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Binding of Mono- and Dianions within Silver Thiazolylurea Tweezers and Capsules

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Supporting Information

ABSTRACT: A silver thiazolylurea complex, $[Ag(TUTh)_2]^+$, has been used as a host species for geometrically differently shaped mono- and dianions: trigonal planar (NO₃⁻), tetrahedral (SO₄²⁻), and octahedral (SiF₆²⁻). In the presence of nitrate a 1:1 near-planar tweezer host–guest species is formed, with poor binding in solution despite excellent geometric complementarity being found between the host and the anion in the solid state. In the presence of either SO₄²⁻ or SiF₆²⁻ a 2:1 host–guest species is formed, whereby the guest is held in a capsulelike arrangement stabilized by an array of eight NH hydrogen-bond donors, as confirmed by X-ray



crystallographic studies. Solution studies in DMSO- d_6 support the host-guest stoichiometry seen in the solid state. The binding constant between SO₄²⁻ and [Ag(TUTh)₂]⁺ was calculated to be $K_{21} = 2511 \text{ M}^{-2}$ and was shown to be the dominant species in solution, in excellent agreement with the solid-state studies. However, upon the addition of SiF₆²⁻ ions different speciation is observed: H₂·G (capsule), H·G (tweezer), and H·G₂ during the course of the study.

INTRODUCTION

Host-guest chemistry has been one of the main driving forces behind the field of supramolecular chemistry.¹ The challenges and motivations associated with designing synthetic receptors for important analytes, typically those that are environmentally or biologically relevant, remain largely unchanged, although there has been significant progress in enhancing our understanding and application of these systems.² Some of the most challenging analytes to selectively target are anionic species, whereby particular difficulties are faced due to nonspherical geometries, higher energies of solvation, and changes in speciation due to pH.

Perhaps the most utilized molecular motifs for the binding of anionic guests are those that can form two parallel N-H hydrogen bonds with the guest.³ Classic examples of this motif are seen in guanidinium and (thio)urea moieties. Another group is the squaramide functionality, which is now being widely incorporated into receptor design.⁴ In particular, this arrangement of hydrogen bond donors lends itself to the recognition of simple oxoanions due to the geometric complementarity between the H…H separation in the donor and the O···O distance in the guest (ca. 2.0-2.4 Å).⁵ Preorganization of these donor groups into organic frameworks or coordination complexes can give rise to very selective binding:⁶ for example, [3]polynorbornane scaffolds,⁷ tris(2aminoethyl)amine,⁸ and trisubstituted benzene.⁹ Effective ureabased receptors can also be constructed around metal ions, which can allow for a significant amount of rotational freedom along the metal–ligand bonds. For example, complexes of the type $[PdL_4]^{2+,10}$ $[CuL_2]^{+,11}$ $[AgL_2]^{+,12}$ and $[FeL_3]^{2+}$ have been reported. 13

Host-guest complexes in which the guest is completely surrounded by the host can offer particularly high affinity and selectivity.¹⁴ Host species can be templated by anions: for example, M_4L_6 cages that contain tetrahedral dianions.¹¹ Molecular receptors containing the tris(2-aminoethyl)amine motif have been shown to either bind H₂PO₄⁻ ions via a tripodal-guest interaction or completely encapsulate SO₄²⁻ ions in a 2:1 cage complex with an array of six urea groups around the saturated anion.¹⁶ Other examples include 4:4 cages that have been shown to encapsulate H_3PO_4 or $H_2PO_4^-$ ions.¹ There have recently been a number of examples whereby flexible receptors form capsules or pseudocapsules containing two or more hosts that self-assemble around the anionic guest(s).¹⁸ Other common scaffolds used are trisubstituted benzene derivatives, which have shown similarly complicated anion encapsulation behavior.¹⁹ Organic bis-urea tweezers have been shown to form complex assemblies with multiple anionic and neutral guests inside a self-assembled cage, to form 2:1 complexes around tetrahedral anions or even to form aniontemplated helicates.²⁰

Herein we report a bis-urea complex, $[Ag(TUTh)_2]^+$, that acts as a host to NO₃⁻ by a simple tweezer receptor and as a

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host to SiF_6^{2-} and SO_4^{2-} through a "scissoring" motif involving two complexes to form a cage that encapsulates the dianionic guest (Figure 1) and the role that subtle structural differences play in host–guest behavior.



Figure 1. Ligand **TUTh** used in this study (with hydrogen atom labeling used in descriptions of binding behavior) and its ML_2 complex formed with AgPF₆ that acts as a tweezer-shaped receptor.

EXPERIMENTAL DETAILS

General Details. All ¹H, ¹³C, ¹⁹F, and ³¹P NMR spectra were recorded on Bruker DPX300, Bruker Avance III 400, and Bruker Avance III 600 spectrometers and were referenced to the resonances of the solvents used or external CFCl3 or H3PO4. Mass spectra were recorded on an Agilent Technologies 5975D inert MSD instrument with a solid-state probe. ATR-FTIR spectra were collected using an Agilent Cary 630 spectrometer. Melting points were determined in glass capillaries and are uncorrected. Microanalyses were carried out at the Science Centre, London Metropolitan University. Tetrabutylammonium salts (NO $_3^-$ and SO $_4^{2-}$) and other reagents were purchased from standard commercial suppliers and used as supplied, except tetrabutylammonium hexafluorosilicate, which was synthesized immediately before use by titrating a dilute aqueous solution of tetrabutylammonium hydroxide against an aqueous solution of hexafluorosilicic acid until neutral. See Figures S1-S4 in the Supporting Information for NMR spectra.

Synthetic Details. N-(Thiazol-2-yl)-N'-(p-tolyl)urea (TUTh). To a solution of 2-aminothiazole (752 mg, 7.51 mmol) in dichloromethane (25 mL) was added p-tolyl isocyanate (1.00 g, 7.51 mmol) dropwise at room temperature. The reaction mixture was heated to reflux and stirred for a further 2 h, forming a white precipitate during this time period. After the reaction mixture was cooled to room temperature, the precipitate was isolated via filtration, washed with dichloromethane $(3 \times 5 \text{ mL})$, and dried in vacuo to give **TUTh** as a white solid (1.51 g, 86%). Mp: 203–207 °C. ¹H NMR (600 MHz, DMSO- d_{6} , 298 K): δ 2.25 (s, 3H, CH₃), 7.09 (d, ${}^{3}J_{HH} = 3.5$ Hz, 1H, SCH), 7.11 (d, ${}^{3}J_{HH} = 8.1$ Hz, 2H, ArH), 7.35 (d, ${}^{3}J_{HH} = 8.1$ Hz, 2H, ArH), 7.36 (d, ${}^{3}J_{HH} = 8.1$ Hz, 2H, ArH), 7.36 (d, ${}^{3}J_{HH} = 3.5$ Hz, 1H, NCH), 8.89 (s, 1H, TolylNH), 10.49 (br s, 1H, NCH) ThiazoleNH). ${}^{13}C{}^{1}H{}$ NMR (101 MHz, DMSO- d_6): δ 20.5 (CH₂), 112.5, 118.8, 129.5, 131.9, 136.1, 137.4 (ArC), 151.8 (C=O), 159.8 (NCS). FTIR (ν/cm^{-1}): 3289 (w), 3027 (w), 1719 (m), 1619 (m), 1546 (m), 1509 (s), 1497 (s), 1314 (s), 1278 (m), 1249 (s), 1191 (s), 1152 (m), 1124 (w), 1063 (w), 1037 (w), 810 (s), 786 (m), 717 (s). MS (EI; m/z (%)): 233.1 ([M]⁺, 58), 100.2 ([ThiazoleNH₂]⁺, 100). Anal. Calcd for C₁₁H₁₁N₃OS: C, 56.63; H, 4.75; N, 18.01. Found: C, 56.54; H, 4.81; N, 17.96.

 $[Ag(TUTh)_2]PF_6$. To a solution of silver hexafluorophosphate (109 mg, 430 μ mol) in methanol (1 mL) was quickly added a warm solution (ca. 60 °C) of TUTh (200 mg, 860 μ mol) in methanol (1 mL) at room temperature. The reaction mixture was briefly stirred before being left to stand in the dark undisturbed for 18 h to give $[Ag(TUTh)_2]PF_6$ as colorless crystals. Yield: 255 mg (83%). Mp: 226–229 °C. ¹H NMR (600 MHz, DMSO- d_{62} 298 K): δ 2.25 (s, 6H,

CH₃), 7.11–7.13 (m, ArH and SCH), 7.35 (d, ${}^{3}J_{HH} = 8.3$ Hz, 4H, ArH), 7.39 (d, ${}^{3}J_{HH} = 3.5$ Hz, 2H, NCH), 8.90 (s, 1H, TolylNH), 10.50 (br. s, 1H, ThiazoleNH). ${}^{13}C{}^{1}H{}$ NMR (75 MHz, DMSO- d_{6}): δ 20.4 (CH₃), 112.7, 118.9, 129.4, 131.9, 135.9, 137.1 (ArC), 151.5 (C=O), 160.8 (NCS). ${}^{19}F$ NMR (282 MHz, DMSO- d_{6}): δ –70.1 (d, ${}^{1}J_{FP} = 710.4$ Hz, 6F, PF₆). ${}^{31}P$ NMR (122 MHz, DMSO- d_{6} , 298 K): δ –144.2 (sept, ${}^{1}J_{PF} = 710.4$ Hz, 1P, PF₆). FTIR (ν /cm⁻¹): 3587 (w), 3404 (w), 1716 (m), 1692 (m), 1604 (m), 1534 (s), 1512 (s), 1458 (m), 1406 (m), 1335 (w), 1314 (m), 1281 (m), 1237 (m), 1198 (m), 1169 (m), 1131 (w), 1042 (w), 889 (w), 835 (s), 804 (s), 732 (s), 699 (s). Anal. Calcd for C₂₂H₂₂AgF₆N₆O₂S₂: C, 36.73; H, 3.08; N, 11.68. Found: C, 36.60; H, 3.14; N, 11.59. PXRD could not be obtained, as the material quickly turned amorphous when it was removed from the mother liquor.

 $[Ag(TUTh)_2]NO_3$. Method A. To a solution of silver nitrate (7.2 mg, 43 µmol) in acetonitrile (2 mL) was added a solution of TUTh (20 mg, 86 µmol) in methanol (2 mL). The reaction mixture was stirred briefly before being left to stand undisturbed in the dark for 18 h to give $[Ag(TUTh)_2]NO_3$ as colorless crystals. Yield: 20 mg (73%).

Method B. A solution of $[Ag(TUTh)_2]PF_6$ (20 mg, 28 μ mol) in acetonitrile (2 mL) was added to a solution of tetrabutylammonium nitrate (8.5 mg, 14 μ mol) in methanol (2 mL) at room temperature. The reaction mixture was stirred briefly before being left to stand undisturbed in the dark for 18 h to produce $[Ag(TUTh)_2]NO_3$ as colorless crystals. Yield: 15 mg (84%). Mp: 215-220 °C. ¹H NMR (400 MHz, DMSO- d_{6} , 298 K): δ 2.24 (s, 6H, CH₃), 7.12 (d, ³ J_{HH} = 8.2 Hz, 4H, ArH), 7.16 (d, ${}^{3}J_{HH}$ = 3.6 Hz, 2H, SCH), 7.37 (d, ${}^{3}J_{HH}$ = 8.2 Hz, 4H, ArH), 7.45 (d, ${}^{3}J_{HH}$ = 3.6 Hz, 2H, NCH), 9.07 (s, 1H, TolylNH), 10.65 (br s, 1H, ThiazoleNH). ${}^{13}C{}^{1}H$ NMR (101 MHz, DMSO-d₆): δ 20.4 (CH₃), 112.6, 118.9, 129.4, 131.9, 136.0, 137.2 (ArC), 151.5 (C=O), 160.8 (NCS). FTIR (ν/cm^{-1}) : 3282 (w), 3203 (w), 3083 (w), 2920 (w), 1702 (s), 1611 (s), 1542 (s), 1508 (s), 1388 (m), 1314 (s), 1278 (m), 1243 (s), 1200 (s), 1161 (s), 1122 (m), 1037 (m), 890 (w), 862 (w), 809 (m), 704 (m). Anal. Calcd for $C_{22}H_{22}AgN_7O_5S_2\!\!:$ C, 41.52; H, 3.48; N, 15.41. Found: C, 41.65; H, 3.35; N, 15.37. Phase purity was confirmed by X-ray powder diffraction (see Figure S8 in the Supporting Information).

 $[Ag(TUTh)_2]_2SiF_6$. A solution of $[Ag(TUTh)_2]PF_6$ (20 mg, 28 μ mol) in methanol (4 mL) was added to a solution of tetrabutylammonium hexafluorosilicate (8.7 mg, 14 μ mol) in methanol (1 mL) at room temperature. The reaction mixture was stirred briefly before being left to stand undisturbed (excluding light) for 18 h to give $[Ag(TUTh)_2]_2SiF_6$ as colorless crystals. Yield: 15 mg (83%). Mp: 243-247 °C. ¹H NMR (400 MHz, d₆-DMSO, 298 K): δ 2.25 (s, 12H, CH₃), 7.08-7.13 (m, 12H, ArH), 7.35-7.42 (m, 12H, ArH), 8.95 (s, 1H, TolylNH), 10.56 (br s, 1H, ThiazoleNH). ¹³C{¹H} NMR (101 MHz, DMSO-d₆): δ 20.4 (CH₃), 112.4, 118.6, 129.3, 131.7, 136.1, 137.3 (ArC), 151.5 (C=O), 160.2 (NCS). ¹⁹F NMR (282 MHz, DMSO- d_6): δ –134.5 (br, 4F), –120.7 (br, 2F). FTIR (ν /cm⁻¹): 3344 (m), 3305 (m), 1699 (s), 1608 (m), 1539 (s), 1509 (s), 1453 (m), 1403 (m), 1312 (s), 1280 (s), 1240 (s), 1199 (s), 1165 (s), 1120 (m), 1070 (m), 1038 (m), 865 (w), 803 (m), 756 (m), 738 (s), 703 (s). Anal. Calcd for C444H44Ag2F6N12O4S4Si: C, 40.94; H, 3.44; N, 13.02. Found: C, 41.07; H, 3.32; N, 13.18. Phase purity was confirmed by Xray powder diffraction (see Figure S9 in the Supporting Information).

Preparation of $[Ag(TUTh)_2]_2SO_4$. To a solution of $[Ag(TUTh)_2]$ -PF₆ (20 mg, 28 μmol) in methanol (4 mL) was added a solution of tetrabutylammonium sulfate (8.1 mg, 14 μmol) in methanol (1 mL) at room temperature. The reaction mixture was stirred briefly before being left to stand undisturbed (excluding light) for 18 h to give $[Ag(TUTh)_2]_2SO_4$ as colorless crystals. Yield: 17 mg (77%). Mp: 240–242 °C. ¹H NMR (300 MHz, DMSO- d_6 , 298 K): δ 2.25 (s, 12H, CH₃), 7.07 (d, ³*J*_{HH} = 8.4 Hz, 8H, ArH), 7.12 (d, ³*J*_{HH} = 3.7 Hz 4H, SCH), 7.39 (d, ³*J*_{HH} = 8.4 Hz, 8H, ArH), 7.51 (d, ³*J*_{HH} = 3.7 Hz, 4H, NCH), 9.62 (s, 1H, TolyINH), 11.35 (br s, 1H, ThiazoleNH). ¹³C{¹H} NMR (101 MHz, DMSO- d_6): δ 20.4 (CH₃), 112.3, 118.6, 129.2, 131.5, 136.3, 137.3 (ArC), 151.5 (C=O), 161.2 (NCS). FTIR (ν /cm⁻¹): 3291 (w), 3124 (w), 2921 (w), 1713 (m), 1689 (m), 1614 (m), 1545 (s), 1512 (s), 1460 (m), 1406 (m), 1313 (m), 1283 (m), 1245 (s), 1198 (s), 1170 (m), 1093 (m), 1063 (s), 1039 (s), 889 (w),

able	1.	Crystal	llographic	Structural	and	Refinement	Parameters	for	All	Structures
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	$[Ag(TUTh)_2]NO_3$	$[Ag(TUTh)_2]_2SO_4 \cdot 2MeCN$	$[Ag(TUTh)_2]_2SiF_6$ ·MeOH	$[Ag(TUTh)_2]PF_6 \cdot 3MeOH$
empirical formula	$C_{22}H_{22}AgN_7O_5S_2$	$C_{48}H_{50}Ag_2N_{14}O_8S_5$	$C_{45}H_{48}Ag_2F_6N_{12}O_5S_4Si$	$\mathrm{C}_{25}\mathrm{H}_{34}\mathrm{AgF_6N_6O_5PS_2}$
formula wt	636.46	1327.06	1323.02	815.54
cryst syst	monoclinic	triclinic	triclinic	triclinic
space group	$P2_{1}/c$	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$
Z	8	2	2	2
a/Å	18.276(4)	13.8336(6)	13.966(3)	8.4917(5)
b/Å	13.899(3)	14.9288(6)	14.348(3)	14.2434(10)
c/Å	20.440(4)	15.3275(6)	15.770(3)	15.9581(12)
α/deg	90	88.020(2)	75.46(3)	113.608(2)
β/\deg	106.09(3)	65.384(2)	67.31(3)	101.284(2)
γ/deg	90	69.584(2)	65.21(3)	97.412(2)
$V/Å^3$	4988.8(17)	2674.1(2)	2631.9(13)	1687.6(2)
temp/K	100	123	100	123
no. of rflns measd	35654	57844	45631	29195
no. of indep rflns	9739	16327	12491	8350
no. of rflns $(I \ge 2\sigma(I))$	8297	7400	11616	5386
$R_{\rm int}$	0.0393	0.1192	0.0235	0.0779
R1 $(I \ge 2\sigma(I)/\text{all data})$	0.0447/0.0514	0.0592/0.1619	0.0371/0.0396	0.0499/0.0898
wR2(F^2) ($I \ge 2\sigma(I)$ /all data)	0.1232/0.1268	0.1089/0.1475	0.0923/0.0937	0.1254/0.1065
GOF	1.053	0.960	1.042	1.003
residual min, max/e	1.454, -0.983	1.196, -0.906	1.599, -1.408	0.820, -0.882
CCDC no.	1554115	1554116	1554117	1554118

864 (w), 814 (m), 789 (m), 705 (m). Anal. Calcd for $C_{44}H_{44}Ag_2N_{12}O_8S_5$: C, 42.45; H, 3.56; N, 13.50. Found: C, 42.57; H, 3.64; N, 13.40. Phase purity was confirmed by X-ray powder diffraction (see Figure S10 in the Supporting Information).

Single-Crystal X-ray Diffraction. Single crystals were mounted on nylon loops using viscous hydrocarbon oil. Data were collected using the MX1 beamline at the Australian Synchrotron ([Ag. (TUTh)₂]NO₃ and [Ag(TUTh)₂]₂SiF₆) or using a Bruker Apex II diffractometer ([Ag(TUTh)₂]₂SO₄·2MeCN and [Ag(TUTh)₂]PF₆· 3MeOH).

Data from the MX1 beamline were collected using an energy of 17.4 keV ($\lambda = 0.7109$ Å), with the sample temperature maintained at 100 K by an open-flow N₂ cryostream, using the BluICE control program.²¹ Data indexing and integration were conducted using the XDS program suite.²² Data from the Bruker Apex II diffractometer were collected using a graphite-monochromated Mo K α source ($\lambda = 0.71073$ Å) with the sample temperature maintained at 123 K by an open-flow N₂ cryostream. Data were collected and processed using the SAINT software suite.²³

Structures were solved by direct methods using SHELXS-2014 or the dual-space method using SHELXT.²⁴ Structures were refined by conventional least-squares methods against F^2 using SHELXL-2014.²⁵ The program X-Seed was used as a graphical interface.²⁶ All nonhydrogen atoms were refined using an anisotropic model, except where indicated below. All hydrogen CH and NH atoms were refined using fixed, idealized X-ray distances and geometries using a riding model with their displacement parameters 1.2 or 1.5 times that of the U_{iso} value of the atom to which they are bound. Additional refinement details are supplied in the Supporting Information.

Crystallographic structural and refinement parameters for all structures are presented in Table 1, and detailed hydrogen bonding tables are provided in the Supporting Information. All structural data have been deposited with, and are available for free from, the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Previous reports of a 3-pyridyl-substituted urea ligand in an $[AgL_2]^+$ complex showed the formation of a molecular tweezer that was selective for NO₃⁻ ions.¹² When the Lewis basic group is switched to a 2-substituted thiazole ring, the angle subtended

by the ligands in a two-coordinate silver complex should differ and will therefore alter the geometry of the potential tweezer complex and hence affect the anion binding properties (vide infra).

The organic species 9N-(thiazol-2-yl)-N'-(p-tolyl)urea (**TUTh**) is synthesized in excellent yield (86%) from the reaction of 2-aminothiazole and p-tolyl isocyanate (see Experimental Details). Reaction of **TUTh** with AgPF₆, AgNO₃, Ag₂SO₄, and AgPF₆/(NBu₄)₂SiF₆ (prepared fresh prior to use) yielded crystalline solids which show structures that suggest the ability of the [Ag(**TUTh**)₂]⁺ cation to act as an effective host species. As is common for silver(I) complexes, addition of halides (X⁻) led to rapid precipitation of AgX.

Solid-State Studies. Crystallization of a 2:1 mixture of TUTh and AgPF₆ in methanol yields the compound [Ag-(TUTh)₂]PF₆·3MeOH. The metal complex contains a near linearly coordinated silver (N-Ag-N = 171°) with the two ligands adopting a trans geometry around the Ag⁺ ion; as a consequence the two urea groups point in opposite directions from the plane of the metal (Figure 2, and Figure S5 in the Supporting Information). The PF₆⁻ anion is a notoriously poor hydrogen bond acceptor. As a consequence, a single N-H…F



Figure 2. Part of the structure of $[Ag(TUTh)_2]PF_6$ ·3MeOH showing the trans conformation of the complex and hydrogen bonding interactions. CH hydrogen atoms and disorder of a tolyl group are omitted for clarity.



Figure 3. Structures of host-guest complexes between $[Ag(TUTh)_2]^+$ and anionic guests as determined by X-ray crystallography: (a) $[Ag(TUTh)_2]NO_3$; (b) $[Ag(TUTh)_2]_2SO_4$; (c) $[Ag(TUTh)_2]_2SiF_6$. CH hydrogen atoms are omitted for clarity (ellipsoid plots in the Supporting Information).



Figure 4. Stack plots of ¹H NMR spectra of TUTh and $[Ag(TUTh)_2]PF_6$ by themselves and upon addition of 1 equiv of anionic guests as their tetrabutylammonium salts (labeling of hydrogen atoms as in Figure 1).

hydrogen bond interaction exists between one urea group of the complex and the counterion. The other urea moiety forms a bifurcated hydrogen-bonding interaction with a single methanol molecule.

Structures containing NO₃⁻, SO₄²⁻, and SiF₆²⁻ as counterions are significantly different, all containing a cis arrangement of the ligands around the metal and good affinity toward the anion. The structure of $[Ag(TUTh)_2]NO_3$ shows the anticipated 1:1 host-guest species, with the asymmetric unit containing two near-identical coordination compounds. The host adopts the anticipated tweezer geometry, with the NO₃⁻ ion residing within the triangular space that is presented by the cation (Figure 3a). The NO_3^- ion is bound by the flanking urea groups with N···O distances in the range 2.764(5) - 3.218(5) Å; longer hydrogen bonds are associated with the oxygen atom closest to the Ag⁺ ion. The NO₃⁻ guest lies close to the Ag⁺ ion with Ag-O distances of approximately 2.7 Å. The previously reported 3-pyridyl-based system did not have close Ag-O contacts, due to the cavity of the tweezer having a concave nature rather than the convex form (i.e., silver protruding into the cleft) that is brought about by the geometry enforced by the thiazole rings in contrast to that of meta-substituted pyridyl rings (Figure 4).¹² This observation is borne out for the dianions as well (vide infra) and demonstrates the significant difference that can be brought about by a subtle change in the geometry of the tweezer.

The adducts of **TUTh** with Ag_2SO_4 and Ag_2SiF_6 both form cages comprising of two $[Ag(TUTh)_2]^+$ units enveloping the central anion (Figure 3b,c). In both instances the two metal

complexes form a near-perpendicular dual-tweezer motif. The structure of $[Ag(TUTh)_2]_2SO_4 \cdot 2MeCN$ contains one unique 2:1 host-guest species in the asymmetric unit. The host-guest complex is not symmetrical, with the two tweezers oriented at 85° with respect to each other (on the basis of the N-Ag-N vectors). The tweezers themselves are nonplanar, with the planes of the thiazole rings being offset by 47 and 38° in the two unique $[Ag(TUTh)_2]^+$ species. As a consequence, the SO_4^{2-} anion does not sit symmetrically within the array of urea groups that face the interior of the cavity. Hydrogen-bonding N···O distances lie in the range 2.757(5) - 3.030(6) Å with two significantly longer, tentative interactions at ca. 3.2 Å (Figure S6 in the Supporting Information). Two nonplanar R_2^2 (8) motifs and two R_2^1 (6) motifs, both of which are commonly associated with urea groups, are present in the host-guest complex (one of each interaction is associated with each tweezer).³ There are close contacts between the $\mathrm{SO_4^{2-}}$ guest and the $\mathrm{Ag^+}$ ions, with Ag…O distances of 2.794(4) and 2.900(3) Å being the closest for the two unique metals.

The SiF₆²⁻ complex $[Ag(TUTh)_2]_2SiF_6$ is similar to that obtained with SO₄²⁻. The tweezers are oriented at ca. 83° with respect to each other and are nonplanar (with angles of 44 and 48° between the planes of the thiazolyl rings). The two tweezers are further separated in the SiF₆²⁻ species than in the SO₄²⁻ complex to account for the larger guest (Ag···Ag = 8.4 Å for SiF₆²⁻, in comparison to 7.4 Å for SO₄²⁻). There are 11 hydrogen bonds between the host and guest within the N···F range 2.767(3)–2.956(3) Å, alongside some longer "interactions" (3.0–3.3 Å; see Table S2 and Figure S7 in the

Supporting Information). As with the SO_4^{2-} complex, there are both R_2^2 (8) motifs and R_2^1 (6) motifs between the tweezers and the SiF_6^{2-} guest, alongside bifurcated NH donor groups. Perhaps the most revealing detail in the structure is the close contact between the anion and the metals, with Ag–F distances of 2.643(2) and 2.597(2) Å. These distances are comparable to those observed in dimeric Ag⁺ cages containing tripodal ligands and can reasonably be expected to significantly enhance the stability of the host–guest complex.²⁷

Solution Studies. The solid-state structure of $[Ag(TUTh)_2]PF_6$ shows that the two ligands are in an anti orientation with respect to the urea groups, whereas in the presence of the NO₃⁻ ions the Ag⁺ coordination compound unambiguously forms a tweezer-shaped host-guest complex.

Our attention turned to solution-based studies to investigate the anion binding ability of $[Ag(TUTh)_2]^+$. We have previously shown that transition-metal ions (Ru^{2+} , Pd^{2+} , and Pt^{2+}) can be used as inorganic backbones that have two pyridinium ligands attached to the metal center, which can bind anions via hydrogen-bonding and electrostatic interactions.²⁸ Therefore, we anticipated that the solution studies of $[Ag(TUTh)_2]PF_6$ will complement the solid-state results described above. The anion binding behavior of $[Ag(TUTh)_2]PF_6$ was assessed by ¹H NMR titration with tetrabutylammonium (TBA) salts of NO_3^{-} , SO_4^{2-} , and SiF_6^{2-} in DMSO- d_6 due to the very limited solubility of the complexes in other solvents (evidenced by their rapid crystallization). The hexafluorophosphate anion was chosen due to its well-known low charge density, causing it to be rapidly displaced by anions that are able to participate in stronger hydrogen bonding interactions (requiring a considerable excess of PF6⁻ to bring about the reverse transformation). Upon the addition of aliquots of the TBA salts, the chemical environments for the hydrogen atoms in [Ag- $(TUTh)_2$]PF₆ experience chemical change upon the binding of the anion (Figures 4 and 5). The hydrogen atom that



Figure 5. ¹H NMR titration curves (NH(tolyl), DMSO- d_6 , 298 K): (a) TUTh plus SiF₆²⁻; (b) [Ag(TUTh)₂]PF₆ plus SiF₆²⁻; (c) [Ag(TUTh)₂]PF₆ plus SO₄²⁻; (d) TUTh plus SO₄²⁻; (e) [Ag(TUTh)₂]PF₆ plus NO₃⁻; (f) TUTh plus NO₃⁻.

showed the greatest chemical shift upon the addition of SO_4^{2-} and SiF_6^{2-} was the urea NH closest to the tolyl group (Figure 1, hydrogen B). However, the ¹H NMR spectrum of $[Ag(TUTh)_2]PF_6$ in the presence of NO_3^- showed very little change (Figure S19 in the Supporting Information), with only a modest change in chemical shift observed for the NH(tolyl) proton (see Figure 1) ($\Delta = 0.08$ ppm). The binding isotherm drawn by plotting chemical shifts vs concentration does show a

typical binding isotherm seen for 1:1 host-guest species (Figures S20 and S21 in the Supporting Information). However, attempts to calculate a binding constant in DMSO- d_6 proved to be difficult; therefore, no thermodynamic data could be obtained. This is presumably due to the relative lack of preorganization and the competitive nature of the DMSO solvent system competing with the anion in equilibrium.

The solution behaviors of $[Ag(TUTh)_2]PF_6$ in the presence of SO₄²⁻ and SiF₆²⁻ are strikingly different from that of NO₃⁻. Upon the addition of SO₄²⁻, a broad band is seen at 4.2 ppm and the NH(tolyl) moiety disappears upon the first addition of the anion (0.1 equiv). This can be explained by deprotonation, and it is reasonable to assume that the species which is being bound in solution is HSO₄⁻; however, there is no evidence of this crystallographically. Nevertheless, this anionic species is still interacting with the silver tweezer complex. The binding isotherms for the other proton chemical environments are significantly different (Figures S22 and S23 in the Supporting Information), and it is clear that the binding isotherms are not representative of a 1:1 binding ratio. Surprisingly, when the binding constant was calculated by least-squares nonlinear fitting, using HYPNMR (see Table 2),²⁹ an excellent fit was

Table 2. Binding Constants Obtained for TUTh and $[Ag(TUTh)_2]PF_6^a$

	NO ₃ ⁻	SO4 ²⁻	SiF ₆ ²⁻
TUTh			
$\log K_{11}$	Ь	0.98	2.47
$[Ag(TUTh)_2]PF_6$			
$\log K_{21}$	d	2.29	1.38
$\log K_{11}$	0.71	negligible ^c	3.39
$\log K_{12}$	d	negligible ^c	0.30

 ${}^{a}K_{11}$ (M⁻¹) and K_{21} (M⁻²), and K_{12} refer to the formation of 1:1, 2:1, and 1:2 host–guest complexes, respectively. Anions were added as their tetrabutylammonium salts. Conditions: DMSO- d_{6} , 298 K. ^bNot determined, ^cThe speciation was included in the binding model to fit data. ^dThe speciation was not needed to fit the data.

obtained for a 2:1 host– SO_4^{2-} complex ($K_{21} = 2511 \text{ M}^{-2}$) (Table 2). The model did have to include 1:1 and 1:2 host– anion ratios, but these species are negligible in solution with the predominant species being the 2:1 host–anion complex (Figure S24 in the Supporting Information), in excellent agreement with the solid-state structure, in which the anion is encapsulated between two Ag tweezers (Figure 3b).

The binding behavior between $[Ag(TUTh)_2]^+$ and SiF_6^{2-} in solution is drastically different from that of the SO_4^{2-} anion. It is evident that different species exist in solution (Figures S25 and S26 in the Supporting Information), unlike the case in the SO_4^{2-} anion study, where only one major species was determined to exist in solution. However, the nonlinear regression calculation required all three species (2:1, 1:1, and 1:2 host-guest complexes) as part of the model to fit the experimental data. At low concentrations ($<2.3 \times 10^{-2}$ mol dm^{-3}) of SiF₆²⁻ ions, it is reasonable to assume that the pseudocapsule is the predominant species in solution, which is supported by the solid-state structure. As the concentration of the guest increases over the course of the titration, the capsule collapses, forming a 1:1 complex, and at high concentrations $(>4.2 \times 10^{-2} \text{ mol dm}^{-3})$ a 1:2 host-anion complex is formed, whereby one anion is presumably associated with each arm of the $[Ag(TUTh)_2]^+$ complex. This is supported by the sigmoidal

behavior of the binding isotherm for the NH(tolyl) functional group (Figure 5), which is indicative of cooperative binding. Furthermore, both the H_2 :G and H:G species can be observed during the course of the titration (Figure S27 in the Supporting Information), whereby distinct signals for each species are seen.

The cooperativity is also supported by investigating the model system (TUTh), whereby only a 1:1 binding isotherm was obtained between **TUTh** plus the anion $(NO_3^{-}, SO_4^{2-}, and$ SiF_6^{2-}). The calculated binding constants are significantly lower than those of the coordination compound $[Ag(TUTh)_2]^+$. Interestingly the binding constants for the model compound (TUTh) with SO_4^{2-} (Figures S14 and S15 in the Supporting Information) and SiF_6^{2-} (Figures S17 and S18 in the Supporting Information) could be determined precisely using nonlinear regression, due to a significant amount of the NH(tolyl) group (Figure 5a,d), whereas the NO_3^- binding constant could not be determined due to the competition with the solvent. However, both the tetrahedral SO_4^{2-} and the octahedral SiF₆²⁻ ion can form R_2^1 (6) and R_2^2 (8) motifs in the solid state, respectively; therefore, we believe that both of these complementary ring systems can stabilize the host-guest interactions in solution (see Figure S28 in the Supporting Information), therefore allowing us to determine the binding constant (Table 2). Interestingly, the R_2^2 (8) motif formed between an SiF_6^{2-} anion and the TuTh model compound appears to hinder the rotation of the thiazole group, thereby "locking" the molecule. As a consequence, a distinctive splitting of the aromatic signals is observed in the ¹H NMR titration, in contrast to the other anions studied, for which there is little movement of these signals (Figure 4a). This is a consequence of the size and shape of the $\mathrm{SiF_6}^{2-}$ ion preventing the rotation of the thiazole group. This is not seen for the NO_3^- or SO_4^{-2} ions, consistent with the small binding constant obtained for SO_4^{2-} and the lack of data for NO_3^{-} (Table 2). Additionally, this is consistent with the significant chemical shift of the NH protons observed during the course of the titration (Figure 5a). While crystallographic information reveals the solid-state structure, this does not always translate to solution-based host-guest behavior. However, in this instance the ¹H NMR titration data support the structural studies.

Overall, the incorporation of two **TUTh** species in the $[Ag(TUTh)_2]^+$ complex gives a significant enhancement in guest binding in comparison to the model system through a combination of charge attraction, preorganization, and the ability of two complexes to form a pseudocapsule around the dianions SO_4^{2-} and SiF_6^{2-} . The complementary hydrogen bonding between host and guest is complemented by weak metal—anion interactions that are allowed by the geometry of the ligands. This highlights the capacity of bis-urea tweezers to be highly complementary toward oxoanions, even in highly competitive solvent.

CONCLUSIONS

The tweezer-type complex $[Ag(TUTh)_2]^+$ is able to act as an effective host for SO_4^{2-} and SiF_6^{2-} in highly competitive media (DMSO) by forming 2:1 host–guest pseudocapsules. Solid-state results show that the PF_6^- complex of the receptor adopts a "splayed" geometry, as opposed to the tweezer form adopted in the presence of more strongly interacting guest species $(NO_3^{-7}, SO_4^{2-}, and SiF_6^{2-})$. The solid-state results concur with the solution-based studies. The geometry of the cleft formed by the ligands around the Ag^+ ion is ideal to present an array of hydrogen bond donors toward the central pocket in which the

anions bind. The combination of eight hydrogen-bonding interactions between the two tweezers and the guest inside the capsule are seemingly strong enough in concert to overcome competition from the highly polar solvent.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b02028.

NMR spectra, PXRD traces, additional crystallographic information, and detailed titration information and plots (PDF)

Accession Codes

CCDC 1554115–1554118 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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REFERENCES

(1) (a) Busschaert, N.; Caltagirone, C.; van Rossom, W.; Gale, P. A. Applications of supramolecular anion recognition. *Chem. Rev.* 2015, *115*, 8038–8155. (b) Steed, J. W.; Turner, D. R.; Wallace, K. J. *Core Concepts in Supramolecular Chemistry and Nanochemistry*; Wiley: Chichester, U.K., 2007.

(2) (a) Li, Y. J.; Liu, H. B.; Li, Y. L. Recent development of anion receptors based on hydrogen bonding. *Chin. J. Inorg. Chem.* 2015, 31, 1687–1704. (b) Gale, P. A. From anion receptors to transporters. *Acc. Chem. Res.* 2011, 44, 216–226. (c) Vargas Jentzsch, A.; Hennig, A.; Mareda, J.; Matile, S. Synthetic ion transporters that work with anion-pi interactions, halogen bonds, and anion-macrodipole interactions. *Acc. Chem. Res.* 2013, 46, 2791–2800. (d) Gale, P. A.; Perez-Tomas, R.; Quesada, R. Anion transporters and biological systems. *Acc. Chem. Res.* 2013, 46, 2801–2813. (e) Jia, C. D.; Zuo, W.; Zhang, D.; Yang, X. J.; Wu, B. Anion recognition by oligo-(thio)urea-based receptors. *Chem. Commun.* 2016, 52, 9614–9627.

(3) (a) Blazek Bregovic, V.; Basaric, N.; Mlinaric-Majerski, K. Anion binding with urea and thiourea derivatives. *Coord. Chem. Rev.* 2015, 295, 80–124. (b) Amendola, V.; Fabbrizzi, L.; Mosca, L. Anion recognition by hydrogen bonding: urea-based receptors. *Chem. Soc. Rev.* 2010, 39, 3889–3915. (c) Gale, P. A. Structural and molecular recognition studies with acyclic anion receptors. *Acc. Chem. Res.* 2006, 39, 465–475. (d) Li, A. F.; Wang, J. H.; Wang, F.; Jiang, Y. B. Anion complexation and sensing using modified urea and thiourea-based receptors. *Chem. Soc. Rev.* 2010, 39, 3729–3745. (e) Hay, B. P.;

Firman, T. K.; Moyer, B. A. Structural design criteria for anion hosts: Strategies for achieving anion shape recognition through complementary placement of urea donor groups. J. Am. Chem. Soc. 2005, 127, 1810–1819. (f) Dydio, P.; Lichosyt, D.; Jurczak, J. Amide- and urea-functionalized pyrroles and benzopyrroles as synthetic, neutral anion receptors. Chem. Soc. Rev. 2011, 40, 2971–2985.

(4) (a) Aleman, J.; Parra, A.; Jiang, H.; Jorgensen, K. A. Squaramides: Bridging from molecular recognition to bifunctional organocatalysis. *Chem. - Eur. J.* **2011**, *17*, 6890–6899. (b) Amendola, V.; Bergamaschi, G.; Boiocchi, M.; Fabbrizzi, L.; Milani, M. The squaramide versus urea contest for anion recognition. *Chem. - Eur. J.* **2010**, *16*, 4368–4380.

(5) Jia, C. D.; Wang, Q. Q.; Begum, R. A.; Day, V. W.; Bowman-James, K. Chelate effects in sulfate binding by amide/urea-based ligands. *Org. Biomol. Chem.* **2015**, *13*, 6953–6957.

(6) Rice, C. R. Metal-assembled anion receptors. *Coord. Chem. Rev.* **2006**, 250, 3190–3199.

(7) Pfeffer, F. M.; Gunnlaugsson, T.; Jensen, P.; Kruger, P. E. Anion recognition using preorganized thiourea functionalized [3]-polynorbornane receptors. *Org. Lett.* **2005**, *7*, 5357–5360.

(8) (a) Zhao, J.; Yang, D.; Zhao, Y. X.; Cao, L. P.; Zhang, Z. B.; Yang, X. J.; Wu, B. Phosphate-induced fluorescence of a tetraphenylethenesubstituted tripodal tris(urea) receptor. *Dalton Trans.* **2016**, *45*, 7360– 7365. (b) Ravikumar, I.; Lakshminarayanan, P. S.; Arunachalam, M.; Suresh, E.; Ghosh, P. Anion complexation of a pentafluorophenylsubstituted tripodal urea receptor in solution and the solid state: selectivity toward phosphate. *Dalton Trans.* **2009**, 4160–4168. (c) Zhuge, F. Y.; Wu, B. A.; Liang, J. J.; Yang, J.; Liu, Y. Y.; Jia, C. D.; Janiak, C.; Tang, N.; Yang, X. J. Full- or half-encapsulation of sulfate anion by a tris(3-pyridylurea) receptro: Effect of the secondary coordination sphere. *Inorg. Chem.* **2009**, *48*, 10249–10256.

(9) (a) Kim, W.; Sahoo, S. K.; Kim, G. D.; Choi, H. J. Novel C-3Vsymmetric trindane based tripodal anion receptor with tris(coumarinurea) extension for optical sensing of bioactive anions. *Tetrahedron* **2015**, *71*, 8111–8116. (b) Turner, D. R.; Paterson, M. J.; Steed, J. W. A conformationally flexible, urea-based tripodal anion receptor: Solidstate, solution, and theoretical studies. *J. Org. Chem.* **2006**, *71*, 1598– 1608.

(10) Bondy, C. R.; Gale, P. A.; Loeb, S. J. Metal-organic anion receptors: Arranging urea hydrogen-bond donors to encapsulate sulfate ions. *J. Am. Chem. Soc.* **2004**, *126*, 5030–5031.

(11) Amendola, V.; Boiocchi, M.; Colasson, B.; Fabbrizzi, L. Metalcontrolled assembly and selectivity of a urea-based anion receptor. *Inorg. Chem.* **2006**, *45*, 6138–6147.

(12) (a) Turner, D. R.; Spencer, E. C.; Tocher, D. A.; Howard, J. A. K.; Steed, J. W. A modular, self-assembled, separated ion pair binding system. *Chem. Commun.* **2004**, 1352–1353. (b) Turner, D. R.; Smith, B.; Radosavljevic-Evans, I.; Goeta, A. E.; Spencer, E. C.; Tocher, D. A.; Howard, J. A. K.; Steed, J. W. Anion binding by Ag(I) complexes of urea-substituted pyridyl ligands. *New J. Chem.* **2005**, *29*, 90–98.

(13) Wu, B.; Yang, X.-J.; Janiak, C.; Lassahn, P. G. Large size anion binding with iron(II) complexes of a 5,5'-disubstituted-2,2'-bipyridine ligand. *Chem. Commun.* **2003**, 902–903.

(14) Emami Khansari, M.; Johnson, C. R.; Basaran, I.; Nafis, A.; Wang, J.; Leszczynski, J.; Hossain, Md.A. Synthesis and anion binding studies of tris(3-aminopropyl)amine-based tripodal urea and thiourea receptors: proton transfer-induced selectivity for hydrogen sulfate over sulfate. *RSC Adv.* **2015**, *5*, 17606–17614.

(15) Custelcean, R.; Bonnesen, P. V.; Duncan, N. C.; Zhang, X. H.; Watson, L. A.; van Berkel, G.; Parson, W. B.; Hay, B. P. Ureafunctionalized M_4L_6 cage receptors: anion-templated self-assembly and selective guest exchange in aqueous solutions. *J. Am. Chem. Soc.* **2012**, 134, 8525–8534.

(16) (a) Custelcean, R.; Moyer, B. A.; Hay, B. P. Chem. Commun. 2005, 5971–5973. (b) Custelcean, R.; Bock, A.; Moyer, B. A. Selectivity principles in anion separation by crystallization of hydrogen-bonding capsules. J. Am. Chem. Soc. 2010, 132, 7177– 7185. (c) Basaran, I.; Emami Khansari, M.; Pramanik, A.; Wong, B. M.; Hossain, Md.A. Binding and selectivity of dihydrogen phosphate by H- bond donors and acceptors in a tripodal-based thiourea receptor. *Tetrahedron Lett.* 2015, 56, 115–118.

(17) Chutia, R.; Dey, S. K.; Das, G. Self-assembly of a tris(urea) receptor as tetrahedral cage for the encapsulation of a discrete tetrameric mixed phosphate cluster ($H_2PO_4^{-}$ · HPO_4^{-}). *Cryst. Growth Des.* **2015**, *15*, 4993–5001.

(18) Dey, S. K.; Basu, A.; Chutia, R.; Das, G. Anion coordinated capsules and pseudocapsules of tripodal amide, urea and thiourea scaffolds. *RSC Adv.* **2016**, *6*, 26568–26589.

(19) (a) Pandurangan, K.; Kitchen, J. A.; Blasco, S.; Boyle, E. M.; Fitzpatrick, B.; Feeny, M.; Kruger, P. E.; Gunnlaugsson, T. Unexpected self-sorting self-assembly formation of a [4:4] sulfate:ligand cage from a preorganized tripodal urea ligand. *Angew. Chem., Int. Ed.* **2015**, *54*, 4566–4570. (b) Wallace, K. J.; Hanes, R.; Anslyn, E. V.; Morey, J.; Kilway, K. V.; Siegel, J. Preparation of 1,3,5-tris(aminomethyl)-2,4,6triethylbenzene from two versatile 1,3,5-tri(halosubstituted)-2,4,6triethylbenzene derivatives. *Synthesis* **2005**, 2005, 2080–2083.

(20) (a) Manna, U.; Nayak, B.; Das, G. Dual guest $[(chloride)_3-DMSO]$ encapsulated cation-sealed neutral trimeric capsular assembly: Meta-substituent directed halide and oxyanion binding discrepancy of isomeric neutral disubstituted bis-urea receptors. *Cryst. Growth Des.* **2016**, *16*, 7163–7174. (b) Jia, C. D.; Wu, B. A.; Li, S. G.; Yang, Z. W.; Zhao, Q. L.; Liang, J. J.; Li, Q. S.; Yang, X. J. A fully complementary, high-affinity receptor for phosphate and sulfate based on an acyclic tris(urea) scaffold. *Chem. Commun.* **2010**, *46*, 5376–5378. (c) Wu, B.; Li, S. G.; Lei, Y. B.; Hu, H. M.; Amadeu, N. D.; Janiak, C.; Mathieson, J. S.; Long, D. L.; Cronin, L.; Yang, X. J. The effect of the spacer of bis(urea) ligands on the structure of A_2L_3 -type (A = anion) phosphate complexes. *Chem. - Eur. J.* **2015**, *21*, 2588–2593.

(21) McPhillips, T. M.; McPhillips, S. E.; Chiu, H. J.; Cohen, A. E.; Deacon, A. M.; Ellis, P. J.; Garman, E.; Gonzalez, A.; Sauter, N. K.; Phizackerley, R. P.; Soltis, S. M.; Kuhn, P. Blu-Ice and the distributed control system: Software for data acquisition and instrument control at macromolecular crystallography beamlines. *J. Synchrotron Radiat.* **2002**, *9*, 401–406.

(22) Kabsch, W. XDS. Acta Crystallogr., Sect. D: Biol. Crystallogr. 2010, 66, 125–132.

(23) SAINT; Bruker AXS Inc., Madison, WI, USA.

(24) Sheldrick, G. M. SHELXT - Integrated space-group and crystalstructure determination. *Acta Crystallogr., Sect. A: Found. Adv.* 2015, 71, 3–8.

(25) Sheldrick, G. M. Crystal structure refinement with SHELXL. Acta Crystallogr, Sect. C: Struct. Chem. 2015, 71, 3–8.

(26) Barbour, L. J. X-Seed - A software tool for supramolecular chemsitry. J. Supramol. Chem. 2001, 1, 189–191.

(27) Du, J.-L.; Hu, T.-L.; Zhang, S.-M.; Zeng, Y.-F.; Bu, X.-H. Tuning silver(I) coordination architectures by ligands design: From dinuclear, trinuclear, to 1D and 3D frameworks. *CrystEngComm* **2008**, *10*, 1866–1874.

(28) Wallace, K. J.; Daari, R.; Belcher, W. J.; Abouderbala, L. O.; Boutelle, M. G.; Steed, J. W. Oxo-anion binding by metal containing molecular 'clefts'. *J. Organomet. Chem.* **2003**, *666*, 63–74.

(29) Gans, P. HypNMR2016; Protonic Software, Leeds, U.K.

(30) Cowieson, N. P.; Aragao, D.; Clift, M.; Ericsson, D. J.; Gee, C.; Harrop, S. J.; Mudie, N.; Panjikar, S.; Price, J. R.; Riboldi-Tunnicliffe, A.; Williamson, R.; Caradoc-Davies, T. MX1: A bending magnet crystallography beamline serving both chemical and macromolecular crystallography communities at the Australian Synchrotron. *J. Synchrotron Radiat.* **2015**, *22*, 187–190.