

## Bis[ $\mu$ -3-[3-(2-pyridyl)pyrazol-1-yl-methyl]pyridine]disilver(I) bis(trifluoromethanesulfonate): effect of counter-anions on the self-assembly of coordination complexes

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Received 17 June 2008

Accepted 29 July 2008

Online 9 August 2008

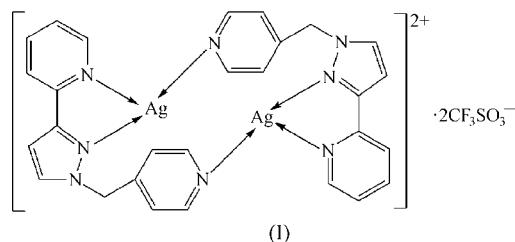
As part of a study on the effect of different counter-anions on the self-assembly of coordination complexes, a new dinuclear  $\text{Ag}^{\text{I}}$  complex,  $[\text{Ag}_2(\text{C}_{14}\text{H}_{12}\text{N}_4)_2](\text{CF}_3\text{SO}_3)_2$ , with the 3-[3-(2-pyridyl)pyrazol-1-ylmethyl]pyridine (*L*) ligand was obtained through the reaction of *L* with  $\text{AgCF}_3\text{SO}_3$ . In this complex, each  $\text{Ag}^{\text{I}}$  center in the centrosymmetric dinuclear complex cation is coordinated by two pyridine and one pyrazole N-atom donor of two inversion-related *L* ligands in a trigonal planar geometry. This forms a unique box-like cyclic dimer with an intramolecular nonbonding  $\text{Ag}\cdots\text{Ag}$  separation of 6.379 (7) Å. Weak  $\text{Ag}\cdots\text{CF}_3\text{SO}_3$  and  $\text{C}-\text{H}\cdots\text{X}$  ( $\text{X} = \text{O}$  and  $\text{F}$ ) hydrogen-bonding interactions, together with  $\pi$ - $\pi$  stacking interactions, link the complex cations along the [001] and  $[1\bar{1}0]$  directions, respectively, generating two different one-dimensional chains and then an overall two-dimensional network of the complex running parallel to the (110) plane. Comparison of the structural differences with previous findings suggests that the presence of different counter-anions plays an important role in the construction of such supramolecular frameworks.

### Comment

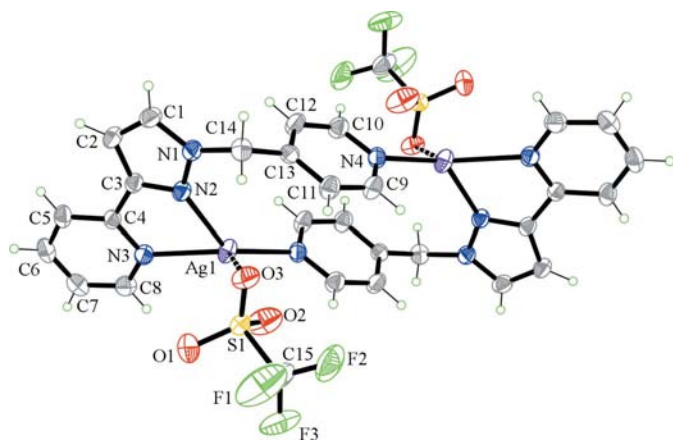
The rational design and synthesis of functional coordination architectures has attracted much attention in recent years owing to their interesting structures and their potential uses as functional materials (Chen *et al.*, 2006; Janiak, 2003; Robin & Fromm, 2006; Steel, 2005; Wang *et al.*, 2008). Although the principles for controlling the solid-state structures of the target products still need to be classified and established, many rational synthetic strategies have been brought forward and have proved significant in the design of metal-based coordination complexes. The selection of suitable ligands as building blocks is undoubtedly a key point in manipulating the final

structures of the complexes (Robin & Fromm, 2006; Steel, 2005). Other factors, such as the coordination geometry or radius of the metal ions (Du *et al.*, 2007; Liu, Wang *et al.*, 2007), the size or coordination ability of the counter-anions (Campos-Fernández *et al.*, 2005; Hirsch *et al.*, 1997; Huang *et al.*, 2004; Xie *et al.*, 2004; Zou *et al.*, 2004), the presence of auxiliary ligands (Liu, Shi *et al.*, 2006; Liu, Wang *et al.*, 2007) or solvents (Kasai *et al.*, 2000; Raehm *et al.*, 2003), metal/ligand ratio (Saalfrank *et al.*, 2001), and even pH value (Du *et al.*, 2002), have also been found to influence significantly the structural topologies of such coordination frameworks.

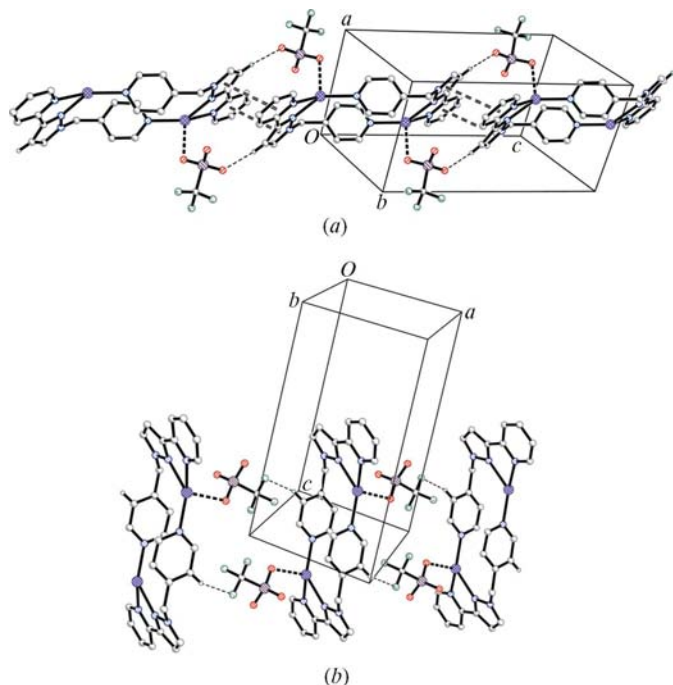
Numerous related bis-heterocyclic chelating or bridging ligands have been synthesized and used extensively to construct functional coordination complexes that contain different heteroaromatic ring systems, for example, pyridine, pyrazine, quinoline, quinoxaline, pyrazole, imidazole, thiazoles and their benzo analogues (Steel, 2005). Ward, Singh and co-workers have reported many coordination architectures involving 3-(2-pyridyl)-1*H*-pyrazole and its derivatives (Bell *et al.*, 2003; Paul *et al.*, 2004; Singh *et al.*, 2003; Ward *et al.*, 2001). In our previous work, a series of 3-(2-pyridyl)pyrazole-based ligands have also been used to construct complexes with various structures, including multinuclear discrete molecules as well as one- and two-dimensional coordination polymers, which also exhibit interesting properties (Liu, Chen *et al.*, 2006; Liu, Li *et al.*, 2007; Liu, Shi *et al.*, 2006; Liu, Zhang *et al.*, 2007; Zhang *et al.*, 2005; Zou *et al.*, 2006). Recently, we have reported the preparation of a nonplanar flexible ligand based on a pyridylpyrazole chelating unit and a pendant pyridyl group, namely 3-[3-(2-pyridyl)pyrazol-1-ylmethyl]pyridine (*L*) (Liu, Li *et al.*, 2007). Its reaction with  $\text{AgClO}_4$  produced a one-dimensional helical chain coordination polymer, *viz.*  $[\text{AgLClO}_4]_{\infty}$ , (II). To further investigate the influence of different counter-anions on the self-assembly process of coordination complexes, we chose to use *L* to construct new functional  $\text{Ag}^{\text{I}}$  complexes through its reaction with  $\text{AgCF}_3\text{SO}_3$ . We report here the crystal structure of  $[\text{Ag}_2\text{L}_2](\text{CF}_3\text{SO}_3)_2$ , (I), and discuss the effect of different counter-anions, *viz.*  $\text{ClO}_4^-$  for (II) and  $\text{CF}_3\text{SO}_3^-$  for (I), on the final structures of the relevant coordination complexes.



The structure of (I) consists of a centrosymmetric dinuclear  $[\text{Ag}_2\text{L}_2]^{2+}$  unit and two uncoordinated  $\text{CF}_3\text{SO}_3^-$  ions. The dinuclear  $[\text{Ag}_2\text{L}_2]^{2+}$  cation (Fig. 1) comprises two *L* ligands and two  $\text{Ag}^{\text{I}}$  centers. Each  $\text{Ag}^{\text{I}}$  center adopts a distorted trigonal planar geometry formed by three N-atom donors, two from the pyridylpyrazole ring system of one *L* ligand, and one from the pendant pyridine ring of another *L* ligand. All  $\text{Ag}-$

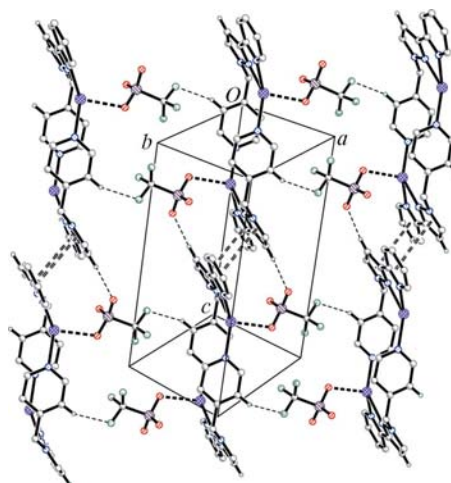
**Figure 1**

The molecular structure of the title complex, showing the weak Ag $\cdots$ O interaction (dashed line). Displacement ellipsoids are drawn at the 30% probability level. The symmetry-related parts in the dinuclear unit are generated by the symmetry operation  $(-x + 1, -y + 1, -z + 2)$ .

**Figure 2**

A view of (a) the one-dimensional chain, running along the [001] direction, formed by  $\pi$ - $\pi$  stacking (double dashed lines), C-H $\cdots$ O hydrogen-bonding (fine dashed lines) and Ag $\cdots$ O (thick dashed lines) interactions, and (b) another one-dimensional chain, running along the  $[1\bar{1}0]$  direction, formed by C-H $\cdots$ F hydrogen-bonding (fine dashed lines) and Ag $\cdots$ O (thick dashed lines) interactions. For clarity, only H atoms involved in the interactions are shown.

N bond distances (Table 1) are in the normal range found in such complexes (Liu, Chen *et al.*, 2006; Liu, Li *et al.*, 2007). Meanwhile, each uncoordinated  $\text{CF}_3\text{SO}_3^-$  anion exhibits a weak interaction with the  $\text{Ag}^{\text{I}}$  center [ $\text{Ag}1\cdots\text{O}2 = 2.660(5) \text{ \AA}$ ]. In addition, adjacent discrete dinuclear  $[\text{Ag}_2\text{L}_2]^{2+}$  units are assembled into different one-dimensional chains, along the [001] and  $[1\bar{1}0]$  directions, by the combined effects of intermolecular face-to-face  $\pi$ - $\pi$  stacking [the

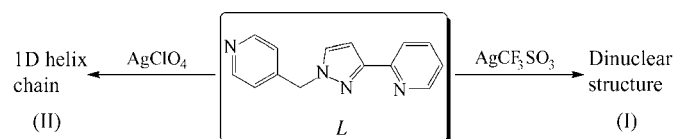
**Figure 3**

The two-dimensional network, parallel to the (110) plane, formed by the intermolecular interactions shown in Fig. 2 (with the same bond coding). For clarity, only H atoms involved in the interactions are shown.

centroid-centroid separation being  $3.804(5) \text{ \AA}$  between the pyridyl-pyrazole ring systems; symmetry code:  $-x + 1, -y + 1, -z + 1$ ] (Janiak, 2000), C-H $\cdots$ X hydrogen-bonding interactions ( $X = \text{O}$  and  $\text{F}$ ; Table 2) (Desiraju & Steiner, 1999) and the weak Ag $\cdots$ O interactions mentioned above (Fig. 2). The net result is a two-dimensional network running parallel to the (110) plane (Fig. 3).

In general, the effect of counter-anions on the self-assembly of coordination complexes can be explained as being due to differences in size, shape and coordination ability (Campos-Fernández *et al.*, 2005; Hirsch *et al.*, 1997; Huang *et al.*, 2004; Xie *et al.*, 2004; Zou *et al.*, 2004).

The structural differences of complexes (I) and (II) serve to exemplify the eventual influence of counter-anions on the construction of supramolecular frameworks. Even if neither the  $\text{ClO}_4^-$  anion in (II) nor the  $\text{CF}_3\text{SO}_3^-$  anion in (I) coordinates to the  $\text{Ag}^{\text{I}}$  cation, owing to their size difference they fulfill quite different template roles, strongly affecting the building of the corresponding final frameworks through weak Ag $\cdots$ O interactions with the different cationic subunits [a dinuclear motif in complex (I) and a one-dimensional (1D) motif in complex (II)]. This analysis shows that changes in



counter-anions could adjust the framework formation of such complexes, and this fact may provide an effective method for controlling the coordination architectures of compounds with potentially useful properties.

## Experimental

Ligand *L* was synthesized according to the method of Liu, Li *et al.* (2007). *L* (0.1 mmol) was added to  $\text{AgCF}_3\text{SO}_3$  (0.1 mmol) in a mixed

solution of methanol (15 ml) and acetonitrile (5 ml). The yellow solid which formed was filtered off and the resulting solution was kept at room temperature. Yellow single crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent after several days (yield ~30%). Elemental analysis calculated for  $C_{15}H_{12}AgF_3N_4O_3S$ : C 36.53, H 2.45, N 11.36%; found: C 36.41, H 2.56, N 11.42%.

## Crystal data

$[Ag_2(C_{14}H_{12}N_4)_2](CF_3SO_3)_2$	$\gamma = 79.16 (3)^\circ$
$M_r = 986.44$	$V = 886.3 (3) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 1$
$a = 7.9430 (16) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 8.5368 (17) \text{ \AA}$	$\mu = 1.31 \text{ mm}^{-1}$
$c = 13.739 (3) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\alpha = 75.64 (3)^\circ$	$0.30 \times 0.28 \times 0.25 \text{ mm}$
$\beta = 86.57 (3)^\circ$	

## Data collection

Bruker SMART CCD area-detector diffractometer	4510 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	3099 independent reflections
$T_{\min} = 0.68, T_{\max} = 0.72$	2678 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.018$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$	245 parameters
$wR(F^2) = 0.095$	H-atom parameters constrained
$S = 1.07$	$\Delta\rho_{\text{max}} = 0.59 \text{ e \AA}^{-3}$
3099 reflections	$\Delta\rho_{\text{min}} = -0.53 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Ag1—N4 <sup>i</sup>	2.196 (3)	Ag1—N3	2.346 (3)
Ag1—N2	2.307 (3)		
N4—Ag1—N2	136.04 (11)	N2—Ag1—N3	72.05 (11)
N4—Ag1—N3	133.89 (11)		

Symmetry code: (i)  $-x + 1, -y + 1, -z + 2$ .

**Table 2**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C2—H2 $\cdots$ O1 <sup>ii</sup>	0.93	2.45	3.375 (6)	171
C12—H12 $\cdots$ F1 <sup>iii</sup>	0.93	2.45	3.326 (7)	156

Symmetry codes: (ii)  $-x + 1, -y + 1, -z + 1$ ; (iii)  $x - 1, y + 1, z$ .

H atoms were included in calculated positions and treated in the subsequent refinement as riding atoms, with C—H = 0.93 (aromatic) or 0.97  $\text{\AA}$  (methylene) and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1998); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL and PLATON (Spek, 2003).

This work was supported by the Startup Fund for PhDs of Natural Scientific Research of Zhengzhou University of Light Industry (No. 2007BSJJ001 to CSL). The authors also gratefully thank Nankai University for supporting this research.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3080). Services for accessing these data are described at the back of the journal.

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