Supporting Information

Spirocyclic, macrocyclic and ladder complexes of coinage metals and mercury with dichalcogeno P_2N_2-supported anions

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Table of Contents

I. Synthesis and Crystal Structure of **10**

II. Packing Diagrams of **13-15**

I. Synthesis and Crystal Structure of [(^{t}Bu(H)NP(Se)(μ-N^{t}Bu)$_2$P(Se)N(H)^{t}Bu)$_2$(μ^4-Ag)][CF_3SO_3] (10)

a) Synthesis of 10.

A suspension of $AgSO_3CF_3$ (100 mg, 0.39 mmol) in toluene (15 mL) was added *via* cannula to a suspension of [(^{t}BuNP(μ-N^{t}Bu)$_2$P^{t}BuN)(μ-Se$_2$)]$_3$ (**9Se**) (200 mg, 0.13 mmol) in toluene (10 mL) at 23°C. The reaction mixture was stirred for ca. 16h and the precipitate was removed by filtration. The solvent was removed under vacuum and recrystallisation of the crude product from *n*-hexane afforded yellow crystals that were identified as **10** by an X-ray crystal structure determination ^{31}P NMR (109.37 MHz, [D$_8$]THF): δ = 23.4 (s, broad).

b) Crystal Structure of 10

The single crystal X-ray analysis of **10** revealed X-ray (Fig. 1) a central Ag^+ cation that is Se,Se′ chelated to two neutral ligands **1Se** (Fig. 1). Charge balance is provided by a triflate anion $[CF_3SO_3]^-$. A similar coordination complex, which features a tetrahedral silver(I) centre with two neutral Se,Se′ chelated ligands ([Ag(Ph$_2$P(Se)NHP(Se)Ph$_2$)$_2$][BF_4]), was reported previously.[1]

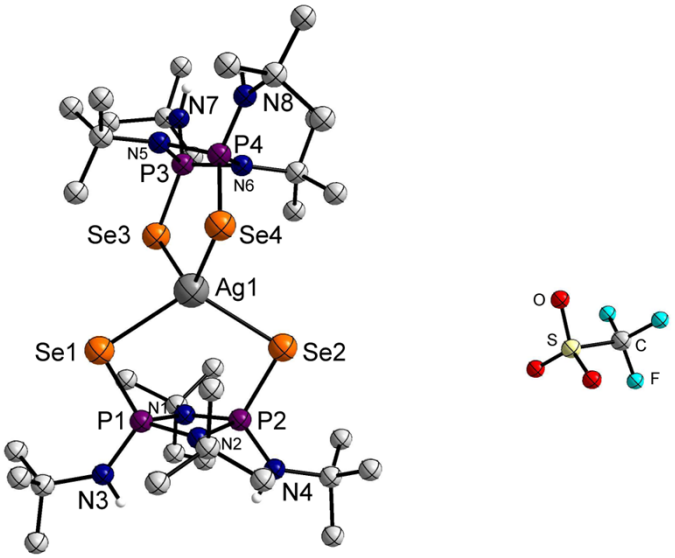


Fig. 1 X-ray crystal structure of **10**. The asymmetric unit contains two [(^{t}Bu(H)NP(Se)(μ-N^{t}Bu)$_2$P(Se)N(H)^{t}Bu)$_2$(μ_4-Ag)][CF_3SO_3] units. Three carbon atoms (C7, C14, C44) are disordered over two positions, which were modelled satisfactorily. H atoms bonded to C atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1–Se1 2.714(2), Ag1–Se4 2.725(2), Ag1–Se2 2.738(2), Ag1–Se3 2.741(2), P1–N3 1.642(12), P1–N2 1.690(13), P1–N1 1.701(12), P1–Se1 2.112(4), P2–N4 1.601(13), P2–N2 1.671(13), P2–N1 1.672(13), P2–Se2 2.120(4), P3–N7 1.625(13), P3–N6 1.676(12), P3–N5 1.701(12), P3–Se3 2.107(4), P3–P4 2.508(5), P4–N8 1.631(11), P4–N6 1.701(12), P4–N5 1.709(12), P4–Se4 2.109(4), S1–O1 1.387(12); Se1–Ag1–Se4 114.31(7), Se1–Ag1–Se2 115.62(6), Se4–Ag1–Se2 102.02(6), Se1–Ag1–Se3 95.62(6), Se4–Ag1–Se3

114.61(6), Se2–Ag1–Se3 115.44(7), N3–P1–N2 111.0(6), N3–P1–N1 110.6(6), N2–P1–N1 82.7(6), N3–P1–Se1 114.7(5), N2–P1–Se1 117.4(5), N1–P1–Se1 116.3(5), N4–P2–N2 111.8(7), N4–P2–N1 110.5(7), N2–P2–N1 84.1(6) N4–P2–Se2 115.0(5), N2–P2–Se2 115.3(5), N1–P2–Se2 116.2(5).

The Ag–Se bond distances in **10** are in the range 2.714(2)-2.741(2) Å, *cf.* 2.634(2)-2.713(3) Å in $[Ag(Ph_2P(Se)NHP(Se)Ph_2)_2][BF_4]$.[1] The bond angles at the Ag centre in **10** are in the range 95.62(6)-115.62(6)°, *cf.* 97.98(9) -117.96(9)° for $[Ag(Ph_2P(Se)NHP(Se)Ph_2)_2][BF_4]$. The P–Se bond lengths in **10** are between 2.107(4) and 2.120(4) Å, somewhat shorter than a single bond. The hydrogen atoms of the *exo*cyclic nitrogen atoms in **10** were included in the structure refinement in the calculated positions. These hydrogen atoms exhibit hydrogen bonding to the fluorine and oxygen molecules of the $[CF_3SO_3]^-$ ion, which leads to the supramolecular structure illustrated in Fig. 2.

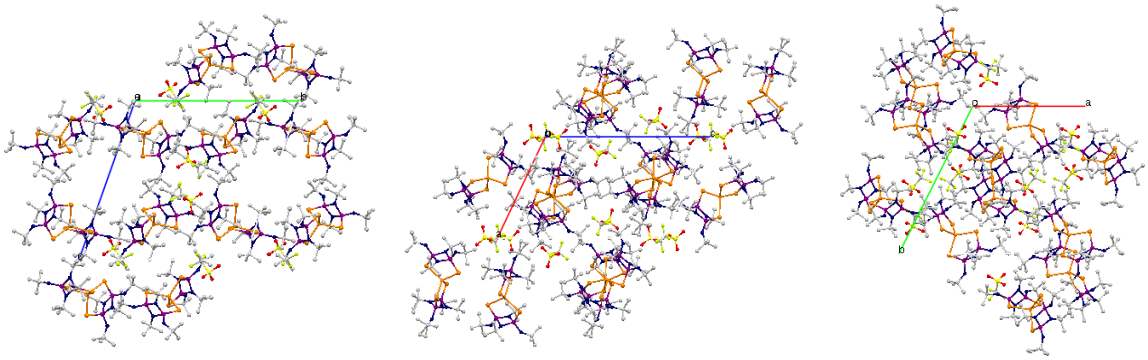


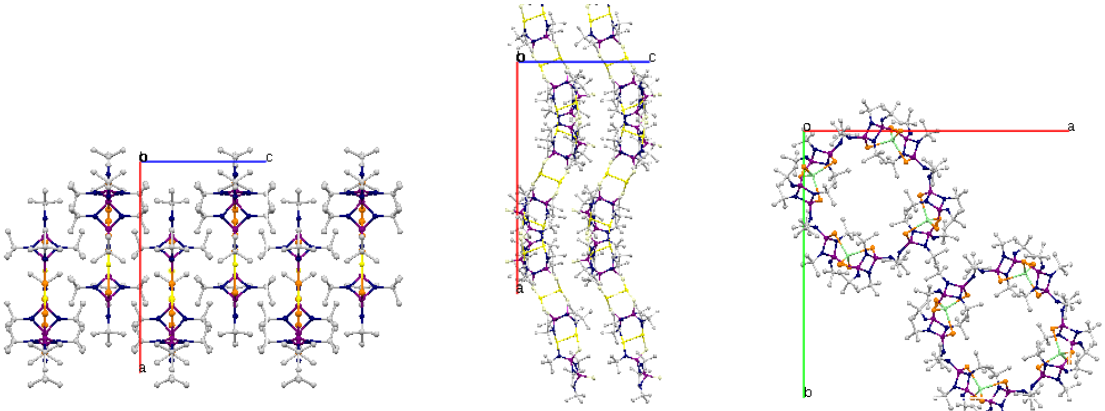
Fig. 2 Packing of **10** along the *a*, *b* and *c* axis (colour scheme: P: purple, Se: orange; N: blue, C: grey. H atoms are omitted.

The ^{31}P NMR spectrum of **10** exhibits a broad resonance at 23.4 ppm in $[D_8]THF$. As was found $Ag(Ph_2P(Se)NHP(Se)Ph_2)_2][BF_4]$,[1] the value of ^1J(P,Se) could not be reliably determined owing to the width of the signals presumably due to the occurrence of rapid exchange equilibria.

1. H. Liu, N. A. G. Bandeira, M. J. Calhorda, M. G. B. Drew, V. Felix, J. Novosad, F. F. de Biani and P. Zanello, *J. Organomet. Chem*., 2004, **689**, 2808.

II. Packing Diagrams for 13-15

The compounds **13-15** exhibit interesting packing arrangements. The packing of the trimeric gold(I) macrocycle **13** is characterised by perfectly planar staggered molecules (Fig. 3a). The ladders of the Au_2 ladder **14** are aligned in S-shaped chains with ^{t}Bu groups providing a buffer between the ladders (Fig. 3b). In the lattice of the Hg(II) complex **15** four molecules are aligned in a cyclic structure when viewed along the *c* axis (Fig. 3c).



(a) (b) (c)

Fig. 3 Packing of (a) **13** (along the *b* axis), (b) **14** (along the *b* axis) and (c) **15** (along the *c* axis).

Table 1 Crystallographic data for compound **10**.

	10
Empirical formula	$C_{66}H_{152}Ag_2F_6N_{16}O_6P_8S_2Se_8$
Formula weight	2539.33
Temperature (°C)	173
Crystal colour, habit	colourless platelet
Crystal dimensions (mm^3)	0.290 x 0.140 x 0.080
Crystal system	triclinic
a (Å)	15.2850(3)
b (Å)	21.2360(3)
c (Å)	21.4390(4)
α (°)	100.0720(10)
β (°)	109.3760(10)
γ (°)	111.0400(10)
Volume ($Å^3$)	5775.45(18)
Space group	P -1
Z value	2
D_{calc} (g/cm^3)	1.460
F_{000}	2560
μ (Mo-K_α) (cm^{-1})	3.062
No. of reflections measured	32567
R_{int}	0.1082
Min. and max. transmissions	0.470, 0.792
Reflection/parameter ratio	16962 (1069)
Residuals: R_1 ($I > 2.00\sigma(I)$)	0.0881
Residuals: wR_2 (all reflections)	0.2718
Goodness of fit indicator	1.117
Max. peak in final diff. map ($e^-/Å^3$)	1.565
Min. peak in final diff. map ($e^-/Å^3$)	−0.911