

Supramolecular framework in *catena*-poly[[*(nitrate-κO)*silver(I)]-*μ*-(*R,S*)-2-(pyridin-4-ylsulfinyl)pyrimidine-*κ*³N,O:N']

Chong-Qing Wan,^{a,b*} Zi-Jia Wang,^a Peng Qiao,^a Zhi-Wei Wang^a and Ai-Min Li^a

^aDepartment of Chemistry, Capital Normal University, Beijing 100048, People's Republic of China, and ^bState Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China

Correspondence e-mail: wanchqing@yahoo.com.cn

Received 16 March 2012

Accepted 5 April 2012

Online 18 April 2012

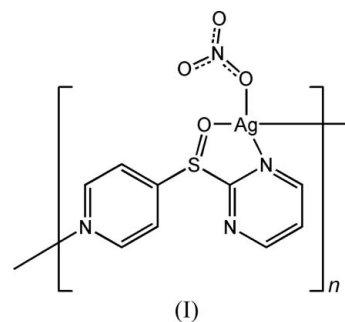
In the title complex, $[\text{Ag}(\text{NO}_3)(\text{C}_9\text{H}_7\text{N}_3\text{OS})]_n$, $\eta^1:\eta^1:\eta^1:\mu_2$ -bridging 2-(pyridin-4-ylsulfinyl)pyrimidine (pypmSO) ligands with opposite chiralities are alternately arranged to link the Ag^{I} cations through two N atoms and one sulfinyl O atom of each ligand, leading to an extended zigzag coordination chain structure along the $[\bar{2}01]$ direction. An FT-IR spectroscopic study shows a decreased stretching frequency for the η^1 -O-bonded S=O group compared with that of the free ligand. The parallel chains are arranged and interconnected *via* $\text{O}(\text{S}=\text{O}) \cdots \pi(\text{pyridine/pyrimidine})$ and $\text{C}-\text{H}(\text{pyridine}) \cdots \text{O}(\text{NO}_3^-)$ interactions to furnish a layer almost parallel to the *ac* plane. Along the *b* axis, the layers are stacked and stabilized through $\text{anion}(\text{NO}_3^-) \cdots \pi(\text{pyrimidine})$ interactions to form a three-dimensional supramolecular framework. The ligand behaviour of the new diheterocyclic sulfoxide and the unconventional $\text{O}(\text{S}=\text{O}) \cdots \pi(\text{pyridine/pyrimidine})$ and $\text{anion}(\text{NO}_3^-) \cdots \pi(\text{pyrimidine})$ interactions in the supramolecular assembly of the title complex are presented.

Comment

Sulfoxides with an asymmetric chiral centre have attracted enormous attention. The interest in these compounds stems from their important synthetic applications in asymmetric synthesis (Posner, 1988; Carreno, 1995) and potential applications in medicinal chemistry (Hogan *et al.*, 2002; Pitchen *et al.*, 1994). The coordination chemistry of sulfoxides with a symmetric or asymmetric centre has also undergone phenomenal development. Much effort has been devoted to the investigation of the variable S=O dimensions of dialkyl sulfoxides upon metal coordination and their related properties (Cotton & Francis, 1960; Alessio, 2004). The C—S(O)—C fragment with C_s local symmetry endows the dialkyl sulfoxide

with flexible coordination sites at the S and/or O atoms, exhibiting η^1 -O-bonded, η^1 -S-bonded and μ -S,O-bonded modes with diverse S=O bond lengths (Calligaris, 2004; Kato *et al.*, 2009). Grafting pyridine groups onto a selected organic fragment is a method generally used by supramolecular chemists to construct various coordination architectures with interesting properties. However, the use of a pyridine-based sulfoxide as a ligand to construct coordination supramolecular architectures remains almost unexplored, except for several well characterized complexes of diphenyl sulfoxide (*L*), such as $\text{HgCl}_2(\text{L})$ (Biscarini *et al.*, 1973), $(\text{Et}_4\text{N})[\text{PtCl}_3(\text{L})]$ (Kukushkin *et al.*, 1992), $\text{K}[\text{PtCl}_3(\text{L})]_3 \cdot \text{Me}_2\text{CO}$ (de Almeida *et al.*, 1992) and the metal complexes with dipyrazinyl sulfoxide reported by our group recently (Wan *et al.*, 2010).

To enrich the coordination chemistry of sulfoxides based on pyridine, we report herein the synthesis and characterization of a new ligand, 2-(pyridin-4-ylsulfinyl)pyrimidine (pypmSO, pyridin-4-yl pyrimidin-2-yl sulfoxide), and its silver(I) complex, $[\text{Ag}(\text{NO}_3)(\text{pypmSO})]_n$, (I). The pypmSO ligand, with one pyridine and one pyrimidine ring attached to the S=O group is, to the best of our knowledge, the first asymmetric diheterocyclic sulfoxide.



As shown in Fig. 1 and Table 1, the silver(I) centre of (I) (Ag^{I}) is coordinated by a pyridine N1 atom of the pypmSO ligand at (x, y, z) with *R* chirality, a pyrimidine N2ⁱ atom and a sulfinyl O1ⁱ atom from a second ligand with *S* chirality

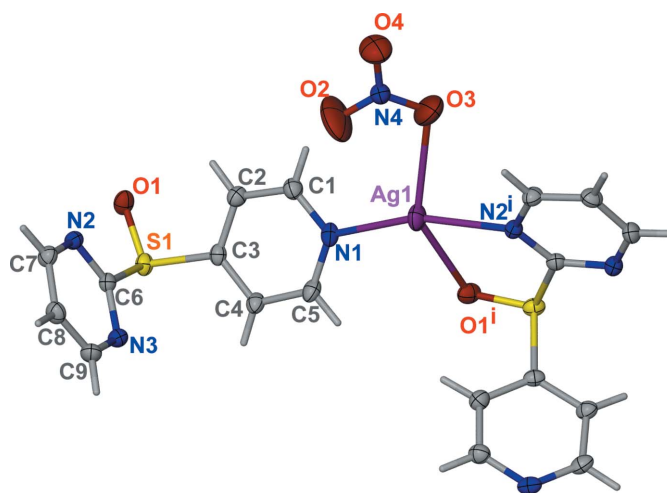


Figure 1
The Ag^{I} coordination environment of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (i) $x - 1, -y + \frac{1}{2}, z + \frac{1}{2}$.]

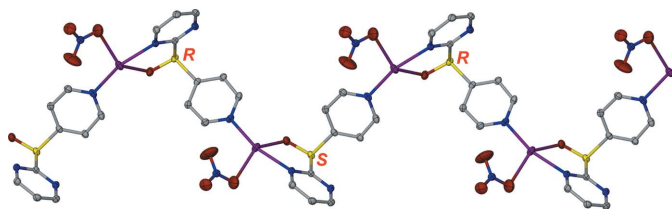


Figure 2
The extended zigzag chain structure of (I).

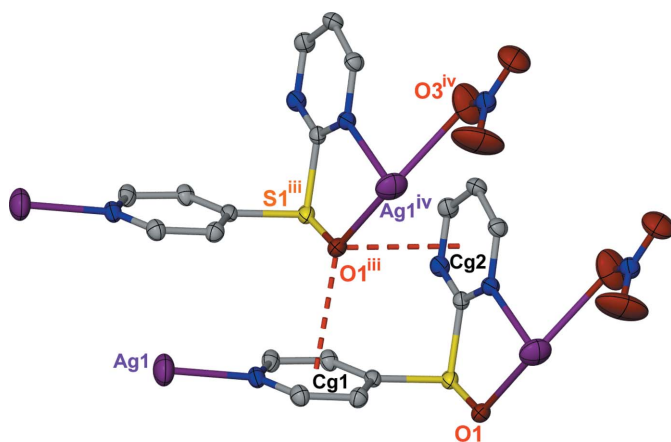


Figure 3
The $\text{S}=\text{O} \cdots \pi$ interactions in (I). Cg1 and Cg2 are the centroids of the pyridine and pyrimidine rings, respectively. [Symmetry codes: (iii) $x - 1, y, z$; (iv) $x, -y + \frac{1}{2}, z - \frac{1}{2}$]

[symmetry code: (i) $x - 1, -y + \frac{1}{2}, z + \frac{1}{2}$], and one nitrate O3 atom. The large $\text{O3}-\text{Ag1}-\text{O1}^{\text{i}}$ angle of $141.73 (17)^\circ$ indicates the presence of a distorted pyramidal N_2O_2 coordination geometry. The pyrimidine N2 and sulfanyl O1 atoms of the pypmSO ligand are in a *cis* relationship, with an $\text{N2}=\text{C6}-\text{S1}=\text{O1}$ torsion angle of $-3.1 (4)^\circ$, and chelate to the Ag1 centre. The planes of the two heterocyclic wings attached to the sulfanyl group exhibit a dihedral angle of $84.14 (1)^\circ$. The $\eta^1\text{-O}$ -bonded $\text{S1}=\text{O1}$ distance is $1.494 (4) \text{ \AA}$, which is slightly longer than the mean for $\eta^1\text{-S}$ -bonded $\text{S}=\text{O}$ [$1.474 (7) \text{ \AA}$] but

shorter than the mean for $\eta^1\text{-O}$ -bonded $\text{S}=\text{O}$ [$1.528 (1) \text{ \AA}$] in metal complexes of dialkyl sulfoxides surveyed by Calligaris (2004). The latter difference can be ascribed to the diheterocyclic feature of pypmSO, which resembles that of $\eta^1\text{-O}$ -bonded $\text{S}=\text{O}$ [$1.496 (3) \text{ \AA}$] in $\{[\text{Cd}(\text{pyz}_2\text{SO})_2(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}\}_n$ (pyz₂SO is dipyrazin-2-yl sulfoxide), another diheterocyclic sulfoxide complex reported by us (Wan *et al.*, 2010). An IR spectroscopic study indicated that the $\nu(\text{S}=\text{O})$ stretching frequency is lower for $\eta^1\text{-O}$ -bonded pypmSO (1041 cm^{-1}) than for the free ligand (1060 cm^{-1}).

Regarding the ligation mode of pypmSO in (I), each ligand links to two symmetry-related Ag^{i} ions through its pyridine N atom, one pyrimidine N atom and the sulfanyl O atom, thereby exhibiting an $\eta^1:\eta^1:\eta^1:\mu_2$ -bridging mode. The pyrimidine N and sulfanyl O atoms exhibit a $\kappa^2\text{N,O}$ -chelating mode. The S atom is not involved in any coordination bonding. The preferred *O*-bonded mode could derive from steric entropic contributions of the $\kappa^2\text{N,O}$ -chelating effect (Calligaris & Carugo, 1996). The different chiralities of the ligands in this centrosymmetric structure exhibit no influence on their ligation mode. Thus, pypmSO ligands with opposite chiralities are alternately arranged to link the Ag^{i} cations into an extended zigzag coordination chain structure which extends parallel to the $[\bar{2}01]$ direction, as shown in Fig. 2.

It is noteworthy that the parallel extended chains thus formed are interconnected through two $\text{S}=\text{O} \cdots \pi$ (pyridine/pyrimidine) contacts between each $\text{S}=\text{O}$ group of one chain and the pyridine and pyrimidine rings of an adjacent chain, as well as a $\text{C5}-\text{H5}(\text{pyridine}) \cdots \text{O2}^{\text{ii}}(\text{NO}_3^-)$ interaction [symmetry code: (ii) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; Table 2]. As shown in Fig. 3, each $\text{S}=\text{O}$ group is embraced by two wings of one pypmSO ligand from an adjacent chain, with $\text{O1}^{\text{iii}} \cdots \text{Cg1}$ and $\text{O}^{\text{iii}} \cdots \text{Cg2}$ distances of $3.117 (3)$ and $3.217 (4) \text{ \AA}$, respectively, and with $\text{S1}^{\text{iii}}-\text{O1}^{\text{iii}} \cdots \text{Cg1} = 101.97 (3)^\circ$ and $\text{S1}^{\text{iii}}-\text{O1}^{\text{iii}} \cdots \text{Cg2} = 99.07 (4)^\circ$ [Cg1 is the centroid of the pyridine ring defined by atoms N1/C1–C5 and Cg2 is the centroid of the pyrimidine ring defined by atoms C6/N2/C7–C9/N3; symmetry code: (iii) $x - 1, y, z$]. These distances are shorter than the sum of the van der Waals radii of the contacting atoms [3.25 \AA ,

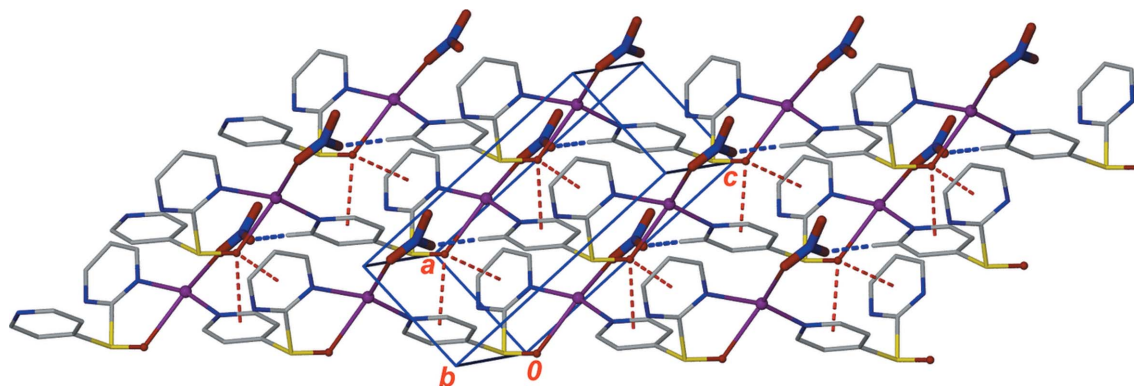


Figure 4
The layer almost parallel to the *ac* plane, constructed by $\text{S}=\text{O} \cdots \pi$ (red dashed lines in the electronic version of the paper) and $\text{C}-\text{H} \cdots \text{O}$ (blue dashed lines) interactions between the chain motifs. The nitrate ligands are shown using thick bonds and all H atoms except those involved in hydrogen bonding have been omitted for clarity.

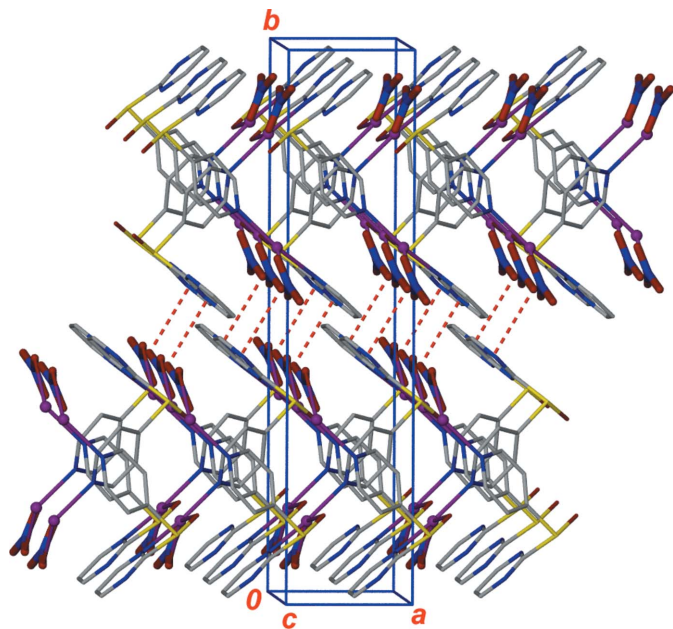


Figure 5

The anion(NO_3^-) $\cdots\pi$ interactions (dashed lines) linking the layers stacked along the b axis.

taking the half thickness of a phenyl ring as 1.85 Å (Malone *et al.*, 1997) and the van der Waals radius of oxygen as 1.40 Å (Pauling, 1960)]. The $\text{O}\cdots\text{centroid}$ distances of the $\text{S}=\text{O}\cdots\pi$ contacts also lie well within the 2.8–3.5 Å range obtained by us (Wan *et al.*, 2009) through a thorough search of the Cambridge Structural Database (CSD, Version 5.22, January 2009 update; Allen, 2002). The corresponding $\text{O}(\text{S}=\text{O})\cdots\text{C}/\text{N}$ (closest ring atom) distances are 3.317 (4) ($\text{O1}^{\text{iii}}\cdots\text{N3}$) and 3.313 (4) Å ($\text{O1}^{\text{iii}}\cdots\text{C3}$). Such $\text{S}=\text{O}\cdots\pi$ contacts represent one type of lone-pair aromatic affinity (Egli & Sarkhel, 2007; Mooibroek, Gamez & Reedijk, 2008), an analogue of anion– π interactions with a bonding energy (20–50 kJ kcal mol $^{-1}$; 1 kcal mol $^{-1}$ = 4.184 kJ mol $^{-1}$) comparable with that of hydrogen bonding. A number of density functional theory (DFT) calculations (Alkorta *et al.*, 2002; Quiñonero *et al.*, 2002) and CSD database searches have indicated that such interactions play an important role in the inducement of supramolecular assembly (Schottel *et al.*, 2006; Zhou *et al.*, 2007) and in molecular recognition (de Hoog *et al.*, 2004; Fairchild & Holman, 2005). The present $\text{S}=\text{O}\cdots\pi$ contacts can be explained in terms of the electrostatic potentials of the sulfinyl O atom and local dipoles of the coordinated heterocyclic rings, as indicated by Gung *et al.* (2008) through a quantitative study of lone-pair aromatic interactions. Herein, due to the $\text{S}=\text{O}\cdots\pi$ affinity, two adjacent chains are stacked together, so the coordinated nitrate anion is pushed away, leading to the flattened pyramidal geometry of the Ag^{I} centre (Figs. 1 and 3).

A layer almost parallel to the ac plane is formed through cooperative $\text{S}=\text{O}\cdots\pi$ and $\text{C}-\text{H}\cdots\text{O}(\text{NO}_3^-)$ interactions between successive chains (Fig. 4). The layers stack along the b axis and are further connected through anion(NO_3^-) $\cdots\pi$ (pyrimidine) interactions to form a three-dimensional supramolecular framework (Fig. 5). The $\text{O4}^{\text{v}}(\text{NO}_3^-)\cdots\text{Cg2}$

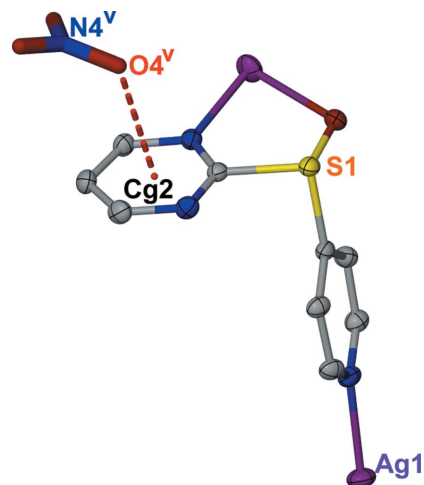


Figure 6

A detailed view of the anion(NO_3^-) $\cdots\pi$ (pyrimidine) interaction. Cg2 represents the centroid of the pyrimidine ring. [Symmetry code: (v) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$]

distance in the anion $\cdots\pi$ interaction is 3.180 (3) Å [Fig. 6; $\text{N4}^{\text{v}}-\text{O4}^{\text{v}}\cdots\text{Cg2} = 103.40 (3)^\circ$; symmetry code: (v) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$], which is comparable with the mean value of 3.190 Å found for $\text{O}(\text{NO}_3^-)\cdots\text{centroid}(\text{pyrimidine})$ distances from a CSD statistical study conducted recently by Mooibroek, Black *et al.* (2008), but slightly longer than the mean value of 3.084 Å in $\text{O}(\text{NO}_3^-)\cdots\text{centroid}(1,2,4\text{-triazine})$ systems, due to the less π -acidic nature of pyrazine than 1,2,4-triazine.

The solid-state structural analysis presented here thus provides further experimental evidence for unconventional lone pair \cdots aromatic and anion $\cdots\pi$ interactions involving heterocycles.

Experimental

2-Bromopyrimidine (500 mg, 3.1 mmol) was added to a solution of sodium pyridine-4-thiolate (3 mmol) in ethanol (50 ml) at room temperature. The mixture was stirred for 10 h. After removal of the solvent *in vacuo*, the resulting solid mixtures were separated and purified by column chromatography on silica gel (eluent dichloromethane–methanol, 95:5 *v/v*). 2-(Pyridin-4-ylsulfanyl)pyrimidine was obtained as a white powder (yield 215.01 mg, 35%). ^1H NMR (600 MHz, CDCl_3): δ 8.634 (*s*, 2H), 8.559–8.567 (*d*, $J = 5$ Hz, 2H), 7.609–7.617 (*d*, $J = 5$ Hz, 2H), 7.085–7.101 (*t*, $J = 10$ Hz, 1H). 2-(Pyridin-4-ylsulfanyl)pyrimidine was prepared following the procedure developed previously for dipyrazin-2-yl sulfoxide (Wan *et al.*, 2010), with 2-(pyridin-4-ylsulfanyl)pyrimidine as the starting material. Racemic 2-(pyridin-4-ylsulfanyl)pyrimidine was obtained as a yellow powder (yield 35%; m.p. 383–389 K). IR (KBr, ν , cm^{-1}): 1060 (*vs*) ($\text{S}=\text{O}$). 2-(Pyridin-4-ylsulfanyl)pyrimidine (20 mg, 0.1 mmol) and AgNO_3 (17 mg, 0.1 mmol) were added to acetonitrile (5 ml) and stirred at room temperature for 3 h. After filtration, slow evaporation from the filtrate yielded block-like yellow crystals of the title complex, (I), suitable for X-ray diffraction (yield 16.85 mg, 45%). Analysis calculated (found) for $\text{C}_9\text{H}_7\text{AgN}_4\text{O}_4\text{S}$ (%): C 28.82 (29.05), H 1.88 (1.85), N 14.94 (14.90). IR (KBr, ν , cm^{-1}): 1041 (*vs*) ($\text{S}=\text{O}$).

Table 1

Selected geometric parameters (Å, °).

Ag1–N1	2.238 (4)	S1–O1	1.494 (4)
Ag1–N2 ⁱ	2.293 (3)	S1–C3	1.806 (4)
Ag1–O1 ⁱ	2.551 (3)	S1–C6	1.840 (4)
Ag1–O3	2.554 (7)		
N1–Ag1–N2 ⁱ	161.48 (13)	N2 ⁱ –Ag1–O1 ⁱ	73.13 (11)
N1–Ag1–O1 ⁱ	89.46 (12)	O1 ⁱ –Ag1–O3	141.73 (17)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C5-H5\cdots O2^{ii}$	0.93	2.39	3.173 (10)	142

 Symmetry code: (ii) $x, -y + \frac{1}{2}, z + \frac{1}{2}$.

Crystal data

[Ag(NO ₃)(C ₉ H ₇ N ₃ OS)]	$V = 1148.82 (5) \text{ \AA}^3$
$M_r = 375.12$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 4.9972 (1) \text{ \AA}$	$\mu = 1.95 \text{ mm}^{-1}$
$b = 21.8972 (6) \text{ \AA}$	$T = 296 \text{ K}$
$c = 10.4994 (3) \text{ \AA}$	$0.36 \times 0.20 \times 0.12 \text{ mm}$
$\beta = 90.668 (1)^\circ$	

Data collection

Bruker APEXII CCD area-detector diffractometer	20256 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2007)	2737 independent reflections
$T_{\min} = 0.652, T_{\max} = 0.791$	2513 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.022$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$	172 parameters
$wR(F^2) = 0.131$	H-atom parameters constrained
$S = 1.07$	$\Delta\rho_{\text{max}} = 1.81 \text{ e \AA}^{-3}$
2737 reflections	$\Delta\rho_{\text{min}} = -1.56 \text{ e \AA}^{-3}$

All H atoms were discernible in difference electron-density maps. They were subsequently added in idealized positions and allowed to ride on their parent atoms, with $C-H = 0.93 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The largest peak and deepest hole of the residual electron density are within 0.8 \AA of the Ag1 atom.

Data collection: APEX2 (Bruker, 2007); cell refinement: APEX2 and SAINT (Bruker, 2007); 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, 2009).

The authors are grateful to the State Key Laboratory of Structural Chemistry in China (grant No. 20110001) and the Natural Science Foundation of Beijing Municipality (grant No. 2122011) for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3150). Services for accessing these data are described at the back of the journal.

References

- Alessio, E. (2004). *Chem. Rev.* **104**, 4203–4242.
- Alkorta, I., Rozas, I. & Elguero, J. (2002). *J. Am. Chem. Soc.* **124**, 8593–8598.
- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Almeida, S. G. de, Hubbard, J. L. & Farrell, N. (1992). *Inorg. Chim. Acta*, **193**, 149–157.
- Biscarini, P., Fusina, L., Nivellini, G. D., Mangia, A. & Pelizzi, G. (1973). *J. Chem. Soc. Dalton Trans.* pp. 159–161.
- Bruker (2007). APEX2, SADABS and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
- Calligaris, M. (2004). *Coord. Chem. Rev.* **248**, 351–375.
- Calligaris, M. & Carugo, O. (1996). *Coord. Chem. Rev.* **153**, 83–154.
- Carreno, M. C. (1995). *Chem. Rev.* **95**, 1717–1760.
- Cotton, F. A. & Francis, R. (1960). *J. Am. Chem. Soc.* **82**, 2986–2992.
- Egli, M. & Sarkhel, S. (2007). *Acc. Chem. Res.* **40**, 197–205.
- Fairchild, R. M. & Holman, K. T. (2005). *J. Am. Chem. Soc.* **127**, 16364–16365.
- Gung, B., Zou, Y., Xu, Z., Amicangelo, J. C., Irwin, D. G., Ma, S. & Zhou, H. C. (2008). *J. Org. Chem.* **73**, 689–693.
- Hogan, P. J., Hopes, P. A., Moss, W. O., Robinson, G. E. & Patel, I. (2002). *Org. Process Res. Dev.* **6**, 225–229.
- Hoog, P. de, Gamez, P., Mutikainen, I., Turpeinen, U. & Reedijk, J. (2004). *Angew. Chem. Int. Ed.* **43**, 5815–5817.
- Kato, M., Takayanagi, T., Fujihara, T. & Nagasawa, A. (2009). *Inorg. Chim. Acta*, **362**, 1199–1203.
- Kukushkin, V. Y., Belsky, V. K., Kononov, V. E., Aleksandrova, E. A., Pankova, E. Y. & Moiseev, A. I. (1992). *Phosphorus Sulfur Silicon Relat. Elem.* **69**, 103–117.
- Malone, J. F., Murray, C. M., Charlton, M. H., Docherty, R. & Lavery, A. J. (1997). *J. Chem. Soc. Faraday Trans.* **93**, 3429–3436.
- Mooibroek, T. J., Black, C. A., Gamez, P. & Reedijk, J. (2008). *Cryst. Growth Des.* **8**, 1082–1093.
- Mooibroek, T. J., Gamez, P. & Reedijk, J. (2008). *CrystEngComm*, **10**, 1501–1515.
- Pauling, L. (1960). *The Nature of the Chemical Bond*, p. 260. Ithaca, New York: Cornell University Press.
- Pitchen, P., France, C. J., McFarlane, I. M., Newton, C. G. & Thompson, D. M. (1994). *Tetrahedron Lett.* **35**, 485–488.
- Posner, G. H. (1988). *The Chemistry of Sulfones and Sulfoxides*, edited by S. Patai, Z. Rappoport & C. J. M. Stirling, ch. 3, p. 55. Chichester: John Wiley & Sons.
- Quiñero, D., Garau, C., Rotger, C., Frontera, A., Ballester, P., Costa, A. & Deyà, P. M. (2002). *Angew. Chem. Int. Ed.* **41**, 3389–3392.
- Schottel, B. L., Chifotides, H. T., Shatruck, M., Chouai, A., Perez, L. M., Bacsa, J. & Dunbar, K. R. (2006). *J. Am. Chem. Soc.* **128**, 5895–5912.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Wan, C. Q., Li, X., Wang, C. Y. & Qiu, X. (2009). *J. Mol. Struct.* **930**, 32–36.
- Wan, C. Q., Zhao, L. & Mak, T. C. W. (2010). *Inorg. Chem.* **49**, 97–107.
- Zhou, X. P., Zhang, X., Lin, S. H. & Li, D. (2007). *Cryst. Growth Des.* **7**, 485–487.