salt ($Na_2[PdCl_4]$, $NiCl_2 \cdot 6H_2O$ or $CuCl_2 \cdot 2H_2O$) (1 mmol) were dissolved in methanol (40 mL). A methanolic sodium methanolate solution (6 or 5 mmol, respectively) was added dropwise. The mixture was then heated to 65 °C for 24 h, after which [PPN]Cl (2 mmol) was added. Upon the addition of water, the products **1**–**12** were obtained as crystalline solids.

Liberation of the cyclotetrapeptide from **8**: HCl gas was passed through a solution of **8** (2 mmol) in absolute MeOH (2 mL) at room temperature. After 15 min, the cyclic peptide precipitated, was washed three times with as little as possible absolute MeOH and subsequently dried. ^1H NMR (400 MHz, $CF_3COOD/CDCl_3$ 8/2): $\delta = 4.08$ (s, 4H, Gly), 3.69 (t, $^3J = 5.28$ Hz, 4H, CH_2CH_2), 2.70 (t, $^3J = 5.28$ Hz, 4H, CH_2CH_2); IR (KBr): $\tilde{\nu} = 3329.3$ (vs), 1646.1 (vs), 1548.0 cm^{-1} (vs); MS (EI): m/z (%): 256 (100) [M^+].

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[11] Single crystals of $\mathbf{1} \cdot 8H_2O \cdot 3CH_3CN$ in the form of large colorless prisms were obtained by slowly cooling a saturated solution of **1** in acetonitrile. Monoclinic, space group $P2_1/n$, $Z = 4$. $M_r = 1703.0$, crystal dimensions $0.3 \times 0.23 \times 0.2$ mm^3. The crystals were covered with perfluoroether oil, mounted on a glass fiber and centered at −80 °C; all reflections in the range $2\theta = 2$–$58°$ were measured by using a Siemens P4 diffractometer equipped with a CCD area detector. $a = 17.0397(3)$, $b = 19.2297(3)$, $c = 26.5244(4)$ Å, $\beta = 102.14(1)°$, $V = 8497(1)$ Å^3, $F(000) = 3560$, $\mu = 0.36$ mm^{-1}; $R(\text{int}) = 0.0819$, 15916 symmetry-independent reflections, 10598 observed with $I > 4\sigma(I)$; refinement: 1078 variables, $R = 0.068$, $R_w = 0.119$, GOF = 1.112, largest residual electron density: 0.74 e Å^{-3}; all calculations using the program SHELXL-97. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-100954. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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The $[Ag\{Se_2C_2(CN)_2\}(Se_6)]^{3-}$, $[Sb\{Se_2C_2(CN)_2\}_2]^{3-}$, and $[As(Se)_3(CH_2CN)]^{2-}$ Anions: Facile Formation of the Maleonitrilediselenolate (mns) Ligand, $[Se_2C_2(CN)_2]^{2-}$**

Donna M. Smith, Thomas E. Albrecht-Schmitt, and James A. Ibers*

Dedicated to Professor Achim Müller
on the occasion of his 60th birthday

Despite numerous reports[1, 2] of complexes containing the maleonitriledithiolate (mnt) ligand, $[Ni\{Se_2C_2(CN)_2\}_2]^{2-}$ is the only reported example of a complex containing the Se analogue maleonitrilediselenolate (mns).[3] Its synthesis involves several steps as well as the use of CSe_2 and dicyanoacetylene, both difficult reagents to synthesize and use.[3] We report here facile syntheses of the complexes **1** and **2**, which

$[K([2.2.2]\text{cryptand})]_3[Ag\{Se_2C_2(CN)_2\}(Se_6)]$ (**1**)

$[K([2.2.2]\text{cryptand})]_3[Sb\{Se_2C_2(CN)_2\}_2] \cdot 2CH_3CN$ (**2**)

$[K([2.2.2]\text{cryptand})]_2[As(Se)_3(CH_2CN)]$ (**3**)

contain the mns ligand, and the synthesis of **3**, as its formation is suggestive of possible mechanisms for the formation of **1** and **2**.

Reaction of $[\{IrCl(cod)\}_2]$ (cod = (*Z*,*Z*)-1,5-cyclooctadiene), $AgBF_4$, and $[K([2.2.2]\text{cryptand})]_2[Se_n]$ ($n = 3, 5, 6$) in liquid ammonia followed by extraction of the residue with CH_3CN results in the formation of **1**. The anion in **1** (Figure 1)

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[*] Prof. J. A. Ibers, D. M. Smith, T. E. Albrecht-Schmitt
Department of Chemistry
Northwestern University
2145 Sheridan Road, Evanston, IL 60208-3113 (USA)
Fax: (+1) 847-491-2976
E-mail: ibers@chem.nwu.edu

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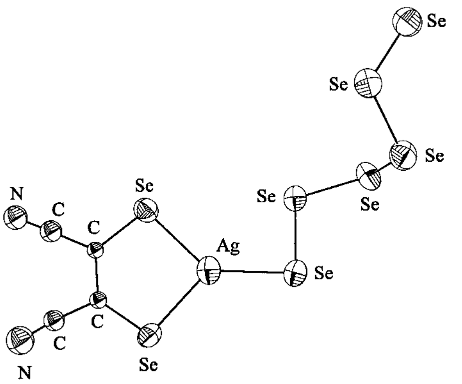

Figure 1. Structure of the anion in **1**. Here and in succeeding figures, 50% displacement ellipsoids are shown.

consists of a Ag^+ ion chelated by a $[Se_2C_2(CN)_2]^{2-}$ ligand and the environment around the Ag^+ center is highly distorted trigonal planar. The Ag–Se bond lengths, which range from 2.524(4) to 2.579(4) Å, are normal.[4] The η^1-Se_6^{2-} ligand is a rarity; chelating and bridging Q_n^{2-} ligands (Q = S, Se, Te) are far more common than η^1-polychalcogenide ligands. $KAuSe_{13}$[5] and $[K([2.2.2]cryptand)]_2[Cr(CO)_5(Te_3)] \cdot 0.5\,en$[6] (en = ethylenediamine) are among the few examples of compounds containing an η^1-Q_n^{2-} ligand. The Se–Se bond lengths in the Se_6^{2-} ligand range, as expected, from 2.313(5) to 2.340(5) Å; the bond length between the two terminal Se atoms is slightly shorter (2.284(5) Å). A similar shortening of the terminal ends of Se_n^{2-} ligands is observed in the structures of virtually all alkali polyselenide compounds.[7] Upon dissolution of **1** in CH_3CN, the $[Ag\{Se_2C_2(CN)_2\}(Se_6)]^{3-}$ anion disproportionates or decomposes; seven ^{77}Se NMR resonances are expected, but fourteen are observed.[8]

The reaction of K, Sb_2Se_3, and Se in the presence of [2.2.2]cryptand in liquid ammonia followed by extraction in CH_3CN results in the isolation of **2**, which features well-separated cations and anions. In the anion of **2** (Figure 2), the central Sb atom is coordinated to two planar mns ligands in a distorted tetrahedron with Se-Sb-Se bond angles ranging from 86.47(7) to 129.27(8)°; the dihedral angle between the two planes is 84.0°. The Sb–Se bond lengths (av 2.654(2) Å) are slightly longer than those observed for $[K([2.2.2]cryptand)]_2[Sb_2^{III}Se_4]$ (av 2.615(1) Å),[9] as would be expected for a reduced charge on the Sb atom. The "noninnocence" of the mnt ligand is well known;[1, 2] one expects the same behavior for the mns ligand. Thus, the Sb atom in **2** only formally has the unusual +I oxidation state. However, $[NEt_4][Sb^{III}(mnt)_2]$ has been synthesized from $Na_2(mnt)$ and SbX_3 (X = Cl, Br, I), although it has not been structurally characterized.[10] In general, the mns ligand resembles the much better known mnt ligand.[1, 2] The Se–C bond lengths are 1.81(2) and 1.89(2) Å in **1**, range from 1.857(17) to 1.874(16) Å in **2**, and are 1.873(4) and 1.878(4) Å in $[PPh_4]_2[Ni\{Se_2C_2(CN)_2\}_2]$.[3]

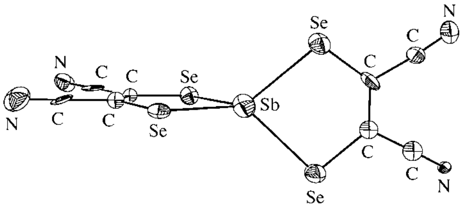

Figure 2. Structure of the anion in **2**.

The reaction of K, As, and Se in the presence of [2.2.2]cryptand followed by extraction in CH_3CN affords **3**. The structure of **3** also features well-separated cations and anions. In the anion of **3** (Figure 3), the central As^V atom is coordinated to three terminal Se^{2-} ligands and one terminal CH_2CN^- ligand in a distorted tetrahedron with C-As-Se bond angles ranging from 99.3(2) to 105.2(2)° and Se-As-Se bond angles ranging from 114.91(6) to 115.46(6)°. The As–Se (2.275(2), 2.280(2), and 2.284(2) Å), As–C (1.973(6) Å), C–C (1.392(12) Å), and C≡N (1.156(10) Å) bond lengths are normal. Structurally characterized main-group compounds containing the CH_2CN^- ligand are rare.[11, 12]

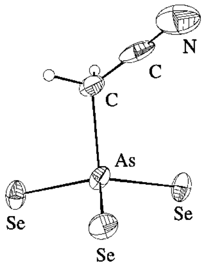

Figure 3. Structure of the anion in **3**.

The syntheses of an Ag^I and an Sb^I complex of the mns ligand (**1** and **2**, respectively) are unexpected and remarkable. At first glance, there is little in common between the two reactions, save for the use of liquid ammonia, potassium, [2.2.2]cryptand, and CH_3CN. Clearly, the source of the cyano groups in the mns ligand is CH_3CN. This strongly suggests that deprotonation of CH_3CN is an important aspect of these reactions, especially since the mono-deprotonated carbanion CH_2CN^- in **3** is attached to the As^V center through an As–C bond.

Acetonitrile reacts with strong bases in one of two competing pathways.[13] The first pathway [Eq. (1)] involves mono-deprotonation of CH_3CN ($pK_a = 31$) to form the mesomeric-stabilized anion CH_2CN^-; the second [Eq. (2)] involves the addition of the base to the carbon atom of the cyano group. The reaction pathway can be controlled by the choice of base and solvent. Pathway (1) is generally favored with bases with high ionic character in polar solvents. In the present instances, what are the bases? The reaction to form the Ag(mns) complex **1** does not occur in the absence of $[\{IrCl(cod)\}_2]$, which presumably generates the required base; it is known that the similar Ir complex $[\{IrCl(coe)_2\}_2]$ (coe = cyclooctene) reacts with liquid ammonia to form stable, amide-bridged, basic dimers.[14–16] Potassium will react catalytically with ammonia to form the stable basic amide KNH_2,[17] which is presumably the base required in the syntheses of **2** and **3**. The reaction of KNH_2 with CH_3CN can proceed by either pathway. However, it is assumed that pathway (1) dominates since subsequent acylation of the resulting CH_2CN^- anion can be achieved in high yield.[18]

$$CH_3CN + B^- \rightarrow HB + [{}^-CH_2{-}C{\equiv}N \leftrightarrow CH_2{=}C{=}N^-] \qquad (1)$$

$$CH_3CN + B^- \rightarrow CH_3C(B){=}N^- \qquad (2)$$

Given the formation of the CH_2CN^- species in these reactions, a variety of ensuing reactions are possible. Clearly, in the synthesis of **3** CH_2CN^- attaches itself to the highly nucleophilic As^V center. Reactions of ACH_2CN ($A^+[CH_2CN^-]$, where A = alkali or alkaline earth metal) are similar to those of Grignard reagents; the anion is nucleophilic and acts as a weak base.[19] ACH_2CN can react "head-to-tail" with the cyano group of another CH_3CN molecule in a manner analogous to the Claisen condensation of esters.[13] Given the ultimate formation of the mns ligand in the present instances, such a reaction is unlikely. "Head-to-head" coupling of two CH_2CN^- species to form a conjugated nitrile is much more attractive, especially if further deprotonation then occurs to afford dicyanoacetylene. This activated alkyne could readily react with a polyselenometalate to form the metal-bound mns ligand in the manner that dimethylacetylenedicarboxylate does to form the metal-bound $[Q_2C_2\{C(O)OCH_3\}_2]^{2-}$ species.[20–22]

It is also possible that the CH_2CN^- species attacks a free selenium source or a polyselenometalate to form a derivatized cyanoaldehyde. Cyanoselenoaldehyde, while too reactive to be isolated, has been trapped with the use of conjugated dienes.[23, 24] Two adjacent selenoaldehydes could also couple by a condensation reaction. Alternatively, if CH_2CN^- attacked a free selenide source, the mns ligand could conceivably form in situ before reaction with the metal center, as observed in reactions with the mnt ligand.

Experimental Section

1: Approximately 10 mL of NH_3 were condensed into a Schlenk flask containing $[\{IrCl(cod)\}_2]$ (134 mg, 0.2 mmol) and $AgBF_4$ (80 mg, 0.41 mmol), and 50 mL of NH_3 were condensed into another flask containing K_2Se (126 mg, 0.8 mmol), Se (316 mg, 4 mmol), and [2.2.2]cryptand (509 mg, 1.8 mmol). Both reaction mixtures were stirred for 1 h at −78 °C, and then the first solution was transfered with a cannula into the second. The reaction mixture was allowed to warm from −78 °C to 24 °C over 48 h. The dark residue was extracted into CH_3CN; the solution was stirred and filtered. The filtrate was layered with Et_2O and stored at 4 °C. Brown plates of **1** were isolated after two weeks in 16 % yield (based on Ag). IR (KBr): $\tilde{\nu} = 2176\ cm^{-1}$ (C≡N). Crystal structure analysis:[25] brown plates, 0.023 × 0.108 × 0.347 mm, triclinic, C_i^1 ($P\bar{1}$), $Z = 2$, $a = 10.407(2)$, $b = 11.285(2)$, $c = 35.190(7)$ Å, $\alpha = 84.60(3)$, $\beta = 87.72(3)$, $\gamma = 77.96(3)°$, $V = 4023(1)$ Å^3. Of 6180 reflections measured ($2\theta_{max} = 80.2°$), 4788 were unique ($R_{int} = 0.12$) and included in the refinement, $\mu = 81\ cm^{-1}$, min./max. transmission = 0.389/0.802, 446 parameters, $R_1 = 0.095$ for reflections with $F_o^2 > 2\sigma(F_o^2)$; $wR_2 = 0.195$; residual electron density = 1.05 e Å^{-3}

2: NH_3 (30 mL) was condensed into a flask charged with [2.2.2]cryptand (189 mg, 0.5 mmol) and K (40 mg, 1 mmol). The blue solution turned colorless within 10 min. More K (40 mg, 1 mmol) was added to regain the blue color. After the solution was stirred for 30 min, Sb_2Se_3 (120 mg, 0.25 mmol) and Se (77 mg, 1 mmol) were added. The reaction mixture was allowed to warm from −78 °C to 24 °C over 48 h. The resulting residue was extracted into CH_3CN (25 mL) to afford a dark red-orange solution and an uncharacterized powder. Filtration of the solution followed by layering with Et_2O gave long red needles of **2** in 13 % yield (based on Sb). IR (KBr): $\tilde{\nu} = 2170\ cm^{-1}$ (C≡N); ^{77}Se NMR (CH_3CN): $\delta = -296$. Crystal structure analysis:[25] red needles, 0.065 × 0.086 × 0.449 mm, monoclinic, C_{2h}^5 ($P2_1/c$), $Z = 4$, $a = 13.945(3)$, $b = 21.764(4)$, $c = 28.283(6)$ Å, $\beta = 98.12(3)°$, $V = 8498(3)$ Å^3. Of 9054 reflections measured ($2\theta_{max} = 98.58°$), 6574 were unique ($R_{int} = 0.072$), $\mu = 64\ cm^{-1}$, min./max. transmission = 0.479/0.687, 897 parameters, $R_1 = 0.079$, $wR_2 = 0.160$, residual electron density = 0.780 e Å^{-3}.

3: NH_3 (30 mL) was condensed into a flask charged with [2.2.2]cryptand (189 mg, 0.5 mmol) and K (40 mg, 1 mmol). After the solution was stirred for 30 minutes at −78 °C, a mixture of As (20 mg, 0.27 mmol) and Se (42 mg, 0.53 mmol) was added. The reaction mixture was allowed to warm from −78 °C to 24 °C over 48 h. The residue was extracted into CH_3CN (25 mL) to afford an orange solution and residual starting material. Filtration of the solution followed by layering with Et_2O afforded yellow blocks of **3** in 23 % yield (based on Se). ^{77}Se NMR (CH_3CN): $\delta = 602$. Crystal structure analysis:[25] yellow blocks, 0.057 × 0.170 × 0.244 mm, triclinic, C_i^1 ($P\bar{1}$), $Z = 2$, $a = 11.701(2)$, $b = 12.216(9)$, $c = 19.703(4)$ Å, $\alpha = 105.01(4)$, $\beta = 92.93(3)$, $\gamma = 106.09(6)°$, $V = 2591(2)$ Å^3. Of 9058 reflections measured ($2\theta_{max} = 96.04°$), 4760 were unique ($R_{int} = 0.042$), $\mu = 52\ cm^{-1}$, min./max. transmission = 0.794/0.858, 534 parameters, $R_1 = 0.043$, $wR_2 = 0.097$, residual electron density = 0.552 e Å^{-3}.

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