$\delta = 13.52$ (s, 4H; NH), 11.88 (s, 4H; NH), 11.86 (s, 4H; NH), 7.80 (d, ^4J(H,H) = 2.3 Hz, 4H; ArH), 5.87 (s, 4H; pyrim); ^{1}H NMR (300 MHz, [D_6]DMSO, 100 °C): $\delta = 10.70-10.00$ (br s, 4H; NH), 9.40 (s, 2H; NH), 7.18 (s, 4H; ArH), 7.04 (d, ^3J(H,H) = 7.5 Hz, 4H; ArH), 6.64 (t, ^3J(H,H) = 7.5 Hz, 2H; ArH), 5.73 (s, 2H; pyrim), 3.80–3.30 (m, 32H; CH_2), 2.42 (t, ^3J(H,H) = 7.5 Hz, 4H; CH_2), 1.63 (m, 4H; CH_2), 1.50–1.20 (m, 24H; CH_2), 1.17 (t, ^3J(H,H) = 7.0 Hz, 6H; CH_3), 1.09 (t, ^3J(H,H) = 7.0 Hz, 6H; CH_3), 0.85 (t, ^3J(H,H) = 7.0 Hz, 6H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, Heteronuclear Multiple Quantum Correlation (HMQC)): major isomer: $\delta = 172.2$, 156.0 (CO), 155.1, 154.8, 152.1, 151.2, 133.3, 133.2, 133.1, 131.3 (ArC, pyrimC), 129.6, 129.5, 123.5, 122.6, 121.4 (ArCH), 105.2 (pyrimCH), 72.3, 72.1, 70.0, 69.7(OCH_2CH_2O), 66.6, 66.1 (OCH_2CH_3), 34.1, 33.5 ($ArCH_2Ar$), 32.9, 31.8, 29.5, 29.3, 29.2, 29.1, 27.3, 22.6 (CH_2), 15.6, 15.3 (OCH_2CH_3), 14.1 (CH_3); IR (KBr): $\tilde{\nu} = 3357$, 1701, 1654, 1587, 1465, 1245 cm^{-1}; positive-ion FAB MS (2-nitrophenyloctyl ether matrix): m/z (%): 2539 (30) [$2M+H$]$^+$, 1270 (100) [$M+H$]$^+$; elemental analysis calcd for $C_{72}H_{100}N_8O_{12}$ (%): C 68.11, H 7.94, N 8.83; found: C 67.77, H 8.28, N 8.68.

1b: 78% yield; (mixture of isomers in proportion 3:1): m.p. 264–266 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): major isomer: $\delta = 13.23$ (s, 4H; NH), 12.10 (s, 4H; NH), 11.89 (s, 4H; NH), 7.84 (d, ^4J(H,H) = 2.3 Hz, 4H; ArH), 7.15–7.05 (m, 8H; ArH), 7.05 (d, ^4J(H,H) = 2.3 Hz, 4H; ArH), 6.60 (t, ^3J(H,H) = 7.0 Hz, 4H; ArH), 4.20–3.40 (m, 64H; CH_2), 2.62–2.30 (m, 16H; CH_2), 1.78 (m, 16H; CH_2), 1.34 (t, ^3J(H,H) = 7.0 Hz, 12H; CH_3), 1.19 (t, ^3J(H,H) = 7.0 Hz, 12H; CH_3); minor isomer (only signals different from those of the major isomer): $\delta = 13.35$ (s, 4H; NH), 12.00 (s, 4H; NH), 11.96 (s, 4H; NH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): major isomer: $\delta = 171.8$, 156.1 (CO), 155.0, 153.6, 152.0, 143.7, 133.7, 133.0 (multiple peaks), 131.9 (ArC, pyrimC), 129.7, 129.5, 123.1, 122.0, 121.3 (ArCH), 114.9 (pyrimCH), 72.2, 71.5, 70.0, 69.6 (OCH_2CH_2O), 66.6, 66.3 (OCH_2CH_3), 34.5, 33.9 ($ArCH_2Ar$), 26.7, 22.3, 21.7 (CH_2), 15.4, 15.3 (CH_3); minor isomer (only signals different from those of the major isomer): $\delta = 154.7$, 153.8, 143.3, 132.2 (ArC, pyrimC), 129.4, 129.2, 121.8, 121.5 (ArCH), 115.4 (pyrimCH), 72.3, 71.8 (OCH_2CH_2O), 66.4 (OCH_2CH_3), 34.1 ($ArCH_2Ar$), 22.0, 21.5 (CH_2), 15.7 (CH_3); IR (KBr): $\tilde{\nu} = 3337$, 1703, 1653, 1584, 1460, 1245 cm^{-1}; positive-ion FAB-MS (m-nitrobenzyl alcohol matrix): m/z (%): 2250 (6) [$2M+H$]$^+$, 1126 (100) [$M+H$]$^+$.

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[8] No heterodimers were observed, however, by addition of 6-*n*-nonyl-2-*n*-octylureidopyrimidin-4(1*H*)-one to **1a**.

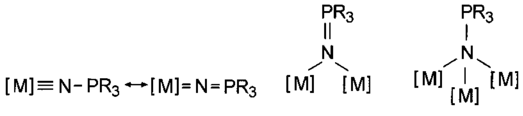
[9] The apparent association constant (K^*_{ass}) was determined from the integrals (I) of the signals of the pyrimidinyl proton in the monomer ($\delta = 5.6$) and dimer ($\delta = 5.9$) using the formula $K^*_{ass} = (1-\alpha_{diss})/4c_0\alpha^2_{diss}$, where $\alpha_{diss} = I_{monomer}/(I_{monomer}+I_{dimer})$ and c_0 is the initial concentration of the dimer. Furthermore, the value of K^*_{ass} determined by integration of one signal of the calixarene unit in the monomer ($\delta = 6.6$, t) and dimer ($\delta = 6.5$, t) was on same order of magnitude.

[10] NH signals were assigned by this experiment.

$[Cu_{12}(NPEt_3)_8]^{4+}$ and $[Ag_{12}(NPEt_3)_8]^{4+}$: Cubane Structures[**]

Ulrike Riese, Naim Faza, Werner Massa, and Kurt Dehnicke[*]

Phosphoraneiminato complexes of transition metals are known in a large variety of forms.[1] The phosphoraneiminato ligands NPR_3^- that are isoelectronic with silanolates $OSiR_3^-$ show great flexibility with regard to coordination chemistry aspects. The terminal bonding mode **A** is preferably realized with electron-deficient transition metals, while increasingly electron-rich transition metals form the μ-bridging type **B** or even the μ_3-type **C**. With divalent transition metals of Mn, Fe, Co, Ni, Zn, and Cd type **C** leads to tetrameric complexes $[XM(NPR_3)]_4$ (X = halogen, organic residue) with M_4N_4 heterocubane structures. With Cu^I, Ag^I, and Au^I such an architecture cannot develop because of their tendency towards sp hybridization. In fact, the build-up of the phosphoraneiminato complexes of Au^I, $[R_3PN\{Au(P'R_3)\}_3]^{2+}$ (R = Ph, NMe_2), leads to coordination type **C** with linear axes N-Au-P′.[2]



A **B** **C**

We have now found that reactions of the silylated phosphaneimine $Me_3SiNPEt_3$ with anhydrous copper(I) trifluoromethanesulfonate (triflate) [Eq. (1)] and of the heterocubane $[BrCo(NPEt_3)]_4$[3] with excess silver triflate [Eq. (2)] provide

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$$8\,Me_3SiNPEt_3 + 12\,Cu(O_3SCF_3) \longrightarrow \underset{\mathbf{1}}{[Cu_{12}(NPEt_3)_8]^{4+}}(O_3SCF_3^-)_4 + 8\,Me_3SiOSO_2CF_3 \quad (1)$$

$$2\,[BrCo(NPEt_3)]_4 + 20\,Ag(O_3SCF_3) \longrightarrow \underset{\mathbf{2}}{[Ag_{12}(NPEt_3)_8]^{4+}}(O_3SCF_3^-)_4 + 8\,Co(O_3SCF_3)_2 + 8\,AgBr \quad (2)$$

access to a new type of phosphoraneiminato complexes with cubane structure. While reaction (2) proceeds in dichloromethane already at 20 °C, the synthesis of **1** according to Equation (1) requires the starting materials to be heated together at 190 °C. An exchange of the reagents $Me_3SiNPEt_3$ and $[BrCo(NPEt_3)]_4$ in the reactions (1) and (2) leads to a drastic loss in yield. Compounds **1** and **2** form colorless, light-sensitive crystals, which dissolve readily in dichloromethane and acetronitrile. According to the crystal structure analyses,[4] the tetracations of **1** (with C_i symmetry) and of **2** (with C_{3i} symmetry) form almost perfect cubane structures of coordination type **C**, in which the metal atoms occupy the edges of the cube skeletons, while the N atoms of the phosphoraneiminato ligands occupy the corner positions (Figures 1 and 2). Thus, these tetracations of **1** and **2** display an inverted population of corners and edges by anions and cations in comparison with those "organometallic boxes" of the $[(C_5Me_4Et)_8Co_4Rh_4(CN)_{12}]^{4+}$ type recently described,[5] in which the eight metal atoms occupy the corners and the twelve cyanide ions occupy the edges of the cube skeletons. Up to now, such an inverted population has been known only with the topologically related tetraanions $[Cu_{12}S_8]^{4-}$[6] and $[Au_{12}S_8]^{4-}$.[7]

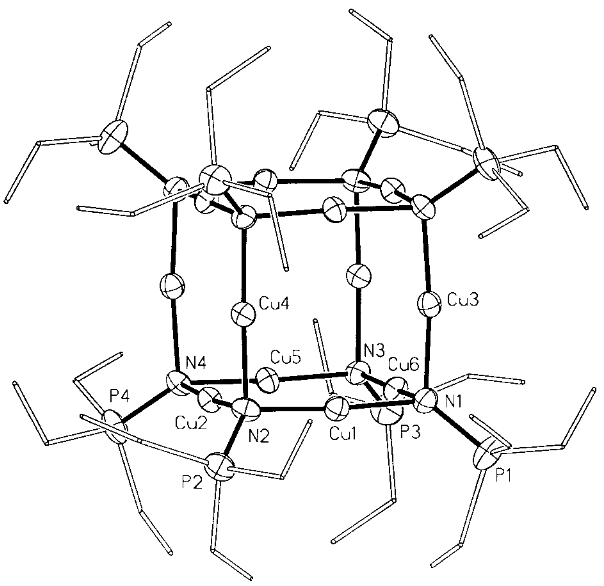

Figure 1. Structure of the cation $[Cu_{12}(NPEt_3)_8]^{4+}$ of **1** in the crystal. In disordered ethyl groups only the more strongly occupied orientation is shown. Selected average bond lengths [pm] and angles [°] (the standard deviations correspond to those of the single values): Cu–N 188.0(7), Cu···Cu 274.6(1), P–N 161.7(6); N-Cu-N 174.5(3), Cu-N-Cu 94.1(3), Cu-N-P 122.5(4).

The $Cu_{12}N_8$ skeleton of **1** can be considered as a molecular section of the structure of the copper nitride Cu_3N,[8] in which the ReO_3 lattice type is realized with an inverted population of corners and edges. The Cu–N distances in Cu_3N (191 pm) are also comparable to the mean value in **1** (188.0 pm); the shortening of the Cu–N distance is due to the tetrapositive charge of **1**. The metal atoms in **1** and **2** deviate only slightly from linearity, showing mean values of the internal angles of 174.3° for Cu and of 173.4° for Ag. The M-N-M bond angles, on the other hand, (93.4° in **1** and 94.5° in **2**) are greater than 90°, therefore the "boxes" are a bit convexed. In Cu_3N, too, the N-Cu-N axes are not exactly linear, due to a slight tilting of the NCu_6 octahedra; the bond angles are 173° at 21 °C and 176° at – 143 °C.[8] Considering the van der Waals radii, **1** only offers a cavity which is 269 pm in free diameter, **2** one of 266 pm; these are too small to take in guest molecules.

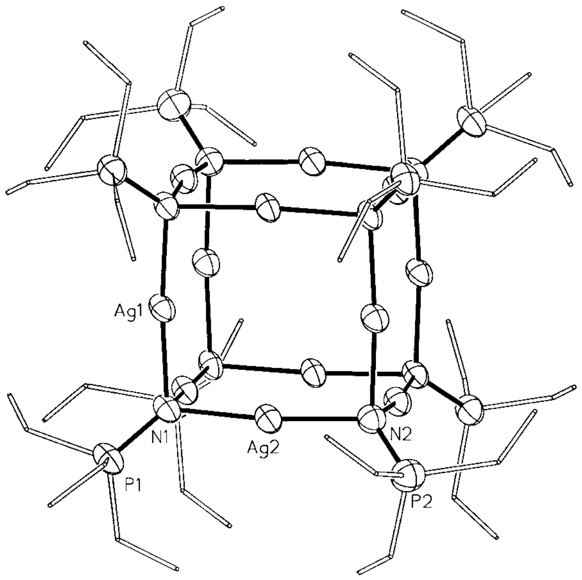

Figure 2. Structure of a cation $[Ag_{12}(NPEt_3)_8]^{4+}$ of **2** in the crystal. Selected average bond lengths [pm] and angles [°] (the standard deviations correspond to those of the single values): Ag–N 208.8(5), Ag···Ag 306.8(1), P–N 159.1(6); N-Ag-N 173.4(3), Ag-N-Ag 94.7(3), Ag-N-P 122.0(3).

The square faces of the cubanes **1** and **2** represent structural elements akin to those in the tetrameric molecular complexes $[M(amide)]_4$ of copper(I)[9a–f] and silver(I)[10] with a planar M_4N_4 skeleton. Analogous building units are also found in the tetrameric ketimine complexes of copper(I),[9g] and—with a planar Cu_4O_4 skeleton—in siloxy complexes $[CuOSiR_3]_4$.[9h,i] In these compounds the Cu···Cu and the Ag···Ag distances are all somewhat shorter than in **1** (av 274.6 pm) and in **2** (av 306.8 pm) because the metal atoms are deflected towards the M_4N_4 ring center; therefore, bonding metal–metal interactions have been assumed time and again.[9, 10] But according to results of recent density functional theory calculations, not even $Cu^I \cdots Cu^I$ distances of only 238 pm can be assumed to signify Cu–Cu bonds.[11]

The ^{109}Ag NMR spectrum[12] of **2** in CD_3CN solution shows only one signal at $\delta = 1106$, consistent with the solid-state structure. Compared with the spectrum of a 3.0 M silver triflate solution in CD_3CN ($\delta = 503$),[13] this signal is shifted downfield in accord with strong deshielding; this can be explained by the neighborhood of the phosphorus atoms—the positive nature of which is increased—of the $NPEt_3^-$ groups. Similarly strong deshielding has recently been observed in the ^{109}Ag NMR spectrum of the imidazolate (im) complex $[Ag(im)(PPh_3)_3]$

with $\delta = 1186$.[14] The phosphonium character of the P atoms in **1** and **2** is also reflected in the downfield position in the ^{31}P NMR spectra, in which a singlet occurs at $\delta = 64.0$ for **1** and at $\delta = 66.0$ for **2**, and lies close to the signal positions in the ^{31}P NMR spectra of tri(phosphorano)borazinium ions[17] with extremely deshielded phosphorus nuclei.

Experimental Section

1: A mixture of anhydrous copper(I) trifluoromethanesulfonate[20] (2.90 g, 13.6 mmol) and trimethylsilyltriethylphosphaneimine[21] (8.00 mL, 36.2 mmol) was heated slowly to 190 °C and maintained at this temperature for 4 h. During this time, emerging trimethylsilyltriflate was continuously distilled off with a Vigreux column. After cooling the mixture, excess $Me_3SiNPEt_3$ was rinsed out with dichloromethane (3×5 mL), the residue washed with *n*-hexane (2×4 mL) and dried in vacuo. Yield 1.69 g (62 %); elemental analysis calcd for $C_{52}H_{120}Cu_{12}F_{12}N_8O_{12}P_8S_4$ (%): C 25.85, H 5.01, N 4.64; found: C 25.61, H 5.04, N 4.64. Single crystals of $\mathbf{1} \cdot 2\,H_2O$ were obtained by cooling and leaving a saturated solution of **1** in acetonitrile/dichloromethane (1:3) at 8 °C. ^{1}H NMR (500 MHz, CD_3CN): $\delta = 1.29$ (dt, ^3J(H,H) = 7.7, ^3J(H,P) = 18 Hz, 72 H; CH_3), 1.87 (dq, ^3J(H,H) = 7.7, ^2J(H,P) = 11 Hz, 48 H; CH_2); ^{13}C NMR (126 MHz, CD_3CN): $\delta = 7.0$ (d, ^2J(C,P) = 4.3 Hz; CH_3), 23.4 (d, ^1J(C,P) = 62 Hz; CH_2).

2: A solution of $[CoBr(NPEt_3]_4$[3] (2.04 g, 1.88 mmol) in dichloromethane (10 mL) was added dropwise under stirring at 20 °C to a suspension of silver(I) trifluoromethanesulfonate (Merck) (4.95 g, 19.3 mmol) in dichloromethane (15 mL). After having been stirred for 5 d, the charge was filtered, the residue washed with dichloromethane (2×5 mL), and the collected filtrates were evaporated in vacuo to 5 mL. Addition of *n*-hexane (5 mL) led to a white precipitate, which was filtered, washed with *n*-hexane, and dried in vacuo. Yield 1.10 g (40 %). Elemental analysis calcd for $C_{52}H_{120}Ag_{12}F_{12}N_8O_{12}P_8S_4$ (%): C 21.19, H 4.10, N 3.80; found: C 21.10, H 4.02, N 4.02. Single crystals of $\mathbf{2} \cdot CH_2Cl_2 \cdot CH_3CN$ were obtained by leaving an oversaturated solution of **2** in dichloromethane/acetonitrile (30:1) at 20 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): $\delta = 1.29$ (dt, ^3J(H,H) = 7.7, ^3J(H,P) = 17 Hz, 72 H; CH_3), 1.86 (dq, ^3J(H,H) = 7.7, ^2J(H,P) = 11 Hz, 48 H; CH_2); ^{13}C NMR (126 MHz, CD_2Cl_2): $\delta = 6.6$ (d, ^2J(C,P) = 4.8 Hz, CH_3), 23.5 (d, ^1J(C,P) = 63 Hz, CH_2).

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[12] A 0.25 M solution in CD_3CN equivalent to a silver ionic concentration of 3.0 mol L^{-1}, 18.6 MHz, 25 °C, external standard saturated solution of $AgClO_4$ in D_2O.

[13] Judging the chemical shifts in the NMR spectra of silver salts in acetonitrile and other N-donor molecules, however, one has to consider their dependence on contact-ion pairs of the solvated silver ions such as $[Ag(NCCH_3)_2]^+$ with their anions.[15, 16] Thus, for example, the chemical shift of a 3.0 M $AgNO_3$ solution in acetonitrile is 380 ppm.[16]

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New Ni–Pt Carbonyl Clusters with a Tetrahedron of Platinum Atoms Encapsulated in an Incomplete Tetrahedron of Nickel Atoms: $[Ni_{36}Pt_4(CO)_{45}]^{6-}$ and $[Ni_{37}Pt_4(CO)_{46}]^{6-}$ **

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Only a limited number of structurally characterized carbonyl or carbonyl-substituted metal clusters containing more than 30 metal atoms is known.[1–3] Metal clusters of high nuclearity provide useful models for experimental[4] and theoretical[5] studies of the metallization process. For instance, we have recently ascertained that carbonyl clusters containing highly connected (coordination number 12 and 13) metal atoms behave as electron sinks; thus, $[H_{6-n}Ni_{38}C_6(CO)_{42}]^{n-}$ ($n=5, 6$)[3b] and $[Ni_{32}C_6(CO)_{36}]^{6-}$ [3d] display an unusually rich redox chemistry[6] that encompasses up to six oxidation states.[7] Furthermore, the almost constant separation of about 0.3 V between the formal potentials of their electrochemically reversible consecutive redox couples indicates the absence of a well defined HOMO–LUMO gap.[7] This finding led us to pursue the synthesis of other carbonyl metal clusters with several interstitial metal atoms to gain a better understanding of the metallization process.

Here we report the synthesis and structural characterization of the complex hexaanions **1** and **2**, which are chemically and structurally related to the previously reported clusters $[H_{6-n}Ni_{38}Pt_6(CO)_{48}]^{n-}$ ($n=4, 5, 6$).[5a] The latter have a cherry structure in which a Pt_6 octahedron is fully encapsulated in a ν_3[8] Ni_{38} octahedron; the present clusters may be considered as being derived by encapsulation of a Pt_4 tetrahedron in an incomplete ν_5 tetrahedron of nickel atoms.

$[Ni_{36}Pt_4(CO)_{45}]^{6-}$ **1**

$[Ni_{37}Pt_4(CO)_{46}]^{6-}$ **2**

The cluster anions **1** and **2** were obtained by reaction of $[NMe_4]_2[Ni_6(CO)_{12}]$ with $K_2[PtCl_4]$ in the molar ratio 2.5:1 in acetonitrile under nitrogen. The final brown mixture of products was separated by extraction with THF ($[Ni_9(CO)_{18}]^{2-}$, $[HNi_9Pt_3(CO)_{21}]^{3-}$),[9, 10] acetone ($[H_2Ni_{38}Pt_6(CO)_{48}]^{4-}$), propionitrile ($[Ni_9Pt_3(CO)_{21}]^{4-}$, $[HNi_{38}Pt_6(CO)_{48}]^{5-}$), and acetonitrile ($[Ni_{36}Pt_4(CO)_{45}]^{6-}$, $[Ni_{37}Pt_4(CO)_{46}]^{6-}$). The hexaanions **1** and **2** are indistinguishable by IR spectroscopy, and their $[NMe_4]^+$ salts cocrystallize when a solution in acetonitrile is layered with diisopropyl ether. The tetramethylammonium salts were converted to other quaternary ammonium and phosphonium salts by metathesis with the corresponding halides in DMSO, precipitation with water, and crystallization from acetonitrile/diisopropyl ether. The **1**/**2** mixture as the $[NMe_3CH_2Ph]^+$ salts shows strong carbonyl absorption bands in acetonitrile at 2003 and 1856 cm^{-1}. The ^1H NMR spectrum ([D$_3$]acetonitrile, 25 °C) only shows signals for the trimethylbenzylammonium cation and organic solvents over the range $\delta=-50$ to $+50$.

The asymmetric unit of the cocrystallized mixture of $[NMe_3CH_2Ph]_6$-**1** and $[NMe_3CH_2Ph]_6$-**2** consists of one anion (**1** or **2**) located on a crystallographic C_3 axis with an average occupancy factor of 0.5, two $[NMe_3CH_2Ph]^+$ cations in general positions, and a disordered isopropanol molecule located on a crystallographic C_3 axis.[11] The idealized metal framework of **1** can be derived from a ν_5 Ni_{56} tetrahedron (Figure 1 top) by

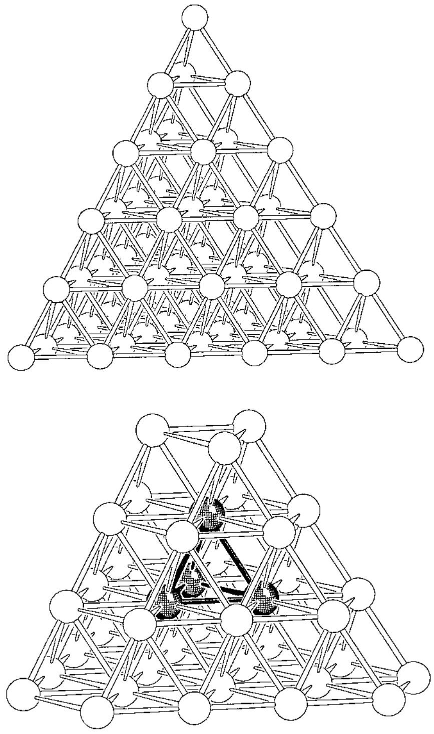

Figure 1. The ν_5 Ni_{56} tetrahedron (top) and the derived idealized $Ni_{36}Pt_4$ metal framework of **1** (bottom).

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