SUPPLEMENTARY INFORMATION

Alloying dichalcogenolate-protected Ag_{21} 8-electron nanoclusters: A DFT investigation

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Content

Table S1. Crystallographic data for the C_1-*I* isomer of $[PtAg_{20}\{S_2P(O^nPr)_2\}_{12}]$.

CCDC number	2091674
Empirical formula	$C_{81}H_{186}Ag_{20}O_{27}P_{12}PtS_{24}$
Crystal system, space group	Trigonal, *R*3
a, Å	22.7267(14)
b, Å	22.7267(14)
c, Å	27.590(2)
α, deg.	90
β, deg	90
γ, deg	120
Volume, Å^3	12341.2(19)
Z	3
ρ_{calcd}, g·cm^{-3}	2.053
μ, mm^{-1}	3.637
Temperature, K	100(2)
θ_{max}, deg. / completeness, %	24.997 / 95.8
Reflections collected / unique	27456 / 9188 [R(int) = 0.1060]
Restraints / parameters	318 / 511
R1[a], wR2[b] [I > 2σ(I)]	0.0491,0.1194
R1[a], wR2[b] (all data)	0.0522,0.1231
Absolute structure parameter	0.020(12)
Goodness of fit on F^2	1.044
Largest diff. peak and hole, e/Å ^{3}	1.978 and -1.077

[a]$R1 = \Sigma \; | \; |F_o| - |F_c| \; | \; / \Sigma |F_o|$. [b]$wR2 = \{ \Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)_2] \}^{1/2}$

Table S2. Computed results for the $[MAg_{20}(S_2(PH_2)_{12}]^q$ species. The first values correspond to structure-type *T* and the values in parentheses to structure-type C_3 (see main text).

S	H-L (eV)	ΔE (kcal/mol)	ΔG (kcal/mol)
CoAg20_I	1.46 (1.36)	0.0 (0.0)	0.0 (0.0)
CoAg20_II	0.48 (0.43-0.52)	40.1 (33.6-39.0)	34.2 (28.1-34.0)
CoAg20_III	0.58 (0.32-0.58)	24.4 (23.3-33.3)	20.5 (21.1-29.0)
RhAg20_I	1.91 (1.73)	0.0 (0.0)	0.0 (0.0)
RhAg20_II	0.88 (0.58-0.83)	41.5 (38.1-38.8)	37.7 (35.3-36.2)
RhAg20_III	0.75 (0.45-0.73)	44.0 (42.2-48.9)	40.2 (39.4-47.0)
IrAg20_I	2.04 (1.84)	0.0 (0.0)	0.0 (0.0)
IrAg20_II	0.90 (0.61-0.82)	48.3 (46.5-54.7)	44.0 (40.7-50.0)
IrAg20_III	0.78 (0.49-0.78)	55.1 (54.9-59.4)	49.9 (51.1-54.8)
NiAg20_I	1.82 (1.72)	0.0 (0.0)	0.0 (0.0)
NiAg20_II	0.91 (0.82-0.93)	22.8 (18.5-22.3)	18.5 (16.6-19.6)
NiAg20_III	1.00 (0.80-0.97)	9.6 (9.1-13.8)	6.0 (8.1-11.8)
PdAg20_I	1.92 (1.81)	0.0 (0.0)	0.0 (0.0)
PdAg20_II	1.39 (1.32-1.33)	21.1 (20.1-21.3)	18.0 (18.5-19.5)
PdAg20_III	1.34 (1.10-1.31)	22.1 (21.4-24.0)	19.0 (18.5-21.1)
PtAg20_I	2.04 (1.91)	0.0 (0.0)	0.0 (0.0)
PtAg20_II	1.39 (1.29-1.33)	30.8 (27.9-30.6)	26.6 (26.6-28.5)
PtAg20_III	1.34 (1.05-1.31)	35.5 (35.2-36.3)	32.0 (31.6-34.0)
CuAg20_I	1.88 (1.74)	4.3 (4.8)	7.0 (5.4)
CuAg20_II	1.82 (1.70-1.72)	8.7 (8.4-9.9)	8.9 (7.0-8.4)
CuAg20_III	1.90 (1.66-1.75)	0.0 (0.0-1.7)	0.0 (0.0-1.1)
AuAg20_I	2.03 (1.87)	0.0 (0.0)	0.0 (0.0)
AuAg20_II	1.80 (1.69-1.74)	9.2 (9.6)	9.2 (9.0-9.2)
AuAg20_III	1.90 (1.68-1.76)	15.8 (14.7-16.0)	15.8 (12.7-14.9)
ZnAg20_I	1.94 (1.72)	3.4 (8.8)	5.8 (8.1)
ZnAg20_II	0.95 (1.66-1.73)	66.1 (8.0-8.8)	57.2 (6.6-7.1)
ZnAg20_III	1.69 (1.32-1.61)	0.0 (0.0-6.4)	0.0 (0.0-4.4)
CdAg20_I	1.98 (1.74)	6.4 (9.1)	7.2 (9.2)
CdAg20_II	1.76 (1.57-1.70)	0.0 (2.1-3.4)	0.0 (2.5-2.8)
CdAg20_III	1.60 (1.22-1.53)	6.5 (0.0-9.8)	5.8-6.6 (0.0-8.8)
HgAg20_I	2.06 (1.81)	5.2 (6.3)	6.3 (4.9)
HgAg20_II	1.57 (1.42-1.56)	0.0 (0.0-1.6)	0.0 (0.0-0.7)
HgAg20_III	0.71-1.44 (1.01-1.39)	15.0-80.1 (5.1-16.7)	14.5-71.5 (5.1-15.0)

Table S3. Computed results for the $[MAg_{20}(Se_2(PH_2)_{12}]^q$ species. The first values correspond to structure-type *T* and the values in parentheses to structure-type C_3 (see main text).

Se	H-L (eV)	ΔE (kcal/mol)	ΔG (kcal/mol)
CoAg20_I	1.36 (1.23)	0.0 (0.0)	0.0 (0.0)
CoAg20_II	0.45 (0.32-0.44)	37.6 (35.8-37.3)	31.9 (29.0-31.7)
CoAg20_III	0.55 (0.36-0.56)	16.0 (20.4-25.3)	15.9-16.1 (15.3-21.5)
RhAg20_I	1.75 (1.53)	0.0 (0.0)	0.0 (0.0)
RhAg20_II	0.81 (0.86-0.92)	40.0 (13.1-36.0)	35.5 (10.9-34.0)
RhAg20_III	0.77 (0.58-0.73)	37.15 (36.7-39.6)	32.6-33.2 (31.8-35.6)
IrAg20_I	1.86 (1.62)	0.0 (0.0)	0.0 (0.0)
IrAg20_II	0.81 (0.60-0.86)	47.1 (41.9-48.6)	42.1 (38.6-41.6)
IrAg20_III	0.78 (0.58-0.76)	46.6 (39.4-48.0)	40.9 (33.5-42.0)
NiAg20_I	1.69 (1.51)	0.0 (0.0)	0.0 (0.0)
NiAg20_II	0.81 (0.71-0.82)	23.9 (20.5-22.4)	19.7 (16.2-18.8)
NiAg20_III	0.99 (0.85-0.97)	10.2-13.5 (10.4-11.4)	6.1-6.6 (7.5-9.5)
PdAg20_I	1.73 (1.54)	0.0 (0.0)	0.0 (0.0)
PdAg20_II	1.25 (1.14-1.17)	20.8 (19.8-20.3)	17.4 (16.6-17.9)
PdAg20_III	1.36 (1.10-1.31)	19.0 (18.5-20.0)	15.7-16.3 (15.7-18.3)
PtAg20_I	1.83 (1.62)	0.0 (0.0)	0.0 (0.0)
PtAg20_II	1.24 (1.13-1.17)	31.9 (26.2-29.1)	26.6 (23.8-26.1)
PtAg20_III	1.36 (1.11-1.30)	32.6-33.2 (28.8-30.9)	27.6 (26.7-28.3)
CuAg20_I	1.70 (1.51)	1.5 (1.5)	4.2 (1.5)
CuAg20_II	1.65 (1.50-1.51)	7.1 (5.9-7.9)	7.6 (6.0-7.0)
CuAg20_III	1.70 (1.49-1.53)	0.0 (0.0-1.6)	0.0 (0.0-1.4)
AuAg20_I	1.83 (1.59)	0.0 (0.0)	0.0 (0.0)
AuAg20_II	1.61 (1.47-1.52)	8.3 (8.5-8.7)	6.6 (6.8-7.7)
AuAg20_III	1.71 (1.45-1.55)	12.9 (12.0-12.9)	10.7-11.3 (11.5-12.2)
ZnAg20_I	1.78 (1.54)	0.0 (3.8)	2.3 (3.8)
ZnAg20_II	1.66 (1.50-1.54)	1.4 (4.8-4.9)	1.00 (4.4-4.8)
ZnAg20_III	1.49 (1.17-1.41)	0.5 (0.0-3.7)	0.0-0.2 (0.0-4.8)
CdAg20_I	1.80 (1.56)	5.3 (6.7)	6.4 (5.6)
CdAg20_II	1.61 (1.43-1.54)	0.0 (0.6-1.7)	0.0 (0.6-0.9)
CdAg20_III	1.42 (1.10-1.37)	6.4 (0.0-7.0)	5.3-6.3 (0.0-7.2)
HgAg20_I	1.87 (1.60)	5.6 (6.6)	6.2 (5.9)
HgAg20_II	1.45 (1.28-1.42)	0.0 (0.0-2.4)	0.0 (0.0-1.4)
HgAg20_III	1.31 (0.92-1.28)	13.7 (4.8-14.1)	12.3-12.9 (5.3-13.7)

Additional comments on experimental data on the *C_1-I* isomer of [$PtAg_{20}\{S_2P(O^nPr)_2\}_{12}$].

The *C_3-I* isomer of [$\{Pt@Ag_{20}\}\{Se_2P(O^nPr)_2\}_{12}$] (Figure 4) is iso-structural with [$Ag_{21}\{S_2P(O^iPr)_2\}_{12}]^+$. The averaged Pt-$Ag_{ico}$ (2.7505 Å) and Ag_{ico}-Ag_{ico} (2.8957 Å) distances in $PtAg_{20}$-C_3 are slightly shorter than those in its previously reported *C_1-I* isomer (Pt-Ag_{ico} :2.7601 Å; Ag_{ico}-Ag_{ico} :2.9022 Å). An opposite trend is found for the peripheral Ag_{ico}-Ag_{cap} (3.017 Å *vs.* 2.902 Å). The metal kernel is protected by 12 ligands exhibiting one binding mode, μ_3: η^2, η^1, in the *C_3-I* isomer, as opposed to two binding modes, μ_4: η^2, η^2 and μ_3: η^2, η^1, in the *C_1-I* isomer. The Ag-S bond lengths in the *C_3-I* isomer range from 2.480 to 2.587 Å, which are slightly shorter than those in *C_1-I* isomer (2.462-2.946 Å).

The ^{31}P NMR spectrum of [$\{Pt@Ag_{20}\}\{Se_2P(O^nPr)_2\}_{12}$] at 293K shows only one sharp peak at 104.1ppm. It splits into four peaks with the same integration ratio at 218K. Four types of resonances correspond to the four chemical environments of the dithiphosphate ligands observed in the *C_3-I* structure. This result indicates that [$PtAg_{20}\{S_2P(O^nPr)_2\}_{12}$] tends to keep C_3 symmetry in solution. Thus, no significantly different optical properties of the two isomers can be observed in solution.

In summary, two isomers of [$\{Pt@Ag_{20}\}\{Se_2P(O^nPr)_2\}_{12}$], of *$C_3$-I* and *$C_1$-I* structure-type, can be obtained in different crystallization conditions, but show the same optical properties in solution. This is the first report of structure isomerism in silver or silver-rich, superatomic nanoclusters.