preparations using a shear-force dependent height-control system. Based on the topographical data, regions of interest on the cell membrane can be identified and spatially addressed with the microelectrode. Current work is directed towards a further decrease of the diameter of the used microelectrodes to submicrometer dimensions and the precise positioning of these fragile microelectrodes in close proximity to individual cells using shear-force interactions. In principle, the application of such miniaturized microelectrodes should allow elucidation of metabolic reactions even at substructures of cells.

Experimental Section

SECM: The SECM with integrated height control and video microscope has been described elsewhere.[10] All electrochemical measurements were carried out using a VA-10 potentiostat (npi electronic GmbH, Tamm, Germany) and an AgCl-coated silver wire as pseudo reference electrode.

Polymer-insulated carbon-fiber electrodes: A single carbon fiber (SGL Technik GmbH, Meitingen, Germany) of diameter 7 μm and length 15 mm was connected to a copper wire by means of silver epoxy glue (H20, EpoTek, Waldbronn, Germany). Parts of the copper wire and the fiber were inserted into a glass capillary and fixed with glue. The capillary was pulled around the fiber with a standard pulling apparatus (Narishige Model PP 830, Science Products, Hofheim, Germany). The electrodeposition was performed as described elsewhere.[13] The fiber was dipped into insulating paint (RS Components, Corby, Northants, UK) and allowed to dry at least 1 h. The ratio of insulator thickness to the fiber radius varied between 0.25 – 1 depending on the amount of coating cycles. Cyclic voltammetry was used to assure the quality of the obtained insulation. A carbon disc was exposed by cutting the insulated fiber with a scalpel. The microelectrode was inspected under the microscope for a smooth cutting and further characterized by means of cyclic voltammetry.

Retzius cells from medicinal leeches were dissected and cultured as described previously.[16] PC12 cells were grown on poly(ornithine)-covered glass slides following a procedure described elsewhere.[17]

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[1] a) R. H. Chow, L. von Rüden, *Single Channel Recording*, Plenum, New York, **1995**, pp. 245 – 275; b) M. J. Logman, E. A. Budygin, R. R. Gainetdinov, R. M. Wightman, *J. Neurosci. Methods* **2000**, *95*, 95 – 102; c) Q. D. Walker, M. B. Rooney, R. M. Wightman, C. M. Kuhn, *Neuroscience* **2000**, *95*, 1061 – 1070; d) D. J. Michael, J. D. Joseph, M. R. Kilpatrick, E. R. Travis, R. M. Wightman, *Anal. Chem.* **1999**, *71*, 3941 – 3947.

[2] a) P. S. Cahill, Q. D. Walker, J. M. Finnegan, G. E. Mickelson, E. R. Travis, R. M. Wightman, *Anal. Chem.* **1996**, *68*, 3180 – 3186; b) C. Amatore, *C. R. Acad. Sci. Ser. 2* **1996**, *23*, 757 – 771; c) Y. E. Korchev, M. Milanovic, C. L. Blashford, D. C. Bennett E. V. Sviderskaya, I. Vodyanov, M. J. Lab, *J. Microsc.* **1997**, *188*, 17 – 23.

[3] a) E. L. Ciolkowski, B. R. Cooper, J. A. Jankowski, J. W. Jorgenson, R. M. Wightman, *J. Am. Chem. Soc.* **1992**, *114*, 2815 – 2821; b) D. Bruns, R. Jahn, *Nature* **1995**, 62 – 65; c) A. Albillos, G. Dernick, H. Horstmann, W. Almers, G. Alvarez de Toledo, M. Lindau, *Nature* **1997**, *389*, 509 – 512; d) R. T. Kennedy, L. Huang, M. A. Atkinson, P. Dush, *Anal. Chem.* **1993**, *65*, 1882 – 1887; e) S. E. Hochstetler, M. Puopolo, S. Gustincich, E. Raviola, R. M. Wightman, *Anal. Chem.* **2000**, *72*, 489 – 496; f) R. M. Wightman, J. M. Finnegan, K. Pihel, *Trends Anal. Chem.* **1995**, *14*, 154 – 158; g) T. J. Schroeder, R. Borges, J. M. Finnegan, K. Pihel, C. Amatore, R. M. Wightman, *Biophys. J.* **1996**, *70*, 1061 – 1068; h) K. D. Kozminski, D. A. Gutman, V. Davila, D. Sulzer, A. G. Ewing, *Anal. Chem.* **1998**, *70*, 3123 – 3130; i) S. E. Zerby, A. G. Ewing, *Brain Res.* **1996**, *712*, 1 – 10; k) T. K. Chen, A. G. Ewing, *Anal. Chem.* **1994**, *66*, 3031 – 3035.

[4] S. C. Land, D. M. Porterfield, R. H. Sanger, P. J. S. Smith, *J. Exp. Biol.* **1999**, *202*, 211 – 218.

[5] T. Yasukawa, I. Uchida, T. Matsue, *Biophys. J.* **1999**, *76*, 1129 – 1135.

[6] Y. E. Korchev, Y. A. Negulyaev, C. R. W. Edwards, I. Vodyanoy, M. J. Lab, *Nat. Cell Biol.* **2000**, *2*, 616 – 619.

[7] a) C. Lee, J. Kwak, A. J. Bard, *Proc. Natl. Acad. Sci. USA* **1990**, *87*, 1740 – 1743; b) M. Tsionsky, Z. G. Cardon, A. J. Bard, R. B. Jackson, *Plant Physiol.* **1997**, *113*, 895 – 901; c) D. T. Pierce, A. J. Bard, *Anal. Chem.* **1993**, *65*, 3598 – 3604.

[8] a) T. Yasukawa, T. Kaya, T. Matsue, *Anal. Chem.* **1999**, *71*, 4637 – 4641; b) T. Yasukawa, Y. Kondo, I. Uchida, T. Matsue, *Chem. Lett.* **1998**, 767 – 768; c) T. Yasukawa, T. Kaya, T. Matsue, *Chem. Lett.* **1999**, 975 – 976; d) T. Yasukawa, T. Kaya, T. Matsue, *Electroanalysis* **2000**, *12*, 653 – 659; e) B. Liu, S. A. Rotenberg, M. V. Mirkin, *Proc. Natl. Acad. Sci. USA* **2000**, *97*, 9855 – 9860.

[9] a) M. Ludwig, C. Kranz, W. Schuhmann, H. E. Gaub, *Rev. Sci. Instrum.* **1995**, *66*, 2857 – 2860; b) C. Kranz, H. E. Gaub, W. Schuhmann, *Adv. Mater.* **1996**, *8*, 634 – 637.

[10] A. Hengstenberg, C. Kranz, W. Schuhmann, *Chem. Eur. J.* **2000**, *6*, 1547 – 1554.

[11] a) J. E. Griffith, D. A. Grigg, M. J. Vasile, P. E. Russell, E. A. Fitzgerald, *J. Vac. Sci. Technol. B* **1991**, *9*, 3586 – 3589; b) L. Montelius, J. O. Tegenfeldt, *Appl. Phys. Lett.* **1993**, *62*, 2628 – 2630.

[12] a) K. Potje-Kamloth, J. Janata, M. Josowicz, *Ber. Bunsenges. Phys. Chem.* **1989**, *93*, 1480 – 1485; b) T. G. Strein, A. G. Ewing, *Anal. Chem.* **1992**, *64*, 1368 – 1373.

[13] A. Schulte, R. H. Chow, *Anal. Chem.* **1996**, *68*, 3054 – 3058.

[14] G. Shi, L. F. Garfias-Mesias, W. H. Smyrl, *J. Electrochem. Soc.* **1998**, *145*, 2011 – 2016.

[15] M. V. Mirkin, F. R. F. Fan, A. J. Bard, *J. Electroanal. Chem.* **1992** *328*, 47 – 62.

[16] I. D. Dietzel, P. Drapeau, J. G. Nicholls, *J. Physiol.* **1986**, *372*, 191 – 205.

[17] L. A. Greene, A. S. Tischler, *Proc. Natl. Acad. Sci. USA* **1976**, *73*, 2424 – 2428.

"Supramolecular" Solid-State Chemistry: Interpenetrating Diamond-Type Frameworks of U^{4+} Ions Linked by *S,S'*-Bidentate $P_2S_6^{2-}$ Molecular Rods in UP_4S_{12}**

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Organic compounds can self-assemble into ordered arrays at low temperature that are capable of molecular recognition, and that can act as biomimetic systems.[1] As a result, organic supramolecular chemistry has afforded many intriguing results,[2] including various three-dimensional (3D) hydrogen-bonded frames of super-diamond-type[3] and super-wurtzite-type structures.[4] In the field of inorganic and coordination polymers, Hoskins and Robson[5] have proposed a strategy for the design of new 3D phases, referred to as

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"scaffolding-like materials", which are assembled by using suitable metal centers (e.g. with tetrahedral, square-planar, or octahedral connectivity) and rodlike or platelike molecular building blocks of different nature and length. This rational has been applied to the synthesis of a number of new compounds, whose structures exhibit interwoven nets.[6–8] Each of a number of simple structures (e.g. diamond, PtS, α-Polonium) may be regarded as prototype for a whole family of new frameworks in which bonds of the parent structure are replaced by a range of molecular rods. Simple bidentate linear ligands with different rod lengths are attractive rodlike connectors.[9] In some cases these polymeric structures evolve as single infinite frameworks leaving relatively large cavities and/or channels; in others, such as in $Zn(CN)_2$,[10] the cavities are filled by one or more identical independent frameworks. Corresponding advances in solid-state reactions have been confined to few examples such as $[Ph_4P]_2[M(Se_6)_2]$,[11] K_2PdSe_{10},[12] or $Ta_4P_4S_{29}$.[13]

Based on the observation that PS_4 and P_2S_6 groups can act as mono-, bi-, or tridentate ligands in early transition metal thiophosphates[14] and the fact that even high coordination numbers of metals such as niobium or uranium can provide low connectivities with chelating ligands, we explored the quasibinary system US_2/P_2S_5 for new compounds containing uranium coordinated by PS_4, P_2S_6, or $S_3P(S)_xPS_3$ groups. Herein we report the synthesis and structural characterization of $U(P_2S_6)_2$ (**1**), a compound with a three-dimensional architecture composed of three interpenetrating SiO_2-type frameworks. The extended structure may be rationalized based on the length of the P_2S_6 connecting rods.

Compound **1** was synthesized in the solid-state reaction of U, P_2S_5, and S in a 1:2:2 ratio at 700 °C.[15] Single crystals were obtained by annealing followed by slow cooling to room temperature. Compound **1** crystallizes in the tetragonal space group $I4_1/a$ with two formula units per cell. The structure[16] of **1** contains three interpenetrating diamond-type frameworks, based on elongated adamandoid cages (Figure 1). The length of shortest vector relating the three independent networks is 9.75 Å. The U atoms are coordinated by eight S atoms of four bidentate P_2S_6 ligands in a square-antiprismatic fashion leading to a pseudotetrahedral arrangement of the dithiophosphate groups. The metal atoms are located on S_4 axes of the cell and display crystallographically imposed D_{2d} coordination symmetry. Each uranium atom has a slightly distorted square-antiprismatic coordination environment (the distortion being caused by S···S repulsion between the P_2S_6 units) with S(2)-U-S(3) angles of 69.96(3)° for the S atoms of each P_2S_6 ligand. The U–S and P–S distances are unexceptional; selected values are compiled in the caption of Figure 2. The S(2)-P-S(3) bite angle of 109.90(8)° and the bridging U-S-P angles of 88.47(5)° and 90.23(5)° are consistent with the presence of essentially planar US_2P rings. The P-U-P angles of 86.54(1)° (2 ×) and 122.02(1)° (4 ×) indicate a compression of the $U(S_2PS_2)_4$ "pseudotetrahedron" in accordance with a *c*/*a* ratio of 0.76.

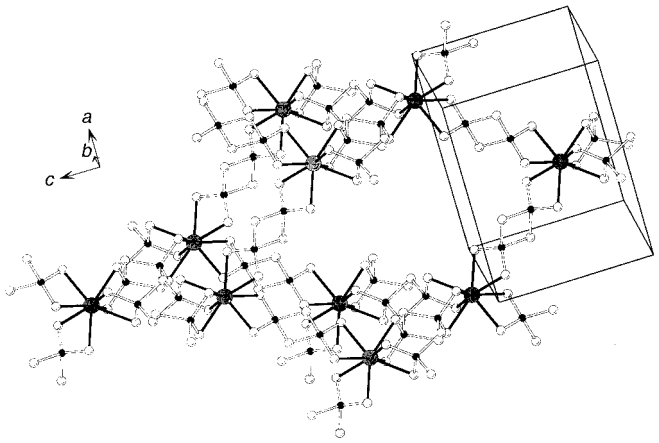

Figure 1. A view of a single adamantoid cage of **1** (U: gray spheres; P: black spheres; S: white spheres). Atom positions (x, y, z, $U_{eq} \times 10^3$): P(1) 0.0062(1), 0.0662(1), 0.3808(1), 113(1); S(1) 0.1681(1), 0.1840(1), 0.6774(1), 117(1); S(2) 0.1195(1), 0.1681(1), 0.3480(1), 119(1); S(3) −0.1812(1), −0.1557(1), −0.0238(1), 16(1) U 0 1/4, 1/8, 11(1). Selected distances [Å]: U-S(2) 2.879(1) (4 ×), U-S(3) 2.812(1) (4 ×), P-S(1) 2.107(2), P-S(1) 2.113(2), P-S(2) 1.989(2), P-S(3) 1.997(2).

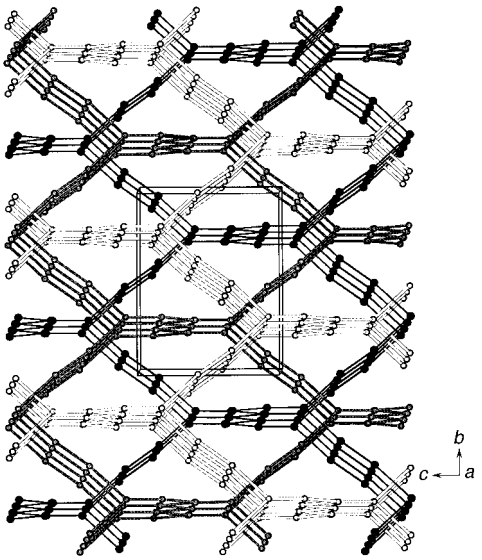

Figure 2. A schematic view of the three equivalent interpenetrating diamondoid frameworks in **1**. The P_2S_6 groups are represented by rods connecting the P atoms of the P_2S_6 ligands.

The title compound **1** is a novel member of the family of super-diamond networks in coordination chemistry. Although there is little precedent in metal/chalcogenide systems, the structure of **1** is closely related to that of methane tetraacetic acid.[18] Interpenetration, which arises by the necessity to fill empty space inside the large cages, is the rule rather than the exception in these species. The structural variability is large, including the presence of different interpenetrating frames, different types of tetrahedral centers, anisobidentate ligand, mixed rods, chiral metallic centers, and polymetal centers.

In an undistorted (cubic) diamond network each adamantane-type unit possesses three mutually perpendicular inversion axes running parallel to the cubic axes of the unit cell. The three interwoven diamond-type networks are oriented in such a way that the nodes of the independent frames are oriented along these inversion axes with identical interframe separations. This is illustrated schematically in Figure 2 for the title compound **1**. Here the frames of two further

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independent nets are located between the upper and lower frame. Furthermore, it is apparent that the frames are distorted in such a way that the adamantane-type units are elongated along one of the S_4 axes; this reduces the symmetry of the structure from cubic to tetragonal. The distance between the uranium atoms in the 3D framework structure determines the size of the adamantane-type cage. To optimize space filling by stuffing empty space in the structure, independent frameworks arrange themselves in such as way as to fill each other's empty cages and tunnels. As an example, Si ··· Si distances of 6.8 Å between the tetrahedral centers in $Si(NCN)_2$[19] are compatible with two interpenetrating diamond-type networks, whereas U ··· U separations of 9.75 Å in **1** require three interpenetrating frameworks for optimum space filling. Rodlike ligands with exceptional length such as 4,4′-biphenyldicarbonitrile (PCN) in $[Ag(BPCN)_2]PF_6$[20] can lead to the formation of a ninefold interwoven diamond-type network with distances of 16.42 Å between the metal centers.

Based on a formal assignment of oxidation states the electronic structure of **1** can be represented by $(U^{4+})(P^{5+})_4(S^{2-})_{12}$. From this formula, an f^2 system with two unpaired electrons may be expected. The molar magnetic susceptibility χ_{mol} of **1** was measured as a function of temperature (4 – 300 K). The effective magnetic moment μ_{eff} of 3.84 μ_B at 300 K is consistent with an f^2 configuration.[21] The magnetic susceptibility of **1** follows a Curie – Weiss type behavior with $C = 3.14\ cm^3\,K\,mol^{-1}$ and $\theta = -270.6$ K, as apparent by the shape of the $1/\chi_{mol}$ versus T and μ_{eff} versus curves (Figure 3). The large negative value of θ indicates that

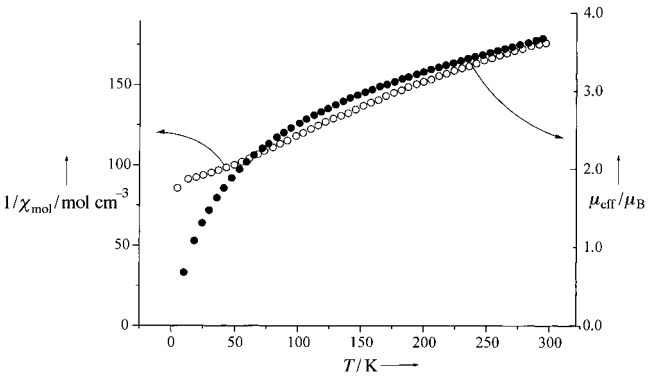

Figure 3. Temperature dependence of $1/\chi_{mol}$ (○) and μ_{eff} (●) for **1**.

antiferromagnetic interactions prevail, although no antiferromagnetic ordering is observed down to 4 K. These observations are in agreement with uranium centers which are magnetically coupled through the P_2S_6 ligands. Magnetic through-bond coupling through five and more atoms is not unusual and has been reported for a number of coordination compounds[22] or electrosodalites.[23] Furthermore, through-space coupling over distances as large as 8 Å has been observed in fullerides.[24] On the other hand, nonmagnetic f^2 ground states in U^{4+} compounds are not known to the best of our knowledge, whereas antiferromagnetic transitions have been observed in many other uranium compounds,[25] although in several cases the data analysis is complicated by the presence of additional 3d metals.[26]

In conclusion, the formation of **1** indicates that interpenetrating framework structures can also be formed in high-temperature solid-state reactions, which are not in the realm of conventional coordination chemistry or soft-chemistry low-temperature approaches. Since the deliberate use of "solid state" ligands is difficult to achieve in high-temperature reactions, only a few examples such as $Ta_4P_4S_{29}$,[13] $ATi_2(PS_4)_3$ (A = Li, Na),[27] $Cr_3P_3S_{9+x}$,[28] or $Li_9B_{19}S_{33}$[29] have been reported so far; nevertheless, a variation of the thiophosphate ligand by deliberate choice of composition and temperature allows the synthesis other framework structures. Apparently, the combination of properties such as rigidity, coordination behavior, ligand dimensions, or thermal stability allows the use of the thiophosphate moieties for the synthesis of "supramolecular" solid-state aggregates.

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[1] H. Ringsdorf, B. Schlarb, J. Venzmer, *Angew. Chem.* **1988**, *100*, 117 – 162; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 113 – 158.
[2] a) G. R. Desiraju, *Crystal Engineering: Design of Organic Solids*, Elsevier, Amsterdam, **1989**; b) A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Clarendon, Oxford, **1984**, p. 432.
[3] O. Ermer, *J. Am. Chem. Soc.* **1988**, *110*, 3747 – 3754.
[4] R. Robson, B. F. Abrahams, S. R. Batten, R. W. Gable, B. F. Hoskins, J. Liu, *ACS Symp. Ser.* **1992**, *499*, 256 – 273.
[5] a) B. F. Hoskins, R. Robson, *J. Am. Chem. Soc.* **1990**, *112*, 1546 – 1548; b) B. F. Abrahams, B. F. Hoskins, D. M. Michail, R. Robson, *Nature* **1994**, *369*, 727 – 729.
[6] S. R. Batten, R. Robson, *Angew. Chem.* **1998**, *110*, 1559 – 1595; *Angew. Chem. Int. Ed.* **1998**, *37*, 1460 – 1494.
[7] R. Robson in *Comprehensive Supramolecular Chemistry*, *Vol. 6* (Eds.: J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle, F. Toda, R. Bishop), Pergamon, Oxford, **1996**, pp. 733 – 755.
[8] a) H. Li, M. Eddaoudi, A. Laine, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **1999**, *121*, 6096 – 6097; b) H. Li, A. Laine, M. O'Keeffe, O. M. Yaghi, *Science* **1999**, *283*, 1145 – 1147.
[9] H. S. Zhdanov, *C. R. Acad. Sci. URSS* **1941**, *31*, 352 – 354; B. F. Hoskins, R. Robson, *J. Am. Chem. Soc.* **1990**, *112*, 1546 – 1554.
[10] a) T. M. Reineke, M. Eddaoudi, D. Moler, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2000**, *122*, 4843 – 4844; b) M. Eddaoudi, H. Li, O. M. H. Yaghi, *J. Am. Chem. Soc.* **2000**, *122*, 1391 – 1397; c) T. M. Reineke, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Angew. Chem.* **1999**, *111*, 682 – 685; *Angew. Chem. Int. Ed.* **1999**, *38*, 2590 – 2594.
[11] S. Dhingra, M. G. Kanatzidis, *Science* **1992**, *258*, 1769 – 1772.
[12] K. W. Kim, M. G. Kanatzidis, *J. Am. Chem. Soc.* **1992**, *114*, 4878 – 4883.
[13] M. Evain, M. Queignec, R. Brec, J. Rouxel, *J. Solid State Chem.* **1985**, *56*, 148 – 157.
[14] "Supramolecular Architecture": J. Rouxel, *ACS Symp. Ser.* **1992**, *499*, 88 – 113.
[15] We have synthesized UP_4S_{12} from a 500 mg mixture of uranium metal, P_2S_5, and sulfur with the molar ratio 1:2:2 in an evacuated quartz tube. The sample was heated in a furnace at a rate of 1 K min^{-1} up to 700 °C and kept at this temperature for seven days; subsequently, it was cooled to room temperature by switching off the furnace. Black crystals with a metallic luster were formed. Microprobe analysis of the crystals indicated the presence of uranium, phosphorus, and sulfur in a 1:4:12 ratio.
[16] Data were collected in on a Siemens (Bruker) SMART platform with a CCD detector using monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å) over more than a hemisphere of reciprocal space ($2\theta <$ 55°). Crystal data: UP_4S_{12}, $M_f = 746.63$, tetragonal, space group $I4_1/a$ (no. 88), $a = 12.8776(9)$, $c = 9.8367(10)$ Å; $V = 1631.25$ Å^3, $Z = 4$,

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$\rho_{calcd} = 3.040\ g\,cm^{-3}$, $\mu = 11.85\ mm^{-1}$. Crystal size $0.08 \times 0.08 \times 0.2\ mm^3$. The SMART software was used for data acquisition and the SAINT software for data extraction.[17a] Unit cell parameters based on 25 reflections ($12^\circ < 2\theta < 30^\circ$). Absorption correction by SADABS,[17a] structure solved and refined by using the SHELXS-86[17b] and SHELXTL program systems,[17c] 1003 independent reflections, 913 with $F > 4\sigma(F_o)$, $R = 0.032/wR2$ (all data) $= 0.061$; max./min. residual electron density 2.2/ – 1.3 e Å^{-3} in the vicinity of the U atoms. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata @fiz-karlsruhe.de), on quoting the depository number CSD-411668.

[17] a) SMART, SAINT V-4, SADABS Programs, Bruker Analytical X-ray Systems Inc., Madison, WI, **1996**; b) G. M. Sheldrick, SHELXS-86: Program for crystal structure solution, University of Göttingen, **1986**; c) G. M. Sheldrick, SHELXL-97: Program for crystal structure refinement, University of Göttingen, **1997**.

[18] O. Ermer, A. Eling, *Angew. Chem.* **1988**, *100*, 856 – 859; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 829 – 833.

[19] R. Riedel, A. Greiner, G. Miehe, W. Dressler, H. Fuess, J. Bill, F. Aldinger, *Angew. Chem.* **1997**, *109*, 657 – 660; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 603 – 606.

[20] a) K. A. Hirsch, D. Venkataraman, S. R. Wilson, J. S. Moore, S. Lee, *J. Chem. Soc. Chem. Commun.* **1995**, 2199 – 2200; b) K. A. Hirsch, S. C. Wilson, J. S. Moore, *Chem. Eur. J.* **1997**, *3*, 765 – 771.

[21] H. Lueken, *Magnetochemie*, Teubner, Stuttgart, **1999**.

[22] a) R. L. Carlin, A. J. van Duyneveldt, *Magnetic Properties of Transition Metal Compounds*, Springer, New York, **1977**; b) "Magnetic Molecular Materials": *NATO ASI Ser. Ser. E* **1991**, *198*.

[23] a) V. I. Srdanov, G. D. Stucky, E. Lippmaa, G. Engelhardt, *Phys. Rev. Lett.* **1996**, *80*, 2449; b) G. K. H. Madsen, C. Gatti, B. B. Iversen, Lj. Damjanovic, G. D. Stucky, V. I. Srdanov, *Phys. Rev. B* **1999**, *59*, 12 359 – 12 369.

[24] P. Allemand, *Science* **1991**, *253*, 301 – 304.

[25] a) H. Noel, J. Padiou, J. Prigent, *C. R. Seances Acad. Sci. Ser. C* **1975**, *280*, 123 – 126; b) H. Noel, *C. R. Seances Acad. Sci. Ser. C* **1973**, *277*, 463 – 464; c) H. Noel, *C. R. Seances Acad. Sci. Ser. C* **1979**, *279*, 513 – 515; d) T. Vovan, N. Rodier, *C. R. Seances Acad. Sci. Ser. C* **1979**, *289*, 17 – 20; e) R. Brochu, J. Padiou, J. Prigent, *C. R. Seances Acad. Sci. Ser. C* **1972**, *274*, 959 – 961; f) H. Noel, J. Daoudi, *J. Solid State Chem.* **1985**, *60*, 131 – 134; g) H. Noel, M. Potel, *J. Less-Common Met.* **1985**, *113*, 11 – 15; h) H. Noel, *J. Less-Common Met.* **1980**, *72*, 45 – 49.

[26] H. Noel, R. Troc, *J. Solid State Chem.* **1979**, *27*, 123 – 135.

[27] a) X. Cieren, J. Angenault, J.-C. Courtier, S. Jaulmes, M. Quarton, F. Robert, *J. Solid State Chem.* **1996**, *121*, 230 – 235; b) V. Derstroff, G. Regelsky, H. Eckert, W. Tremel, *J. Mater. Chem.* **2001**, submitted.

[28] P. Fragnaud, M. Evain, E. Prouzet, R. Brec, *J. Solid State Chem.* **1993**, *102*, 390 – 399.

[29] F. Hiltmann, P. zum Hebel, A. Hammerschmidt, B. Krebs, *Z. Anorg. Allg. Chem.* **1993**, *619*, 293 – 302.

σ-Bishomoconjugation (σ-Bishomoaromaticity) in 4C/3(2)e Cations—Scope and Limitations**

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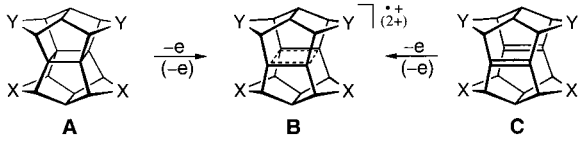
The experimental verification of σ-bishomoconjugation (σ-bishomoaromaticity) in the 4C/3e radical cation and the 4C/2e dication **B**, generated by one- and two-electron oxidation of the [1.1.1.1]pagodane **A** (X = Y = CH_2) and of the respective [1.1.1.1]pagodadiene **C** ("bisseco-dodecahedradiene"), respectively, was a prominent spin-off from our search for versatile synthetic routes to pentagonal dodecahedranes.[1] In order to



assess the geometrical prerequisites of these novel bonding motifs,[2] modification of the cage structures has been pursued in three directions: a) by formal rotation of a molecular "half" (→"isopagodanes"),[3] b) by homologation at the X- and/or Y-positions (→[2.2.1.1]/[2.2.2.2](iso)pagodanes),[3] and c) by bridging the X,Y positions (→(homo)dodecahedradienes).[4] A particularly attractive triad of this latter series consists of the parent bisseco-(**1**), seco-(**2**), and 1,16-dodecahedradienes (**3**) (Scheme 1).[5]

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