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FULL PAPER

Characterization of $Cu_{11}(\mu_9\text{-Se})(\mu_3\text{-I})_3[Se_2P(OR)_2]_6$ (R = Pr, Pr^i) by X-ray diffraction and multinuclear NMR†

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Two types of products were isolated from the reaction of $NH_4Se_2P(OR)_2$ (R = Pr, Pr^i), $Cu(CH_3CN)_4PF_6$, and Bu_4NI in a 3 : 2 : 2 molar ratio in diethyl ether. The formulation of **1**, $Cu_8(\mu_8\text{-Se})[Se_2P(OR)_2]_6$, and **2**, $Cu_{11}(\mu_9\text{-Se})(\mu_3\text{-I})_3[Se_2P(OR)_2]_6$, was confirmed by elemental analyses, positive FAB mass spectrometry, multinuclear NMR (^1H, ^{31}P, and ^{77}Se), and X-ray diffraction (**1a** and **2b**). The geometry in **1** can be described as a selenide-centered, slightly distorted Cu_8 cube with each edge of the cube being bridged by a selenium atom of the diselenophosphato (dsep) ligands . The sx dsep ligands, each capped on the square face of the cube, adopt a tetrametallic tetraconnective coordination pattern. The eleven copper atoms in **2** adopt the geometry of a 3,3,4,4,4-pentacapped trigonal prism with a selenium atom in the center. The coordination geometry for the central selenium atom is tricapped trigonal prismatic. In addition, the central core ($Cu_{11}Se$ in **2**) is further stabilized by three iodides and six dsep ligands. A unique ^{77}Se NMR pattern for the dsep ligands clearly indicates that local C_{3h} symmetry was retained in solution. Moreover, the octacoordinated and nonacoordinated selenium atoms in **1** and **2** are unequivocally characterized by the ^{77}Se NMR spectra, whose resonance frequencies are centered around −1150 and −1200 ppm, respectively.

Introduction

The chemistry of hypercoordination for the main group elements continues to be an active research field.[1] Some of this success is related to anionic binding and recognition, an important subject in supramolecular chemistry.[2] For spherical substrates, the halide ions are the dominant species being studied to the greatest extent, and the coordination polyhedra for the halides can be planar,[3] tetrahedral,[4] octahedral,[5] and cubic.[6] Especially interesting is the halide-centered M_8 cube. In addition to the molecular aggregate $(\mu_8\text{-I})Cd_8(SCH_2CH_2OH)_{12}I_3$, characterized by Burgi *et al.*, only one type of discrete M_8 cluster, containing dithiophosphato ligands,[6a] was known prior to our study of $\{Cu_8(\mu_8\text{-Br})[Se_2P(OR)_2]_6\}(PF_6)$, even though they had been identified in the core unit of several mixed-metal mixed-valence species of the type $M^{II}_6M^I_8(\mu_8\text{-Cl})L_{12}$,[7] of which the copper clusters[7a] had been used to elucidate the possible role of *D*-penicillamine in chemotherapy for Wilson disease.[8]

Following our initial report[9] of the bromide-centered Cu_8 cube, in which each edge of the cube was bridged by a selenium atom of the diselenophosphato ligand (dsep), we turned our attention to the larger iodide ion, with the hope of building an hitherto unknown iodo-centered M^I_8 (M = Cu or Ag) cube. It turned out that the iodide is too large to fit into the Cu_8 cube and only a selenide-centered Cu_8 cube capped by six dsep ligands and a selenide-centered undecacopper cage capped by three iodo ions and six dsep ligands were isolated. The coordination geometry for the central selenium atom of the latter is tricapped trigonal prismatic, which is identical to that revealed in its bromide analogue, $Cu_{11}(\mu_9\text{-Se})(\mu_3\text{-Br})_3[Se_2P(OPr^i)_2]_6$.[9] Herein, we report detailed characterizations of this undecanuclear copper structure in both solid and solution states.

Results and discussion

Synthesis and structural characterization

Two types of products were isolated from the reaction of $NH_4Se_2P(OR)_2$, $Cu(CH_3CN)_4PF_6$, and Bu_4NI in a 3 : 2 : 2 molar ratio in diethyl ether (Scheme 1). They can be separated by column chromatography (eluent: ethyl acetate–hexane = 10:7.5) and are stable in air as solids. The formulations of **1**, $Cu_8(\mu_8\text{-Se})[Se_2P(OR)_2]_6$, and **2**, $Cu_{11}(\mu_9\text{-Se})(\mu_3\text{-I})_3[Se_2P(OR)_2]_6$, were confirmed by elemental analyses, positive FAB mass spectroscopy, multinuclear NMR (^1H, ^{31}P, and ^{77}Se), and X-ray diffraction (**1a** and **2b**). Unlike the previous reaction with the bromide ion,[9] the iodo-centered Cu_8 cube has not been detected to date. Compound **1b** was reported before without the presence of halide ion in solution.[10] The synthetic details of **1**, involving a plausible cluster transformation from $Cu_4[Se_2P(OR)_2]_4$ to $Cu_8(Se)[Se_2P(OR)_2]_6$ under acidic conditions, as well as detailed DFT calculations of the bonding properties will be reported elsewhere.

Scheme 1

Compounds **2** can be isolated from THF and halocarbon solvents, but the highest yield is achieved in Et_2O. Further reaction of **1** with n-butyl ammonium iodide does not appear to produce clusters **2**. Nevertheless, the cluster nuclearity does increase from eight to eleven in the presence of iodide or bromide ions in solution.

The cluster **1a** crystallizes in the trigonal space group $R\bar{3}$, and its structure is shown in Fig. 1. There are two copper atoms

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† Metal dialkyl diselenophosphates. Part 6. For part 5, see ref. 21.

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Table 1 Selected bond lengths (Å) and angles (°) for **1a**[a]

Se(01)–Cu(2)	2.504(2)	Se(2)–Cu(1)#2	2.461(2)
Se(01)–Cu(1)	2.520(1)	Cu(1)–Se(1)#3	2.452(2)
Se(1)–Cu(1)#4	2.452(2)	Cu(1)–Se(2)#2	2.460(2)
Se(1)–Cu(1)	2.456(2)	Cu(1)–Cu(2)	2.899(2)
Cu(1)–Cu(1)#4	2.912(2)	Cu(2)–Se(2)#5	2.456(1)
Se(1)–P(1)	2.146(4)	Se(2)–P(1)	2.160(4)
P(1)–O(1)	1.633(13)	P(1)–O(2)	1.533(11)
Se(1) ··· Se(2)	3.776		
Cu(2)–Se(01)–Cu(2)#1	180.0	Cu(2)–Se(01)–Cu(1)#1	109.52(3)
Cu(2)–Se(01)–Cu(1)#2	70.48(3)	Cu(1)#2–Se(01)–Cu(1)#1	70.57(3)
Cu(1)#4–Se(1)–Cu(1)	72.71(5)	Cu(1)#3–Se(01)–Cu(1)#1	109.43(3)
P(1)–Se(2)–Cu(2)	104.33(10)	P(1)–Se(1)–Cu(1)#4	101.39(10)
P(1)–Se(2)–Cu(1)#2	101.71(10)	P(1)–Se(1)–Cu(1)	103.62(10)
Cu(2)–Se(2)–Cu(1)#2	72.28(6)	Se(1)#3–Cu(1)–Se(2)#3	114.75(6)
Se(1)#3–Cu(1)–Se(1)	115.30(5)	Se(1)–Cu(1)–Se(2)#3	116.61(6)
Cu(2)–Cu(1)–Cu(1)#4	89.85(3)	Se(1)#3–Cu(1)–Se(01)	102.56(5)
Se(2)#3–Cu(2)–Se(2)#2	115.37(4)	Se(1)–Cu(1)–Se(01)	102.49(5)
Se(2)–Cu(2)–Se(01)	102.61(5)	Se(2)#3–Cu(1)–Se(01)	102.03(5)
Cu(1)–Cu(2)–Cu(1)#2	90.40(6)	Cu(1)#4–Cu(1)–Cu(1)#3	89.85(3)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x, -y, -z$; #2 $-y, x-y, z$; #3 $x-y, x, -z$; #4 $y, -x+y, -z$; #5 $-x+y, -x, z$.

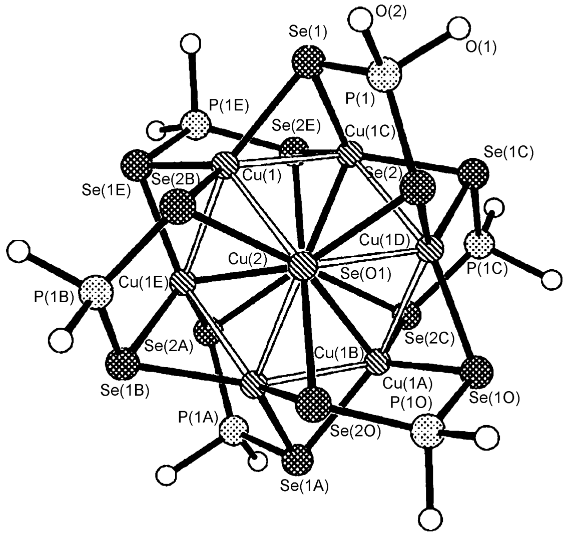

Fig. 1 Structure of **1a**. Hatched, cross-hatched, dotted, and white spheres represent Cu, Se, P, and O atoms, respectively; the n-propyl groups have been omitted for clarity.

(Cu1 and Cu2) in the asymmetric unit and a dsep ligand with Se(01) located at the inversion center. The shape of the molecule can be described as a selenide-centered, slightly distorted Cu_8 cube, with each edge of the cube being bridged by a selenium atom of a dsep ligand. The deviation from the perfect cube is revealed along the threefold rotational axis, where the Se(01)–Cu(2) distance is 0.016 Å shorter in comparison with the other Se(01)–Cu distances [2.504(2) and 2.520(1) Å, respectively]. Consequently, two kinds of Cu–Cu distances are revealed, 2.899(2) and 2.912(2) Å, as required by the symmetry. Six dsep ligands, each capped on the square face of the cube, adopt a tetrametallic tetraconnective coordination pattern. The Cu–μ_2-Se distances lie in the range 2.452(2) and 2.461(2) Å and the Cu–μ_2-Se–Cu angles average 72.47(5)°. The Se–Cu–Se angles range from 102.03(5) to 116.61(6)°. The Se ··· Se "bite distance" is 3.776 Å and the Se–P–Se angle is 122.6(1)°. Due to the lack of a fourfold rotational axis, complex **1a** has an idealized T_h point group symmetry. The central selenide anion associated with the twelve outer selenium atoms of the dsep ligands form a body-centered icosahedron. Selected bond distances and angles for **1a** are listed in Table 1.

Basically, clusters **1a** and **1b**[10] are isostructural but crystallize in two different space groups, $R\bar{3}$ and $P2_1/n$, respectively. These two clusters belong to a rare class of octacoordinated bridging selenido ligands in cubic geometry. In fact, the first example was identified in the core unit of the mixed-valence molecule $Cu_{20}(\mu_8\text{-}Se)Se_{12}(PEt_3)_{12}$.[11]

X-Ray analysis reveals that the eleven copper atoms in **2b** adopt the geometry of a 3,3,4,4,4-pentacapped trigonal prism (Fig. 2), with a selenium atom in the center. A pseudo-threefold axis passes through the Cu(1), Se(01), and Cu(2) atoms. A group of six copper atoms, Cu(6)–Cu(11), comprise an idealized trigonal prism, of which each rectangular face is further capped by an additional copper atom. The edges of the trigonal prism are in the range 3.489–3.714 Å, while the heights (Cu7–Cu8, Cu6–Cu9, and Cu10–Cu11) are, on average, 3.175(4) Å. Significantly shorter Cu–Cu distances are revealed between the capping atoms and the prism; they are in the range 2.805(2)–3.154(2) Å, slightly longer than the sum of the van der Waals

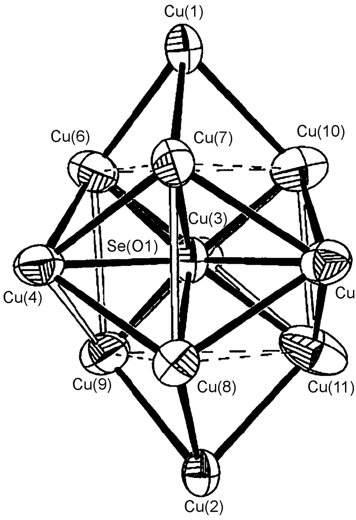

Fig. 2 The $Cu_{11}Se$ core in **2b**. Cu–Se and Cu–Cu distances (Å): Se(01)–Cu(3) 2.672(2), Se(01)–Cu(4) 2.725(2), Se(01)–Cu(5) 2.681(2), Se(01)–Cu(6) 2.596(2), Se(01)–Cu(7) 2.595(2), Se(01)–Cu(8) 2.500(2), Se(01)–Cu(9) 2.630(2), Se(01)–Cu(10) 2.563(2), Se(01)–Cu(11) 2.766(3), Se(01) ··· Cu(1) 3.541, Se(01) ··· Cu(2) 3.615, Cu(1)–Cu(6) 2.823(2), Cu(1)–Cu(7) 2.876(2), Cu(1)–Cu(10) 2.921(2), Cu(2)–Cu(8) 2.821(2), Cu(2)–Cu(9) 2.895(2), Cu(2)–Cu(11) 2.904(3), Cu(3)–Cu(9) 2.805(2), Cu(3)–Cu(6) 2.897(2), Cu(3)–Cu(10) 2.928(2), Cu(3)–Cu(11) 3.154(2), Cu(4)–Cu(8) 2.814(2), Cu(4)–Cu(7) 2.866(2), Cu(4)–Cu(6) 2.913(2), Cu(4)–Cu(9) 3.095(2), Cu(5)–Cu(11) 2.829(2), Cu(5)–Cu(8) 2.858(2), Cu(5)–Cu(10) 2.879(2), Cu(5)–Cu(7) 2.918(2), Cu(6)–Cu(9) 3.224(2), Cu(7)–Cu(8) 3.134(2), Cu(10)–Cu(11) 3.169(2), Cu(7) ··· Cu(10) 3.571, Cu(7) ··· Cu(6) 3.546, Cu(6) ··· Cu(10) 3.635, Cu(8) ··· Cu(9) 3.489, Cu(8) ··· Cu(11) 3.551, Cu(9) ··· Cu(11) 3.714.

radii for copper (2.80 Å).[12] Alternatively, the undecanuclear copper cage can be described as a combination of nine Cu_4 butterflies, where the wing-tip positions are represented by five capping copper atoms with each edge and height of the trigonal prism being the hinges. Clusters or cages having pentacapped trigonal prismatic geometry are not common. Examples containing main-group elements as capping atoms are $Ni_6(\mu_3\text{-}Se)_2(\mu_4\text{-}Se)_3(PPh_3)_6$[13] and $[Cu_6(\mu_3\text{-}I)_2(\mu_4\text{-}I)_3I_6]^{5-}$.[14] The geometry with capping metal atoms on all five faces of a trigonal prism is even rarer. Besides clusters **2**, the closest examples are found in the undecanuclear silver clusters $Ag_{11}(\mu_5\text{-}E)(\mu_4\text{-}Et_2NCS_2)_3(\mu_3\text{-}Et_2NCS_2)_6$ ($E = S^{2-}$, Se^{2-}).[15]

The Cu–Se(01) bond distances in **2b** are noteworthy. Whereas two on the C_3 rotational axis are quite long, 3.541 and 3.615 Å, the rest are in the range 2.500(2)–2.766(3) Å and are within the reported limits.[16] Consequently, the nonacoordinate bridging selenido ligand in a tricapped trigonal prismatic geometry is afforded. While the angles Cu(5)–Se(01)–Cu(4), Cu(4)–Se(01)–Cu(3), and Cu(3)–Se(01)–Cu(5) are close to 120° [121.89(6)–117.95(6)°], the rest of the Cu–μ_9-Se–Cu angles range between 62.57(5) and 144.03(7)°. This is the second example of a copper cluster exhibit such a coordination geometry for a main group element.

The central core in **2b** is further stabilized by three iodides and six dsep ligands. (Fig. 3). The Cu_4 butterflies containing a copper atom on the C_3 axis are each capped by a dsep ligand containing a tetrametallic tetraconnective (μ_2, μ_2) coordination pattern. The Cu–μ_2-Se distances lie in the range between 2.358(2) and 2.504(2) Å and the Cu–μ_2-Se–Cu angles range between 70.35(7) and 80.02(8)°. Although the Se–P–Se angles range between 117.12(13) and 120.26(13)°, and P–Se distances average 2.170(3) Å and are normal, the "bite" distances average 3.727 Å and are slightly shorter than those (3.776 and 3.784 Å) found in the Cu_8 cube.[10] This is as expected when taking into account the difference in the capping faces: butterfly and square. The remaining three, where hinge positions are the heights of the prism, are each capped by a triply bridging iodide atom over an alternating set of three of the six triangular faces. The Cu–I bond distances are, on average, 2.692(2) Å and comparable with those found in $[Cu_6(\mu_3\text{-}I)_2(\mu_4\text{-}I)_3I_6]^{5-}$.[14] The Cu–$\mu_3$-I–Cu angles are in the range 62.51(5) and 71.59(7)°. Overall, due to the existence of three alternating triply bridging iodides, the idealized D_{3h} symmetry depicted in Fig. 2 is lowered to C_{3h}. Hence, all the dsep ligands are related to each other by virtual $3/m$ symmetry. Selected bond distances and angles are listed in Table 2.

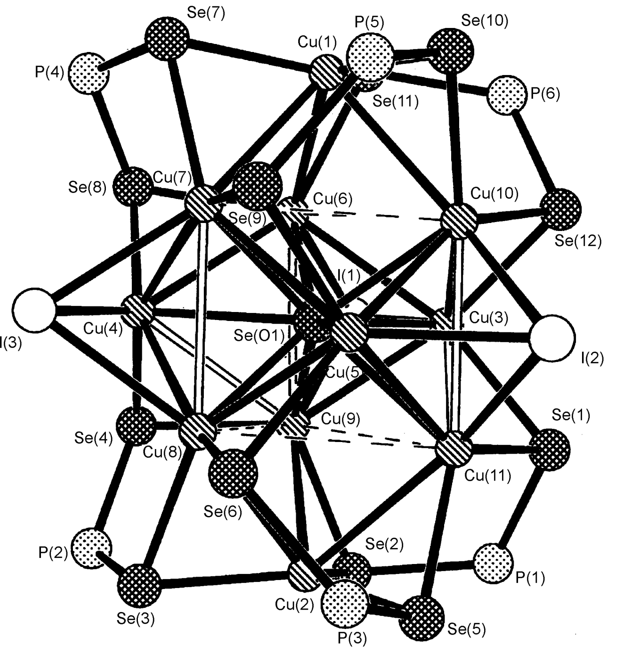

Fig. 3 Structure of **2b**. Hatched, cross-hatched, dotted, and white spheres represent Cu, Se, P, and I atoms, respectively; the isopropoxyl groups have been omitted for clarity.

Spectroscopy

Based on the symmetry properties of structure **1** mentioned above, only one singlet flanked with a set of satellites was observed in the $^{31}P\{^1H\}$ NMR spectrum. This suggests that the cluster remains intact in solution. Accordingly, the $^{77}Se\{^1H\}$ NMR spectrum of **1b** displays two chemical shifts: a doublet peak and a singlet. The latter can be reasonably assigned to the resonance frequency of the central selenide anion, while the former arises from the dsep ligands, for which the $^1J(^{77}Se, ^{31}P)$ value is in good agreement with that observed in the ^{31}P NMR spectrum. Astonishingly, the peak centered at *ca.* −1150 ppm (−1172.6 and −1147.4 for **1a** and **1b**, respectively) shows a huge upfield shift by comparison with K_2Se (−527 ppm)[17] in alkaline aqueous solution and $(NH_4)_2Se$ (−511ppm).[18] K_2Se is known to have an antifluorite structure,[19] a cubic arrangement of cations with the anion at its center. It is worthwhile emphasizing that a long accumulation time (four to five days) is required in order to collect the ^{77}Se NMR data.

In sharp contrast to **1**, the $^{31}P\{^1H\}$ NMR spectrum of **2** at ambient temperature showed a singlet accompanied by two sets of satellites arising from $^1J(^{77}Se, ^{31}P)$. The inequivalence of the two Se environments supports the assignment of local C_{3h} symmetry in solution (*vide supra*). Hence, the two Se environments could not be interchanged by any symmetry operations of the C_{3h} point group. This is further supported by the observation of two distinct sets of chemical shifts for the alkyl groups in the ^1H NMR spectrum. The ^{77}Se NMR spectrum of **2** is of particular interest. The $^{77}Se\{^1H\}$ NMR spectrum of **2b** is depicted in Fig. 4(b) and displays two sets of resonances due to the dsep ligand. The both chemically and magnetically inequivalent selenium nuclei of the dsep ligand exhibit intriguingly different scalar coupling patterns with the adjacent chemically equivalent but magnetically non-equivalent phosphorus nuclei. The large coupling constants (651.3 and 677.4 Hz for **2a**, 644.9 and 673.0 Hz for **2b**) of each set are due to one-bond coupling to P_x, to which the Se is directly connected. These coupling constants are in good agreement with the ^{31}P NMR results. The remaining coupling pattern results from three-bond coupling to the other two phosphorus nuclei. The chemical shift centered at 12.5 ppm can be reasonably assigned to the Se_A atom coordinated to the tetracapped copper atom. The larger scalar coupling (~35 Hz) is due to the adjacent P_y atom related to the threefold symmetry axis, and the torsion angle Se_A–Cu–Se–Py averages 170.4°. The small scalar coupling (~14 Hz) is due to $P_{z'}$ generated by the mirror plane, having an averaged torsion angle of 160.8°. Surprisingly, the resonance centered at 50.3 ppm does not exhibit a similar coupling pattern to that at 12.5 ppm. Therefore, this signal must due to Se_B connected to the tricapped copper atom. The small coupling constant could result from the two adjacent P atoms (P_y and P_z) related to each other by the C_3 rotational axis. Presumably, these two ^3J(Se, P) have opposite signs (positive and negative values), reflected in their different averaged torsion angles of 177.5 and 20.5°, respectively. Due to the low natural abundance of ^{77}Se nuclei (less than 8%), it is unlikely that the coupling patterns observed in **2b** are from ^2J(Se, Se) scalar coupling. Thus, it is of interest to carry out more detailed NMR experiments, such as ^{77}Se–^{31}P shift-correlated 2D NMR,[20] in order to corroborate the above assignment. Nevertheless, the simulated spectrum [Fig 4(c)] matches well with the above assignment. The observed ^{77}Se NMR spectrum of **2a** exhibited a similar pattern to that depicted in Fig. 4.

Table 2 Selected bond lengths (Å) and angles (°) for **2b**

I(1)–Cu(3)	2.623(2)	Se(5)–Cu(11)	2.427(2)
I(1)–Cu(9)	2.718(2)	Se(6)–P(3)	2.158(3)
I(1)–Cu(6)	2.725(2)	Se(6)–Cu(8)	2.478(2)
I(2)–Cu(5)	2.624(2)	Se(6)–Cu(5)	2.480(2)
I(2)–Cu(11)	2.660(2)	Se(7)–P(4)	2.176(3)
I(2)–Cu(10)	2.733(2)	Se(7)–Cu(1)	2.367(2)
I(3)–Cu(4)	2.633(2)	Se(7)–Cu(7)	2.445(2)
I(3)–Cu(7)	2.725(2)	Se(8)–P(4)	2.180(3)
I(3)–Cu(8)	2.783(2)	Se(8)–Cu(4)	2.447(2)
Se(1)–P(1)	2.171(3)	Se(8)–Cu(6)	2.504(2)
Se(1)–Cu(11)	2.432(2)	Se(9)–P(5)	2.156(3)
Se(1)–Cu(3)	2.472(2)	Se(9)–Cu(5)	2.426(2)
Se(2)–P(1)	2.173(3)	Se(9)–Cu(7)	2.469(2)
Se(2)–Cu(2)	2.377(2)	Se(10)–P(5)	2.180(3)
Se(2)–Cu(9)	2.457(2)	Se(10)–Cu(1)	2.361(2)
Se(3)–P(2)	2.179(3)	Se(10)–Cu(10)	2.433(2)
Se(3)–Cu(2)	2.369(2)	Se(11)–P(6)	2.182(4)
Se(3)–Cu(8)	2.453(2)	Se(11)–Cu(1)	2.358(2)
Se(4)–P(2)	2.157(3)	Se(11)–Cu(6)	2.461(2)
Se(4)–Cu(4)	2.456(2)	Se(12)–P(6)	2.161(3)
Se(4)–Cu(9)	2.456(2)	Se(12)–Cu(3)	2.449(2)
Se(5)–P(3)	2.177(3)	Se(12)–Cu(10)	2.481(2)
Se(5)–Cu(2)	2.366(2)	Se(1) ··· Se(2)	3.709
Se(3) ··· Se(4)	3.700	Se(5) ··· Se(6)	3.724
Se(7) ··· Se(8)	3.724	Se(9) ··· Se(10)	3.760
Se(11) ··· Se(12)	3.747		
Cu(10)–Se(01)–Cu(7)	87.62(6)	Cu(8)–Se(01)–Cu(10)	133.38(7)
Cu(8)–Se(01)–Cu(6)	131.27(7)	Cu(8)–Se(01)–Cu(7)	75.93(6)
Cu(10)–Se(01)–Cu(6)	89.59(6)	Cu(9)–Se(01)–Cu(3)	63.89(5)
Cu(7)–Se(01)–Cu(6)	86.21(6)	Cu(8)–Se(01)–Cu(5)	66.85(6)
Cu(8)–Se(01)–Cu(9)	85.75(6)	Cu(10)–Se(01)–Cu(5)	66.56(6)
Cu(10)–Se(01)–Cu(9)	131.63(7)	Cu(7)–Se(01)–Cu(5)	67.14(5)
Cu(7)–Se(01)–Cu(9)	135.75(6)	Cu(6)–Se(01)–Cu(5)	144.03(7)
Cu(6)–Se(01)–Cu(9)	76.21(6)	Cu(9)–Se(01)–Cu(5)	139.75(7)
Cu(8)–Se(01)–Cu(3)	141.23(7)	Cu(3)–Se(01)–Cu(5)	121.89(6)
Cu(10)–Se(01)–Cu(3)	67.98(5)	Cu(8)–Se(01)–Cu(4)	65.00(5)
Cu(7)–Se(01)–Cu(3)	142.73(7)	Cu(10)–Se(01)–Cu(4)	143.75(7)
Cu(6)–Se(01)–Cu(3)	66.70(6)	Cu(7)–Se(01)–Cu(4)	65.12(5)
Cu(6)–Se(01)–Cu(4)	66.34(6)	Cu(7)–Se(01)–Cu(11)	129.71(7)
Cu(9)–Se(01)–Cu(4)	70.63(6)	Cu(6)–Se(01)–Cu(11)	137.58(7)
Cu(3)–Se(01)–Cu(4)	120.16(6)	Cu(9)–Se(01)–Cu(11)	87.04(6)
Cu(5)–Se(01)–Cu(4)	117.95(6)	Cu(3)–Se(01)–Cu(11)	70.92(6)
Cu(8)–Se(01)–Cu(11)	84.73(6)	Cu(5)–Se(01)–Cu(11)	62.57(5)
Cu(10)–Se(01)–Cu(11)	72.87(6)	Cu(4)–Se(01)–Cu(11)	142.94(7)
Cu(3)–I(1)–Cu(9)	63.35(5)	Cu(11)–I(2)–Cu(10)	71.97(7)
Cu(3)–I(1)–Cu(6)	65.56(6)	Cu(4)–I(3)–Cu(7)	64.64(5)
Cu(9)–I(1)–Cu(6)	72.69(6)	Cu(4)–I(3)–Cu(8)	62.52(5)
Cu(5)–I(2)–Cu(11)	64.74(6)	Cu(7)–I(3)–Cu(8)	69.39(5)
Cu(5)–I(2)–Cu(10)	64.98(6)	Cu(1)–Se(7)–Cu(7)	73.38(7)
Cu(11)–Se(1)–Cu(3)	80.07(8)	Cu(4)–Se(8)–Cu(6)	72.09(6)
Cu(2)–Se(2)–Cu(9)	73.54(7)	Cu(5)–Se(9)–Cu(7)	73.18(6)
Cu(2)–Se(3)–Cu(8)	71.59(6)	Cu(1)–Se(10)–Cu(10)	75.06(7)
Cu(4)–Se(4)–Cu(9)	78.16(7)	Cu(1)–Se(11)–Cu(6)	71.70(7)
Cu(2)–Se(5)–Cu(11)	74.58(7)	Cu(3)–Se(12)–Cu(10)	72.88(7)
Cu(8)–Se(6)–Cu(5)	70.39(6)	Se(1)–P(1)–Se(2)	117.26(12)
Se(3)–P(2)–Se(4)	117.12(13)	Se(5)–P(3)–Se(6)	118.42(14)
Se(7)–P(4)–Se(8)	117.56(12)	Se(9)–P(5)–Se(10)	120.28(12)
Se(11)–P(6)–Se(12)	119.29(14)		
P(1)–Se(1)–Cu(3)–Se(12)	161.85(9)	P(6)–Se(12)–Cu(3)–Se(1)	165.26(10)
P(2)–Se(4)–Cu(4)–Se(8)	159.50(9)	P(4)–Se(8)–Cu(4)–Se(4)	161.83(9)
P(3)–Se(6)–Cu(5)–Se(9)	152.97(9)	P(5)–Se(9)–Cu(5)–Se(6)	163.37(9)
P(5)–Se(10)–Cu(10)–Se(12)	170.02(9)	P(3)–Se(5)–Cu(11)–Se(1)	170.71(11)
P(6)–Se(11)–Cu(6)–Se(8)	175.12(11)	P(1)–Se(2)–Cu(9)–Se(4)	175.46(10)
P(4)–Se(7)–Cu(7)–Se(9)	161.43(10)	P(2)–Se(3)–Cu(8)–Se(6)	169.72(9)
P(5)–Se(10)–Cu(1)–Se(11)	179.93(10)	P(3)–Se(5)–Cu(2)–Se(2)	177.39(10)
P(6)–Se(11)–Cu(1)–Se(7)	175.71(10)	P(1)–Se(2)–Cu(2)–Se(3)	179.33(10)
P(4)–Se(7)–Cu(1)–Se(10)	176.44(9)	P(2)–Se(3)–Cu(2)–Se(5)	176.6(10)
P(4)–Se(7)–Cu(1)–Se(11)	24.50(12)	P(2)–Se(3)–Cu(2)–Se(2)	17.28(11)
P(5)–Se(10)–Cu(1)–Se(7)	20.56(11)	P(3)–Se(5)–Cu(2)–Se(3)	23.10(12)
P(6)–Se(11)–Cu(1)–Se(10)	17.62(12)	P(1)–Se(2)–Cu(2)–Se(5)	19.94(11)

On the other hand, the chemical shift for the central nonacoordinated selenium atom is −1210.8 ppm. Listed in the Table 3 are chemical shifts for the hypercoordinated selenide species characterized in this laboratory. The coordination number can be eight, nine, or ten, and the geometries are cubic, tricapped trigonal prismatic, and *cis*-bicapped trapezoidal prismatic, respectively. Previously, the resonance frequency for the decacoordinated selenium ion was reported at −1396.1 ppm.[21] For a nonacoordinated selenium atom, the resonance appears to be centered at *ca.* −1200 ppm, no matter whether the tricapping atoms surrounding the copper framework are iodides or bromides. It seems to us that the chemical shifts for

Table 3 ^{77}Se NMR data for hypercoordinated selenide-containing species

Compound	$Se_2P(OR)_2^-$ δ/ppm, (*J*/Hz)	Se^{2-} δ/ppm
$Cu_8(\mu_8\text{-}Se)[Se_2P(OPr^i)_2]_6$	-54.7, ($^1J_{SeP} = 671$)	-1147.4
$Cu_8(\mu_8\text{-}Se)[Se_2P(OPr)_2]_6$	-17.1, ($^1J_{SeP} = 670$)	-1172.6
$Cu_{11}(\mu_9\text{-}Se)(\mu_3\text{-}Br)_3[Se_2P(OPr^i)_2]_6$	61.7, ($^1J_{BX} = 645.7$, $^3J_{BZ} + {}^3J_{BY} = 9.4$)	-1201.3
	0.1, ($^1J_{AX} = 668.9$, $^3J_{AY} = 34.8$, $^3J_{AZ} = 14.7$)	
$Cu_{11}(\mu_9\text{-}Se)(\mu_3\text{-}I)_3[Se_2P(OPr^i)_2]_6$	50.3, ($^1J_{BX} = 644.9$, $^3J_{BZ} + {}^3J_{BY} = 8.5$)	-1210.8
	12.5, ($^1J_{AX} = 673.0$, $^3J_{AY} = 35.2$, $^3J_{AZ} = 14.4$)	
$Cu_{11}(\mu_9\text{-}Se)(\mu_3\text{-}I)_3[Se_2P(OPr)_2]_6$	34.0, ($^1J_{BX} = 651.3$, $^3J_{BZ} + {}^3J_{BY} = 8.8$)	-1187.6
	-12.1, ($^1J_{AX} = 677.4$, $^3J_{AY} = 33.3$, $^3J_{AZ} = 14.3$)	
$Ag_{10}(\mu_{10}\text{-}Se)[Se_2P(OEt)_2]_8$	77.9, ($^1J_{SeP} = 672$)	-1396.1
$Ag_{10}(\mu_{10}\text{-}Se)[Se_2P(OPr^i)_2]_8$	108.0, ($^1J_{SeP} = 668$)	-1395.4

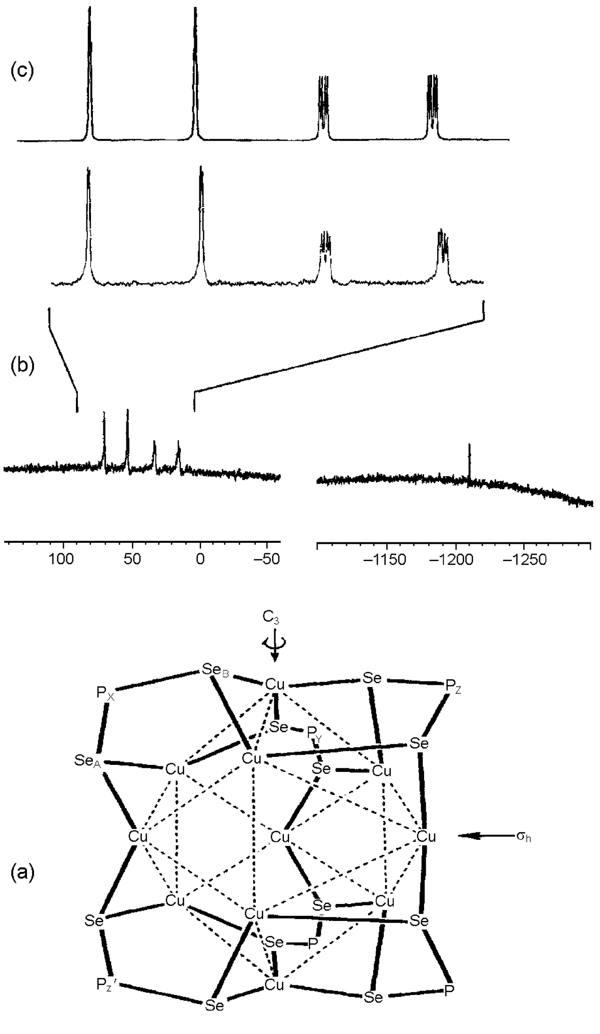

Fig. 4 (a) The $Cu_{11}Se_{12}P_6$ skeleton of **2b**. (b) $^{77}Se\{^1H\}$ NMR spectrum ($CDCl_3$) of cluster **2b**. (c) Simulated $^{77}Se\{^1H\}$ NMR spectrum for **2b**.

these hypercoordinated selenium atoms roughly correlate to the number of peripheral metal atoms, where electron transfer from the s orbital of copper and/or silver to the p orbital of selenium leads to extreme shielding of the selenium.[22] Clearly, these hypercoordinated selenide complexes deserve merit investigation in order to understand these large ^{77}Se chemical shift differences, and to see if the ^{77}Se shielding can be used to monitor the bonding situation prior to detailed crystallographic studies.

Clusters **1** and **2** were also characterized by positive FAB mass spectroscopy. For **1**, two major peaks arising from the molecular ion and the molecular ion minus a dsep ligand, $\{Cu_8(\mu_8\text{-}Se)[Se_2P(OR)_2]_5\}^+$, were observed. In addition to the molecular ion peak for **2**, two major fragment bands corresponding to the molecular ion minus an iodide ion, $\{Cu_{11}(\mu_9\text{-}Se)(\mu_3\text{-}I)_2[Se_2P(OR)_2]_6\}^+$, and a dsep ligand, $\{Cu_{11}(\mu_9\text{-}Se)(\mu_3\text{-}I)_3[Se_2P(OR)_2]_5\}^+$, were identified.

Experimental

NMR spectra were recorded on Bruker AC-F200 and Avance-300 Fourier transform spectrometers. The $^{31}P\{^1H\}$ and $^{77}Se\{^1H\}$ NMR are referenced externally against 85% H_3PO_4 (δ = 0 ppm) and PhSeSePh (δ = 463 ppm), respectively. Positive FAB mass spectroscopy was performed on VG 70-250S mass spectrometer with nitrobenzyl alcohol as the matrix. Elemental analyses were obtained with a Perkin Elmer 2400 CHN analyzer. $[Cu(CH_3CN)_4](PF_6)$[23] was prepared according to literature report. All reactions were performed in oven-dried Schlenk glassware using standard inert-atmosphere techniques. Commercial CH_2Cl_2 and C_3H_7OH were distilled from P_4O_{10} and Mg, respectively, before use. Hexanes and diethyl ether were distilled from Na–K.

General procedure for reaction of $Cu(CH_3CN)_4PF_6$ and $NH_4Se_2P(OR)_2$

$NH_4Se_2P(OPr^i)_2$ (1.23 g, 3.78 mmol) in Et_2O (50 mL) at 0 °C was stirred for 30 min, then Bu_4NI (931 mg, 2.52 mmol) and $Cu(CH_3CN)_4PF_6$ (940 mg, 2.52 mmol) were added sequentially. The reaction was lasted for 4 h and the solution changed from colorless to yellow during this time. After filtration, the yellow filtrates were evaporated under vacuum. Then, the residue was subjected to silica gel column chromatography using 10:7.5 ethyl acetate–n-hexane as the eluent, which yielded a yellow band of **1** (340 mg, 44%) and an orange–yellow band of **2** (250 mg, 36%).

The n-propyl derivatives (**1a** and **2a**) were prepared in a similar fashion.

$Cu_8(\mu_8\text{-}Se)[Se_2P(OPr)_2]_6$, 1a. Elemental analysis: $C_{36}H_{84}Cu_8O_{12}P_6Se_{13}$ calcd C, 17.80; H, 3.48; found C, 18.80; H, 3.78%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 78 (J_{SeP} 670 Hz). ^{1}H NMR ($CDCl_3$): δ 0.94 (t, $^3J_{HH}$ 7 Hz, 36H; CH_3), 1.71 (m, 24H; CH_2), 4.00 (m, 24H; CH_2). $^{77}Se\{^1H\}$ NMR ($CDCl_3$): δ −1172.6 (1Se), −17.1 (J_{SeP} 670 Hz, 12Se). Positive ion FAB-MS (nitrobenzyl alcohol): *m*/*z* (m/z_{calcd}) 2429 (2428.8) $[M]^+$, 2122 (2121.9) $[M - dsep]^+$.

$Cu_8(\mu_8\text{-}Se)[Se_2P(OPr^i)_2]_6$, 1b. Elemental analysis: $C_{36}H_{84}Cu_8O_{12}P_6Se_{13}$ calcd C, 17.80; H, 3.46; found C, 17.66; H, 3.34%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 73 (J_{SeP} 671 Hz). ^{1}H NMR ($CDCl_3$): δ 1.37 (d, $^3J_{HH}$ 6 Hz, 72H; CH_3), 4.88 (m, 12H; CH). $^{77}Se\{^1H\}$ NMR ($CDCl_3$): δ −1147.4 (1Se), −54.7 (J_{SeP} 671 Hz, 12Se). Positive ion FAB-MS (nitrobenzyl alcohol): *m*/*z* (m/z_{calcd}) 2429 (2428.8) $[M]^+$, 2122 (2121.9) $[M - dsep]^+$.

$Cu_{11}(\mu_9\text{-}Se)(\mu_3\text{-}I)_3[Se_2P(OPr)_2]_6$, 2a. Elemental analysis: $C_{48}H_{108}Cu_{11}O_{12}P_6Se_{13}I_3$ calcd C, 17.61; H, 3.32; found C, 18.19; H, 3.43%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 83.0 (J_{SeP} 651.3, 677.4 Hz). ^{1}H NMR ($CDCl_3$): δ 0.94 (t, $^3J_{HH}$ 7 Hz, 18H; CH_3), 0.95 (t, $^3J_{HH}$ 7 Hz, 18H; CH_3), 1.73 (m, 24H; CH_2), 4.01 (m, 12H; CH_2), 4.77 (m, 12H; CH_2). $^{77}Se\{^1H\}$ NMR ($CDCl_3$): δ −1187.6 (1Se), −12.1 (6Se), 34.0 (6Se). Positive ion FAB-MS (nitrobenzyl alcohol): *m*/*z* (m/z_{calcd}) 2997.8 (3001.1) $[M]^+$, 2873.5 (2874.2) $[M - I]^+$, 2691.4 (2694.0) $[M - dsep]^+$.

Table 4 Crystallographic data for $Cu_8(\mu_8\text{-}Se)[Se_2P(OPr)_2]_6$, **1a**, and $Cu_{11}(\mu_9\text{-}Se)(\mu_3\text{-}I)_3[Se_2P(OPr^i)_2]_6$, **2b**

	1a	**2b**
Formula	$C_{36}H_{84}Cu_8O_{12}P_6Se_{13}$	$C_{36}H_{84}Cu_{11}I_3O_{12}P_6Se_{13}$
Fw	2429.65	3000.97
T/°C	25	25
Space group	$R\bar{3}$	$P2_1/n$
a/Å	22.7362(8)	14.3367(8)
b/Å	22.7362(8)	23.2385(13)
c/Å	12.3205(7)	24.3538(14)
β/°		91.670(1)
V/Å^3	5515.6(4)	8110.3(8)
Z	3	4
μ/mm^{-1}	8.876	9.958
Measured/independent reflections (R_{int})	5191/2121 (0.0363)	22317/12974 (0.0416)
Final $R1^a$ ($wR2^b$)	0.0589 (0.1532)	0.0548 (0.1071)

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

$Cu_{11}(\mu_9\text{-}Se)(\mu_3\text{-}I)_3[Se_2P(OPr^i)_2]_6$, 2b. Elemental analysis: $C_{36}H_{84}Cu_{11}O_{12}P_6Se_{13}I_3$ calcd C, 15.29; H, 2.82; found C, 14.41; H, 2.85%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 76.2 (J_{SeP} 644.9, 673.0 Hz). ^1H NMR ($CDCl_3$): δ 1.32 (d, $^3J_{HH}$ 6 Hz, 36H; CH_3), 1.35 (d, $^3J_{HH}$ 6 Hz, 36H; CH_3), 4.77 (m, 6H; CH), 5.14 (m, 6H; CH). $^{77}Se\{^1H\}$ NMR ($CDCl_3$): δ −1210.8 (1Se), 12.5 (6Se), 50.3 (6Se). Positive ion FAB-MS (nitrobenzyl alcohol): m/z (m/z_{calcd}) 3000.3 (3000.1) $[M]^+$, 2873.6 (2874.1) $[M - I]^+$, 2692.9 (2694.0) $[M - dsep]^+$.

X-Ray structure determination

Crystals were mounted on the tips of glass fibers with epoxy resin. Data were collected at 298 K on a Siemens SMART CCD (charged coupled device) diffractometer. For both crystals, data were measured with omega scans of 0.3° per frame for 90 s. A total of 1271 frames were collected, with a maximum resolution of 0.84 Å. Cell parameters were retrieved with SMART software[24] and refined with SAINT software[25] on all observed reflections [$I > 10\sigma(I)$]. Data reduction was performed with SAINT, which corrects for Lorentz and polarization effects. An empirical absorption correction was applied for both **1** and **2**. The structure was solved by direct methods and refinement was performed by least-squares methods on F^2 with the SHELXL-97 package,[26] incorporated in SHELXTL/PC V5.10.[27] The propyl groups were found to be disordered in **1a** and their bond lengths were constrained to the ideal distances (C–C = 1.540, O–C = 1.430 Å) during the structural refinement. Due to the unresolved disorder problem, the C atoms of the propyl group were refined isotropically. H-atoms were added in calculated positions in both structures. Pertinent crystallographic data for both compounds are listed in Table 4.

CCDC reference numbers 182802 and 182803.

See http://www.rsc.org/suppdata/dt/b2/b202633n for crystallographic data in CIF or other electronic format.

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