), N2-Ag1 = 2.153(4), N4-Ag2 = 2.164(4). (Middle) View showing the weak intermolecular interaction. (Bottom) View down the a -axis illustrating the crystal packing. Symmetry codes: (N2A) $-x, -y, 1-z$; (N4A) $-$

1-x, 1-y, 1-z; (Ag1A) $-\frac{1}{2}+x$, $\frac{1}{2}-y$, $-\frac{1}{2}+z$; (Ag1B) $-\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$; (Ag1C) $\frac{1}{2}-x$, $\frac{1}{2}+y$, $1\frac{1}{2}-z$; (Ag1D) $-\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$.

As a result of these interactions, the molecules assemble into squares of silver atoms lying in the *bc*-plane (Fig. 4, bottom), which produces channels running down the *a*-axis that are occupied by the tetrafluoroborate anions.

The structure of the silver nitrate complex (4) is related but different. It crystallises in the triclinic space group P-1, again with two molecules of Pzo, two independent silver atoms, both lying on crystallographic centres of inversion, and a disordered nitrate counteranion in the asymmetric unit (Fig. 5, top). The environment of the silver atoms is similar to that in complex 3. However, in 3 the two independent Ag(Pzo)₂ cations were oriented in an orthogonal manner, whereas in 4 they are parallel. As a result, the crystal packing is somewhat different (Fig. 5, bottom) with the cations arranged in a parallel fashion with the disordered nitrate anions lying between them and with each nitrate making weak Ag-O interactions with four nearby silver atoms.

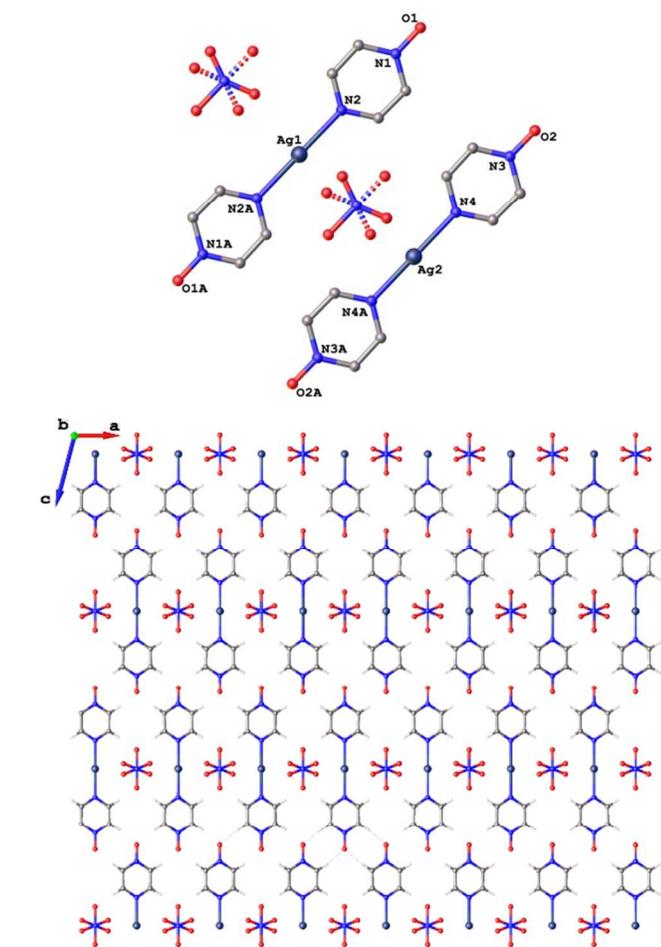


Fig. 5 (Top) The two independent units of complex 4. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): N1-O1 = 1.282(2), N3-O2 = 1.281(2), N2-Ag1 = 2.1806(16), N4-Ag2 = 2.1743(16). Symmetry codes: (N2A) $-1-x$, $-y$, $1-z$; (N4A) $1-x$, $1-y$, $1-z$. (Bottom) View down the *a*-axis showing the crystal packing.

The silver trifluoroacetate complex (5) crystallises in the monoclinic space group $P2_1/n$ with a 1:1 M:L ratio, which is different to the 1:2 M:L ratio found in complexes 1-4. This is because the trifluoroacetate counteranion is coordinated to silver in complex 5, whereas the anions were non-coordinating in complexes 1-4. There are two independent silver atoms, each of which is three-coordinate, with distorted T-shaped geometries (Fig.

6). Ag1 is coordinated to a Pzo nitrogen, an oxygen atom of a disordered trifluoroacetate anion and has a weak Ag-Ag bond [3.2201(3) Å] to a symmetry related silver. Ag2 binds to a Pzo nitrogen, a trifluoroacetate oxygen and a coordinated water molecule. Although the Pzo oxygens are non-coordinating, they each experience weak contacts with two symmetry related silver atoms. The hydrogen atoms of the coordinated water molecule are hydrogen bonded to oxygen atoms of nearby trifluoroacetates, with OH...O separations of 2.714 Å (O4) and 2.690 Å (O6A) and O-H...O angles of 161° and 157°, respectively. Interestingly, the trifluoroacetates are monodentate. In our experience, silver complexes involving trifluoroacetate anions usually have an O,O'-bidentate coordination mode.¹¹

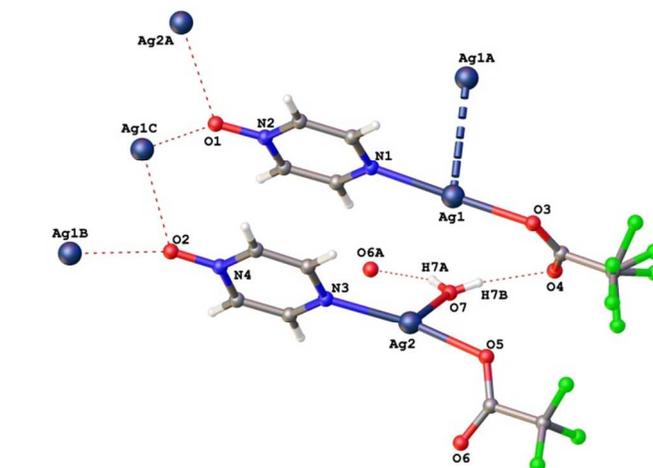


Fig. 6 The asymmetric unit of complex 5. Hydrogen atoms are excluded for clarity. Symmetry related atoms in the adjacent asymmetric unit are shown with dashed bonds. Selected bond lengths (Å) and bond angles (°): N2-O1 = 1.2894(19), N4-O2 = 1.2911(19), N1-Ag1 = 2.1840(15), N3-Ag2 = 2.2129(15), Ag1-O3 = 2.1744(13), Ag2-O5 = 2.2418(12), Ag2-O7 = 2.4119(15), Ag1-Ag1Aⁱ = 3.2201(3), N3-Ag2-O5 = 155.81(5), N3-Ag2-O7 = 110.44(5), O5-Ag2-O7 = 93.60(5), O3-Ag1-Ag1Aⁱ = 105.51(4), O3-Ag1-N1 = 170.07(5), N1-Ag1-Ag1Aⁱ = 76.92(4). Symmetry codes: (i) $1-x$, $-y$, $1-z$. (Ag1B) $-\frac{1}{2}+x$, $-\frac{1}{2}-y$, $-\frac{1}{2}+z$; (Ag1C and Ag2A) $\frac{1}{2}-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$.

Due to the several weak intermolecular interactions mentioned above, the crystal packing of complex 5 is rather complicated (Fig. 7). It also involves π - π interactions between the Pzo ligands coordinated to Ag1 and Ag2 with a separation of 3.552 Å along the *a*-axis.

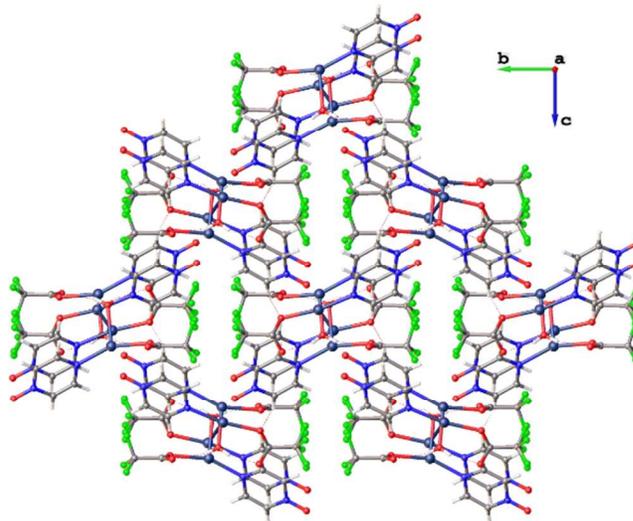


Fig. 7 Crystal packing of complex 5 viewed down the *a*-axis.

Conclusions

We have shown that pyrazine mono-N-oxide can be reacted with silver salts to form either discrete complexes involving monodentate N-coordination or 1D coordination polymers in which the ligand acts in a N₂O-bridging bidentate coordination mode. However, unlike pyridine N-oxide the oxygen is not hyperdentate. In all the structures there are numerous additional weak intermolecular interactions that control the supramolecular packing. In the complexes the geometry of the Pzo ligand is similar to that in the crystal structure of the free ligand itself.¹² Anion control in the assembly of silver coordination polymers is a common phenomenon¹³ and is clearly operating here, as the only difference in the synthetic procedures is the nature of the anion. However, the promiscuity of silver as a metallosupramolecular synthon is such that it is not possible to rationalise or predict the nature of the assemblies formed simply from a knowledge of the anion involved.

Experimental Section

General

Unless otherwise specified, all reagents and starting materials were reagent grade, purchased from standard suppliers and used as received. Melting points were recorded on an Electrothermal melting point apparatus and are uncorrected. Elemental analysis was carried out by Campbell Microanalytical Laboratory, University of Otago. Infrared spectra were recorded on Bruker Alpha instrument equipped with a diamond ATR prism. Mass spectra were recorded with a Bruker MaXis 4G spectrometer, operated in high resolution positive ion electrospray mode. Pyrazine mono-N-oxide was prepared as previously described.¹⁴

Preparation of complexes

WARNING: Perchlorate salts of metal complexes are potentially explosive. Care should be taken while handling such complexes.

Complex (1)

Silver(I) perchlorate (43 mg, 0.21 mmol) dissolved in methanol (2 ml) was added to a solution of the ligand (10 mg, 0.104 mmol) dissolved in water (2 ml). The solution was left in darkness to evaporate slowly to give colourless blocks suitable for X-ray crystallography. Yield 31%, m.p. 123°C. Calculated for 2(C₄H₄N₂O).AgClO₄: C, 24.05; H, 2.02; N, 14.02. Found: C, 23.83; H, 2.26; N, 14.57. IR $\nu_{\max}/\text{cm}^{-1}$: 1444, 1408, 1228, 1173, 1013, 837, 769, 705, 625, 570, 513. ESI-MS *m/z*: Found [L+Ag]⁺ 202.9366, C₄H₄AgN₂O requires [L+Ag]⁺ 202.9369.

Complex (2)

Silver(I) hexafluorophosphate (52 mg, 0.21 mmol) dissolved in acetonitrile (2 ml) was added to a solution of the ligand (10 mg, 0.104 mmol) dissolved in methanol (2 ml). The solution was left in darkness to evaporate slowly to give colourless block-like crystals suitable for X-ray crystallography. Yield 45%, m.p. 198°C. Calculated for 2(C₄H₄N₂O).AgPF₆: C, 21.59; H, 1.81; N, 12.59. Found: C, 21.41; H, 1.71; N, 12.36. IR $\nu_{\max}/\text{cm}^{-1}$: 1595, 1484, 1463, 1316, 1273, 1206, 1031, 831, 554, 474. ESI-MS *m/z*: Found [L+Ag]⁺ 202.9366, C₄H₄AgN₂O requires [L+Ag]⁺ 202.9369.

Complex (3)

Silver(I) tetrafluoroborate (40 mg, 0.21 mmol) dissolved in methanol (2 ml) was added to a solution of the ligand (10 mg, 0.104 mmol) dissolved in acetonitrile (2 ml). The solution was left in darkness to evaporate slowly to give colourless blocks suitable for X-ray crystallography. Yield 47%, m.p. 148°C. Calculated for 2(C₄H₄N₂O).AgBF₄: C, 24.72; H, 2.08; N, 14.48. Found: C, 24.80; H, 2.41; N, 14.03. IR $\nu_{\max}/\text{cm}^{-1}$: 3131, 1600, 1461, 1439, 1281, 1203, 1809, 1021, 860, 831, 540, 478. ESI-MS *m/z*: Found [L+Ag]⁺ 202.9367, C₄H₄AgN₂O requires [L+Ag]⁺ 202.9369.

Complex (4)

Silver(I) nitrate (35 mg, 0.21 mmol) dissolved in water/acetone (1:1, 2 ml) was added to a solution of the ligand (10 mg, 0.104 mmol) dissolved in methanol/dichloromethane (1:1, 4 ml). The solution was left in darkness to evaporate slowly to give colourless blocks suitable for X-ray crystallography. Yield 40%, m.p. 118°C. Calculated for 2(C₄H₄N₂O₂).AgNO₃: C, 26.54; H, 2.23; N, 19.34. Found: C, 26.51; H, 2.00; N, 18.96. IR $\nu_{\max}/\text{cm}^{-1}$: 1595, 1463, 1436, 1273, 1198, 1082, 850, 831, 542, 489.

Complex (5)

Silver(I) trifluoroacetate (46 mg, 0.21 mmol) dissolved in methanol (2 ml) was added to a solution of the ligand (10 mg, 0.104 mmol) dissolved in acetonitrile (2 ml). The solution was left in darkness to evaporate slowly to give colourless block crystals suitable for X-ray crystallography. Yield 27%, m.p. 86°C. Calculated for 2(C₄H₄N₂O).(AgOCOCF₃).H₂O: C, 22.11; H, 1.55; N, 8.59. Found: C, 22.04; H, 1.51; N, 8.38. IR $\nu_{\max}/\text{cm}^{-1}$: 1643, 1444, 1312, 1258, 1190, 1132, 836, 822, 721, 699. ESI-MS *m/z*: Found [L+Ag]⁺ 202.9367, C₄H₄AgN₂O requires [L+Ag]⁺ 202.9369.

Crystallography

X-Ray crystallographic data collection was carried out with an Agilent Supernova instrument, using Mo K α ($\lambda = 0.71073 \text{ \AA}$) radiation. All structures were solved using direct methods with SHELXS¹⁵ and refined on F² using all data by full matrix least-squares procedures with SHELXL.¹⁵ All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.2 times the isotropic equivalent of their carrier atoms. Experimental details are listed in Table 1.

Acknowledgements

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Notes and references

Electronic Supplementary Information (ESI) available: X-ray crystallographic data as CIFs for compounds **1** - **5**. CCDC numbers: 986756 (**1**), 986757 (**2**), 986758 (**3**), 986759 (**4**) and 986760 (**5**). See DOI: 10.1039/b000000x/

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Table 1. X-Ray crystallography experimental details.

Complex	1	2	3	4	5
Empirical formula	C ₈ H ₈ N ₄ O ₆ ClAg	C ₈ H ₈ N ₄ O ₂ P ₂ F ₆ Ag	C ₈ H ₈ N ₂ O ₄ BF ₄ Ag	C ₈ H ₈ N ₅ O ₅ Ag	C ₁₂ H ₁₀ N ₄ O ₇ F ₆ Ag ₂
Formula weight	399.50	445.02	386.86	362.06	651.98
Temperature (K)	120	120	120	120	120
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	<i>P2₁/n</i>	<i>P2₁/c</i>	<i>P2₁/n</i>	<i>P-1</i>	<i>P2₁/n</i>
<i>a</i> (Å)	10.25413(18)	10.2884(5)	4.88685(15)	6.5100(13)	11.3257(3)
<i>b</i> (Å)	12.90075(16)	12.7097(4)	15.4949(3)	7.0870(14)	12.5005(2)
<i>c</i> (Å)	18.8342(3)	10.3360(4)	15.4356(3)	12.645(3)	13.7721(3)
α (°)	90	90	90	95.60(3)	90
β (°)	100.9954(16)	103.593(4)	97.643(2)	103.58(3)	112.254(3)
γ (°)	90	90	90	99.50(3)	90
Volume / Å ³	2445.77(7)	1313.70(9)	1158.42(5)	553.63(19)	1804.58(7)
Z	8	4	4	2	4
Density (calculated) Mg/m ³	2.170	2.250	2.218	2.172	2.400
Absorption Coefficient mm ⁻¹	1.900	1.741	1.800	1.849	2.278
F(000)	1568	864	752	356	1256
Crystal size (mm ³)	0.27 x 0.14 x 0.03	0.20 x 0.19 x 0.04	0.20 x 0.17 x 0.13	0.40 x 0.29 x 0.05	0.24 x 0.18 x 0.04
2 θ range for data collection (°)	5.14 to 55.00	5.96 to 55.00	5.32 to 55.00	5.88 to 55.00	516 to 55.00
Reflections collected [R(int)]	39526 [0.0243]	13012 [0.0213]	18970 [0.0240]	13702 [0.0227]	30718 [0.0237]
Independent reflections	5625	3022	2663	2547	4145
Data completeness (%)	100	100	100	99.9	100
Data/ restraints/ parameters	5625 /0/361	3022/0/255	2663 /0/184	2547/0/203	4145/0/316
Goodness-of-fit on F ²	1.099	1.073	1.270	0.985	1.071
Final R ₁ indices [I>2sigma(I)]	R ₁ = 0.0172 wR ₂ = 0.0417	R ₁ = 0.0184 wR ₂ = 0.0491	R ₁ = 0.0457 wR ₂ = 0.1089	R ₁ = 0.0137 wR ₂ = 0.0407	R ₁ = 0.0178 wR ₂ = 0.0429
Final R indices [all data]	R ₁ = 0.0185 wR ₂ = 0.0423	R ₁ = 0.0208 wR ₂ = 0.0531	R ₁ = 0.0466 wR ₂ = 0.1092	R ₁ = 0.0210 wR ₂ = 0.0482	R ₁ = 0.0200 wR ₂ = 0.0443

Anion dependent silver(I) complexes of pyrazine mono-N-oxide

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Graphical Abstract

Pyrazine mono-N-oxide reacts with silver salts to form either discrete complexes involving monodentate N-coordination or 1D coordination polymers in which the ligand acts in a N,O-bridging bidentate coordination mode.

