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Control of Silver(I)–Dialkyl Chalcogenide Coordination by a Synthetic Cavity**

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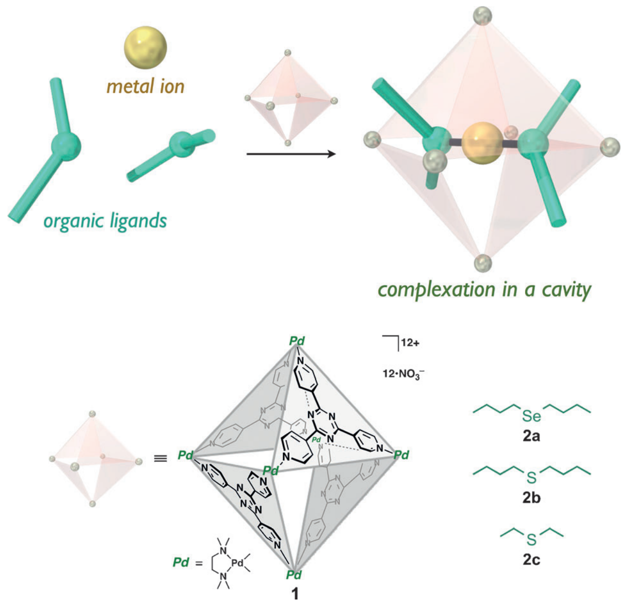
Abstract: *The discrete cavity of a self-assembled palladium–tris(4-pyridyl)triazine cage dictates the ratio of metal, ligand, and a non-coordinative molecule in the formation of silver(I)–dialkyl chalcogenide (Et, nBu; S, Se) complexes and defines their coordination arrangement.*

The coordination number and geometry of a metal ion are fundamental concerns in transition-metal chemistry and these factors are usually controlled by changing the structure of the ligands. For example, a sterically bulky ligand offers an active metal site with a low coordination number,[1] and a multidentate ligand restricts the coordination geometry, which affects the metal activity.[2] Recent development of self-assembled host cages[3] has made it possible to control the reactivity and stability of various transition metal complexes[3f–j,4] inside host cavities, but in all cases the accommodated metal complexes are synthesized prior to inclusion within the cavity. Herein, we show that the confined cavity of cage **1** (Scheme 1) can control the coordination of organic ligands to an Ag^I ion, which can, in general, adopt a variety of coordination numbers and geometries.[5] The number of organic ligands (dialkyl chalcogenides in this study) and the coordination geometry of the complexes formed in situ are clearly defined by the cavity size and shape, which enables us to generate otherwise unobtainable Ag^I complexes. Coexistence of a non-coordinative molecule in the cavity decreases the number of organic ligands coordinated to the Ag^I ion.

Upon addition of dibutyl selenide (**2a**; 33.0 μmol, 3 equiv) to a D_2O solution of cage **1** (5 mM, 2.20 mL, 1 equiv), the colorless solution turned yellow (Figure 1 a). The solution was stirred at room temperature for 10 min, and the excess selenide **2a** was removed by filtration. Based on integral ratios, ^1H NMR spectroscopy revealed the formation of inclusion complex $\mathbf{1}\cdot(\mathbf{2a})_2$ in 78% yield (Figure 1 b,c). The signals of the alkyl chains of **2a** were shifted upfield ($\Delta\delta = -1.98$ ppm for H_a). UV/Vis spectroscopy displayed a new absorption ($\lambda_{max} \approx 420$ nm), which was presumably derived from charge transfer (CT) from the electron rich selenium atom of **2a** to the electron-deficient triazine ligands of cage **1** (Supporting Information, Figure S8).[6] Furthermore, ^{77}Se NMR spectroscopy showed a large upfield shift ($\Delta\delta = -19.3$ ppm, Figure 1 e,f), which was mainly due to the chalcogen–π interactions.[7] One equivalent of silver(I) nitrate was then added to the yellow solution,[8] and the solution immediately reverted to its colorless state (Figure 1 a).



Scheme 1. Representation of metal complexation in the cavity of self-assembled cage **1**. Silver(I) ions and dialkyl chalcogenide ligands **2** were employed in this study.

After 5 min, the ^1H NMR spectrum showed that the signals of the alkyl chains of **2a** were broadened and shifted downfield, which indicated that the selenide atom was coordinated to the silver(I) center (Figure 1 d). The integral ratio of selenide **2a** to cage **1** remained unchanged, and these combined results strongly suggested the formation of ternary complex $\mathbf{1}\cdot[Ag^I\cdot(\mathbf{2a})_2]$. Selenide coordination was also supported by the upfield-shifted signal in the ^{77}Se NMR spectrum (Figure 1 g),[5f–h] and the disappearance of the CT absorption band (Supporting Information, Figure S8). When an additional selenide ligand **2a** was introduced into the solution of $\mathbf{1}\cdot[Ag^I\cdot(\mathbf{2a})_2]$, the number of ligand **2a** coordinated to the silver center did not increase. This was confirmed by NMR spectroscopy (Supporting Information, Figure S7), and is presumably due to the fact that further coordination was restricted by the volume limitation of the cage.

The $\mathbf{1}\cdot[Ag^I\cdot(\mathbf{2a})_2]$ host–guest structure and the coordination geometry of the Ag^I complex were confirmed by X-ray crystallographic analysis. A single crystal suitable for analysis

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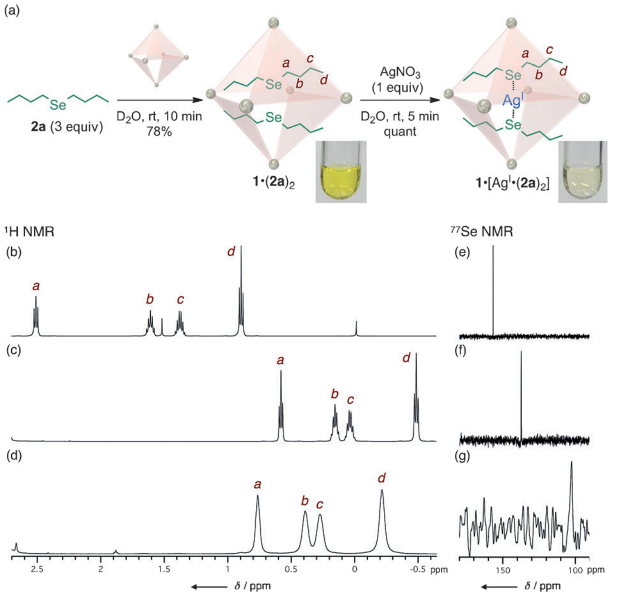

Figure 1. a) Encapsulation of dialkyl selenide **2a** within self-assembled cage **1** and subsequent incorporation of a silver(I) ion. Photographs of the sample solution before and after addition of silver(I) are shown as insets. ^{1}H NMR spectra (500 MHz, 300 K) of b) dialkyl selenide **2a** in $CDCl_3$, c) inclusion complex **1**·(**2a**)$_2$ in D_2O, and d) ternary complex **1**·[Ag^I·(**2a**)$_2$] in D_2O. ^{77}Se NMR spectra (95 MHz, 300 K) of e) **2a** in $CDCl_3$, f) **1**·(**2a**)$_2$ in D_2O, and g) **1**·[Ag^I·(**2a**)$_2$] in D_2O.

was obtained by slow evaporation of water from the aqueous solution (15 mM) at 15 °C over 15 days. In the crystal structure, two disordered Ag^I·(**2a**)$_2$ complexes were observed inside the highly symmetrical cage: one was associated with NO_3^- (70 % occupancy; Figure 2 a) and the other with OH^- or H_2O (30 % occupancy; Figure 2 b).[9] In both cases, the silver atom was located at the center of cage **1** and all of the alkyl chains of selenide ligand **2a** passed through the cage portals. As shown in Figure 2 a, the nitrate anion coordinates to Ag^I in a η^2-fashion and holds the whole silver complex inside the cage.

Despite their lower affinity for Ag^I,[5f,10] sulfide ligands also formed the corresponding silver(I)–bis(dialkyl sulfide) complexes in the cage using the same procedure. When dibutyl sulfide **2b** was employed, inclusion complex **1**·[Ag^I·(**2b**)$_2$] was obtained quantitatively (Figure 3 a), as observed when dibutyl selenide **2a** was used. As the size of the complex is limited by the cavity volume, a less bulky sulfide ligand was necessary to increase the number of sulfide ligands coordinated to the silver(I) ion: four molecules of diethyl sulfide **2c** were included in cage **1** to give 1:4 complex [Ag^I·(**2c**)$_4$] (Figure 3 b).

More interestingly, co-enclathration of an inert guest that reduced the effective cavity volume resulted in lower numbers of coordinated organic ligands, and a 1:1 silver(I)–sulfide complex with one coordinated sulfide could even be obtained. Sulfide **2b** (1 equiv) and a linear guest, 1,3-diyne **3** (8 equiv), were added to an aqueous solution of cage **1** (Figure 4 a). After stirring for 2 h at room temperature, the excess guests were removed by filtration, and the formation of ternary complex **1**·(**2b**·**3**) in 73 % yield was confirmed by

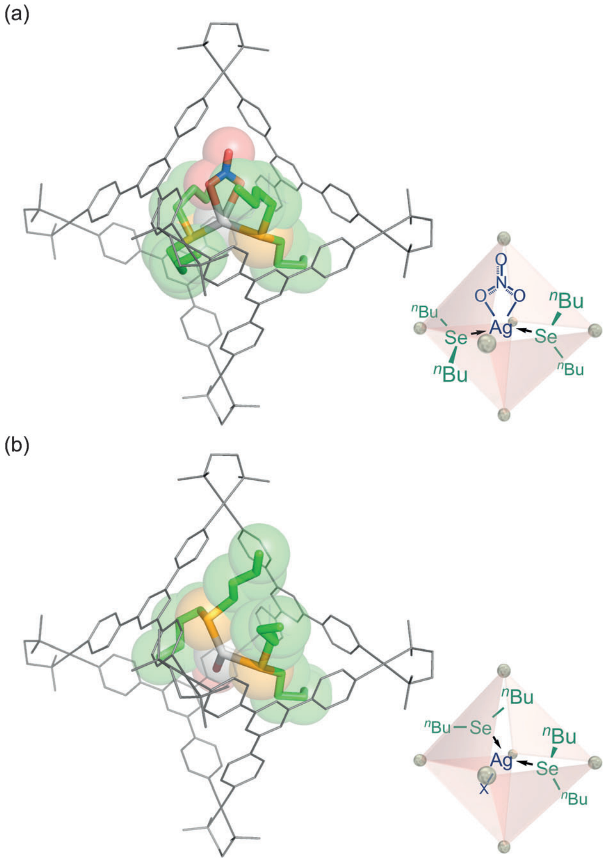

Figure 2. X-ray structures of the encapsulated Ag–Se complex **1**·[AgX·(**2a**)$_2$]. Two disordered structures of guest complex [AgX·(**2a**)$_2$] were observed within host cage **1**: a) X = NO_3 (70 % occupancy) and b) X = OH or H_2O (30 % occupancy). Hydrogen atoms have been omitted for clarity.

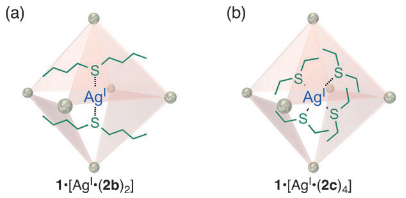

Figure 3. Silver–dialkyl sulfide complexes within cage **1**: a) **1**·[Ag^I·(**2b**)$_2$], b) **1**·[Ag^I·(**2c**)$_4$].

^{1}H NMR spectroscopy, which showed the upfield shift of **2b** and **3** (Figure 4 c). The pairwise encapsulation of **2b** and **3** was also confirmed by a NOESY experiment, in which NOE correlations between the *n*-butyl moiety of **2b** and the *tert*-butyl moiety of **3** were clearly observed (Supporting Information, Figure S14). One equivalent of silver(I) nitrate was then added to this solution. In the ^{1}H NMR spectrum, the signals of the alkyl chains of **2b** were shifted downfield and broadened; this again shows the sulfide coordination to the Ag^I center (Figure 4 d). In contrast, the signal of the *tert*-butyl groups of **3** was not shifted. ^{13}C NMR spectroscopy revealed that the signals of the diyne part of **3** did not change after addition of silver, which indicates that there was no coordination of **3** to the Ag^I center. Thus, the inclusion complex

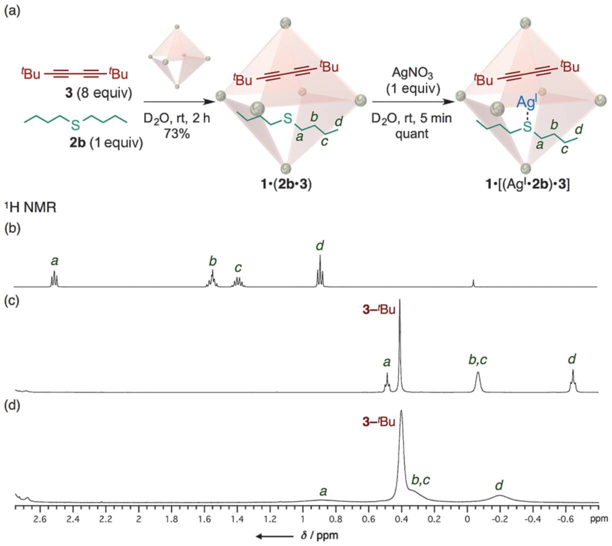

Figure 4. a) Pairwise encapsulation of dialkyl sulfide **2b** and diyne **3** within self-assembled cage **1**, and subsequent incorporation of a silver(I) ion. ^{1}H NMR spectra (500 MHz, 300 K) of b) dialkyl sulfide **2b** in CDCl$_3$, c) ternary complex **1**·(**2b**·**3**) in D$_2$O, and d) quaternary complex **1**·[(Ag^I·**2b**)·**3**] in D$_2$O.

formed is described as **1**·[(Ag^I·**2b**)·**3**], in which 1:1 complex Ag^I·**2b** and inert guest **3** are coenclathrated inside cage **1** (Supporting Information, Figure S17).

In summary, we have controlled the coordination of organic ligands for Ag^I complexation with dialkyl chalcogenide ligands through inclusion in the cavity of a self-assembled cage. Despite the fact that the coordination pattern of Ag^I is variable, the number of dialkyl chalcogenide coordinated was precisely restricted by the rigid architecture of the host cage. Ligand fluctuations are not observed in any of the examples, which suggests that the silver(I)–chalcogenide complexes that form in the cavity are stabilized. The cavity-directed control of the number and geometry of coordinated molecules and the close proximity of a metal and an inert molecule are reminiscent of events that occur in enzyme pockets. Further development of enzymatic reactions in the proximity of a low-valent metal and a substrate in the synthetic cavity is one of our next goals in this work.

Experimental Section

Stepwise preparation of ternary complex **1**·[Ag^I·(**2a**)$_2$]: Dibutyl selenide **2a** (5.82 μL, 33.0 μmol, 3 equiv) was added to a solution of cage **1** (5 mM, 2.20 mL, 11.0 μmol, 1 equiv) in D$_2$O in a screw tube. The mixture was shaken with a vortex mixer for several seconds and stirred at room temperature for 10 min to give selenide-inclusion complex **1**·(**2a**)$_2$. The excess guest **2a** was removed by filtering the emulsion. ^{1}H NMR spectroscopy showed the formation of selenide inclusion complex **1**·(**2a**)$_2$ in 78% yield (Supporting Information, Figure S3). A D$_2$O solution of silver(I) nitrate (0.1 g mL^{-1}, 4.17 μL, 2.45 μmol, 1 equiv) was added to the D$_2$O solution of selenide inclusion complex **1**·(**2a**)$_2$ (5 mM, 78% inclusion, 0.630 mL, 2.46 μmol, 1 equiv) in a screw tube. The mixture was shaken with a vortex mixer for several seconds and stirred at room temperature for 5 min. ^{1}H NMR spectroscopy showed the formation of ternary complex **1**·[Ag^I·(**2a**)$_2$] in quantitative yield.

Crystal data of **1**·[Ag^I·(**2a**)$_2$]: Space group $I4_1/a$, $T=90(2)$ K, $a=b=26.216(7)$, $c=31.195(9)$ Å, $\alpha=\beta=\gamma=90°$, $V=21439(10)$ Å^3, $Z=4$, $\rho_{\text{calcd}}=1.389$ Mg m^{-3}, $F(000)=9077$, reflections collected/unique 248 794/12 287 ($R_{\text{int}}=0.0310$). The structure was solved by direct methods (SHELXS-97) and refined by fill-matrix least-squares methods (SHELXL-97) on F^2 with 784 parameters. $R_1=0.0584$ ($I>2\sigma(I)$), $wR_2=0.1760$, GOF 1.096. CCDC 987499 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) A. F. Littke, G. C. Fu, *Angew. Chem. Int. Ed.* **2002**, *41*, 4176–4211; *Angew. Chem.* **2002**, *114*, 4350–4386; b) G. C. Fu, *Acc. Chem. Res.* **2008**, *41*, 1555–1564.

[2] a) M.-N. Birkholz née Gensow, Z. Freixa, P. W. N. M. van Leeuwen, *Chem. Soc. Rev.* **2009**, *38*, 1099–1118; b) H. Hirao, D. Kumar, L. Que, S. Shaik, *J. Am. Chem. Soc.* **2006**, *128*, 8590–8606; c) L. Bernasconi, M. J. Louwerse, E. J. Baerends, *Eur. J. Inorg. Chem.* **2007**, 3023–3033; d) T. Hatakeyama, T. Hashimoto, Y. Kondo, Y. Fujiwara, H. Seike, H. Takaya, Y. Tamada, T. Ono, M. Nakamura, *J. Am. Chem. Soc.* **2010**, *132*, 10674–10676.

[3] For reviews of self-assembled host cages, see: a) J. Rebek, Jr., *Angew. Chem. Int. Ed.* **2005**, *44*, 2068–2078; *Angew. Chem.* **2005**, *117*, 2104–2115; b) R. Chakrabarty, P. S. Mukherjee, P. J. Stang, *Chem. Rev.* **2011**, *111*, 6810–6918; c) L. Marchetti, M. Levine, *ACS Catal.* **2011**, *1*, 1090–1118; d) H. Amouri, C. Desmarets, J. Moussa, *Chem. Rev.* **2012**, *112*, 2015–2041; e) M. Raynal, P. Ballester, A. Vidal-Ferran, P. W. N. M. van Leeuwen, *Chem. Soc. Rev.* **2014**, *43*, 1734–1787; f) D. M. Vriezema, M. Comellas Aragonès, J. A. A. W. Elemans, J. J. L. M. Cornelissen, A. E. Rowan, R. J. M. Nolte, *Chem. Rev.* **2005**, *105*, 1445–1489; g) S. J. Lee, J. T. Hupp, *Coord. Chem. Rev.* **2006**, *250*, 1710–1723; h) T. S. Koblenz, J. Wassenaar, J. N. H. Reek, *Chem. Soc. Rev.* **2008**, *37*, 247–262; i) M. Yoshizawa, J. K. Klosterman, M. Fujita, *Angew. Chem. Int. Ed.* **2009**, *48*, 3418–3438; *Angew. Chem.* **2009**, *121*, 3470–3490; j) M. J. Wiester, P. A. Ulmann, C. A. Mirkin, *Angew. Chem. Int. Ed.* **2011**, *50*, 114–137; *Angew. Chem.* **2011**, *123*, 118–142.

[4] a) M. L. Merlau, M. del Pilar Mejia, S. T. Nguyen, J. T. Hupp, *Angew. Chem. Int. Ed.* **2001**, *40*, 4239–4242; *Angew. Chem.* **2001**, *113*, 4369–4372; b) S. J. Lee, S. Cho, K. L. Mulfort, D. M. Tiede, J. T. Hupp, *J. Am. Chem. Soc.* **2008**, *130*, 16828–16829; c) A. W. Kleij, J. N. H. Reek, *Chem. Eur. J.* **2006**, *12*, 4218–4227; d) V. F. Slagt, P. W. N. M. van Leeuwen, J. N. H. Reek, *Angew. Chem. Int. Ed.* **2003**, *42*, 5619–5623; *Angew. Chem.* **2003**, *115*, 5777–5781; e) J. Flapper, J. N. H. Reek, *Angew. Chem. Int. Ed.* **2007**, *46*, 8590–8592; *Angew. Chem.* **2007**, *119*, 8744–8746; f) A. Cavarzan, A. Scarso, P. Sgarbossa, G. Strukul, J. N. H. Reek, *J. Am. Chem. Soc.* **2011**, *133*, 2848–2851; g) D. H. Leung, D. Fiedler, R. G. Bergman, K. N. Raymond, *Angew. Chem. Int. Ed.* **2004**, *43*, 963–966; *Angew. Chem.* **2004**, *116*, 981–984; h) D. H. Leung, R. G. Bergman, K. N. Raymond, *J. Am. Chem. Soc.* **2006**, *128*, 9781–9797; i) D. H. Leung, R. G. Bergman, K. N. Raymond, *J. Am. Chem. Soc.* **2007**, *129*, 2746–2747; j) Z. J. Wang, K. N. Clary, R. G. Bergman, K. N. Raymond, F. D. Toste, *Nat. Chem.* **2013**, *5*, 100–103; k) S. Horiuchi, T. Murase, M. Fujita, *Angew. Chem. Int. Ed.* **2012**, *51*, 12029–12031; *Angew. Chem.*

2012, *124*, 12195 – 12197; l) Y. Kohyama, T. Murase, M. Fujita, *J. Am. Chem. Soc.* **2014**, *136*, 2966 – 2969; m) M. A. Sarmentero, H. Fernández-Pérez, E. Zuidema, C. Bo, A. Vidal-Ferran, P. Ballester, *Angew. Chem. Int. Ed.* **2010**, *49*, 7489 – 7492; *Angew. Chem.* **2010**, *122*, 7651 – 7654.

[5] a) M. Johnsson, I. Persson, *Inorg. Chim. Acta* **1987**, *130*, 215 – 220; b) J. Clarkson, R. Yagbasan, P. J. Blower, S. C. Rawle, S. R. Cooper, *J. Chem. Soc. Chem. Commun.* **1987**, 950 – 951; c) J. R. Black, N. R. Champness, W. Levason, G. Reid, *J. Chem. Soc. Dalton Trans.* **1995**, 3439 – 3445; d) M. A. Carvajal, J. J. Novoa, S. Alvarez, *J. Am. Chem. Soc.* **2004**, *126*, 1465 – 1477; e) A. G. Young, L. R. Hanton, *Coord. Chem. Rev.* **2008**, *252*, 1346 – 1386; f) T. Shimizu, M. Kawaguchi, T. Tsuchiya, K. Hirabayashi, N. Kamigata, *J. Org. Chem.* **2005**, *70*, 5036 – 5044; g) F. R. Knight, R. A. M. Randall, L. Wakefield, A. M. Z. Slawin, J. D. Woollins, *Molecules* **2012**, *17*, 13307 – 13329; h) F. R. Knight, R. A. M. Randall, L. Wakefield, A. M. Z. Slawin, J. D. Woollins, *Dalton Trans.* **2013**, *42*, 143 – 154.

[6] J. E. Frey, T. Aiello, D. N. Beaman, H. Hutson, S. R. Lang, J. J. Puckett, *J. Org. Chem.* **1995**, *60*, 2891 – 2901.

[7] The chemical shift in the ^{77}Se NMR spectrum was also affected by conformational changes of the alkyl chains and intermolecular interactions (Se–Se or Se–H interactions) between the two molecules of **2a** within cage **1**. See also: a) H. Duddeck, P. Wagner, B. Rys, *Magn. Reson. Chem.* **1993**, *31*, 736 – 742; b) H. Duddeck in *Encyclopedia of Nuclear Magnetic Resonance*, *Vol. 7* (Eds.: D. M. Grant, R. K. Harris), Wiley, Chichester, **1996**, pp. 4623 – 4635.

[8] The counterion of the silver salt was the same as that of cage **1** (NO_3^-) to avoid the influence of anion exchange in this process.

[9] The number of protons on the coordinating oxygen cannot be determined from the X-ray diffraction analysis.

[10] L. D. Pettit, A. Royston, C. Sherrington, R. J. Whewell, *Chem. Commun.* **1967**, 1179 – 1180.