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Synthesis and Characterization of the Silver Maleonitrilediselenolates and Silver Maleonitriledithiolates $[K([2.2.2]\text{-cryptand})]_4[Ag_4(Se_2C_2(CN)_2)_4]$, $[Na([2.2.2]\text{-cryptand})]_4[Ag_4(S_2C_2(CN)_2)_4]\cdot 0.33MeCN$, $[NBu_4]_4[Ag_4(S_2C_2(CN)_2)_4]$, $[K([2.2.2]\text{-cryptand})]_3[Ag(Se_2C_2(CN)_2)_2]\cdot 2MeCN$, and $[Na([2.2.2]\text{-cryptand})]_3[Ag(S_2C_2(CN)_2)_2]$

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Reaction of $AgBF_4$, KNH_2, K_2Se, Se, and [2.2.2]-cryptand in acetonitrile yields $[K([2.2.2]\text{-cryptand})]_4[Ag_4(Se_2C_2(CN)_2)_4]$ (**1**). In the unit cell of **1** there are four $[K([2.2.2]\text{-cryptand})]^+$ units and a tetrahedral Ag_4 anionic core coordinated in μ_1-Se, μ_2-Se fashion by each of four mns ligands (mns = maleonitrilediselenolate, $[Se_2C_2(CN)_2]^{2-}$). Reaction of $AgNO_3$, Na_2(mnt) (mnt = maleonitriledithiolate, $[S_2C_2(CN)_2]^{2-}$), and [2.2.2]-cryptand in acetonitrile yields $[Na([2.2.2]\text{-cryptand})]_4[Ag_4(mnt)_4]\cdot 0.33MeCN$ (**2**). The Ag_4 anion of **2** is analogous to that in **1**. Reaction of $AgNO_3$, Na_2(mnt), and $[NBu_4]Br$ in acetonitrile yields $[NBu_4]_4[Ag_4(mnt)_4]$ (**3**). The anion of **3** also comprises an Ag_4 core coordinated by four mnt ligands, but the Ag_4 core is diamond-shaped rather than tetrahedral. Reaction of $[K([2.2.2]\text{-cryptand})]_3[Ag(mns)(Se_6)]$ with KNH_2 and [2.2.2]-cryptand in acetonitrile yields $[K([2.2.2]\text{-cryptand})]_3[Ag(mns)_2]\cdot 2MeCN$ (**4**). The anion of **4** comprises an Ag center coordinated by two mns ligands in a tetrahedral arrangement. Reaction of $AgNO_3$, 2 equiv of Na_2(mnt), and [2.2.2]-cryptand in acetonitrile yields $[Na([2.2.2]\text{-cryptand})]_3[Ag(mnt)_2]$ (**5**). The anion of **5** is analogous to that of **4**. Electronic absorption and infrared spectra of each complex show behavior characteristic of metal−maleonitriledichalcogenates. Crystal data (153 K): **1**, $P2/n$, $Z = 2$, $a = 18.362(2)$ Å, $b = 16.500(1)$ Å, $c = 19.673(2)$ Å, $\beta = 94.67(1)°$, $V = 5941(1)$ Å^3; **2**, $P\bar{4}$, $Z = 4$, $a = 27.039(4)$ Å, $c = 15.358(3)$ Å, $V = 11229(3)$ Å^3; **3**, $P2_1/c$, $Z = 6$, $a = 15.689(3)$ Å, $b = 51.924(11)$ Å, $c = 17.393(4)$ Å, $\beta = 93.51(1)°$, $V = 14142(5)$ Å^3; **4**, $P2_1/c$, $Z = 4$, $a = 13.997(1)$ Å, $b = 21.866(2)$ Å, $c = 28.281(2)$ Å, $\beta = 97.72(1)°$, $V = 8578(1)$ Å^3; **5**, $P2/n$, $Z = 2$, $a = 11.547(2)$ Å, $b = 11.766(2)$ Å, $c = 27.774(6)$ Å, $\beta = 91.85(3)°$, $V = 3772(1)$ Å^3.

Introduction

Tetrahedral Ag_4 clusters, some with coordinating chalcogen-containing ligands, are well-known.[1,2] For example, clusters with dithiolate ligands, such as $[Ag_4(S_2C_2H_4(C_6H_4))_3]^{2-}$ [3] and $[Ag_4(S_2C{=}C(CN)_2)_4]^{4-}$,[4] and the polyselenide species $[Ag_4(Se_4)_3]^{2-}$,[5] $[Ag_4(Se_4)_4]^{4-}$,[5] and $[Ag_4(Se_4)_{3-x}(Se_5)_x]^{2-}$ [6,7] have been reported. Cation size has an important effect on which Ag−chalcogenide species are formed.[5,7] Noncluster complexes of Ag with chalcogen-containing ligands are also common.[5,8−16] However, Ag complexes with the dithiolate ligand maleonitriledithiolate (= mnt = $[S_2C_2(CN)_2]^{2-}$) are limited primarily to the Ag_2(mnt) salt,[17,18] polymeric $(Ag_4(mnt)_3)_n^{2-}$,[19] and $[Ag(PPh_3)_2][Ag(PPh_3)_2(mnt)]$.[20−22] There is also a claim of $[Ag(mnt)_2]^{2-}$,[23] but no evidence is provided. $[Ag(PR_3)_2]^+$ complexes with $[M(mnt)_2]^{2-}$ species (M = Ni,[24−28] Pd,[27] and Pt[27]) and Ag complexes with mnt derivatives, such as oxa-crown

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ethers ([15]-crown-$O_3(S_2C_2(CN)_2)$)[29−31] and alkylated mnt ($R_2S_2C_2(CN)_2$),[32] are also known. We recently reported the synthesis of [K([2.2.2]-cryptand)]$_3$[Ag(mns)(Se$_6$)],[33,34] an Ag complex of the maleonitrilediselenolate (= mns = $[Se_2C_2(CN)_2]^{2-}$) ligand, the Se analogue of mnt. Here we report the synthesis and characterization of new Ag−mns and Ag−mnt complexes with structures unlike those of any reported mnt complexes.

Experimental Section

All processes were carried out under N_2 with the use of standard Schlenk and air-free manipulation techniques.[35] Infrared spectra were collected on a Bio-Rad Digilab FTS-60 FTIR as KBr mulls. Electronic absorption spectra were collected on a Cary 1E UV−visible spectrophotometer. Energy dispersive spectroscopy (EDS) was performed on a Hitachi S-4500 field emission scanning electron microscope. Melting point determinations were made in glass capillaries with a Mel-Temp device. Electrospray mass spectroscopic analyses were performed on a Micromass Quattro II triple quadrupole instrument operated in negative ion mode with CH_2Cl_2 as the solvent. Se (99.9%), $AgBF_4$ (98%), [NBu$_4$]Br (98%), KBr (98%), $AgNO_3$ (99+%), and [2.2.2]-cryptand (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) (98%) were purchased from Aldrich Chemicals, Milwaukee, WI, and used without further purification. K_2Se was prepared by the stoichiometric combination of the elements in liquid ammonia. KNH_2 was prepared by reaction of KH with liquid ammonia. [K([2.2.2]-cryptand)]$_3$[Ag(mns)(Se$_6$)][34] and Na$_2$(mnt)[36] were prepared by published methods. All solvents were dried and distilled prior to use.

Preparation of [K([2.2.2]-cryptand)]$_4$[Ag$_4$(Se$_2$C$_2$(CN)$_2$)$_4$] (1). Method 1. A mixture of 11 mg (0.2 mmol) of KNH_2, 63 mg (0.4 mmol) of K_2Se, 158 mg (2 mmol) of Se, 340 mg (0.9 mmol) of [2.2.2]-cryptand, and 40 mg (0.2 mmol) of $AgBF_4$ was dissolved in 10 mL of acetonitrile. The flask containing the resultant green solution was wrapped in foil to keep out light. After it was stirred for 24 h, the solution was filtered and the red-green filtrate was cooled to 4 °C and then layered with 11 mL of diethyl ether/toluene (10:1). Orange block-shaped crystals of **1** were isolated after 7 days. Yield: 51.7 mg (21% based on Ag). UV−vis (CH_2Cl_2) (λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 287 (11000), 329 (2500), 383 (1400). IR (ν, CN region, cm^{-1}): 2177. EDS: K:Ag:Se = 1.1:1:2.3. Anal. Calcd for $C_{88}H_{144}Ag_4K_4N_{16}O_{24}Se_8$: C, 34.89; H, 4.79; N, 7.40. Found: C, 33.82; H, 4.33; N, 7.09. Mp 242−246 °C.

Method 2. A mixture of 27 mg (13 μmol) of [K([2.2.2]-cryptand)]$_3$[Ag(mns)(Se$_6$)], 11 mg (56 μmol) of $AgBF_4$, 7 mg (0.16 mmol) of KNH_2, and 50 mg (0.13 mmol) of [2.2.2]-cryptand was dissolved in 10 mL of acetonitrile. The flask containing the resultant red-brown solution was wrapped in foil to keep out light. The solution was stirred for 24 h and then filtered. The red-green filtrate was cooled to 4 °C and layered with 11 mL of diethyl ether/toluene (10:1). Orange block-shaped crystals of **1** were isolated after 2 days.

Preparation of [Na([2.2.2]-cryptand)]$_4$[Ag$_4$(S$_2$C$_2$(CN)$_2$)$_4$]·0.33MeCN (2). Acetonitrile (5 mL) was added to a flask charged with 42 mg (0.25 mmol) of $AgNO_3$ to afford a colorless solution. In a separate flask, 47 mg (0.25 mmol) of Na$_2$(mnt) and 5 mL of acetonitrile were combined to yield a yellow suspension. After 1 h the Ag solution was added dropwise to the mnt suspension to produce an orange solution. After 16 h a solution of acetonitrile (3 mL) containing 374 mg (1 mmol) of [2.2.2]-cryptand was added dropwise to the Ag/mnt solution. The color of the solution darkened. The solution was stirred for 2 h and then filtered; the red-orange filtrate was cooled to 4 °C and then layered with 11 mL of diethyl ether/toluene (10:1). Yellow block-shaped crystals of **2** were isolated after 2 days. Yield: 180.6 mg (68% based on Ag). UV−vis (CH_2Cl_2) (λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 269 (33600), 306 (13200), 369 (35100), 380 (26200). IR (ν, CN region, cm^{-1}): 2180. ESI (−): 248.8 (*m/z*, $[Ag_4(S_2C_2(CN)_2)_4]^{4-}$), 425.8 (*m/z*, $[Ag_4(S_2C_2(CN)_2)_3]^{2-}$), 851.8 (*m/z*, $[Ag_4(S_2C_2(CN)_2)_3]^{-}$). EDS: Na:Ag:S = 0.68:1:1.51. Anal. Calcd for $C_{88.67}H_{145}Ag_4N_{16.33}Na_4O_{24}S_8$: C, 40.90; H, 5.61; N, 8.78. Found: C, 40.46; H, 5.64; N, 8.28. Mp 161−166 °C.

Preparation of [NBu$_4$]$_4$[Ag$_4$(S$_2$C$_2$(CN)$_2$)$_4$] (3). $AgNO_3$ (38 mg, 0.22 mmol) in 5 mL of acetonitrile was added via cannula to 43 mg (0.23 mmol) of Na$_2$(mnt) in 5 mL of acetonitrile, and the resultant orange solution was stirred for 16 h. Then 73.5 mg (0.23 mmol) of [NBu$_4$]Br in 3 mL of acetonitrile was added dropwise to the solution. The orange solution was filtered, cooled to 4 °C, and layered with 11 mL of diethyl ether/toluene (10:1). Yellow needles of **3** were isolated after 2 days. Yield: 49.0 mg (45% based on Ag). Complex **3** was also prepared with [NBu$_4$][BF$_4$] in place of [NBu$_4$]Br. UV−vis (CH_2Cl_2) (λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 268 (35400), 302 (16500), 369 (23800), 382 (23400). IR (ν, CN region, cm^{-1}): 2196. ESI (−): 247.8 (*m/z*, $[Ag_4(S_2C_2(CN)_2)_4]^{4-}$). EDS: Ag:S = 1:1.7. Mp 176−180 °C.

Preparation of [K([2.2.2]-cryptand)]$_3$[Ag(Se$_2$C$_2$(CN)$_2$)$_2$]·2MeCN (4). Acetonitrile (10 mL) was added to a flask charged with 25 mg (12 μmol) of [K([2.2.2]-cryptand)]$_3$[Ag(mns)(Se$_6$)], 7 mg (0.16 mmol) of KNH_2, and 50 mg (0.13 mmol) of [2.2.2]-cryptand. The color of the solution changed from red-brown to deep orange over 20 min. After 24 h the solution was filtered and the orange filtrate was cooled to 4 °C and layered with 11 mL of diethyl ether/toluene (10:1). Red needles of **4** were isolated after 4 days. Yield: 5 mg (22% based on Ag). UV−vis (CH_2Cl_2) (λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 290 (16800), 333 (4700), 392 (2700) 248 (11100). IR (ν, CN region, cm^{-1}): 2168. EDS: K:Ag:Se = 2.9:1:3.8. Mp 206−208 °C. Limited amounts of material made bulk analyses impractical.

Preparation of [Na([2.2.2]-cryptand)]$_3$[Ag(S$_2$C$_2$(CN)$_2$)$_2$] (5). Acetonitrile (5 mL) was added to a flask charged with 15.6 mg (0.09 mmol) of $AgNO_3$ to give a colorless solution. In a separate flask, 41 mg (0.20 mmol) of Na$_2$(mnt) and 5 mL of acetonitrile were combined to yield a yellow suspension. After 1 h the Ag solution was added dropwise to the mnt suspension to produce an orange solution. After 16 h a solution of acetonitrile (3 mL) containing 139 mg (0.37 mmol) of [2.2.2]-cryptand was added dropwise to the Ag/mnt solution. The solution was stirred for 2 h and then filtered. The red-orange filtrate was cooled to 4 °C and layered with 11 mL of diethyl ether/toluene (10:1). Yellow plate-shaped crystals of **5** were isolated after 2 days. Yield: 72 mg (50% based on Ag). UV−vis (CH_2Cl_2) (λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 270 (15300), 374 (11100), 395 (10700). IR (ν, CN region, cm^{-1}): 2171. ESI (−): 236.8 (*m/z*, $[HAg(S_2C_2(CN)_2)_2\cdot CH_2Cl_2]^{2-}$), 246.7 (*m/z*, $[Ag(S_2C_2(CN)_2)]^{-}$). Mp 164−168 °C.

X-ray Crystallography. A crystal of **1**, **2**, **3**, **4**, or **5** was mounted on the end of a fiber on a goniometer head. The head was placed in the cold stream of a Bruker-AXS SMART-1000 diffractometer equipped with a CCD area detector and graphite-monochromated Mo Kα radiation. Data were collected at 153 K with 0.3° steps in ω for 606 frames each, with $\phi = 0°, 120°, 240°$ for **1**, **4**, and **5** and $\varphi = 0°, 90°, 180°, 270°$ for **2** and **3**. An additional 50 frames at $\varphi = 0°$ were collected for **1**−**5** at the end of each data collection. Data were processed with the program SAINT+.[37] A face-indexed absorption correction was applied with the use of the program XPREP of the SHELXTL-PC suite.[38] Data were further corrected for frame variations with the program SADABS,[37] which relies on redundant data. Structure solutions were obtained by direct methods and refined on F^2 with the use of full-matrix least-squares techniques.[38] Except where noted, all non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined with a riding model.

Of the two unique [K([2.2.2]-cryptand)]$^+$ units in **1**, one is well-behaved, whereas the second shows some disorder in the flexible C_2H_4-

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Table 1. Crystallographic Data for [K([2.2.2]-cryptand)]$_4$[Ag$_4$(Se$_2$C$_2$(CN)$_2$)$_4$] (**1**), [Na([2.2.2]-cryptand)]$_4$[Ag$_4$(S$_2$C$_2$(CN)$_2$)$_4$]·0.33MeCN (**2**), [NBu$_4$]$_4$[Ag$_4$(S$_2$C$_2$(CN)$_2$)$_4$] (**3**), [K([2.2.2]-cryptand)]$_3$[Ag(Se$_2$C$_2$(CN)$_2$)$_2$]·2MeCN (**4**), and [Na([2.2.2]-cryptand)]$_3$[Ag(S$_2$C$_2$(CN)$_2$)$_2$] (**5**)[a]

	1	**2**	**3**	**4**	**5**
formula	$C_{88}H_{144}Ag_4K_4N_{16}O_{24}Se_8$	$C_{88.67}H_{145}Ag_4N_{16.33}Na_4O_{24}S_8$	$C_{80}H_{144}Ag_4N_{12}S_8$	$C_{66}H_{108}AgK_3N_{12}O_{18}Se_4$	$C_{62}H_{108}AgN_{10}Na_3O_{18}S_4$
fw	3029.75	2603.80	1962.03	1904.70	1586.66
a, Å	18.362(2)	27.039(4)	15.689(3)	13.997(1)	11.547(2)
b, Å	16.500(1)	27.039(4)	51.924(11)	21.866(2)	11.766(2)
c, Å	19.673(1)	15.358(3)	17.393(4)	28.281(2)	27.774(6)
β, °	94.67(1)	90	93.51(1)	97.72(1)	91.85(3)
V, Å^3	5941(1)	11229(3)	14142(5)	8578(1)	3772(1)
ρ_{calcd}, g cm^{-3}	1.694	1.541	1.382	1.475	1.397
T, K	153(2)	153(2)	153(2)	153(2)	153(2)
space group	$P2/n$	$P\bar{4}$	$P2_1/c$	$P2_1/c$	$P2/n$
Z	2	4	6	4	2
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073
μ, cm^{-1}	33.10	9.25	10.41	21.45	4.67
$R(F)^b$	0.076	0.047	0.082	0.036	0.081
w$R(F_o^2)^c$	0.143	0.098	0.153	0.070	0.132

[a] Crystal data for [K([2.2.2]-cryptand)]$_2$[Cu(Se$_2$C$_2$(CN)$_2$)$_2$]: $C_{44}H_{72}CuK_2N_8O_{12}Se_4$, monoclinic, $P2_1/c$, $a = 12.211(2)$ Å, $b = 16.086(3)$ Å, $c = 15.158(3)$ Å, $\beta = 107.05(3)°$, $V = 2847(1)$ Å^3, $T = -120$ °C, $Z = 2$. [b] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR(F_o^2) = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.03F_o^2)^2$ for $F_o^2 > 0$; $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 \leq 0$.

OC$_2$H$_4$OC$_2$H$_4$ arms and has been refined isotropically. As refinement in both $P2/n$ and Pn produced similar results, the higher symmetry space group $P2/n$ was used.

Compound **2** crystallizes with 0.333(4) molecules of acetonitrile in the asymmetric unit. Atom N20 of the acetonitrile is too close to its symmetry-generated counterpart (0.90(3) Å) for both to be present simultaneously. No evidence of a supercell was found. Although $P\bar{4}$ is a noncentrosymmetric space group, the $\bar{4}$ axis precludes the possibility of enantiomorphs. However, a metric of racemic cocrystallization, the Flack parameter,[39] refined to 0.41(1). Examination of the atomic coordinates of the anions with the program MISSYM in the PLATON suite of programs did not suggest the presence of any additional symmetry.[40,41]

In **3**, five of the six unique [NBu$_4$]$^+$ cations refined well but the other showed some disorder of a butyl group. This was modeled accordingly.

Compound **4** solved and refined routinely.

Compound **5** contains 1.5 crystallographically unique [Na([2.2.2]-cryptand)]$^+$ cations. The half cation with Na located at $^1/_4$,0.4891,$^1/_4$ showed disorder in several C and N positions of the flexible cryptand and was modeled accordingly. No evidence of a supercell was found.

Crystallographic details are summarized in Table 1 and in the Supporting Information.

Results and Discussion

Syntheses. The reaction of AgBF$_4$, KNH$_2$, K$_2$Se, Se, and [2.2.2]-cryptand in acetonitrile yields [K([2.2.2]-cryptand)]$_4$[Ag$_4$(mns)$_4$] (**1**). Compound **1** can also be formed by reaction of [K([2.2.2]-cryptand)]$_3$[Ag(mns)(Se$_6$)] with AgBF$_4$, KNH$_2$, and [2.2.2]-cryptand in acetonitrile. The reaction of AgNO$_3$, Na$_2$(mnt), and [2.2.2]-cryptand in acetonitrile yields [Na([2.2.2]-cryptand)]$_4$[Ag$_4$(mnt)$_4$]·0.33MeCN (**2**), the anion of which is analogous to that of **1**. The reaction of AgNO$_3$, Na$_2$(mnt), and [NBu$_4$]Br in acetonitrile yields [NBu$_4$]$_4$[Ag$_4$(mnt)$_4$] (**3**). The syntheses of **2** and **3** differ only in the cation added to the reaction mixture. The reaction of [K([2.2.2]-cryptand)]$_3$[Ag(mns)(Se$_6$)] with KNH$_2$ and [2.2.2]-cryptand in acetonitrile yields [K([2.2.2]-cryptand)]$_3$[Ag(mns)$_2$]·2MeCN (**4**). An analogous anion is observed in complex **5**, [Na([2.2.2]-cryptand)]$_3$[Ag(mnt)$_2$], obtained by reaction of AgNO$_3$, 2 equiv of Na$_2$(mnt), and [2.2.2]-cryptand in acetonitrile. Unoptimized yields range from 21% to 68%.

Structure of [K([2.2.2]-cryptand)]$_4$[Ag$_4$(Se$_2$C$_2$(CN)$_2$)$_4$] (1). The crystal structure of [K([2.2.2]-cryptand)]$_4$[Ag$_4$(mns)$_4$] (**1**) consists of well-separated anions and cations. The anion, [Ag$_4$(mns)$_4$]$^{4-}$, has crystallographically imposed C_2 symmetry but idealized S_4 symmetry (Figure 1). The central Ag$_4$ core contains Ag···Ag distances of 3.026(1)−3.103(1) Å, which are typical for tetrahedral clusters[5−7] but are longer than Ag−Ag bonding distances (Ag−Ag = 2.89 Å in Ag metal).[42−44] The mns ligands in **1** have C=C and CN distances and angles typical for the ligand.[33,34,45,46] Selected distances and angles are presented in Table 2.

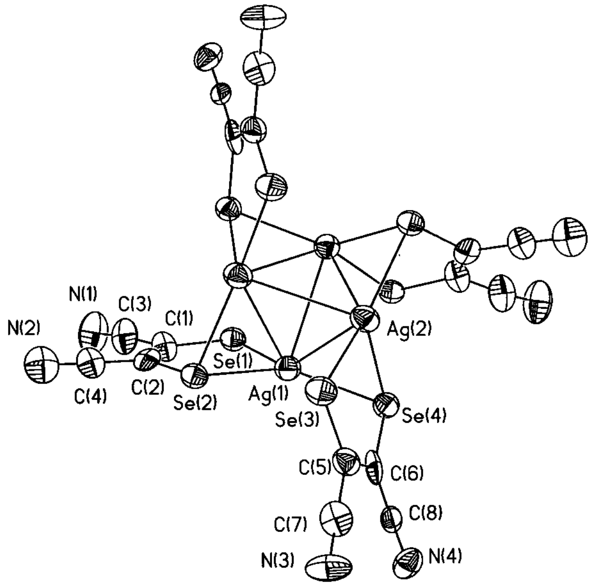

Figure 1. Displacement ellipsoid plot of the [Ag$_4$(mns)$_4$]$^{4-}$ anion in [K([2.2.2]-cryptand)]$_4$[Ag$_4$(mns)$_4$] (**1**). Here and in subsequent figures displacement ellipsoids are drawn at the 50% probability level. The anion has crystallographically imposed symmetry 2.

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Table 2. Average[a] Bond Distances (Å) and Bond Angles (deg) in Metal−mns Complexes[b]

	Ag (**1**)[c]	Ag (**4**)[c]	Sb[d]	Ag[d]
M−Se	μ_1-Se 2.562(1) μ_2-Se 2.608(1)	2.6579(4)	2.654(2)	2.567(4)
Se−C	μ_1-Se 1.880(8) μ_2-Se 1.936(9)	1.888(3)	1.87(2)	1.853(2)
C═C	1.379(11)	1.368(4)	1.36(2)	1.38(3)
C−CN	1.390(13)	1.434(4)	1.44(2)	1.43(3)
C−N	1.159(11)	1.131(4)	1.14(2)	1.116(3)
Se−M−Se (same ligand)	91.22(3)	87.96(1)	87.81(7)	91.4(1)
M−Se−C	95.8(3)	97.11(8)	96.7(5)	97.54(8)
Se−C═C	128.0(7)	128.0(2)	128(1)	128(2)
C═C−CN	119.0(8)	118.4(2)	118(2)	114(2)
C−C−N	176.9(10)	178.4(3)	177(2)	176(3)

[a] Average values are unweighted arithmetic means with the largest esd of the series as the esd. [b] Some bond lengths and angles for [K([2.2.2]-cryptand)]$_2$[Cu(mns)$_2$]: Cu−Se, 2.3823(8); Se−C, 1.880(3); C═C, 1.351(3); C−CN, 1.431(4); C≡N, 1.149(3) Å; ∠Se−Cu−Se, 91.93(2)°; ∠Cu−Se−C, 100.27(8)°; ∠C−C≡N, 179.1(1)°. See Supporting Information. [c] [Ag$_4$(mns)$_4$]$^{4-}$ (**1**) and [Ag(mns)$_2$]$^{3-}$ (**4**); this work. [d] [Sb(mns)$_2$]$^{3-}$ and [Ag(mns)(Se$_6$)]$^{3-}$; ref 33.

In the [Ag$_4$(mns)$_4$]$^{4-}$ anion of **1** (Figure 1), each mns ligand has a μ_1-Se bond to a Ag atom and a μ_2-Se bond to that same Ag atom and to an adjacent Ag atom. For example, for one mns ligand of **1**, Se(1) is μ_1 to Ag(1) whereas Se(2) is μ_2 between Ag(1) and Ag(2). This unusual bridging arrangement is also seen in one Se$_4^{2-}$ ring in [Ag$_4$(Se$_4$)$_4$]$^{4-}$.[5] In **1**, the average μ_1-Se−Ag distance of 2.562(1) Å is significantly shorter than the average μ_2-Se−Ag distance of 2.608(1) Å. However, the μ_2-Se−Ag distance to the neighboring mns ligand is the same (2.560(1) Å) and is significantly shorter than the μ_2-Se−Ag distance of 2.655(1) Å to the “attached” ligand. The Se$_{\mu1}$−CCN bond is shorter than the Se$_{\mu2}$−CCN bond (1.880(9) vs 1.938(9) Å), probably because the bridging Se atom possesses less electron density. Each Ag is coordinated to three Se atoms in a trigonal planar environment. A trigonal planar environment of chalcogens around each Ag is unusual,[47,48] but is also found in [PPh$_4$]$_2$[Ag$_4$(S$_2$C$_2$H$_4$(C$_6$H$_4$))$_3$], which has an [Ag$_4$S$_6$] core.[3]

Structure of [Na([2.2.2]-cryptand)]$_4$[Ag$_4$(S$_2$C$_2$(CN)$_2$)$_4$]·0.33MeCN (2). The crystal structure of [Na([2.2.2]-cryptand)]$_4$[Ag$_4$(mnt)$_4$]·0.33MeCN (**2**) consists of well-separated anions and cations and partially occupied acetonitrile molecules. The structural solution contains three distinct [Ag$_4$(mnt)$_4$]$^{4-}$ anionic moieties and four unique [Na([2.2.2]-cryptand)]$^+$ units. Two of the anions, centered at Wyckoff positions 1*a* and 1*c*, exhibit S_4 symmetry (Figure 2), whereas the remaining anion, centered at Wyckoff position 2*g*, exhibits C_2 symmetry crystallographically. The anion of **2** is analogous to that of **1**. As in **1**, the three central Ag$_4$ cores contain Ag···Ag interactions that are longer than Ag−Ag bond distances; two Ag$_4$ cores have distances similar to those seen in **1** (2.9732(6)−3.1832(6) Å) whereas the other Ag$_4$ core has longer interactions (3.0031(7)−3.4320(9) Å). Each mnt ligand has a μ_1-S bond to a Ag atom and a μ_2-S bond to that same Ag atom and to an adjacent Ag atom, and these distances show the same trends as the Ag−Se distances in **1**. The mnt ligands in **2** have S−C, C═C, and CN distances and angles typical for the ligand.[21,22,49−52] Selected distances and angles are presented in Table 3.

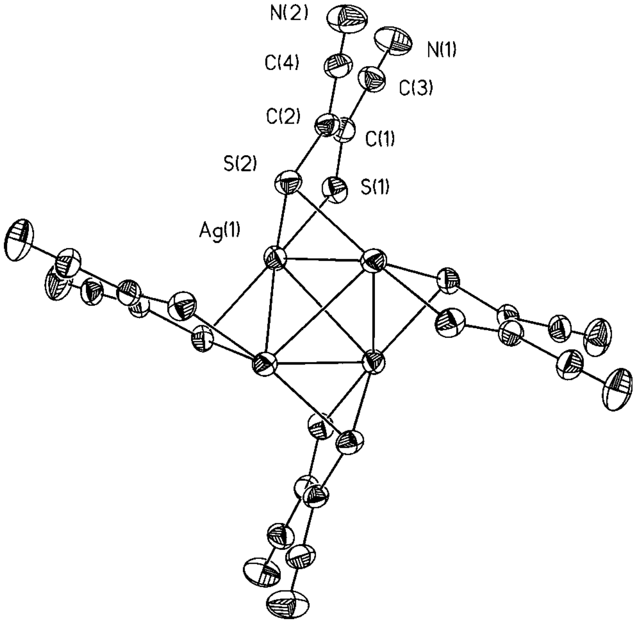

Figure 2. Displacement ellipsoid plot of the tetrahedral [Ag$_4$(mnt)$_4$]$^{4-}$ anion of [Na([2.2.2]-cryptand)]$_4$[Ag$_4$(mnt)$_4$]·0.33MeCN (**2**). The anion has crystallographically imposed symmetry $\bar{4}$.

Structure of [NBu$_4$]$_4$[Ag$_4$(S$_2$C$_2$(CN)$_2$)$_4$] (3). The crystal structure of [NBu$_4$]$_4$[Ag$_4$(mnt)$_4$] (**3**) consists of planar [Ag$_4$(mnt)$_4$]$^{4-}$ anions and well-separated [NBu$_4$]$^+$ cations. The structure contains two unique but very similar cluster units, one with no crystallographically imposed symmetry (Figure 3) and one with an imposed inversion center. The anion comprises an Ag$_4$ diamond bound by four mnt ligands. The mnt ligands have distances and angles typical for mnt.[21,22,49−52] Average bond distances and angles for selected portions of the anion are summarized in Table 3.

In this planar [Ag$_4$(mnt)$_4$]$^{4-}$ anion, each mnt ligand has two distinct S atoms, as was seen in the anion of **2**. Again, each mnt ligand has a μ_1-S bond to a Ag atom and a μ_2-S bond to that same Ag atom and to an adjacent Ag atom. The average Ag···Ag interaction is 3.0211(8) Å for adjacent Ag atoms, and the interactions are even longer between opposing Ag atoms of the diamond. The Ag−S distances in the anion of **3** are significantly longer than those in the anion of **2**.

Binding Modes in the Ag$_4$ Clusters 1, 2, and 3. Both [K([2.2.2]-cryptand)]$_4$[Ag$_4$(mns)$_4$] (**1**) and [Na([2.2.2]-cryptand)]$_4$[Ag$_4$(mnt)$_4$]·0.33MeCN (**2**) comprise encapsulated alkali-metal cations and an Ag$_4$ tetrahedron bound by four bidentate mns or mnt ligands. [NBu$_4$]$_4$[Ag$_4$(mnt)$_4$] (**3**), however, comprises [NBu$_4$]$^+$ cations and an Ag$_4$ planar diamond bound by four bidentate mnt ligands. For [Ag$_4$(mns)$_4$]$^{4-}$, tetrahedral [Ag$_4$(mnt)$_4$]$^{4-}$, and planar [Ag$_4$(mnt)$_4$]$^{4-}$, the bidentate ligands have one μ_1-Q (Q = S, Se) atom bound to one Ag atom and one μ_2-Q atom bridging the same Ag atom and an adjacent Ag atom. One Se$_4$ ring of [Ag$_4$(Se$_4$)$_4$]$^{4-}$ [5] also bridges in this fashion. Similar bridging is seen in [Ag(PPh$_3$)$_2$][Ag(PPh$_3$)$_2$(mnt)],[21,22] with one μ_1-S atom bound to a Ag atom and a μ_2-S atom bridging the two Ag(PPh$_3$)$_2$ moieties. More typically, the bridging that occurs

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Table 3. Average[a] Bond Distances (Å) and Bond Angles (deg) in Ag−mnt Complexes

	$[Ag_4(mnt)_4]^{4-}$ (**2**)[b]	$[Ag_4(mnt)_4]^{4-}$ (**3**)[c]	$[Ag(mnt)_2]^{3-}$ (**5**)[d]	$[(PPh_2)_4Ag_2(mnt)]$[e]
Ag−S	μ_1-S 2.451(1)	μ_1-S 2.485(2)	2.563(2)	μ_1-S 2.568(7)
	μ_2-S 2.467(1)	μ_2-S 2.494(2)		μ_2-S 2.566(7)
S−C	μ_1-S 1.725(5)	μ_1-S 1.721(6)	1.730(6)	1.740(17)
	μ_2-S 1.749(5)	μ_2-S 1.751(6)		
C=C	1.375(7)	1.373(8)	1.387(8)	1.35(2)
C−CN	1.438(7)	1.439(9)	1.444(8)	1.44(3)
C−N	1.146(7)	1.149(8)	1.132(7)	1.13(3)
S−Ag−S (same ligand)	88.57(4)	87.59(6)	86.51(5)	82.2(2)
Ag−S−C	μ_1-S 98.9(2)	μ_1-S 98.7(2)	98.8(2)	97.9(6)
	μ_1-S_{intra} 96.3(2)	μ_1-S_{intra} 97.0(2)		
	μ_2-S_{inter} 102.6(2)	μ_2-S_{inter} 103.7(2)		
S−C=C	127.8(4)	127.4(5)	127.9(4)	121(1)
C=C−CN	117.4(5)	118.1(5)	117.3(5)	117(2)
C−C−N	177.8(7)	178.1(9)	178.1(7)	176(2)

[a] Average values are unweighted arithmetic means with the largest esd of the series as the esd. [b] $[K([2.2.2]\text{-cryptand})]_4[Ag_4(mnt)_4]$ (**2**), this work. [c] $[NBu_4]_4[Ag_4(mnt)_4]$ (**3**), this work. [d] $[K([2.2.2]\text{-cryptand})]_3[Ag(mnt)_2]$ (**5**); this work. [e] $[(PPh_2)_4Ag_2(mnt)]$; ref 22.

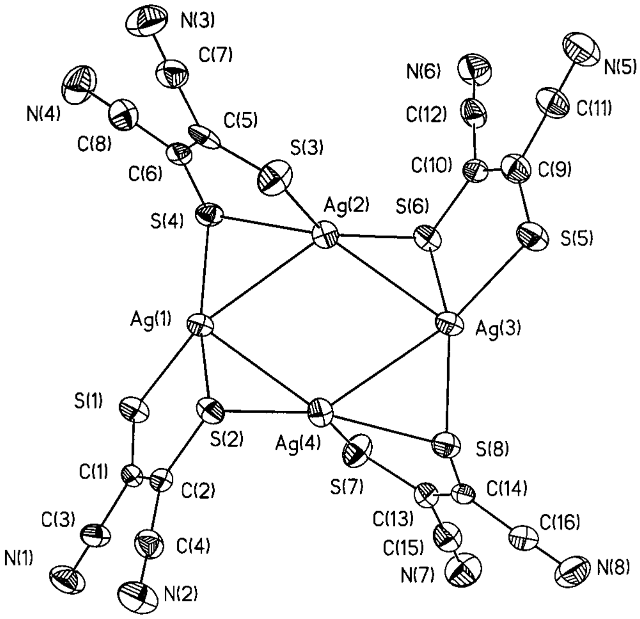

Figure 3. Displacement ellipsoid plot of the planar $[Ag_4(mnt)_4]^{4-}$ anion of $[NBu_4]_4[Ag_4(mnt)_4]$ (**3**).

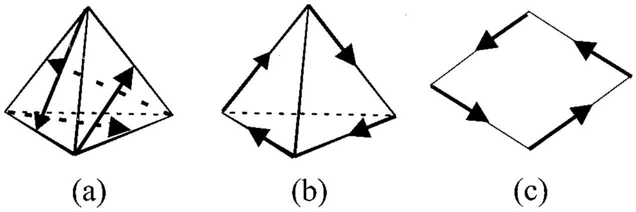

Figure 4. Representation of the Ag_4 core and binding dichalcogenate ligands in (a) $[Ag_4(i\text{-mnt})_4]^{4-}$, ref 4; (b) $[Ag_4(mns)_4]^{4-}$ (**1**) and $[Ag_4(mnt)_4]^{4-}$ (**2**), this work; and (c) $[Ag_4(mnt)_4]^{4-}$ (**3**), this work. Each arrow represents a bridging mns or mnt ligand. The tail of each arrow represents a μ_1-chalcogen, and the head is a μ_2-chalcogen.[4]

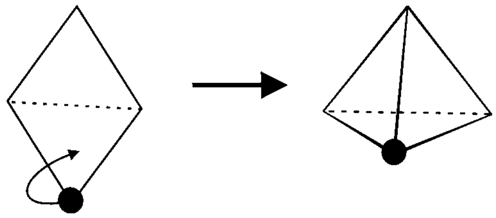

Figure 5. Conceptual transformation of the planar $[Ag_4(mnt)_4]^{4-}$ of **3** to the tetrahedral $[Ag_4(mnt)_4]^{4-}$ of **2**.

in dichalcogenates is akin to that seen in the $[Ag_4(i\text{-mnt})_4]^{4-}$-anion (*i*-mnt = isomaleonitriledithiolate, $[S_2C{=}C(CN)_2]^{2-}$).[4] This anion also has two different S environments, with one μ_1-S atom and one μ_2-S atom; however, one S atom of the *i*-mnt ligand is μ_1 to one Ag atom and the other S atom is μ_2 between two additional Ag atoms. In $[Ag_4(i\text{-mnt})_4]^{4-}$, the *i*-mnt bridges across each face of the Ag_4 core, whereas in **1** and **2** the ligands bridge along four of six of the edges of the Ag_4 core and in **3** the ligands bridge along all four edges of the Ag_4 core. The geometries of these complexes are sketched in Figure 4. There the central polygon represents the Ag_4 core, and each arrow represents a bridging bidentate dichalcogenate ligand. The tail of each arrow is a μ_1-Q atom and originates from the vertex of the Ag atom to which Q is bound. The head of each arrow is a μ_2-Q atom with the head terminus lying on the line connecting the two atoms bridged by the μ_2-Q atom.[53] The cores of $[Ag_4(i\text{-mnt})_4]^{4-}$, **1**, and **2** have idealized S_4 symmetry whereas the core of **3** has idealized C_2 symmetry. In another dithiolate-bound Ag_4 species, $[Ag_4(S_2C_2H_4(C_6H_4))_3]^{2-}$, each S atom is μ_2 and only three ligands surround the Ag_4 tetrahedron; the ligands bridge across three faces of the Ag_4 core.[3] The $[Ag_4S_6]$ species ideally has C_3 symmetry. The differences in the structures of this dithiolate and the mns/mnt species may be attributed to the differences in the bite angles of the ligands involved. The *o*-xylene-1,2-dithiolate ligand of the $[Ag_4S_6]$ species has a much larger bite angle than either the mns or mnt ligand (112.62(4)° vs 91.22(3)° or 88.07(6)°). Perhaps the smaller bite angle and lower steric hindrance (CN in lieu of m-$(CH_2)_2(C_6H_4)$) of mns/mnt allow a higher coordination number around the Ag_4 core. The structure of $[Ag_4(i\text{-mnt})_4]^{4-}$, where four *i*-mnt ligands fit around the Ag_4 center (bite angle = 92.6°),[54] is consistent with this notion. However, as noted, the *i*-mnt units possess a different binding mode from the mns and mnt units.

In both **2** and **3** the anions are completely surrounded by cations, but neither forms discrete anion or cation layers. The differences in the Ag_4 core of **2** and **3** must arise from the cations used for crystallization, as the syntheses for the two materials are otherwise identical. Cation effects on crystallization have been known for many years[55−57] and have been noted in the

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(53) For a complete description of this notation, see ref 4.

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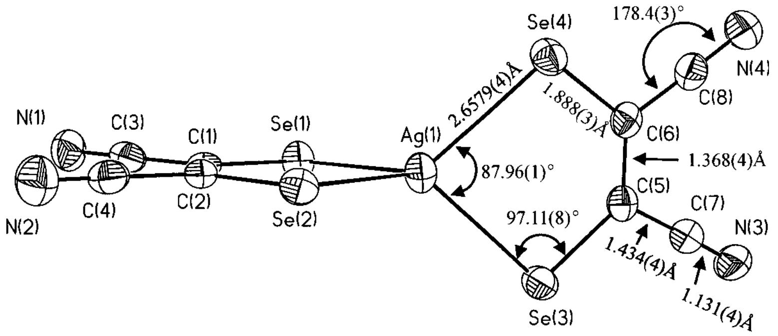

Figure 6. Displacement ellipsoid plot of the $[Ag(mns)_2]^{3-}$ anion of $[K([2.2.2]\text{-cryptand})]_3[Ag(mns)_2]\cdot 2MeCN$ (**4**) showing selected average bond distances and angles.

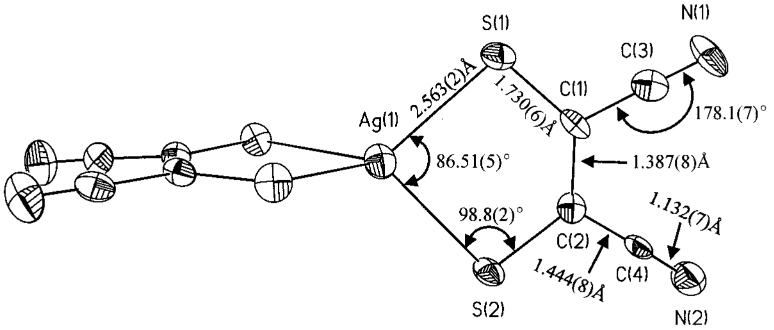

Figure 7. Displacement ellipsoid plot of the $[Ag(mnt)_2]^{3-}$ anion of $[Na([2.2.2]\text{-cryptand})]_3[Ag(mnt)_2]$ (**5**) showing selected average bond distances and angles. The anion has crystallographically imposed symmetry 2.

Ag−chalcogenide literature as well; in mixing $AgNO_3$ with K_2Se_5 and a cation in *N,N*-dimethylformamide, $[Ag_4(Se_4)_3]^{2-}$ crystallizes in the presence of $[NPr_4]^+$,[7] whereas the use of $[K(18\text{-crown-}6)]^+$ [58] or $[PPh_4]^+$ [6] affords $[Ag_4(Se_4)_{3-x}(Se_5)_x]^{2-}$, and the use of $[NMe_4]^+$ [5] or $[NEt_4]^+$ [59] instead yields polymeric structures. In the present instance the use of $[Na([2.2.2]\text{-cryptand})]^+$ affords a tetrahedral Ag_4 core (**2**) whereas the use of $[NBu_4]^+$ results in a planar diamond-shaped Ag_4 core (**3**). The conversion between the structures of the two anions may be accomplished conceptually by folding the Ag_4 diamond in half such that one Ag corner of the diamond becomes positioned above the plane to form a tetrahedron (Figure 5).

Structure of $[K([2.2.2]\text{-cryptand})]_3[Ag(Se_2C_2(CN)_2)_2]\cdot 2MeCN$ (4). The crystal structure of $[K([2.2.2]\text{-cryptand})]_3[Ag(mns)_2]\cdot 2MeCN$ (**4**) comprises well-separated cations and anions. The anion of **4** contains a nominally Ag^+ center tetrahedrally coordinated by two mns ligands. The anion, $[Ag(mns)_2]^{3-}$, has idealized D_{2d} symmetry; it is shown in Figure 6. Complex **4** is isostructural with $[K([2.2.2]\text{-cryptand})]_3[Sb(mns)_2]\cdot 2MeCN$.[33] The anion contains bond distances typical for Ag−Se complexes[5−7,33] and bond distances and angles consistent with literature values for the mns ligand.[33,34,45,46] Selected distances and angles are summarized in Table 2 and in Figure 6.

Structure of $[Na([2.2.2]\text{-cryptand})]_3[Ag(S_2C_2(CN)_2)_2]$ (5). The anion of **5** is the mnt analogue of the $[Ag(mns)_2]^{3-}$ anion seen in complex **4**. The tetrahedrally coordinated Ag center has Ag−S distances ranging from 2.549(2) to 2.577(2) Å, and the ligands have bond distances and angles typical for mnt. The anion of **5** has crystallographically imposed C_2 symmetry and is shown in Figure 7. Selected bond distances and angles are shown in Table 3 and Figure 7.

Spectroscopy. The UV−vis spectra for **1** and **4** are consistent with those of other metal−maleonitrilediselenolates.[34,46] For such complexes the dominant transition has been attributed to a ligand−metal charge transfer, by comparison with the analogous mnt complexes.[60] Therefore, the electronic transitions of complexes **1** and **4** are expected to be similar, since both metal and ligand are identical. The UV−vis spectra for **2**, **3**, and **5** are very similar to one another—**2** and **3** are nearly identical—and are consistent with those of other metal−maleonitriledithiolates.[60]

The infrared spectrum of **1** shows a ν_{CN} stretch at 2177 cm^{-1}, much like the spectrum of $[K([2.2.2]\text{-cryptand})]_3[Ag(mns)(Se_6)]$ and other metal−mns species.[33,34] In contrast, **4** shows a ν_{CN} stretch at 2168 cm^{-1} much like the lower energy peak of 2170 cm^{-1} seen in $[Na([2.2.2]\text{-cryptand})]_3[Ag(mnt)_2]$ (**5**) and $[K([2.2.2]\text{-cryptand})]_3[Sb(mns)_2]\cdot 2MeCN$.[33] Lower energy ν_{CN} stretches in $[M(mnt)_2]^{3-}$ complexes have been noted.[61] The infrared spectrum of **2** shows a ν_{CN} stretch at 2180 cm^{-1}, much like the spectrum of $[K([2.2.2]\text{-cryptand})]_4[Ag_4(mns)_4]$ (**1**), whereas **3** has shows a ν_{CN} stretch at 2196 cm^{-1} with the much higher energy value ν_{CN} peak consistent with that for other mnt complexes.[61]

Reactivity. Since acetonitrile is the source of CN in a variety of mns complexes, it is likely that formation of the mns ligand proceeds through the deprotonation of acetonitrile. Clearly base has a role, whether it be deprotonation or not, as the preparation of $[K([2.2.2]\text{-cryptand})]_4[Ag_4(mns)_4]$ (**1**) only differs from that for $[K([2.2.2]\text{-cryptand})]_3[Ag(mns)(Se_6)]$ in the quantity of base used. Substitution of KNH_2 by similar molar quantities of KOH, Et_3N, Ph_3N, or Aliquat 336 (= tricaprylmethylammonium chloride = $[NCH_3(C_8H_{17})_3]Cl$) leads only to the formation of $[K([2.2.2]\text{-cryptand})]_3[Ag(mns)(Se_6)]$, whereas the use of ex-

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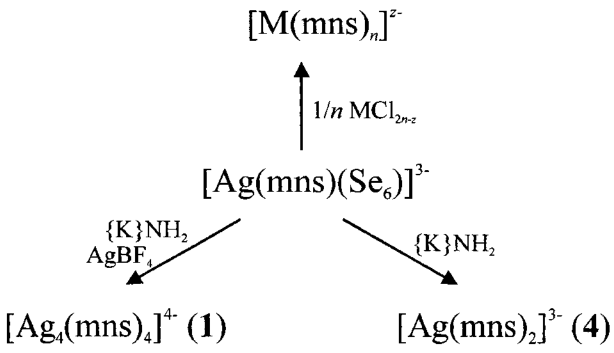

Figure 8. Summary of the reactivity of the $[Ag(mns)(Se_6)]^{3-}$ anion. {K} is [K([2.2.2]-cryptand)].

cess of these bases affords **1**. Reaction with CuCl in lieu of $AgBF_4$ under both sets of conditions led instead to $[K([2.2.2]\text{-cryptand})]_2[Cu(mns)_2]$, which contains a Cu^{2+} center and is isostructural with other known $[K([2.2.2]\text{-cryptand})]_2[M^{2+}(mns)_2]$ complexes.[34,46]

Some insight has been gained into the reactivity of $[K([2.2.2]\text{-cryptand})]_3[Ag(mns)(Se_6)]$ (Figure 8). The addition of $AgBF_4$ and $[K([2.2.2]\text{-cryptand})][NH_2]$ to $[K([2.2.2]\text{-cryptand})]_3[Ag(mns)(Se_6)]$ in acetonitrile yields $[K([2.2.2]\text{-cryptand})]_4[Ag_4(mns)_4]$ (**1**). However, the addition of just $[K([2.2.2]\text{-cryptand})][NH_2]$ to $[K([2.2.2]\text{-cryptand})]_3[Ag(mns)(Se_6)]$ in acetonitrile yields $[K([2.2.2]\text{-cryptand})]_3[Ag(mns)_2]\cdot 2MeCN$ (**4**). It is unlikely that **4** is merely an intermediate in the process to form **1**, as repeated efforts to form **1** from **4** with Ag sources have been unsuccessful. It is more likely that $[Ag(mns)(Se_6)]^{3-}$ is an intermediate in the formation of **1**; attempts to synthesize **4** directly led only to the synthesis of **1** or $[K([2.2.2]\text{-cryptand})]_3[Ag(mns)(Se_6)]$.

The substitution chemistry of $[K([2.2.2]\text{-cryptand})]_3[Ag(mns)(Se_6)]$ has also been explored. Metal chlorides can be reacted with $[K([2.2.2]\text{-cryptand})]_3[Ag(mns)(Se_6)]$ to form other metal−mns complexes, e.g., $[Ni(mns)_2]^{2-}$ from $NiCl_2$.[34,46] $[K([2.2.2]\text{-cryptand})]_3[Ag(mns)(Se_6)]$ is an effective synthon to make a variety of metal mns complexes.

Silver−mnt analogues of **1** and **4**, i.e., **2** and **5**, were prepared by direct reaction of $AgNO_3$ with $Na_2(mnt)$. As many M−mnt complexes are known and readily prepared by other methods, the substitution chemistry of **2** and **5** was not explored.

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Supporting Information Available: Crystallographic data for $[K([2.2.2]\text{-cryptand})]_4[Ag_4(mns)_4]$ (**1**), $[Na([2.2.2]\text{-cryptand})]_4[Ag_4(mns)_4]\cdot 0.33MeCN$ (**2**), $[NBu_4]_4[Ag_4(mns)_4]$ (**3**), $[K([2.2.2]\text{-cryptand})]_3[Ag(mns)_2]\cdot 2MeCN$ (**4**), $[Na([2.2.2]\text{-cryptand})]_3[Ag(mnt)_2]$ (**5**), and $[K([2.2.2]\text{-cryptand})]_2[Cu(mns)_2]$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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