

Supplementary Information for:

A coordination–polymer strategy for anion encapsulation: anion– π interactions in (4,4) nets formed from Ag(I) salts and a flexible pyrimidine ligand

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4-(Chloromethyl)pyrimidine was prepared via literature methods.¹ All ¹H NMR spectra were measured with a 300 or 500 MHz Varian UNITY INOVA spectrometer at 298 K. All ¹³C and two-dimensional NMR spectra were collected on a 500 MHz Varian UNITY INOVA spectrometer at 298 K. NMR Spectra were collected in CDCl₃ and referenced to the solvent signal. IR spectra were measured with a Perkin Elmer Spectrum BX FT-IR System using Nujol, KBr disks, or as neat samples. Elemental microanalyses were carried out at the Campbell Microanalytical Laboratory at the University of Otago.

Synthesis of bis(4-pyrimidylmethyl)sulfide L

KOH (2.2 g, 39 mmol) in H₂O (5 mL) together with 4-(chloromethyl)pyrimidine (5.0 g, 39 mmol) and thioacetamide (1.5 g, 20 mmol) were refluxed for 19 h in a 250 mL benzene/ethanol (1:1 v/v) solution. The black suspension was filtered and solvent removed. The resulting black oil was dissolved in CH₂Cl₂ (150 mL), washed with saturated Na₂CO₃ solution (2 x 100 mL) and then H₂O (5 x 100 mL), and the solvent removed. Purification on a silica gel column (5 % hydrated v/v) eluted with ethyl acetate/acetone (80 : 20) gave **L** as a yellow oil (1.2 g, 27 %). NMR: δ_{H} (CDCl₃, 300 MHz) 9.13 (2H, br s, *H*(2)), 8.66 (2H, d, *H*(6), *J* = 5.0 Hz), 7.39 (2H, dd, *H*(5), *J* = 5.0, 1.5 Hz), 3.74 (4H, s, *H*(7)); δ_{C} (CDCl₃, 500 MHz) 166.62 (*C*4), 158.79 (*C*2), 157.34 (*C*6), 120.60 (*C*5), 36.51 (*C*7). Selected IR (Nujol)/cm⁻¹: 2724 (*w*), 2670 (*w*), 1579 (*s*), 1548 (*m*), 1309 (*m*), 1157 (*w*), 1074 (*w*) 990 (*w*). Found: C, 52.63; H, 4.92; N, 24.38; S, 13.85. Calc. for C₁₀H₁₀N₄S·0.5H₂O: C, 52.84; H, 4.88; N, 24.65; S, 14.11%.

Single crystal X-ray diffraction:

X-Ray diffraction data for **1** were collected at the University of Otago on a Bruker APEX II CCD diffractometer, data for **2** were collected at the University of Strathclyde, Glasgow, on a Nonius Kappa-CCD diffractometer and data for **3** were collected at the University of Canterbury on a Bruker SMART CCD diffractometer; all had graphite monochromated Mo-K α (λ = 0.71073 Å) radiation. Intensities were corrected for Lorentz polarisation effects² and a multiscan absorption correction³ was applied to all structures collected at Otago and Canterbury universities. The structures were solved by direct methods (SHELXS⁴ or SIR-97⁵) and refined on *F*² using all data by full-matrix least-squares procedures (SHELXL 97⁶). All calculations were performed using the WinGX interface.⁷ Detailed analyses of the extended structure were carried out using PLATON⁸ and MERCURY⁹ (Version 1.4.1). Topological analyses were conducted using OLEX (Version 2.55).¹⁰

References

- 1 (a) Wietzke, R.; Mazzanti, M.; Latour, J.-M.; Pécaut, J.; Cordier, P.-Y.; Madić, C. *Inorg. Chem.* **1998**, *37*, 6690–6697. (b) Rubina, K. I.; Iovel, I. G.; Gol'dberg, Y. S.; Shimanskaya, M. V. *Khim. Geterotsikl. Soedin.* **1989**, *4*, 543–546. (c) Newkome, G. R.; Kiefer, G. E.; Xia, Y.-J.; Gupta, V. K. *Synthesis* **1984**, *8*, 676–679.
- 2 (a) Otwinowski, Z.; Minor, W. In *Processing of X-Ray Diffraction Data Collected in Oscillation Mode*; Carter C. W., Jr., Sweet, R. M., Eds.; Methods in Enzymology, Vol. 276; Academic Press: New York, 1997; pp 307–326. (b) SAINT V4, *Area Detector Control and Integration Software*; Siemens Analytical X-Ray Systems Inc.: Madison, WI, 1996.
- 3 Sheldrick, G. M. *SADABS, Program for Absorption Correction*, University of Göttingen: Göttingen, Germany, 1996.
- 4 Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.
- 5 Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Cryst.* **1999**, *32*, 115–119.
- 6 Sheldrick, G. M. *SHELXL-97, Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.
- 7 Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837–838.
- 8 Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, C34.
- 9 (a) Macrae, C. F.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Shields, G. P.; Taylor, R.; Towler, M.; van de Streek, J. *J. Appl. Cryst.* **2006**, *39*, 453–457. (b) Bruno, I. J.; Cole, J. C.; Edgington, P. R.; Kessler, M. K.; Macrae, C. F.; McCabe, P.; Pearson, J.; Taylor, R. *Acta Crystallogr., Sect. B* **2002**, *58*, 389–397.
- 10 Dolmanov, O. V.; Blake, A. J.; Champness, N. R.; Schröder, M. *J. Appl. Crystallogr.* **2003**, *36*, 1283–1284.