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[27] See for example: a) $[Cp_2Zr(CPh_2H)_2]$: Zr–C 2.379(6), 2.396(6) Å (J. L. Atwood, G. K. Barker, J. Holton, W. E. Hunter, M. F. Lappert, R. Pearce, *J. Am. Chem. Soc.* **1977**, *99*, 6645–6652); b) $[Cp_2Zr(CH(CH_3)($6-ethylpyrid-2-yl$)Cl]$: Zr–C 2.421(4) Å (A. S. Guram, D. C. Swenson, R. F. Jordan, *J. Am. Chem. Soc.* **1992**, *114*, 8991–8996); c) $[\{Cp_2Zr(CH(Me)CH_2CH_2O)\}_2]$: Zr–C 2.382(11) Å (H. Takaya, M. Yamakawa, K. Mashima, *J. Chem. Soc. Chem. Commun.* **1983**, 1283–1284).

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[30] Preparation of **2**. All experimental manipulations were performed under rigorously anaerobic conditions using Schlenk techniques or an argon-filled glovebox. To a pale yellow-brown solution of $[Zr(CH_2C_6H_5)_4]$[17] (0.2 g, 0.44 mmol) in toluene (10 mL) at room temperature was added solid **1** (0.273 g, 0.88 mmol). The reaction mixture was stirred for four days, then concentrated to half of the original volume and finally left at room temperature. After two days a pale brown crystalline solid deposited which was isolated by filtration and washed with few mL of hexane (0.09 g). A second fraction of product (0.02 g) was obtained after cooling the filtrate at −15 °C for 8 h. (Total Yield: 0.11 g, 0.155 mmol, 35.4 %). IR (Nujol mull): $\tilde{\nu}$1457w, 1381s, 1287m, 1278m, 1243s, 1068s, 1038s, 940m, 924s, 897w, 838s, 765s, 751s, 725s, 712w, 685w, 670m, 645m, 615m; ^{1}H NMR (400.1 MHz, C_6D_6, 298 K): $\delta = 1.58$ (t, $^2J_{P,H} = 6$ Hz, 24 H), 0.39 (s, 36 H; $SiMe_3$); $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 298 K): $\delta = 77.8$ (t, $^1J_{P,C} =$ 188 Hz, 2 C; PCP), 25.4 (t, $J_{P,C} = 32$ Hz, 8 C; P-CH_3), 4.6 (s, 12 C, CH_3-$SiMe_3$); $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6, 298 K): $\delta = 2.9$ (4 P); elemental analysis (%) calcd for $C_{22}H_{60}N_4P_4Si_4Zr$: C 37.31, H 8.54, N 7.91; found: C 37.61, H 8.48, N, 7.64.

[31] Crystal structure analysis for **2**: tetragonal, $P4_2/n$ (no. 86), $a =$ 13.5050(4), $c = 10.5817(5)$ Å, $V = 1929.9(12)$ Å^3, $Z = 2$,. $\rho_{calcd} =$ 1.219 g cm^{-3}, $\mu = 0.593$ mm^{-1} ($Mo_{K\alpha}$, $\lambda = 0.71073$ Å), $T = 193$ K; the structure was solved by direct methods and refined by full-matrix least-squares procedures: $R_1 = 0.0248$ and $wR_2 = 0.0738$ for 1982 reflections with $F_o^2 > 2\sigma(F_o^2)$ and all data respectively. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-171868. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Syntheses and Structures of Niobium Copper Chalcogenido Clusters: $[Cu_4Nb_6Se_{12}O(PMe_3)_{10}][Cu_4NbSe_4Cl_2(PMe_3)_4]\cdot 1.5\,DMF$, $[Cu_4Nb_2Se_6(PMe_3)_8]$, $(NEt_4)[Cu_6Nb_2S_6Cl_5(PEt_3)_6]$, and $[Cu_6NbTe_3(Te_2)_2(PEt_3)_6][CuCl_2]$[**]

Alexander Lorenz and Dieter Fenske[*]

Chalcogenometalates of molybdenum, tungsten, and vanadium, in particular the tetrachalcogenometalates $[ME_4]^{n-}$ (M = Mo, W, $n = 2$, E = S, Se; M = V, $n = 3$, E = S), have been successfully used as complexing ligands for the synthesis of heterodimetallic clusters, since Müller et al. first synthesized $(PPh_4)_2[Ni(WS_4)_2]$[1] in 1971.[2] As a result of the biochemical[3] and industrial[4] interest in the coordination chemistry of chalcogenomolybdates, -tungstenates, and -vanadates, these compounds have been extensively researched, and a multitude of M-M′-E clusters have been synthesized (M = V, Mo, W, M′ = Fe, Cu, Ag, Au, etc., E = S, Se). In contrast, the coordination chemistry of chalcogenoniobates or -tantalates has remained relatively unexplored. Recently, we reported on the reactivity of soluble chalcogenoniobates towards coinage metal salts in which a series of novel Nb–Cu or Nb–Au chalcogenide clusters were prepared by reactions of $Li_3[NbS_4]\cdot 4\,CH_3CN$,[5a,b] $(NEt_4)_4[Nb_6S_{17}]\cdot 3\,CH_3CN$,[5c] and $(NEt_4)_2[NbE_3(E'tBu)]$ (E = S, Se; E′ = S;[5d,e] E = E′ = Se[6]) with copper or gold salts in the presence of phosphane ligands.[6] For example, polynuclear complexes containing a $[Cu_2Nb_2E_4]$ heterocubane unit, such as $[Cu_2Nb_2E_4Cl_2(PMe_3)_6]\cdot DMF$ **I** (E = S, Se, DMF = *N*,*N*-dimethylformamide) with two terminal chloro ligands, can be isolated. Initial attempts to link the cluster units in **I** through bridging Se atoms by the use of $(Me_3Si)_2Se$ (and accompanying loss of Me_3SiCl) have not yet produced crystalline reaction products. However, Wu et al. reported the successful in situ condensation of cluster complexes.[7] Following this concept, we allowed $(NEt_4)_2[NbSe_3(SetBu)]$ and $[CuCl(PMe_3)_3]$ to react in DMF[8] and isolated two novel Nb–Cu cluster compounds, the nature of which was dependent on the amount of $(Me_3Si)_2Se$ added during the reaction. The molecular structures of the ionic compound **1** and the neutral cluster **2** (Scheme 1) were determined by X-ray diffraction.[9] Compound **2** might have been formed by a reaction of intermediate $[Cu_2Nb_2Se_4Cl_2(PMe_3)_6]$ with $[CuCl(PMe_3)_3]$ and $(Me_3Si)_2Se$.

Compound **1** crystallizes in the orthorhombic space group *Pbcn* with eight formula units per unit cell. The ionic compound contains two heterodimetallic Nb-Cu-Se cluster ions, $[Cu_4NbSe_4Cl_2(PMe_3)_4]^{2-}$ and $[Cu_4Nb_6Se_{12}O(PMe_3)_{10}]^{2+}$. The anion is formed by a $[NbSe_4]$ tetrahedron, in which four

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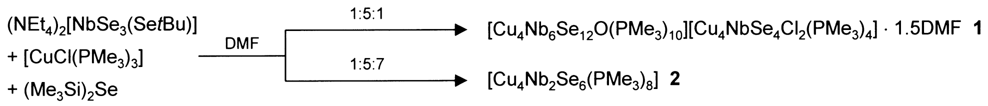
[**] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.



Scheme 1. Syntheses of the Nb–Cu clusters **1** and **2**.

of the six edges are occupied by two [CuCl] and two $[Cu(PMe_3)_2]^+$ units (Figure 1, top). The copper atoms Cu5–Cu8 surround Nb7 in a slightly distorted square-planar geometry (Cu-Nb-Cu angles: 88.48(7)–91.69(7) and 175.04(8)–175.74(8)°). Cu7 and Cu8 are coordinated in a trigonal-planar fashion, each bound to one Cl^- and two Se^{2-} ligands. In contrast, Cu5 and Cu6 show a distorted tetrahedral coordination geometry, each bound to two Se^{2-} ligands and two P atoms of the PMe_3 ligands. All Se atoms of the $[NbSe_4]$ unit act as μ_3-bridging selenido ligands; Nb–Se distances are 243.7(2)–244.6(2) pm. As expected, Cu–Se bonds involving four-coordinate Cu atoms are significantly longer (247.3(3)–249.2(3) pm) than those involving three-coordinate Cu atoms (238.6(2)–238.9(2) pm). The same observation is made for the Nb–Cu distances that vary even more distinctly (292.0(2) (Nb7–Cu5) or 291.4(2) (Nb7–Cu6) and 275.6(2) (Nb7–Cu7) or 275.8(2) pm (Nb7–Cu8)). Several Nb-Cu-E clusters were synthesized so far that contain tetrahedral $[NbE_4]$ units with two, three, four, five, or six edges of the tetrahedron occupied by copper atoms.[6] The anion in **1** is closely related to these compounds and bridges a gap in the series of these Nb–Cu chalcogenide clusters. A novel molecular cationic structure is observed in **1** (Figure 1, bottom). The metal–chalcogen framework is formed by three concentric deltahedra of either niobium, selenium, or copper atoms, which surround a central O^{2-} ion (Figure 2). The first sphere is represented by a slightly distorted Nb_6 octahedron (Nb1–Nb6) at a mean distance of 220.9 pm from O1. The Nb–Nb distances lie between 310.1(2) and 315.8(2) pm. The second sphere consists of twelve Se atoms (Se1–Se12) that form a cubooctahedron. At distances between 362.1(5) and 366.3(5) pm from O1, the Se_{12} cubooctahedron is on average 65 % further away from O1 than the Nb_6 octahedron. Another 10 % out from the center, at 387.3(5)–388.8(8) pm from O1, four copper atoms occupy the corners of a tetrahedron (Cu1–Cu4). The latter cap four of the eight triangular faces of the Se_{12} cubooctahedron. A niobium atom is positioned at each of the six edges of the tetrahedron (Cu-Nb-Cu 175.88(6)–179.01(6)°). Alternatively, the cationic substructure of **1** can be described as an oxygen-centered Nb_6 octahedron, in which four of its eight triangular faces are alternately capped by nearly tetrahedral $[Se_3Cu(PMe_3)]$ units. All copper and niobium atoms bind to a terminal PMe_3 ligand. Whereas the copper atoms are four-coordinate, the niobium atoms are six-coordinate. Four Se

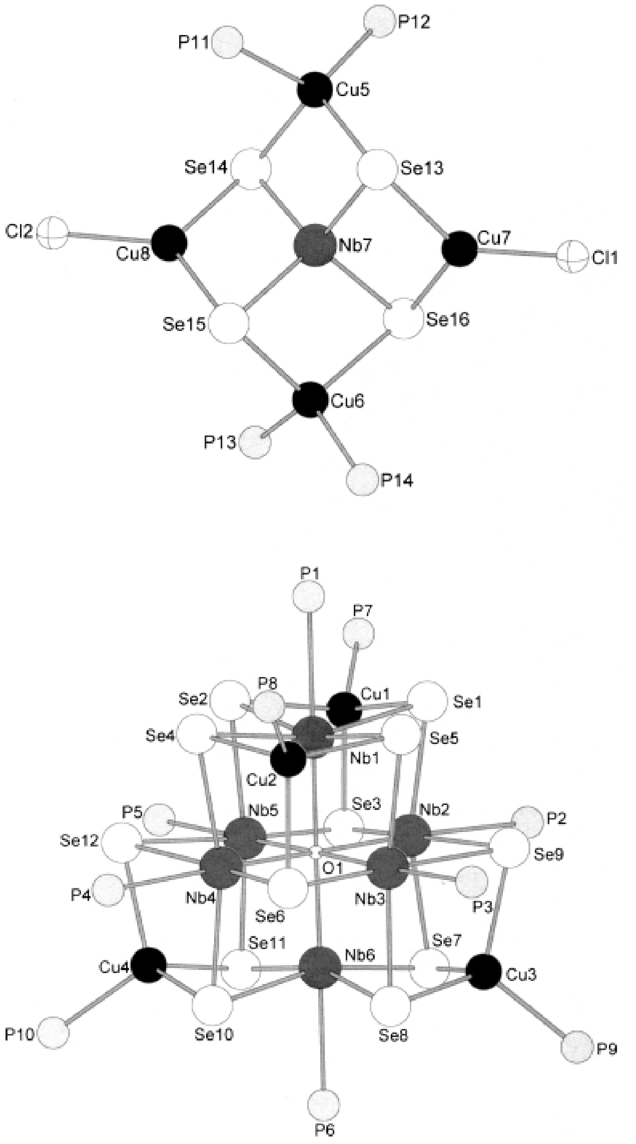


Figure 1. Top: Molecular structure of the $[Cu_4NbSe_4Cl_2(PMe_3)_4]^{2-}$ cluster anion in **1** in the crystal. Selected distance ranges [pm] (CN = coordination number): Nb-Cu(CN 3) 275.6(2)–275.8(2), Nb-Cu(CN 4) 291.4(2)–292.0(2), Nb-Se 243.7(2)–244.6(2), Cu(CN 3)-Se 238.6(2)–238.9(2), Cu(CN 4)-Se 247.3(3)–249.2(3), Cu-P 225.2(6)–226.0(5), Cu-Cl 218.6(4)–218.7(4). Bottom: Molecular structure of the $[Cu_4Nb_6Se_{12}O(PMe_3)_{10}]^{2+}$ cluster cation in **1** in the crystal. Selected distance ranges [pm]: Nb-Nb 310.1(2)–315.8(2), Nb-Cu 302.8(2)–330.0(2), Nb-Se 258.4(2)–264.1(2), Nb-O 219.8(10)–221.9(10), Nb-P 265.4(4)–268.2(4), Cu-Se 237.0(2)–246.1(2), Cu-P 223.1(4)–224.4(4).

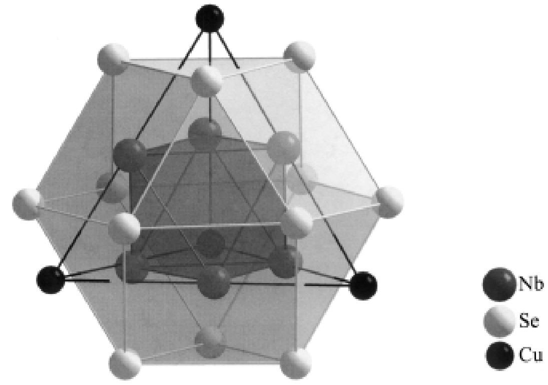


Figure 2. Illustration of the packing of three concentric polyhedra (Nb_6 octahedron, Se_{12} cubooctahedron, Cu_4 tetrahedron) in the cluster cation in **1**.

atoms, the interstitial oxygen atom O1, and the P atom of the respective PMe_3 ligand surround each Nb center in a distorted octahedral geometry. All twelve Se atoms act as μ_3 bridges. Cu–Se bonds (237.0(2) – 246.1(2) pm) are shorter, and Nb–Se bonds (258.4(4) – 264.1(2) pm) are significantly longer than the respective bonds in the anionic substructure of **1** (Cu–Se 247.3(3) – 249.2(3) pm; Nb–Se 243.7(2) – 244.6(2) pm). All Nb–Cu distances lie between 302.8(2) and 330.0(2) pm. They are longer than those in the molecular structures of the anion or in any Nb-Cu-Se cluster reported so far.

Compound **2** crystallizes in the monoclinic space group *C2/c* with four molecules per unit cell. The complex possesses an inversion center and shows a close structural relationship to the cluster observed in **I**. Two of the $[Cu_2Nb_2E_4]$ heterocubane units found in **I** are formally condensed sharing an Nb_2E_2 face (Figure 3). The coordination numbers of Cu as well as those of Nb atoms remain unchanged during the formal condensation. Se atoms of the Nb_2Se_2 face are now μ_4-bridging ligands (Se1), and therefore show significantly longer distances to neighboring Nb atoms (266.3(5), 264.5(6) pm) than μ_3-bridging Se atoms Se2 and Se3 (254.8(7) and 256.6(8) pm, respectively). However, the bridging mode of the Se atoms has no mentionable effect on the observed Cu–Se bond lengths. The Cu-μ_3-Se bonds (247.9(6) – 251.2(7) pm) are on average 4.4 pm longer than the Cu-μ_4-Se bonds (243.4(9), 246.5(8) pm). This is a result of the significant shortening of the Cu-μ_4-Se bonds perpendicular to the Cu_2E_2 and Nb_2E_2 faces, which has been already observed in **I**. The Nb–Nb distance in **2** (301.9(7) pm) is significantly longer than that observed in **I** (293.6(3) pm). However, although the heterocubane unit is extended in **2** compared to that in **I**, the Cu–Cu distance is 25.8 pm shorter (261.8(7) pm). Under the assumption of a formal oxidation state of +I for the copper centers in the anion in **1** and in **2**, all Nb atoms obtain the formal charge +IV. Preliminary experiments show paramagnetic behavior for **1** and **2**, as expected. Further investigations on the magnetic properties are in progress.

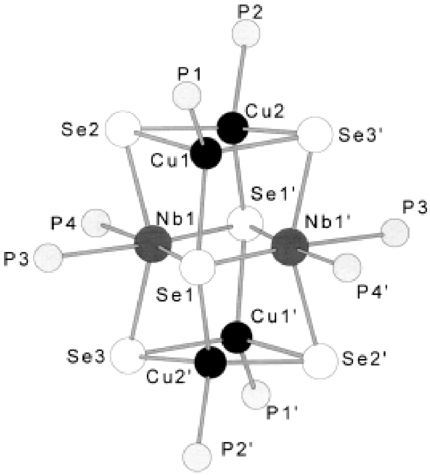
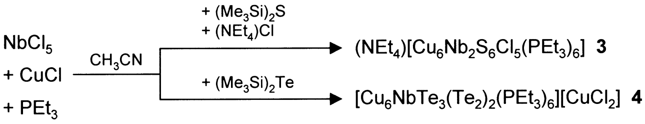


Figure 3. Molecular structure of $[Cu_4Nb_2Se_6(PMe_3)_8]$ (**2**) in the crystal. Selected distance ranges [pm]: Nb-Nb 301.9(7), Nb-Cu 303.0(8) – 305.7(7), Cu-Cu 261.8(7), Nb-μ_3-Se 254.8(7) – 256.6(8), Nb-μ_4-Se 266.3(5) – 264.5(6), Nb-P 269.7(12) – 271.4(11), Cu-μ_3-Se 247.9(6) – 251.2(7), Cu-μ_4-Se 243.4(9) – 246.5(8), Cu-P 224.3(14) – 224.5(16).

The Nb–Cu chalcogenide clusters can also be synthesized directly by the reaction of $NbCl_5$ with CuCl, PEt_3, and $(Me_3Si)_2E$ (E = S, Te). Orange crystals of the ionic compound **3** are formed upon addition of $(NEt_4)Cl$ in CH_3CN (Scheme 2). However, the analogous reaction of $NbCl_5$ with CuCl, PEt_3, and $(Me_3Si)_2Te$ yields an Nb-Cu-Te cluster **4**. Both compounds were characterized by X-ray diffraction.[9]



Scheme 2. Syntheses of the Nb – Cu clusters **3** and **4**.

Compound **3** crystallizes in the orthorhombic space group *Pnma* with four formular units per unit cell. The cluster anion (Figure 4) has a mirror plane and is formed by two $[Cu_3NbS_3Cl]$ heterocubane units that are linked by three μ_2-bridging chlorine ligands (Cl2, Cl3, Cl4). Such a heterocubane unit was already observed in $[Cu_3NbS_3Cl_2(PPh_3)_3(dmf)_2]\cdot 1.5\,DMF$ (**II**).[6] Interatomic distances within the $[Cu_3NbS_3Cl]$ fragment are very similar to those in **II**. However, the bonds between the Cu atoms (Cu1 – Cu3) and the μ_3-Cl ligand (Cl1) are about 8 pm longer in **3** (av 272.4 pm). Additionally, as expected, the bonds from Nb1 to the μ_2-bridging Cl ligands (263.9(2) – 265.0(3) pm) are longer than the Nb–Cl bonds involving terminal Cl ligands in **II** (253.4(2) pm). In **3**, the Nb atoms have the formal charge +V, and the Nb–Nb distance is very large (377.5(2) pm). Several compounds have already been reported that possess two μ_2-Cl-bridged Nb atoms. However, most of them are complexes of Nb^{+III} featuring a metal – metal bond between the Nb centers. Accordingly, one observes significantly shorter Nb–Nb distances (270.8(3) pm) or Nb–μ_2-Cl distances (248.2(5) – 252.4(5) pm) in $(NnBu_4)[Nb_2Cl_7(PEt_3)_2]$.[10]

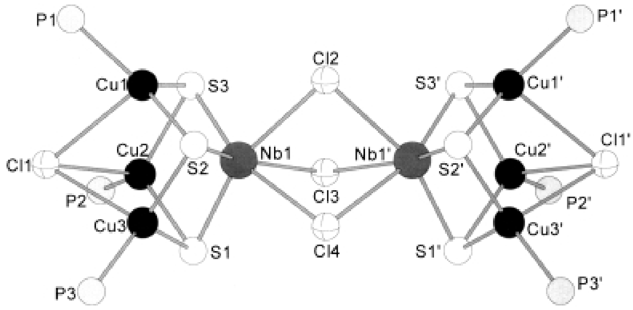


Figure 4. Molecular structure of the $[Cu_6Nb_2S_6Cl_5(PEt_3)_6]^-$ cluster anion in **3** in the crystal. Selected distance ranges [pm]: Nb-Nb 377.5(2), Nb-Cu 272.9(1) – 275.7(2), Cu-Cu 303.8(2) – 305.8(2), Nb-S 233.6(2) – 234.5(3), Nb-Cl 263.9(2) – 265.0(3), Cu-S 224.3(3) – 225.7(3), Cu-P 219.6(3) – 220.7(3), Cu-Cl 263.5(3) – 280.7(3).

The ionic compound **4** crystallizes in the triclinic space group $P\bar{1}$ with two formular units in the unit cell. The cation is formed by a distorted, Nb-centered (Nb1) Cu_6 trigonal prism (Figure 5). One of the three edges that define the rectangular

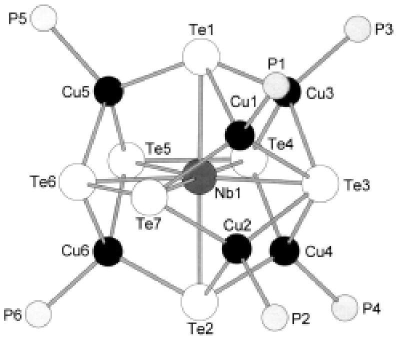


Figure 5. Molecular structure of the $[Cu_6NbTe_3(Te_2)_2(PEt_3)_6]^+$ cluster cation in **4** in the crystal. Selected distance ranges [pm]: Nb-Cu 280.7(4) – 285.1(3), Cu-Cu 260.3(3) – 423.9(4), Te-Te(Te_2^{2-}) 274.9(2) – 279.6(2), Nb-Te 282.3(3) – 351.4(4), Cu-Te 251.4(2) – 274.1(2), Cu-P 221.2(5) – 223.8(5).

faces of the prism is much shorter (Cu1–Cu2 260.3(3) pm) than the other two (365.8(4) and 367.4(4) pm, respectively). The Nb–Cu distances vary slightly (280.7(4) – 285.1(3) pm) and are among the longest observed in Nb–Cu chalcogenide compounds so far. The two triangular faces and one of the distorted rectangular faces of the Cu_6 prism are each capped by a tellurido ligand (Te1, Te2, Te3), the two remaining Cu_4 faces are each capped by a ditellurido ligand (Te4, Te5; Te6, Te7). The atoms Te3 – Te7 describe the equatorial plane of a highly distorted pentagonal Te_7 bipyramid, Te1 and Te2 form the respective vertices (Te $\cdots$ Te 274.9(2) – 462.8(5) pm). The Te atoms of the Te_2^{2-} units are bonded to two Cu atoms and the central Nb atom (Nb1), but show different Nb–Te bond lengths. The Nb1–Te5 bond (290.9(3) pm) is about 8 pm longer than the Nb1–Te4 bond (282.3(3) pm); the difference between the Nb1–Te6 and the Nb1–Te7 bond is even greater (Nb1–Te6 298.1(2), Nb1–Te7 351.4(4) pm). Te1 and Te2 are μ_4-bridging ligands and bind to three Cu atoms and the Nb1 atom. In contrast, Te3 acts as μ_5-bridge between four Cu centers and Nb1. In **4**, Nb1 has the coordination number 6+1. The smaller Nb–Te bond lengths lie within the range of the values for $K_6[Nb_4OTe_4(CN)_{12}] \cdot K_2CO_3 \cdot KOH \cdot 8H_2O$[11] (283.2(2) – 285.9(1) pm) and $[Nb_2S(Te_2)(Et_2NCS_2)_4]$[12] (284.2(3) – 285.4(3) pm). The atoms Cu1 – Cu6 each bind to three Te ligands and the P atom of one PEt_3 ligand, and are thus nearly tetrahedrally surrounded. The Cu–Te distances cover a wide range (251.4(2) – 274.1(2) pm). This was also observed in other tellurium-bridged compounds such as $[Cu_{23}Te_{13}(PiPr_3)_{19}]$[13] (253 and 284 pm). A nearly linear coordination geometry around Cu occurs in the counterion $[CuCl_2]^-$ (Cl-Cu-Cl 177.9(3)°). The formation of $[CuCl_2]^-$ ions was reported to occur likewise in the synthesis of other heterodimetallic clusters such as $(PPh_4)_3[MoOS_3(CuCl)_3]$-$[CuCl_2]$.[14]

As in **3**, formal oxidation states of +I (Cu) and +V (Nb) are assigned to the metal centers in **4**. Accordingly, both compounds are diamagnetic. Compounds **1** – **4** are obtained in yields of 45% maximum. Eviently, other soluble compounds are formed during the reactions shown in Schemes 1 and 2, which we have not yet characterized. Compounds **1** – **4** are unsuitable for characterization by further analytical techniques (e.g. NMR spectroscopy), since the crystalline material decomposes as soon as it is dissolved in organic solvents. The products are binary copper and niobium chalcogenides.

Experimental Section

All reaction steps were carried out with strong exclusion of air and moisture in a dry nitrogen atmosphere. Solvents were dried prior to use. C, H, P, and Cu elemental analyses are consistent with the formulas given.

1: $(Me_3Si)_2Se$ (0.065 mL, ca. 0.065 g, ca. 0.290 mmol) was added to a solution of $[CuCl(PMe_3)_3]$ (0.475 g, 1.450 mmol) and $(NEt_4)_2[NbSe_3(SetBu)]$ (0.211 g, 0.290 mmol) in DMF (15 mL), after the solution had been stirred for 90 min. Slow reduction of the volume in vacuum led to the crystallization of reddish black crystals of compound **1** within two weeks. Yield: 0.026 g (17% with respect to Nb).

2: $(Me_3Si)_2Se$ (0.340 mL, ca. 0.338 g, ca. 1.498 mmol) was added to a solution of $[CuCl(PMe_3)_3]$ (0.350 g, 1.070 mmol) and $(NEt_4)_2[NbSe_3(SetBu)]$ (0.155 g, 0.214 mmol) in DMF (12 mL), after the solution had been stirred for 60 min. Black crystals of compound **2** were formed within four weeks. Yield: 0.020 g (12% with respect to Nb).

3: $(Me_3Si)_2S$ (0.103 mL, ca. 0.087 g, ca. 0.487 mmol) was added to a suspension of $NbCl_5$ (0.131 g, 0.485 mmol), CuCl (0.060 g, 0.606 mmol), and PEt_3 (0.215 mL, 0.172 g, 1.455 mmol) in CH_3CN (10 mL), whereafter the reaction mixture was stirred for 60 min. The reaction mixture was then filtered, and $(NEt_4)Cl$ (0.120 g, 0.724 mmol) was added to the dark red filtrate. On stirring the mixture for a few minutes, an orange-red, crystalline precipitate of compound **3** was formed. Yield: 0.080 g (45% with respect to Cu).

4: $(Me_3Si)_2Te$ (0.056 mL, ca. 0.066 g, ca. 0.241 mmol) was added to a suspension of $NbCl_5$ (0.055 g, 0.204 mmol), CuCl (0.020 g, 0.202 mmol) and PEt_3 (0.090 mL, 0.072 g, 0.609 mmol) in CH_3CN (5 mL), whereafter the reaction mixture was stirred for 60 min. The reaction mixture was then filtered, and the reddish black filtrate was reduced to half the volume in vacuum. Slow condensation of Et_2O onto the solution led to the formation of black crystals of compound **4** after three weeks. Yield: 0.012 g (16% with respect to Cu).

Received: July 10, 2001 [Z17461]

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[8] Compound **I** can be isolated from the reaction of $(NEt_4)_2[NbSe_3(StBu)]$ and $[CuCl(PMe_3)_3]$ (1:5) in DMF. We have so for not been able to crystallize the analogous Nb-Cu-Se compound starting from $(NEt_4)_2[NbSe_3(SetBu)]$.

[9] X-ray structural analyses: STOE-IPDS; data collection and refinement (SHELXS-97, SHELXL-97). **1**: orthorhombic, space group *Pbcn* (no. 60), $Z = 8$, $T = 200$ K, $a = 2216.8(4)$, $b = 2167.3(4)$, $c = 4766.9(10)$ pm, $V = 22902(8) \times 10^6$ pm^3, $\mu(Mo_{K\alpha}) = 74.80$ cm^{-1},

1433-7851/01/4023-4405 $ 17.50+.50/0

$2\Theta_{max} = 41°$, 57352 reflections collected, 11223 independent reflections ($R_{int} = 0.070$), 9132 observed reflections with $I > 2\sigma(I)$, 733 parameters, max residual electron denisty $0.78 \times 10^{-6}\,e^-pm^{-3}$, $R_1 = 0.055$, $wR_2 = 0.143$. Nb, Cu, Se, Cl, P refined anisotropically. **2**: monoclinic, space group *C*2/*c* (no. 15), $Z = 4$, $T = 190$ K, $a = 1806.3(4)$, $b = 1300.4(3)$, $c = 2209.4(4)$ pm, $\beta = 92.73(3)°$, $V = 5183.8(18) \times 10^6$ pm^3, $\mu(Mo_{K\alpha}) = 65.16$ cm^{-1}, $2\Theta_{max} = 40°$, 3536 reflections collected, 1654 independent reflections ($R_{int} = 0.103$), 1183 observed reflections with $I > 2\sigma(I)$, 139 parameters, max residual electron denisty $0.69 \times 10^{-6}\,e^-pm^{-3}$, $R_1 = 0.113$, $wR_2 = 0.256$. Nb, Cu, Se, P refined anisotropically. **3**: orthorhombic, space group *Pnma* (no. 62), $Z = 4$, $T = 190$ K, $a = 2092.5(4)$, $b = 3235.5(7)$, $c = 1228.9(3)$ pm, $V = 8320(3) \times 10^6$ pm^3, $\mu(Mo_{K\alpha}) = 22.20$ cm^{-1}, $2\Theta_{max} = 43°$, 11702 reflections collected, 3621 independent reflections ($R_{int} = 0.035$), 3146 observed reflections with $I > 2\sigma(I)$, 278 parameters, max residual electron denisty $0.83 \times 10^{-6}\,e^-pm^{-3}$, $R_1 = 0.057$, $wR_2 = 0.153$. Nb, Cu, S, Cl, P refined anisotropically. **4**: triclinic, space group $P\bar{1}$ (no. 2), $Z = 2$, $T = 180$ K, $a = 1348.9(8)$, $b = 1532.1(8)$, $c = 1782.7(9)$ pm, $\alpha = 104.33(3)$, $\beta = 105.41(3)$, $\gamma = 100.05(3)°$, $V = 3325(3) \times 10^6$ pm^3, $\mu(Mo_{K\alpha}) = 56.17$ cm^{-1}, $2\Theta_{max} = 42°$, 4338 reflections collected, 3629 independent reflections ($R_{int} = 0.082$), 3366 observed reflections with $I > 2\sigma(I)$, 352 parameters, max residual electron denisty $1.12 \times 10^{-6}\,e^-pm^{-3}$, $R_1 = 0.064$, $wR_2 = 0.169$. Nb, Cu, Te, Cl, P refined anisotropically. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-165897–165900 (**1**–**4**, respectively). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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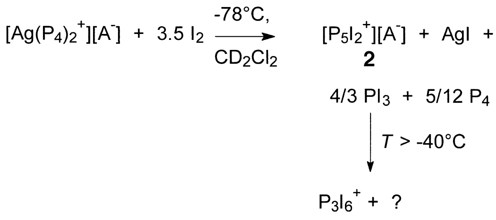
$P_5X_2^+$ (X = Br, I), a Phosphorus-Rich Binary P–X Cation with a C_{2v}-Symmetric P_5 Cage**

Ingo Krossing* and Ines Raabe

Dedicated to Jack Passmore

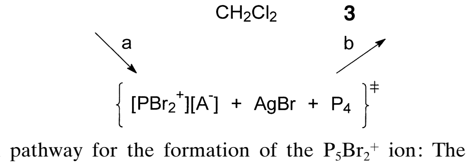
Our knowledge on simple cations with a polyphosphorus skeleton is still very limited owing to the poor capability of the phosphorus atom to bear positive charge. With mass spectrometric methods naked polyphosphorus cations up to P_{89}^+[1, 2] and binary P–X cations (X = halogen) were shown to exist in the gas phase.[3] Their structures have been elucidated by quantum-chemical methods.[4, 5] In the solid state only the PX_4^+ (X = F–I)[6] and $P_2I_5^+$ ions[7, 8] are known—in contrast to numerous polyphosphorus(Zintl-)anion structures.[9] Classical weakly basic counteranions only led to decomposition.[10] Recently we reported on nonoxidizing, weakly coordinating anions of the type $Al(OR)_4^-$ (OR = polyfluorinated aliphatic alkoxide).[11, 12] These anions stabilize binary Ag–P cations, such as D_{2h}-symmetric $Ag(P_4)_2^+$, $\mathbf{1}^+$.[13, 14] The reaction of $[\mathbf{1}^+][A^-]$ ($A^- = Al[OC(CF_3)_3]_4^-$) with X_2 (X = Br, I) provided evidence for the intermediate formation of the elusive P_5^+ ion but finally only led to the first subvalent binary P–X cation, the C_2-symmetric $P_3I_6^+$ ion with a P_3 backbone.[15]

Herein we reinvestigate this reaction by using low-temperature in situ NMR spectroscopy: Reaction of $[Ag(P_4)_2^+][A^-]$ in CD_2Cl_2 with 3.5 equivalents of I_2 at −78 °C revealed one major product in the in situ ^{31}P NMR spectrum at −78 °C (see Supporting Information): $[P_5I_2^+][A^-]$ (**2**) (Scheme 1). A scaled-up preparation verified these conclusions (mass balance, Raman spectrum of **2**, PI_3 and P_4 formation). The reaction mixture reacted according to Scheme 1 already at −40 °C to give $P_3I_6^+$ and other yet unidentified species.[15] The formation and decomposition of $P_5I_2^+$ possibly proceed as follows: it is known that P_4 reacts with iodine to immediately give PI_3 (and only then to give P_2I_4).[16] The PI_3 reacted with the polarizing silver cation of $Ag^+[A^-]$ to give AgI and PI_2^+. This "carbenoid"[5] cation inserted into one P–P bond of the P_4 tetrahedron leading to the formation of $P_5I_2^+$. Upon warming the sample, the excess PI_3 and P_4 react to give P_2I_4 (Raman), which at about −40 °C becomes slightly soluble and then reacts with $P_5I_2^+$ to form $P_3I_6^+$ and P_4. The latter reaction in CH_2Cl_2 is exergonic by 26 kJ mol^{-1} (COSMO[17, 18] solvation model and MP2/TZVPP[26–29]).



Scheme 1. Reaction pathway for the formation and subsequent decomposition of the $P_5I_2^+$ ion.

To confirm the PI_2^+ insertion hypothesis, we reacted P_4, PBr_3, and $Ag^+[A^-]$ according to Scheme 2 at −78 °C. Indeed, in situ ^{31}P NMR spectroscopy at −80 °C showed that $[P_5Br_2^+][A^-]$ (**3**) was the only P-containing product visible after a reaction time of 10 days at this temperature. This confirms the insertion mechanism proposed in the steps a and



Scheme 2. Reaction pathway for the formation of the $P_5Br_2^+$ ion: The intermediate PBr_2^+ ion (a) inserts into the P–P bond of the P_4 cage (b).

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[**] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Prof. H. Schnöckel for valuable discussions.

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