

**Ag(I) bipyridyl coordination polymers containing functional anions.**

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**Abstract**

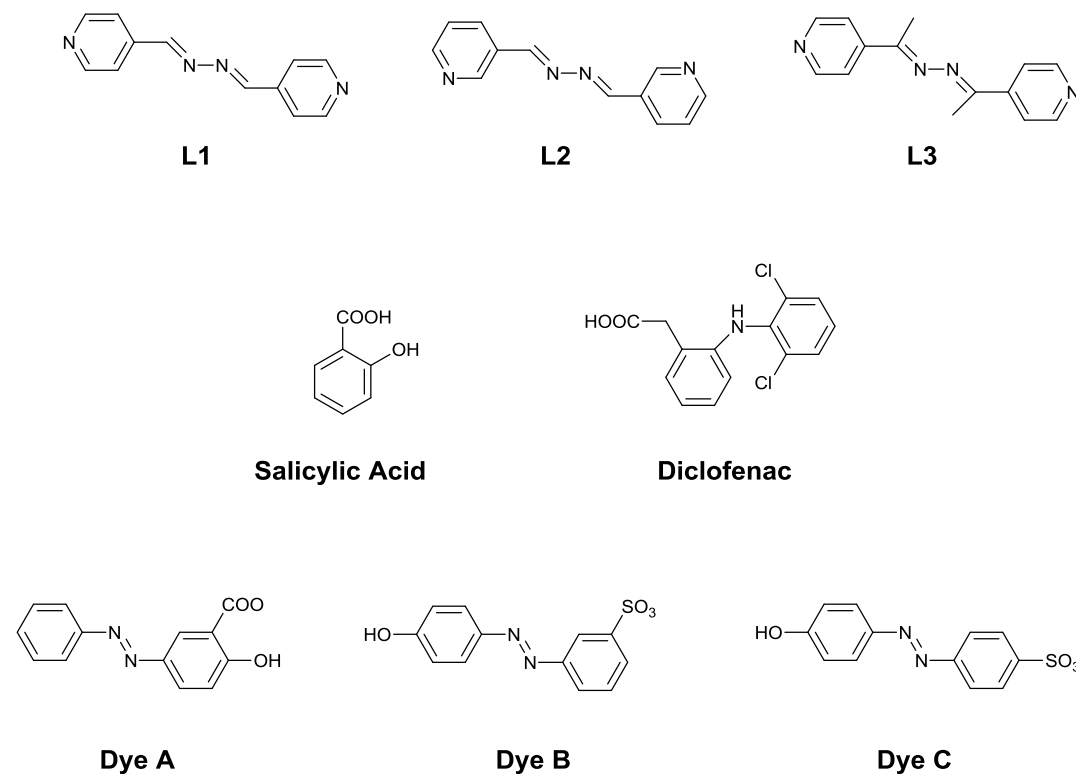
The single crystal diffraction structures of seven coordination polymers formed by Ag(I) and bipyridyl azine ligands are described and compared. All contain organic anions derived from intrinsically functional molecules, either Active Pharmaceutical Ingredients (API = salicylate or diclofenac) or carboxylate or sulfonate monoazo dyes. Five of the seven coordination polymers, including all those that feature API species, are found to display variations on a common structural motif, with polymeric  $[\text{Ag}(\text{azine})]_n$  chains linked into pairs through argentophilic Ag-Ag contacts supported by a pair of AgOXOAg (X = C or S) bridges. Also reported are the crystal structures of two Ag(I) complexes of sulfonated monoazo dyes, including the first such structure to feature a Ag to azo dative bond.

## Introduction

Coordination polymers and metal organic frameworks (MOFs) can be formed from a wide variety of metal ions and bipyridyl-based ligands. These species normally also contain an anionic counterion. Discussions on chemical functionality typically concentrate on the nature of the metal ion and of the bipyridyl ligand, with the counterion relegated to being a chemically inactive bystander which is of interest only in as much as it influences the final three dimensional structure of the solid. The structural roles of typical small counterions (e.g.  $\text{NO}_3^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{SO}_4^{2-}$ ) have been much discussed for Ag(I) bipyridyl coordination polymers.[1,2] These polymers have outwardly simple structures where two coordinate Ag(I) centres and approximately linear ligands give one dimensional polymeric molecules. However, when investigated the structural roles of even these simple counterions are non-trivial. They can form a wide variety of short range Ag<sup>+</sup>-anion contacts and thus, together with other non-covalent intermolecular interactions, they strongly influence how the polymeric Ag-bipyridyl chains interact and pack. [1,2]

Similar Ag(I) structures with larger, organic anions are less common and are mostly limited to aromatic anions bearing multiple carboxylate or sulfonate groups. [3-7] These functionalised anions are of course designed to interact with Ag(I) and thus they are usually introduced for structural reasons rather than due to any great interest in the chemical properties of the ions themselves. There are relatively few examples of coordination polymers or MOFs where the counterion is a large organic species that is chemically active in its own right. [7] Herein we present the structures of seven Ag(I) coordination polymers with chemically active counterions. Ag(I) was chosen as it is relatively well tolerated by the body and is used pharmaceutically for its antibacterial functionalities. [8,5] The bipyridyl ligands are chosen partly as earlier work on these ligands allows comparisons to be made with equivalent simple anion containing species and partly with the long term aim of utilising their central chromophores as signalling devices. The counterions used are derived either from well known Active Pharmaceutical Ingredients (APIs) that contain carboxylic acid groups (salicylic acid, diclofenac) or from azo dyes that contain carboxylic or sulfonic acid groups, see scheme 1. The chemico-physical properties of such API and dye molecules are routinely tailored either by salt formation or (for the APIs) by cocrystal formation. [9, 10] The structures of the chosen counterion formers' salt forms and cocrystal forms have thus been widely studied. [11-24] We present these new structures both to investigate the structural effect of

introducing large anions into Ag(I) bipyridyl structures and because including such counterions within coordination polymers opens up the possibility of dramatic changes to the chemico-physical properties of the counterion (e.g. aqueous solubility, dissolution rate and mechanical strength) and thus is a potential route to new and improved formulations. [5, 8]



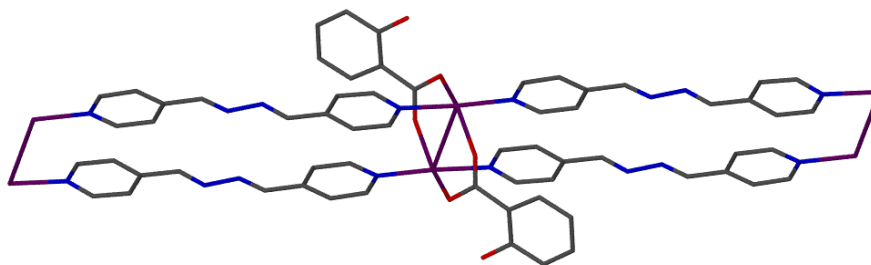
Scheme 1. Ligands used showing their given names. Monoazo dye species are shown in their anionic forms.

## Results and Discussion

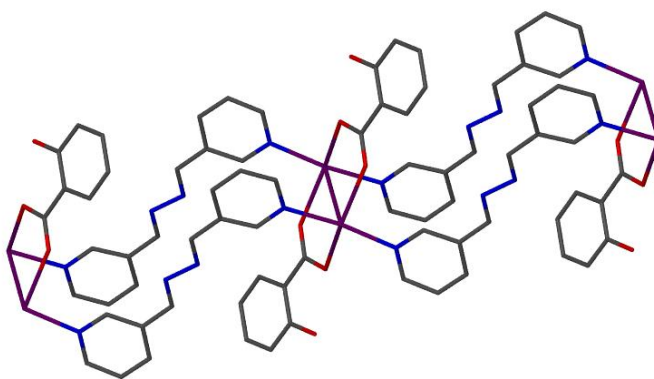
All complexes were prepared by first isolating the Ag(I) complex of the desired API or dye. This was accomplished by simple reaction of  $\text{AgNO}_3$  with Na salts of the relevant organic acid (HY). Suitable crystals of the bipyridyl (L) coordination complexes were then prepared by layering solutions of  $\text{AgY}$  with solutions of the bipyridyl ligands thus allowing slow mixing of the reagents.

*Ag API coordination polymers:* Four acceptable quality crystal structures containing  $[\text{AgL}][\text{Y}]$  complexes were obtained for API relevant carboxylate counterions, see Table 1. Both  $[\text{AgL1}][\text{sal}]$  (sal = salicylate) and  $[\text{AgL2}][\text{sal}]$  have structures that share many of the structural features typical of the related

compounds with small anions that have already been reported in the literature [1,2]. Dative Ag-N(pyridyl) bonding thus creates 1-dimensional  $[\text{AgL}]_n$  chains formed by the 2-coordinate Ag(I) centres and the approximately linear ligands.  $[\text{AgL2}][\text{sal}]$  contains an azine ligand with the *meta* pyridyl geometry and this forms a more pronounced zig-zag polymer than is seen for the L1 complex, compare Figures 1 and 2. This is also shown by the Ag-N...N angles (where N...N represents the two pyridyl N atoms of a single ligand). For  $[\text{AgL1}][\text{sal}]$  there are two crystallographically independent Ag centres and these angles are 165.7 and 168.6°, whilst the equivalent angle for  $[\text{AgL2}][\text{sal}]$  is 122.6°.



**Figure 1.** Part of the polymeric structure of  $[\text{AgL1}][\text{sal}]$  showing two  $[\text{AgL1}]_n$  chains linked by Ag-Ag interactions and by bridging carboxylate groups. Here and in the following figures; Ag = purple, O = red, N = blue, C = grey.



**Figure 2.** Part of the polymeric structure of  $[\text{AgL2}][\text{sal}]$ . As with  $[\text{AgL1}][\text{sal}]$ , shown in Figure 1, there are two  $[\text{AgL}]_n$  chains linked by Ag-Ag interactions and by bridging carboxylate groups. Note that the  $[\text{AgL2}]_n$  chains are not as linear as the equivalent chains in  $[\text{AgL1}][\text{sal}]$ .

Table 1: Selected crystallographic parameters for API containing silver(I) coordination polymers.

Compound	[AgL1][sal]	[AgL2][sal]	[AgL2] [diclofenac]	[AgL3] [diclofenac]. Hdiclofenac
Formula	C <sub>19</sub> H <sub>15</sub> Ag N <sub>4</sub> O <sub>3</sub>	C <sub>19</sub> H <sub>15</sub> Ag N <sub>4</sub> O <sub>3</sub>	C <sub>26.64</sub> H <sub>21.14</sub> Ag Cl <sub>2.72</sub> N <sub>5.14</sub> O <sub>2</sub>	C <sub>42</sub> H <sub>35</sub> Ag Cl <sub>4</sub> N <sub>6</sub> O <sub>4</sub>
Included solvent			MeCN/DCM (28:72)	
Formula weight	455.22	455.22	649.66	937.43
Crystal system	triclinic	monoclinic	triclinic	triclinic
Space Group	P-1	P2 <sub>1</sub> /n	P-1	P-1
$\lambda$ Å	0.71073	0.71073	0.71073	0.71073
$a$ Å	10.0038(5)	8.1200(6)	6.8116(1)	13.3362(6)
$b$ Å	13.3770(7)	9.7869(6)	13.5608(2)	16.5265(8)
$c$ Å	14.291898)	21.6736(16)	28.7557(6)	20.1331(7)
$\alpha$ °	71.640(3)	90	95.438(2)	66.518(4)
$\beta$ °	78.179(3)	97.433(7)	95.833(2)	75.035(3)
$\gamma$ °	78.327(3)	90	96.716(2)	89.409(4)
Volume Å <sup>3</sup>	1757.03(16)	1707.9(2)	2608.96(8)	3910.3(3)
Temp. K	123(2)	123(2)	100(2)	100(2)
$Z$	4	4	4	4
$Z'$	2	1	2	2
Refls. Collected	26245	16401	31146	47857
Refls. Unique	26245 <sup>a</sup>	4437	11757	16978
Rint	n.a. <sup>a</sup>	0.0340	0.0199	0.0468
Goodness of Fit	0.982	1.051	1.049	1.016

<b>R[<math>I &gt; 2\sigma(I)</math>], <i>F</i></b>	0.0635	0.0285	0.0247	0.0451
<b>R<sub>w</sub>, <math>F^2</math></b>	0.1439	0.0693	0.0567	0.1053

<sup>a</sup> This structure was found to be twinned and was refined against a hklf5 formatted reflection file. See ESI for further information.

Table 2. Geometric parameters that describe the Ag(I) environment of the polymeric species.

	[AgL1][sal]	[AgL1][sal]'	[AgL2][sal]	[AgL2][diclofenac]	[AgL2][diclofenac]'	[AgL3][diclofenac].Hdiclofenac	[AgL3][diclofenac].Hdiclofenac'	[AgL2] [DyeA]	[AgL3] [DyeB]	[AgL3] [DyeC]
<b>Dative bonds</b>										
Ag-N(Py)	2.170(5)	2.154(6)	2.19419(17)	2.1881(15)	2.1918(16)	2.176(2)	2.172(2)	2.205(6)	2.158(3)	2.161(2)
Ag-N(Py)	2.175(6)	2.154(6)	2.1976(17)	2.1970(14)	2.1964(15)	2.178(2)	2.173(2)	2.264(6)	2.162(3)	2.167(2)
Py-Ag-Py	173.3(2)	175.3(3)	169.30(6)	161.53(6)	163.36(6)	168.53(9)	166.57(9)	144.2(2)	171.63(10)	172.68(9)
<b>Ag---anion</b>										
Ag---O	2.594(6)	2.671(6)	2.6630(16)	2.5109(14)	2.4887(14)	2.682(2)	2.689(2)	2.357(5)	2.643(2)	2.630(2)
Ag---O	2.821(6)	3.069(6)	2.7072(15)	2.985(4)	2.927(4)	2.734(2)	2.845(2)	2.842(6)	2.881(2)	2.924(3)
Ag---O	3.237(6)	3.164(6)						3.214(7)		
<b>Ag---<math>\pi</math></b>										
Ag---C or N (shortest)			3.2526(19) (azine N)	3.590(1) (py C)	3.466(1) (py C)				3.423(3) (py C)	3.480(3) (pheno l C)
<b>Ag---Ag</b>										
Ag---Ag	3.4944(12)	3.4238(12)	2.9962(4)	3.0597(3)	3.0164(3)	3.1650(5)	3.1051(5)		3.2235(6)	

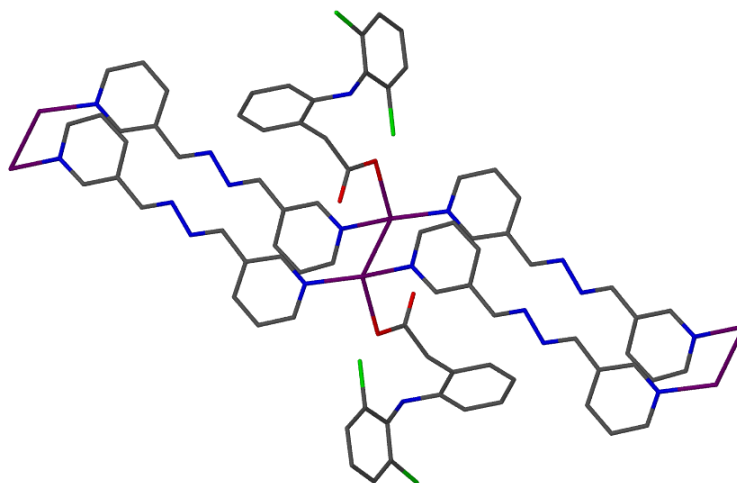


Figure 3. The structure of  $[\text{AgL2}][\text{diclofenac}]$  differs from the salicylate species shown in figures 1 and 2 in having a highly asymmetric interaction between the Ag-Ag unit and the carboxylate group.

In both compounds each Ag centre makes 4 short contacts, in addition to the two dative Ag-N bonds, giving a *pseudo*-octahedral geometry. The individual dative chains are linked into pairs by argentophilic Ag-Ag short contacts [1,2,25] which are each supported by two COO bridges from the benzoate anions, giving pairs of  $[\text{AgAgOCO}]$  five-membered rings. A difference between the two structures lies in the geometric detail of these rings. The Ag-Ag contact in  $[\text{AgL1}][\text{sal}]$  is much longer than that in  $[\text{AgL2}][\text{sal}]$  and indeed is longer than any of the other Ag-Ag contacts reported in Table 2. Additionally, the two Ag-O distances per ring are asymmetric for  $[\text{AgL1}][\text{sal}]$  but near equivalent in  $[\text{AgL2}][\text{sal}]$ , see distances given in Table 2. Both compounds described so far thus give rather similar double-chain, 1-dimensional polymers. However, the 6<sup>th</sup> contact site of each Ag centre is that *trans* to the Ag-Ag bond and differs between the compounds and thus so does the method of double-chain to double-chain interaction, Table 3. In the structure of  $[\text{AgL1}][\text{sal}]$  both independent Ag centres make a short contact with an O atom of the salicylate anion of a neighbouring double chain, but one Ag centre contacts an O atom of a COO group whilst the other interacts with the O atom of the phenolic group. These contacts link double chains in the crystallographic *b* direction. In contrast, the sixth site in  $[\text{AgL2}][\text{sal}]$  is a  $\pi$  contact between Ag and a N atom of the central azine linker fragment. This interaction is supported by short  $\pi$ - $\pi$  contacts between the azine ligands (closest C to C contact 3.3248(2) Å). These  $\pi$  interactions combine to link the double chains of  $[\text{AgL2}][\text{sal}]$ . In both cases the resulting packed structure is layered with alternating



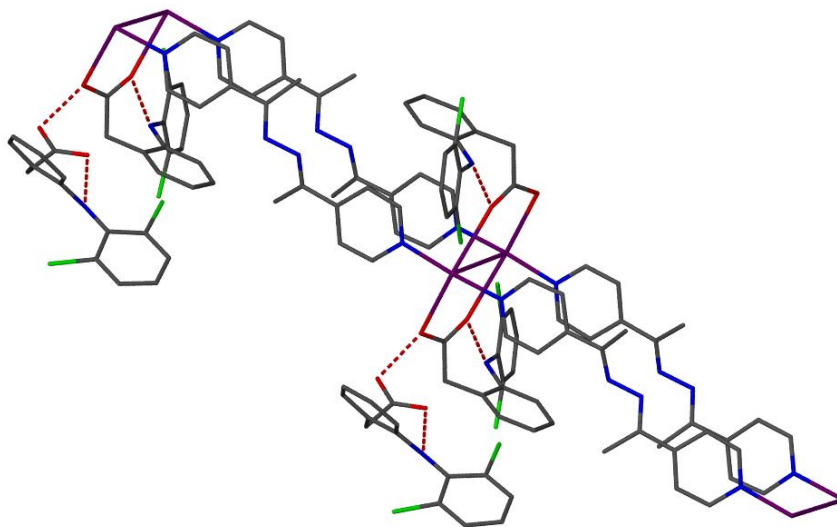
organic (hydrophobic) and inorganic (hydrophilic) layers. A related Ag(I) structure with the carboxylate-based ibuprofen anion and a bipyridyl ligand with a C<sub>3</sub>H<sub>6</sub> linker between its pyridyl rings has been published. [7] Despite a very different pyridyl ligand geometry caused by the flexibility of the C<sub>3</sub>H<sub>6</sub> alkyl linkage, this has a somewhat similar structure featuring chains of [AgL]<sub>n</sub> bridged by Ag-Ag contacts. However, in this literature compound the COO group does not bridge between the Ag-Ag centres and the Ag-Ag bonds link the chains not into pairs but into 2-dimensional sheets.

Table 3. Summary of pertinent structural features of the polymeric species.

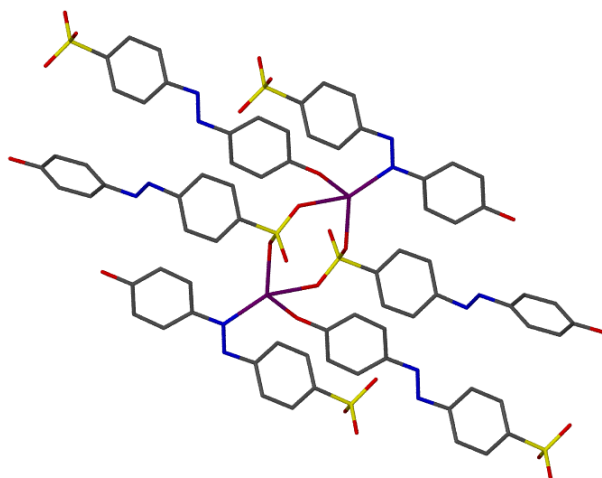
Compound	[AgL1][sal]	[AgL2][sal]	[AgL2] [diclofenac]	[AgL3] [diclofenac]. Hdiclofenac	[AgL2] [DyeA]	[AgL3] [DyeB]	[AgL3] [DyeC]
Double chain structure	yes	yes	yes	yes	no	yes	no
Ag-Ag bonding	yes	yes	yes	yes	no	yes	no
OCO or OSO bridging Ag-Ag	yes	yes	yes	yes	no	yes	no
Coordination number of Ag	6	6	6	5	5	6	5/6
Interaction type at 6 <sup>th</sup> coordination site	Ag...O	Ag...π(azine)	Ag...π(py))	none	none	Ag...π(py))	Disordered solvent. Ag...Cl 3.419(4)

Two silver structures containing the diclofenac anion were also obtained. Despite the larger anion size, [AgL2][diclofenac] is very similar to the two salicylate structures described above. Both of its crystallographically independent AgL2 units propagate into 1-dimensional chains through Ag-N bonds and double chains are formed by Ag-Ag interactions that are bridged by the anions' COO groups. The bridging Ag-O contacts are even more asymmetrical than in the structure of [AgL1 sal] (Table 2). As with [AgL2][sal], the sixth short contact is a π contact to the azine ligand, but here the bond is to the pyridyl ring rather than to the central azine fragment. A further difference is that π-π contacts between the

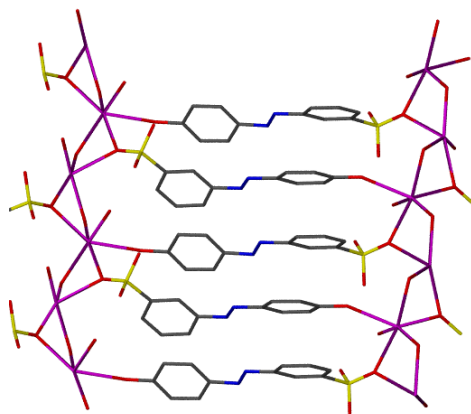
azine ligands are only found between the ligands of a double chain and do not link neighbouring double chains to one another. The second Ag/diclofenac structure is chemically rather different. It contains both diclofenac anions and neutral, free-acid, molecules of diclofenac and has formula  $[AgL_3][diclofenac].Hdiclofenac$ . This is another  $Z' = 2$  structure although, unlike  $[AgL_1][sal]$  and  $[AgL_2][diclofenac]$ , both of the independent Ag centres are part of the same polymeric coordination chain rather than forming crystallographically independent coordination chains. Despite the inclusion of free acid molecules, the same core 1-dimensional polymeric motif of a double chain of  $[AgL]_n$  units supported by an Ag-Ag interaction and its COO bridges is retained. Once again the Ag...O contacts are asymmetric but here there are no short azine to azine  $\pi$ - $\pi$  contacts and the Ag centre is best described as 5-coordinate rather than as 6-coordinate. The preeminent intermolecular contact formed by the free acid groups are donation of O-H...O hydrogen bonds from the carboxylic acid groups to the anionic diclofenac COO groups that bond to Ag. Both Ag(I) diclofenac structures pack so as to give layered structures with alternating AgL and diclofenac layers. The diclofenac layer of  $[AgL_2][diclofenac]$  also contains disordered solvent molecules.



**Figure 4.** Part of the polymeric structure of  $[AgL_3][diclofenac].Hdiclofenac$  showing the free acid hydrogen bonded to and pendant upon the coordination polymer.



**Figure 5.** Part of the polymeric structure of [AgDyeB] showing the tetrahedral coordination geometry at Ag(I) centres and the central [AgOSO]<sub>2</sub> ring motif.



**Figure 6.** Part of the structure of [Ag<sub>x</sub>Na<sub>(1-x)</sub>(DyeC)(OH<sub>2</sub>)<sub>2</sub>] showing the azo anions acting as links between hydrophilic zones that contain metal ions and water.

Table 4: Selected crystallographic parameters for azo dye containing complexes.

Compound	[Ag(DyeB)]	[Na(DyeC)]	[AgNa(DyeC)]	[AgL2] [DyeA] BASF 0.4593(16)	[AgL3] [DyeB]	[AgL3] [DyeC]
<b>Formula</b>	C <sub>12</sub> H <sub>9</sub> Ag N <sub>2</sub> O <sub>4</sub> S	C <sub>12</sub> H <sub>13</sub> N <sub>2</sub> Na O <sub>6</sub> S	C <sub>12</sub> H <sub>13</sub> Ag <sub>0.87</sub> N <sub>2</sub> Na <sub>0.13</sub> O <sub>6</sub> S	C <sub>25</sub> H <sub>19</sub> Ag N <sub>6</sub> O <sub>3</sub>	C <sub>28</sub> H <sub>26</sub> Ag N <sub>7</sub> O <sub>4</sub> S	C <sub>27.5</sub> H <sub>25.5</sub> Ag Cl N <sub>6.5</sub> O <sub>4</sub> S
<b>Included solvent</b>		2H <sub>2</sub> O	2H <sub>2</sub> O		MeCN	MeCN/DCM (50:50)
<b>Formula weight</b>	385.14	336.29	410.03	559.33	664.49	686.02
<b>Crystal system</b>	monoclinic	orthorhombic	orthorhombic	triclinic	triclinic	triclinic
<b>Space Group</b>	P2 <sub>1</sub> /n	Pbca	Pbca	P-1	P-1	P-1
<b>λ Å</b>	0.71073	0.71073	0.71073	1.5418	0.71073	0.71073
<b>a Å</b>	8.3838(2)	7.1227(3)	7.0886(3)	7.1538(5)	7.1356(5)	11.1773(4)
<b>b Å</b>	9.7225(3)	11.9399(2)	11.8816(6)	12.9587(15)	14.0212(11)	11.6004(4)
<b>c Å</b>	14.9340(4)	32.5608(9)	32.9373(17)	13.2859(14)	15.4526(9)	12.1880(4)
<b>α°</b>	90	90	90	67.835(10)	109.697(4)	81.629(2)
<b>β°</b>	94.352(2)	90	90	82.451(7)	101.688(3)	73.899(2)
<b>γ°</b>	90	90	90	76.606(8)	98.473(30)	70.341(2)
<b>Volume Å<sup>3</sup></b>	1213.78(6)	2769.11(15)	2774.1(2)	1108.29(19)	1385.85(17)	1427.43(9)
<b>Temp. K</b>	123(2)	150(2)	123(2)	123(2)	100(2)	120(2)
<b>Z</b>	4	8	8	2	2	2
<b>Z'</b>	1	1	1	1	1	1
<b>Refs. Collected</b>	25790	5649	19356	10036	25884	31937

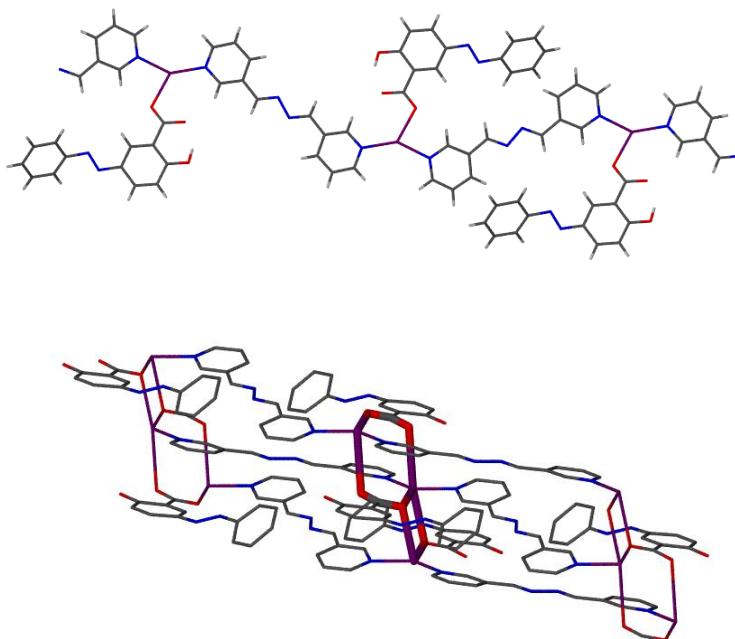
<b>Refls.</b>	3549	3048	3015	10036 <sup>a</sup>	6336	6545
<b>Unique</b>						
<b>Rint</b>	0.0409	0.0826	0.0630	na <sup>a</sup>	0.0681	0.0595
<b>Goodness of Fit</b>	1.067	0.991	1.020	1.066	1.052	1.035
<b>R[<math>I &gt; 2\sigma(I)</math>], <i>F</i></b>	0.0229	0.0473	0.0319	0.1044	0.0567	0.0392
<b>Rw, <math>F^2</math></b>	0.0485	0.1052	0.0599	0.2934	0.0932	0.0917

<sup>a</sup> This structure was found to be twinned and was refined against a hklf5 formatted reflection file. See ESI for further information.

*Ag salts of Dye B and Dye C:* Two structures were elucidated for the “starting materials” which were expected to be Ag(I) salts of DyeB and DyeC, Table 4. Few structures of Ag salts of sulfonated azo dyes are known from the literature, but in those structures that are known [3, 21, 26] the Ag(I) centre performs the same structural role as is performed by the heavier alkali metal ions (Na, K, Rb) in equivalent compounds. [18-21] For the *meta*-sulfonated DyeC, the compound isolated was predominately a silver salt where as expected Ag performs the same structural role as a heavy alkali metal. Indeed the structure obtained was found to be isomorphous and isostructural with the Na salt form of DyeC (given in the ESI for comparison) and even features metal sites with mutual substitution disorder with a mix of Ag(I) and Na(I) sharing the same metal site such that the refined formula is  $[Ag_xNa_{(1-x)}(DyeC)(OH_2)_2]$  ( $x = 0.867(2)$ ). However, the structure of  $[Ag(DyeB)]$  is different from what has been observed previously, with the main and obvious difference being that a Ag-N dative bond (Ag-N 2.2437(15) Å) has formed between Ag(I) and a N atom of the azo group. No such M-N bond has been found for any previously reported alkali metal sulfonated azo dye structure. [18] The closest analogue found was a Ag(I) complex of azobenzene - an azo ligand which offers no Lewis base atoms as potential bonding sites apart from its azo group. [31] The Ag-N bond formation does not alter the azo bond length (compare 1.264(2) and 1.266(3) Å in  $[Ag(DyeB)]$  and  $[Ag_xNa_{(1-x)}(DyeC)(OH_2)_2]$ ). Gas phase calculations suggest that sulphonated azo ions prefer planar (and presumably conjugated) conformations.[18] However, the aromatic rings in the azo anion of  $[Ag(DyeB)]$  are considerably twisted out of plane, the angle between ring planes is 49.75(6) °. The solid state structures of such anions do sometimes feature

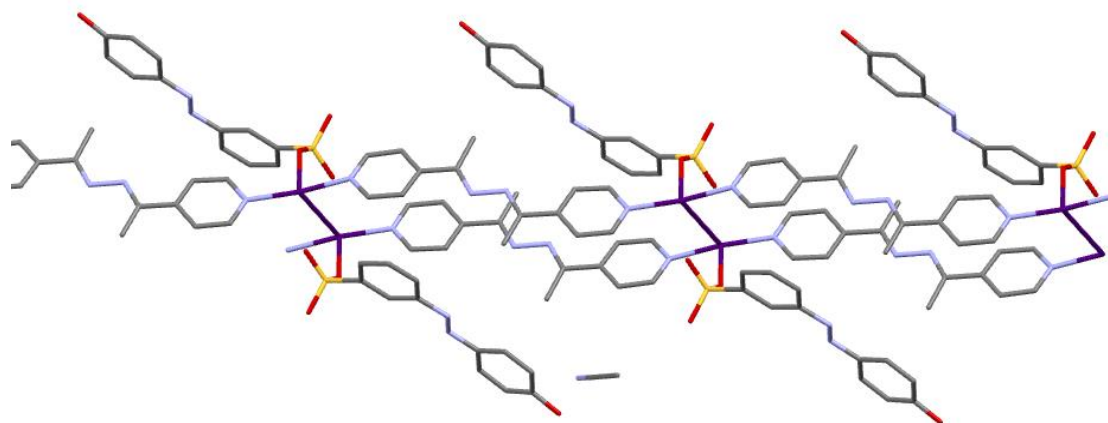
non-planar conformations but these are rarely as pronounced as is the case here. Thus it may be that the twist is directly related to the Ag-N bond formation. [18]

*Ag dye coordination polymers:* The first of the three Ag(I) bipyridyl and azo dye-containing structures, [AgL2][Dye A], is chemically similar to the Ag(I) API containing complexes, above, in as far as the organic anion is a carboxylate. Further, it is a derivative of salicylic acid and retains the salicylate metal ion bonding groups. Largely due to twinning of the crystals, the quality of this structure is rather low. However, the data clearly demonstrates that this structure is different from the API-containing structures. There are no Ag-Ag interactions here. Each Ag centre makes 2 dative bonds to pyridyl N atoms as usual, but the N-Ag-N angle is bent away from 180 to 144.2(2)° by the presence of a Ag-OCO bond that is much shorter than the others described herein (2.357(5)Å, see Table 2) . These three dative bonds result in the 1-dimensional coordination polymer illustrated in Figure 7 (top). Note that the bipyridyl ligands have crystallographically imposed centres of symmetry at the middle of the N-N bonds, giving two crystallographically independent ligands. Two longer Ag...O contacts are also present and have unusual Ag-π type geometries. These contacts are to neighbouring COO groups and they complete the Ag bonding which is thus approximately trigonal bipyramidal. The long Ag-O interactions link individual [AgL2]<sub>n</sub> chains in the crystallographic *a* direction. [AgOAgO] and [Ag(OCO)Ag(OCO)] rings are formed and these result in the structure being a 2-dimensional polymer.

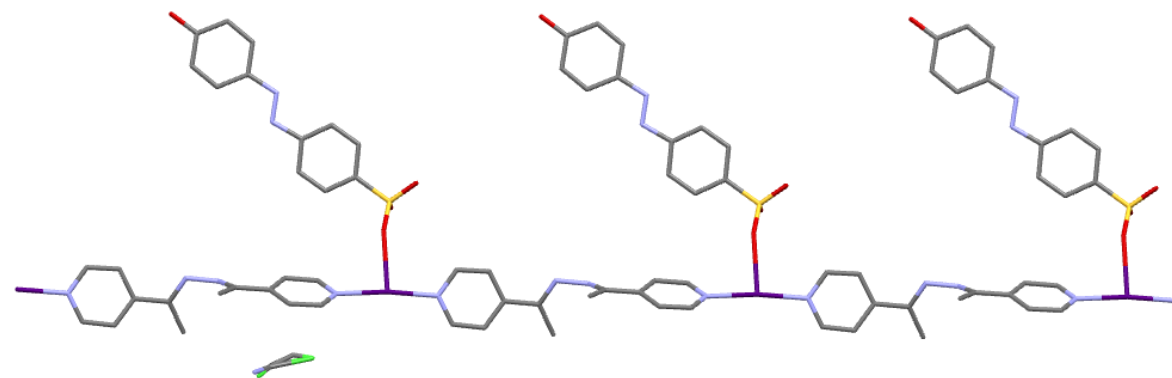


**Figure 7.** *Top*, part of the 1-dimensional coordination polymer formed by dative bonding in [AgL2][Dye A]. The azo dye anions are pendant to the polymeric chain. *Bottom*, longer Ag-OCO contacts have  $\pi$  geometries and link the 1-dimensional coordination polymers in a second dimension. One such series of Ag-O interactions has been picked out with thick bonds.

Of the two Ag(I) complexes that contain sulfonated monoazo dyes as anions, one has a structure that is a close relative of the Ag(I) API complexes. The simple difference is that in the structure of [AgL3][DyeB].NCMe asymmetrically bridging  $\text{SO}_3$  units replace the bridging COO groups seen for the API complexes and these perform an equivalent structural role by bridging Ag-Ag argentophilic bonds. The sixth site involves a Ag...C  $\pi$  interaction with a pyridyl ring and these interactions form links connecting neighbouring double chain units. Short  $\pi$ - $\pi$  interactions between azine ligands exist within the double chains but also occur between the azo anions of neighbouring molecules – and this latter interaction also connects neighbouring double chains to each other. The final Ag(I) structure is a solvate of [AgL3][DyeC], where Dye C is the *para* isomer of *meta*-sulfonated azo dye, DyeB. Despite this relatively small difference, the structure is very different, with no Ag-Ag bond (Ag to Ag distances  $> 4.39 \text{ \AA}$ ). The usual two *trans* Ag-N bonds to pyridyl are present giving a 1-dimensional coordination polymer, but the remainder of the Ag centre's short contacts are made up of two contacts to O atoms of sulfonate groups and one  $\pi$ -interaction with the phenol ring of an azo anion. The three dimensional packed structure results from these Ag to sulfonate ion interactions combining to link single chains of  $[\text{AgL3}]_n$ . The potential sixth contact site for Ag is unusual. This space is filled by a mixture of disordered solvent (a 50:50 mix of MeCN and DCM) and the only contact that is less than the sum of van der Waals radii is a Ag...Cl interaction ( $3.419(4) \text{ \AA}$ ). This highlights a difference between the currently reported structures and similar species with small anions.[2] When prepared using the same methods and solvents, almost half of the small counterion containing structures had MeCN present as a ligand bound to Ag. Three of the seven relevant structures reported herein have MeCN in the crystal structure – but none features a Ag-NCMe bond. A further oddity of this structure is that although the aromatic rings of the azo anion are mutually coplanar, the azine ligand adopts a very twisted conformation (angle between least squares planes  $65.79(9)^\circ$ ). Such a twisted conformation of the azine ligand has been seen before, for example in the complex [AgL1][NO<sub>3</sub>], but is uncommon. [2]



**Figure 8.** Part of the 1-dimensional double chain structure of  $[AgL3][DyeB].NCMe$ , showing structural similarity to the salicylate and diclofenac structures reported above.



**Figure 9.** Part of the 1-dimensional polymeric chain structure of  $[AgL3][DyeC].solvate$  illustrating the twisted nature of the azine ligand and pendant monoazo anions. These chains are interconnected by  $Ag-O_3S$  contacts and by  $Ag-\pi$  contacts.

## Conclusions

This work shows the successful inclusion of functional carboxylate and sulfonate anions into  $Ag(I)$  bipyridyl coordination polymers. Four structures are reported that contain anionic forms of the Active



Pharmaceutical Ingredients (APIs) salicylate and diclofenac, and three structures contain anionic monoazo dyes. In addition the structure of a silver salt of a meta-sulfonated azo dye, [Ag(DyeB)], is reported and is found to contain an unexpected Ag-N(azo) dative bond. All Ag(azine) polymers have a 1:1:1 stoichiometry for the Ag:bipyridyl:anion ratio and all have the expected 1-dimensional [Ag(bipyridyl)]<sub>n</sub> polymeric chain structure formed through Ag-N(pyridyl) bonds. Five of the seven structures, including all of the API structures, share a further bonding motif of individual chains being linked into pairs through Ag-Ag contacts and twin AgOXOAg (X = C or S) bridges. Similar bonding motifs are also known for related species with smaller anions. [1,2] Further intermolecular interactions between the double-chain structures are highly variable. Two structures, both with sulfonated azo dye anions, do not show the otherwise common bonding mode of Ag-Ag contacts and OXO (X= C or S) bridges. In these two cases, single chain [Ag(bipyridyl)]<sub>n</sub> structures with pendant anions are formed and inter-chain linkage is by long Ag-O, silver-to-anion contacts.

## Experimental

*Single Crystal Diffraction.* Measurements were made at low temperature with Rigaku/Oxford Diffraction or Enraf Nonius instruments. Monochromated Mo ( $\lambda = 0.71073 \text{ \AA}$ ) radiation was used for all data collections except that for [AgL2][Dye A] where Cu radiation was used ( $\lambda = 1.5418 \text{ \AA}$ ). Data for the diclofenac containing compounds and for [AgL3][DyeB].NCMe and [AgL3][DyeC].solvate were measured by the NCS at the University of Southampton.[28] All structures were refined to convergence against  $F^2$  and against all independent reflections using programs from the SHELX family. [29] Figures were drawn using MERCURY. [30] [AgL1][sal] and [AgL2][Dye A] were modelled as twins. Selected crystallographic and refinement parameters are given in Tables 1 and 4 and full data has been deposited in cif format with the CCDC as CCDC 1517174 to 1517183.

## *Synthesis.*

*General Preparation of Ag salts.* Example. Sodium salicylate (2 g, 12.8 mmol) was dissolved in water (10 ml). Silver nitrate (3.6 g, 21 mmol (excess)) was dissolved in water (20 ml). The silver nitrate solution was then added to the salicylate solution and a white precipitate formed immediately. The precipitate was separated by filtration, washed with water and dried. Mass of product = 2.93 g (11.95 mmol). Yield = 93.35 %. All other Ag salts were formed in similar fashion and were generally used without further

characterization. The exceptions being the Ag salt forms of Dye B and Dye C which were characterized crystallographically (see above). This showed that “AgDyeC” in fact contained 13 to 14 % of residual Na.

*General Preparation of Ag azine complexes.* The azine ligands L1 to L3 were synthesised as described in reference 2. They gave IR spectra identical to the ligands previously reported. Sample preparation was also based on the methodology of reference 2. Thus in general dichloromethane solutions of the azine ligands were pipetted into nmr tubes. After leaving time to settle, acetonitrile solutions of the Ag salts were slowly pipetted into the tubes such that two layers were formed. Leaving the sealed tubes to sit resulted in slow mixing of the two solutions and their reagents with crystals forming within 1 to 7 days. Larger scale reactions for the salicylate and dye compounds, performed with mixing of reagents rather than layering, gave the same products (by comparison of IR spectra) as powders. Yields were 50 to 85 %. All possible combinations of L1, L2 and L3 with Ag salts of sal, diclofenac, Dye B and Dye C were attempted, but only the structures reported herein gave identifiable crystalline products that were not starting materials.

*[AgL1][sal].* L1 (0.02 g, 0.1 mmol) was dissolved in dichloromethane (0.5 ml) and filtered. The solution was then pipetted into an NMR tube, a layer of blank acetonitrile (1 ml) was then pipetted into the NMR tube. Silver salicylate (0.05 g, 0.2 mmol) was dissolved in acetonitrile (1 ml), the silver salicylate solution was then pipetted into the same NMR tube giving two distinct layers. After one week crystalline material was obtained. IR ( $\text{cm}^{-1}$ ) KBr: 750, 820, 1142, 1248, 1309, 1354, 1390, 1419, 1456, 1487, 1554, 1599, 3413. Raman,  $\lambda = 633 \text{ nm}$  ( $\text{cm}^{-1}$ ): 1003, 1212, 1241, 1327, 1536, 1585, 1615.

*[AgL2][sal].* L2 (0.02 g, 0.1 mmol) was dissolved in dichloromethane (0.5 ml) and filtered. The solution was then pipetted into an NMR tube, a layer of blank acetonitrile (1 ml) was then pipetted into the NMR tube. Silver salicylate (0.05 g, 0.2 mmol) was dissolved in acetonitrile (1 ml), the silver salicylate solution was then pipetted into the same NMR tube giving two layers. After five days yellow crystalline material was present. IR ( $\text{cm}^{-1}$ ): 639, 689, 765, 796, 948, 1001, 1124, 1196, 1292, 1383, 1423, 1446, 1579, 1636, 2925.

*[AgL2][diclofenac].* L2 (0.02 g, 0.1 mmol) was dissolved in dichloromethane (0.5 ml) and filtered. The solution was then pipetted into an NMR tube, a layer of blank acetonitrile (1 ml) was then pipetted into the NMR tube. Silver diclofenac (0.02 g, 0.05 mmol) was dissolved in acetonitrile (1 ml), the silver diclofenac solution was then pipetted into the same NMR tube forming two distinct layers. After 4 days

crystalline material was present. IR ( $\text{cm}^{-1}$ ): 689, 764, 798, 943, 1038, 1105, 1167, 1195, 1256, 1312, 1352, 1420, 1454, 1560, 1577, 2922, 2954.

*[AgL3][diclofenac]*. L3 (0.027 g, 0.1 mmol) was dissolved in dichloromethane (0.5 ml) and filtered. The solution was then pipetted into an NMR tube, a layer of blank acetonitrile (1 ml) was then pipetted into the NMR tube. Silver diclofenac (0.02 g, 0.05 mmol) was dissolved in acetonitrile (1 ml), the silver diclofenac solution was then pipetted into the same NMR tube forming two layers. After 5 days crystalline material was present.

*[AgL2][DyeA]*. L2 (0.033 g, 0.16 mmol) was dissolved in 1 ml of dichloromethane and filtered. The solution was pipetted into a nmr tube. AgDyeA (0.055 g, 0.16 mmol) was dissolved in 1 ml of acetonitrile and filtered. This solution was carefully layered onto the L3 solution and the tube was sealed. After 24 hours, crystalline material appeared. IR ( $\text{cm}^{-1}$ ): 702, 822, 866, 949, 971, 1023, 1083, 1120, 1188, 1225, 1247, 1307, 1337, 1419, 1486, 1591, 1628, 2942.

*[AgL3][DyeB]*. L3 (0.019 g, 0.08 mmol) was dissolved in dichloromethane and filtered. A second filtered solution was prepared using AgDyeB (0.013 g, 0.04 mmol) and acetonitrile. Layering the two solutions in a nmr tube resulted in crystal growth at the interface after approximately 4 days. IR ( $\text{cm}^{-1}$ ) KBr: 581, 613, 719, 833, 1029, 1131, 1222, 1282, 1422, 1605, 3452.

*[AgL3][DyeC]*. L3 (0.19 g, 0.8 mmol) was dissolved in dichloromethane and filtered. A second filtered solution was prepared using AgDyeC (0.12 g, 0.31 mmol) and acetonitrile. The solutions were layered together, split between several narrow tubes. This resulted in crystal growth at the interface after approximately 5 days. IR ( $\text{cm}^{-1}$ ) KBr: 573, 622, 708, 850, 1024, 1118, 1195, 1424, 1605, 3426.

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