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New cationic clathrate: synthesis and structure of $[Si_{40}P_6]I_{6.5}$

Kirill A. Kovnir,[a,b] **Alexei N. Uglov,**[a] **Julia V. Zaikina**[a] **and Andrei V. Shevelkov***[a]

[a] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119992 Moscow, Russian Federation. Fax: +7 095 939 4788; e-mail: shev@inorg.chem.msu.ru*

[b] *Department of Materials Science, M. V. Lomonosov Moscow State University, 119992 Moscow, Russian Federation. E-mail: kovnir@inorg.chem.msu.ru*

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The $[Si_{40}P_6]I_{6.5}$ cationic clathrate possessing the type-I clathrate structure with a minimal known unit-cell volume and a remarkably high vacancy concentration in the guest sublattice was synthesised.

The supramolecular organisation of semiconducting clathrates[1] attracts considerable attention. First, the role of the host–guest interaction in assembling supramolecular architectures from electrically charged hosts and guests is the basic issue that is not yet established. Second, the clathrates based on Group 14 elements exhibit superconductivity[2] and abnormally low thermal conductivity,[3] opening horizons of their application. Within a large family of semiconducting clathrates, there is a small number of compounds featuring cationic frameworks encapsulating guest anions, halides or Te^{2-}.[4–7] Here we report the $[Si_{40}P_6]I_{6.5}$ cationic clathrate, a type-I clathrate with the lowest known unit-cell volume, which exhibits an unusually high vacancy concentration in the guest substructure.

The title compound was prepared by a high-temperature ampoule synthesis at 925 K for 6 days using powdered silicon, red phosphorus and iodine as starting materials.[†] The XRD analysis of the product (Guinier-type Nonius FR-552 chamber, $\lambda = 1.54060$ Å, Ge as an internal standard, $a = 5.6576$ Å) showed that it contained a new phase together with traces of SiP_2. The indexing of all the reflections of the XRD pattern belonging to the main phase was successful in a cubic system. The least-squares refinement led to the unit cell parameter $a = 10.130(1)$ Å. A suitable single crystal was selected from the reaction product for the X-ray single crystal structure determination.[‡]

The title compound crystallises with the type-I clathrate structure typical of various gas hydrates[8,9] and semiconducting clathrates based on Group 14 elements.[1] The crystal structure is built of a three-dimensional framework composed of silicon and phosphorus atoms, trapping guest iodine atoms in the cavities of two types (Figure 1). In total, there are 46 atoms per formula forming the clathrate framework. Though the accuracy of distinguishing silicon and phosphorus atoms upon the communal occupation of two positions in the structure is typically low, the quality of the experimental data enabled us to determine the overall Si:P ratio as 40(1):6(1), which is in good agreement with the microprobe analysis data, 40.7:5.3:6.5 for the Si:P:I ratio normalised to 6.5 iodine atoms per formula (PHILIPS XL30 scanning electron microscope equipped with an EDXS analyser). The co-ordination of all atoms of the framework is best described as slightly distorted tetrahedral. The separation between the silicon atoms in the 24-fold position is 2.39 Å. Two other positions of the framework, 16-fold and 6-fold, are jointly occupied by silicon and phosphorus atoms, the phosphorus content being 32 and 8%, respectively. The bonding distance between these atoms is shorter, the minimal one being 2.33 Å for the separation between two atoms in the 16-fold position, which is most populated by phosphorus atoms, reflecting the trend of decreasing the homonuclear single bond on going from silicon to phosphorus. As a consequence, the unit cell volume of $[Si_{40}P_6]I_{6.5}$ is the smallest in the very broad family of semiconducting clathrates based on Group 14 elements.

The iodine atoms reside in the large cavities of the clathrate framework. The I(2) atom is surrounded by 24 atoms forming a tetrakaidecahedron. The co-ordination polyhedron of the I(1) atom is a slightly distorted dodecahedron. The I(1) position is only 25% occupied, which is typical of gas hydrates rather than semiconducting clathrates. Only one example with even lower (22%) occupancy of the respective position by rubidium atoms in $Rb_{6.168}Si_{45.27}$ was reported.[10] It is unclear, which factors determine the occupation of the 20-vertex position by a guest atom. However, note that the title compound, in comparison to other cationic clathrates of type-I, displays a greater difference in the clathrate cage volume. The calculated r_2/r_1 ratio, where r_2 and r_1 are the effective radii of the bigger and smaller cages, respectively, is 1.108, which is significantly higher (9 to 10%) than the corresponding values of 1.010 and 1.003 reported for $Sn_{24}P_{19.3}I_8$ and $Sn_{24}P_{19.5}Br_8$,[11] respectively. Another problem that seems to associate with the vacancy concentration in the guest sublattice is the charge balancing or the electron count. Applying the Zintl electron counting scheme[12] to the phases with the reversed polarity,[13] one arrives at the compositions with the equal numbers of phosphorus and iodine atoms. Taking into

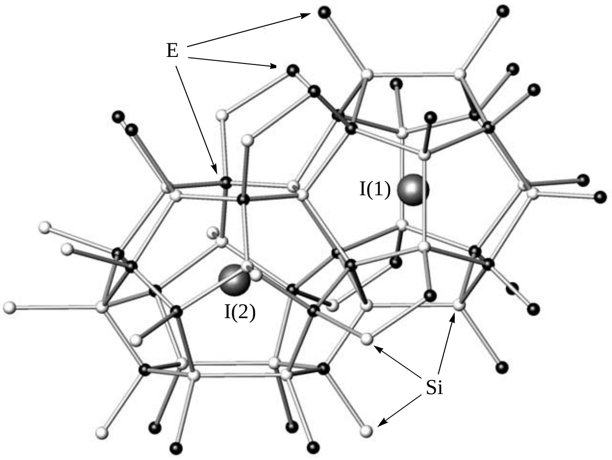

Figure 1 Two adjacent cages of the crystal structure of $[Si_{40}P_6]I_{6.5}$. The mixed Si/P sites are designated as E. Bond distances (Å) and valence angles (°) in the structure of $[Si_{40}P_6]I_{6.5}$: E(1)–Si(3) 2.3686(7), E(2)–E(2) 2.326(1), E(2)–Si(3) 2.3385(6), Si(3)–Si(3) 2.388(1); Si(3)–E(1)–Si(3) 108.61(1), Si(3)–E(1)–Si(3) 111.21(3), E(2)–E(2)–Si(3) 108.40(2), Si(3)–E(2)–Si(3) 110.52(2), E(1)–Si(3)–E(2) 106.24(3), E(1)–Si(3)–Si(3) 124.40(1), E(2)–Si(3)–E(2) 105.47(3), E(2)–Si(3)–Si(3) 106.57(1).

[†] A stoichiometric mixture of the starting materials was sealed under a vacuum (10^{-2} Torr) in a silica ampoule (50 mm in length, 7 mm in inner diameter). The ampoule was placed vertically in a furnace and heated to 925 K at a rate of 25 K h^{-1}. After annealing at 925 K for 6 days, the ampoule was cooled with the furnace.

[‡] *Crystal data for* $[Si_{40}P_6]I_{6.5}$: $M = 2135.68$, cubic, $Pm\bar{3}n$ (No. 223), $a = 10.1293(9)$ Å, $V = 1039.3(1)$ Å^3, $Z = 1$, $d_{calc} = 3.412$ g cm^{-3}, μ(MoKα) = 6.275 mm^{-1}, $T = 291$ K, dark-gray cube; 1597 measured reflections [$2.84 < \theta < 29.91$], 298 independent reflections ($R_{int} = 0.0513$), 18 parameters, $R_1 = 0.0186$, $wR_2 = 0.0346$. Data were collected on a Nonius CAD-4 diffractometer using ω–2θ scans. The structure was solved by direct methods and refined against F^2 using SHELX-97 programs.[15] Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: +49 7247 808 666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-414081.

account the very high accuracy of the occupancy determination of the I(1) atom, the composition of the electron-precise inverted Zintl phase[13] is expected to be $[Si_{39.5}P_{6.5}]I_{6.5}$, which is slightly off the Si:P ratio found from both crystal data and microprobe analysis. Note that the title compound is a point phase and has no detectable phase range; all the prepared samples of $[Si_{46-x}P_x]I_{6.5}$ (x = 5.5, 6.0, 6.5, 7.0 and 7.5) contain a clathrate phase with the same cubic parameter a = 10.130(1) Å. Because the accuracy of the Si:P ratio determination is low, it is impossible to conclude whether the composition conforms to the Zintl scheme or $[Si_{40}P_6]I_{6.5}$ is an electron-deficient compound. Noteworthy, silicon-based clathrates are frequently electron-rich compounds; this is attributed[10] to the remarkable stability of the Si–Si bond (222 kJ mol^{-1})[14] withstanding the promotion of electrons to the conduction band. Careful resistivity measurements are required to conclude on the nature of the new clathrate on the basis of the conductivity type.

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References

1 S. Bobev and S. C. Sevov, *J. Solid State Chem.*, 2000, **153**, 92.
2 H. Fukuoka, J. Kiyoto and S. Yamanaka, *Inorg. Chem.*, 2003, **42**, 2933.
3 B. B. Iversen, A. E. C. Palmqvist, D. E. Cox, G. S. Nolas, G. D. Stucky, N. P. Blake and H. Metiu, *J. Solid State Chem.*, 2000, **149**, 455.
4 H. G. von Schnering and H. Menke, *Angew. Chem.*, 1972, **84**, 30.
5 R. Nesper J. Curda and H. G. von Schnering, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 350.
6 M. M. Shatruk, K. A. Kovnir, A. V. Shevelkov, I. A. Presniakov and B. A. Popovkin, *Inorg. Chem.*, 1999, **38**, 3455.
7 N. Jaussaud, P. Toulemonde, M. Pouchard, A. San Miguel, P. Gravereau, S. Pechev, G. Goglio and C. Cros, *Solid State Sci.*, 2004, **6**, 401.
8 L. Pauling and R. E. Marsh, *Proc. Natl. Acad. Sci.*, 1952, **36**, 112.
9 D. Mootz, E.-J. Oellers and M. J. Wiebcke, *J. Am. Chem. Soc.*, 1987, **109**, 1200.
10 G. K. Ramachandran, P. F. McMillan, J. Dong and O. F. Sankey, *Solid State Chem.*, 2000, **154**, 626.
11 K. A. Kovnir, J. V. Zaikina, L. N. Reshetova, A. V. Olenev, E. V. Dikarev and A. V. Shevelkov, *Inorg. Chem.*, 2004, **43**, 3230.
12 G. J. Miller, in *Chemistry, Structure, and Bonding of Zintl Phases and Ions*, ed. S. M. Kauzlarich, VCH, New York, 1996, pp. 1–59.
13 A. V. Shevelkov and M. M. Shatruk, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 321 (*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 337).
14 D. M. P. Mingos, *Essential Trends in Inorganic Chemistry*, Oxford University Press, Oxford, 1998.
15 G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Solution*, and *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, Germany, 1997.

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