vacuo, and filtered over silica gel with petroleum ether/ethyl acetate (20:1 v/v) to give **2** as a colorless liquid; yield: 1.02 g (2.9 mmol, 60 %). ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 4.17$ (t, $J = 7$ Hz, 2H; $OCOCH_2$), 2.52 (q, $J = 7$ Hz, 2H; $HSCH_2$), 1.94 (s, 6H; CH_3), 1.70 – 1.57 (m, 4H; CH_2), 1.40 – 1.24 (m, 14H; CH_2); ^{13}C NMR ($CDCl_3$, APT, 100 MHz): $\delta = 171.72$, 66.12, 55.99, 34.01, 30.78, 29.43, 29.42, 29.41, 29.12, 29.03, 28.34, 28.32, 25.75, 24.62; MS: m/z (%): 354 (2) [M^+], 87 (100).

Site-exchange process: C_{12} colloid (385 mg) and thiol initiator **2** (69 mg, 0.2 mmol) were dissolved in toluene (190 mL) and stirred for 24 h at room temperature. The solution was evaporated to dryness in vacuo and the crude product intensively washed with ethanol to give initiator-functionalized Au-NPs (390 mg).

Tris(2-dimethylaminoethyl)amine (Me_6Tren) was synthesized according to the method given in reference [9].

ATR polymerization and cleavage of the grafted polymer chains: Initiator-functionalized Au-NPs (66 mg) were dissolved in toluene (1 mL) and *n*-butylacrylate (2 mL, 14.0 mmol), and CuBr (3.8 mg, 26 μmol) and Me_6Tren (7.0 mg, 30 μmol) were dissolved in *n*-butylacrylate (3 mL, 20.9 mmol). Both solutions were degassed with argon and combined. After the mixture had been stirred for 24 h at room temperature, the product precipitated in methanol, yielding a dark brown, viscous substance. The supernatant liquid was decanted, the residue was repeatedly washed with methanol and dried in vacuo to give the product (527 mg). The polymer-coated Au-NPs (38 mg) were dissolved in toluene (20 mL), and *n*-butanol (2 mL) and *p*-toluenesulfonic acid (20 mg) were added. Heating overnight under reflux, filtration over silica gel, and drying in vacuo gave the cleaved polymer.

TEM images were recorded on a Philips CM-300 microscope working at 300 kV. SFM measurements were performed on a Digital Instruments Multimode SPM with a Nanoscope IIIa controller in the tapping mode. The resonance frequency dependent on the Si-cantilever ($K \cong 42\,\mathrm{N\,m^{-1}}$, Nanosensors) was set to about 330 kHz. Samples were prepared by spin casting of a dilute $CHCl_3$ or THF solution with a concentration of $0.01\,\mathrm{mg\,mL^{-1}}$ at 2000 rpm on mica as a substrate. GP chromatograms were recorded on a Spectra-Physics SP 8100 (polystyrene calibration). Thermogravimetric measurements were carried out on a Netzsch TG 209.

Received: February 6, 2001
Revised version: June 1, 2001 [Z16568]

---

[1] a) A. C. Templeton, W. P. Wuelfing, R. W. Murray, *Acc. Chem. Res.* **2000**, *33*, 27 – 36; b) M. J. Hostetler, R. W. Murray, *Curr. Opin. Colloid Interface Sci.* **1997**, *2*, 42 – 50; c) R. L. Whetten, J. T. Khoury, M. M. Alvarez, S. Murthy, I. Vezmar, Z. L. Wang, P. W. Stephens, C. L. Cleveland, W. D. Luedtke, U. Landman, *Adv. Mater.* **1996**, *8*, 428 – 433.

[2] a) L. He, M. D. Musick, S. R. Nicewarner, F. G. Salinas, S. J. Benkovic, M. J. Natan, C. D. Keating, *J. Am. Chem. Soc.* **2000**, *122*, 9071 – 9077; b) W. P. McConnell, J. P. Novak, L. C. Brousseau III, R. R. Fuierer, R. C. Tenent, D. L. Feldheim, *J. Phys. Chem. B* **2000**, *104*, 8925 – 8930; c) J. J. Storhoff, A. A. Lazarides, R. C. Mucic, C. A. Mirkin, R. L. Letsinger, G. C. Schatz, *J. Am. Chem. Soc.* **2000**, *122*, 4640 – 4650; d) S. Chen, R. S. Ingram, M. J. Hostetler, J. J. Pietron, R. W. Murray, T. G. Schaaff, J. T. Khoury, M. M. Alvarez, R. L. Whetten, *Science* **1998**, *280*, 2098 – 2101.

[3] M. J. Hostetler, J. E. Wingate, C.-J. Zhong, J. E. Harris, R. W. Vachet, M. R. Clark, J. D. Londono, S. J. Green, J. J. Stokes, G. D. Wignall, G. L. Glish, M. D. Porter, N. D. Evans, R. W. Murray, *Langmuir* **1998**, *14*, 17 – 30.

[4] a) M. J. Hostetler, A. C. Templeton, R. W. Murray, *Langmuir* **1999**, *15*, 3782 – 3789; b) A. C. Templeton, M. J. Hostetler, E. K. Warmoth, S. Chen, C. M. Hartshorn, V. M. Krishnamurthy, M. D. E. Forbes, R. W. Murray, *J. Am. Chem. Soc.* **1998**, *120*, 4845 – 4849; c) M. J. Hostetler, S. J. Green, J. J. Stokes, R. W. Murray, *J. Am. Chem. Soc.* **1996**, *118*, 4212 – 4213.

[5] a) R. Jordan, N. West, A. Ulman, Y.-M. Chou, O. Nuyken, *Macromolecules* **2001**, *34*, 1606 – 1611; b) K. J. Watson, J. Zhu, T. Nguyen, C. A. Mirkin, *J. Am. Chem. Soc.* **1999**, *121*, 462 – 463.

[6] T. E. Patten, K. Matyjaszewski, *Adv. Mater.* **1998**, *10*, 901 – 915.

[7] a) H. Böttcher, M. L. Hallensleben, H. Wurm, DE Patent 19838241, **1998**; b) H. Böttcher, M. L. Hallensleben, S. Nuß, H. Wurm, *Polym. Bull.* **2000**, *44*, 223 – 229; c) J.-B. Kim, M. L. Bruening, G. L. Baker, *J. Am. Chem. Soc.* **2000**, *122*, 7616 – 7617; d) R. R. Shah, D. Mecerreyes, M. Husemann, I. Rees, N. L. Abbott, C. J. Hawker, J. L. Hedrick, *Macromolecules* **2000**, *33*, 597 – 605; e) M. Husemann, E. E. Malmström, M. McNamara, M. Mate, D. Mecerreyes, D. G. Benoit, J. L. Hedrick, P. Mansky, E. Huang, T. P. Russell, C. J. Hawker, *Macromolecules* **1999**, *32*, 1424 – 1431.

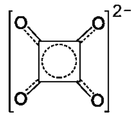
[8] J. Xia, S. G. Gaynor, K. Matyjaszewski, *Macromolecules* **1998**, *31*, 5958 – 5959.

[9] M. Ciampolini, N. Nardi, *Inorg. Chem.* **1966**, *5*, 41 – 44.

Solvothermal Synthesis of a 24-Nuclear, Cube-Shaped Squarato-oxovanadium(IV) Framework: $[N(nBu)_4]_8[V_{24}O_{24}(C_4O_4)_{12}(OCH_3)_{32}]$

Johann Spandl, Irene Brüdgam, and Hans Hartl*

Polyoxometalates with organic oxygen donor groups show an impressive structural and electronic diversity. As a result, extensive synthetic research has been carried out in this field in the past few years, with the aim of synthesizing compounds with interesting magnetic or catalytic properties,[1] as well as precursors for metal oxides of high purity.[2] Notable successes were achieved in synthesizing polyoxo-alkoxo-metalates with chelating trisalkoxy ligands.[3] Polyoxometalate fragments that are otherwise usually unstable can be stabilized by using suitable, highly symmetrical polydentate coligands such as oxalate and squarate. The high symmetry of the bis-bidentate squarato group **1**, as well as the suitable spacing of the four oxygen donor atoms favors the interconnection of small polyoxo-alkoxo-vanadate units to highly symmetric supermolecular polyoxometalate derivatives. Until now, suprisingly few squarato-oxovanadium compounds have been structurally characterized. In the anions $[V_2O_2(C_4O_4)_2(OH)(H_2O)_3]^-$,[4, 5] $[V_2O_3(C_4O_4)_2(H_2O)_3]^-$,[5] $[V_2O_2(C_4O_4)_2F_4]^{4-}$,[4] $[V_3O_3(C_4O_4)_3F_4]^{4-}$,[6] and $[V_4O_6(C_4O_4)_5(H_2O)_4]^{4-}$,[5] the squarato group is a μ_2-bridging ligand; only in the polymeric compounds ${}^2_\infty[V(OH)(C_4O_4)]$ and ${}^3_\infty[V(OH)(C_4O_4)(H_2O)]$,[7] is the squarato ligand found to be μ_3- and μ_4-bridging, respectively.[7] Herein, we report the solvothermal synthesis and structure of the cube-shaped 24-nuclear oxo-alkoxo-squarato complex $[N(nBu)_4]_8[V_{24}O_{24}(C_4O_4)_{12}(OCH_3)_{32}]$ (**2**) (Figure 1), which is an astonishing example of a compound with μ_4-bridged oxo-alkoxo-vanadium fragments.



1

Vanadium(V) oxytrialkoxides prove to be auspicious starting materials for the synthesis of new polyoxometalates.[8] In

---

[*] Prof. Dr. H. Hartl, Dipl.-Chem. J. Spandl, I. Brüdgam
Freie Universität Berlin
Institut für Chemie/Anorganische und Analytische Chemie
Fabeckstrasse 34 – 36, 14195 Berlin (Germany)
Fax: (+49) 30-83854003
E-mail: hartl@chemie.fu-berlin.de

1433-7851/01/4021-4018 $ 17.50+.50/0

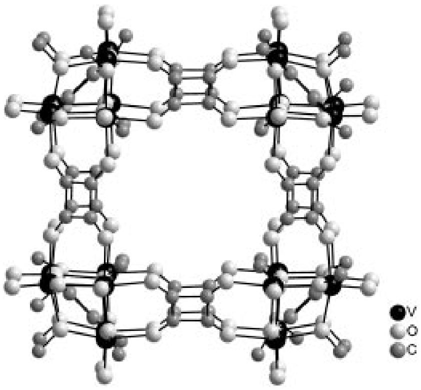


Figure 1. Structure of the cubic anion in **2** viewed on one of the cubic faces.

the course of dissolving vanadium(v)oxytri-(*tert*-butoxide), VO(O*t*Bu)$_3$, in methanol, an almost complete exchange of the O*t*Bu groups for the methoxy groups in the solvent takes place. The resulting solution contains oligomeric fragments cut out of the infinite chains of solid vanadium(v) oxytrimethoxide ${}^{1}_{\infty}[\mathrm{VO(OMe)_3}]$.[8, 9] Solvothermal conditions and the presence of a stochiometric amount of squaric acid and tetra-*n*-butylammonium hydroxide reduce $\mathrm{V^V}$ to $\mathrm{V^{IV}}$ in these solutions; excess methanol functions as the main reducing agent. This resulted in the formation of **2**, which was characterized by X-ray structure analysis.[10]

The cube-shaped framework of **2** is made up of eight $\{\mathrm{(VO)_3(OMe)_4O_6}\}$ subunits at its corners. Each of these trinuclear units is built up of three edge-sharing, distorted $\mathrm{VO_6}$ octahedra with one corner oxygen atom in common (Figures 2 and 3). This structural unit can be considered an incomplete, distorted heterocubane unit, in which one of the vanadium positions remains unoccupied. A comparable arrangement of atoms occurs in the isolated anion $[\mathrm{V_3O_3(C_4O_4)_3F_4}]^{4-}$;[6] however, it contains fluoro ligands instead of methoxy groups.

The edge-sharing oxygen atoms in this trinuclear component come from three μ_2- and one μ_3-bridging methoxy groups. The $\{\mathrm{VO_6}\}$ coordination sphere is completed by a terminal oxo group located *trans* to the triply bridging methoxy group and two oxygen atoms of one squarato ligand perpendicular to the quadrangular arrangement of the $\mathrm{V_2(OMe)_2}$ groups. Eight $\{\mathrm{(VO)_3(OMe)_4}\}$ subunits are connected by twelve μ_4-bridging squarato ligands to form edges of the cube (Figures 1 and 3).

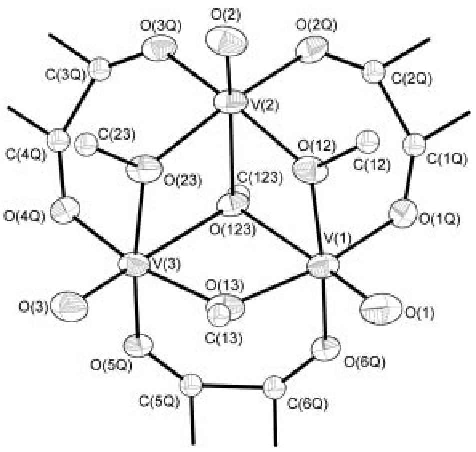


Figure 2. Section of the structure of **2** with selected bond lengths [Å]: V(1)-O(1) 1.604(5), V(1)-O(12) 1.974(4), V(1)-O(123) 2.220(4), V(1)-O(1Q) 2.019(4).

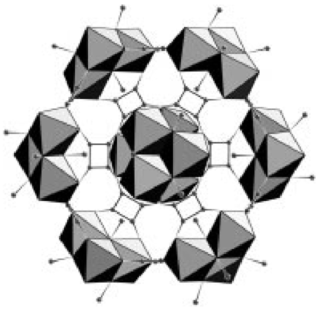


Figure 3. Polyhedral representation of the anion structure, $[\mathrm{V_{24}O_{24}(C_4O_4)_{12}(OCH_3)_{32}}]^{8-}$, viewed along the space diagonal of the cube.

The eight μ_3-bridging methoxy groups point towards the center of the cube, whereas the 24 μ_2-methoxy groups face outwards. The tetra-*n*-butylammonium cations form unexpectedly close contacts with the anions. Six of the eight cations are located on top of the cube faces such that one of their butyl groups always protrudes into the hydrophobic cavity inside the anion (Figure 4). Thus, the anion and the six tetra-*n*-butylammonium cations accumulate to a twofold negatively charged array, $\{[\mathrm{N}(n\mathrm{Bu})_4]_6[\mathrm{V_{24}O_{24}(C_4O_4)_{12}(OCH_3)_{32}}]\}^{2-}$, in which the vanadium–oxygen framework is completely surrounded by a hydrophobic shell that consists of 24 methyl and 18 *n*-butyl groups (outside) as well as eight methyl groups and six *n*-butyl groups (inside). The two remaining tetra-*n*-butylammonium cations and the huge anion are arranged to form a bulky ionic framework in which weakly bound solvent molecules are incorporated. Crystals lose the enclosed methanol even at low temperatures. For this reason, the number and positions of the remaining disordered methanol molecules could not be determined with a high degree of accuracy.[10]

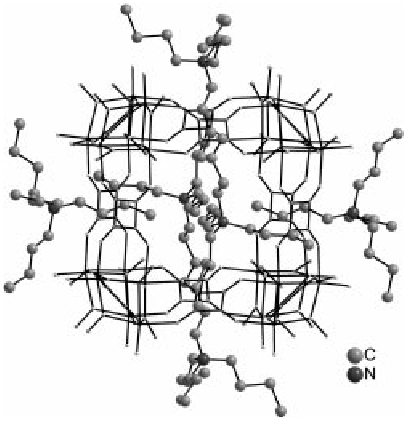


Figure 4. Cation–anion network in the structural unit $\{[\mathrm{N}(n\mathrm{Bu})_4]_6[\mathrm{V_{24}O_{24}(C_4O_4)_{12}(OCH_3)_{32}}]\}^{2-}$.

By replacing the tetra-*n*-butylammonium hydroxide in the synthesis with an equivalent amount of an alkali metal hydroxide or ammonia, it is possible to synthesize other salts with the anion, $[\mathrm{V_{24}O_{24}(C_4O_4)_{12}(OCH_3)_{32}}]^{8-}$. The formation of this anion can be verified with aid of IR spectroscopy, because the cation exchange implies almost no change in the range of the O–C(H_3) and V–O vibrations. For the potassium salt $K_8[V_{24}O_{24}(C_4O_4)_{12}(OCH_3)_{32}]$ (**3**), the cubic structure of the anion, analgous to that of **2**, was determined by difference-Fourier analyis, whereas the potassium cations coordinated by methanol molecules as well as free solvent molecules in the crystal lattice were disordered and could not be clearly localized by crystal-structure analysis.[11] Exchanging the cations led to a change in the environment of the anion, which led to significant differences in the cation–anion interactions. Because of the ion-pair formation with tetra-*n*-butylammonium, a low charge formed, which is more likely a hydrophobic anion to be protected by the *n*-butyl groups. In the case of the potassium cation, the anion is highly charged, and balanced by the solvated potassium cations. This inevitably leads to compounds with different solubility behavior. Furthermore, the composition of the vanadium–oxygen compounds obtained by thermal decomposition can be controlled by the choice of cation. It is also advantageous that the squarato and methoxy ligands can be removed easily with a simultaneous reduction of the vanadium.

Experimental Section

A 0.2 M solution of VO(O*t*Bu)$_3$ (23 mL, 4.6 mmol) in methanol (Merck p.a.), $H_2C_4O_4$ (0.27 g, 2.4 mmol) and a 0.8 M solution of tetra-*n*-butylammonium hydroxide (2 mL, 1.6 mmol) in methanol (Fluka) were heated for 24 h at 125 °C in a 50 mL Teflon-lined autoclave (Berghof). After the autoclave was cooled to room temperature, the content was left to stand for one day at −30 °C to complete crystallization. The extremly temperature-sensitive, green crystals of $\mathbf{2}\cdot x$ MeOH were filtered in an argon atmosphere at room temperature, washed with methanol, and dried under vacuum for a complete removal of the weakly bound methanol. Yield (based on the solvent-free compound): 0.71 g (0.12 mmol), 63 %. Elemental analysis calcd (%, based on the solvent-free compound) for $C_{208}H_{384}N_8O_{104}V_{24}$ ($M = 5883.90\ \mathrm{g\,mol^{-1}}$): C 42.5, H 6.58, N 1.90; found: C 42.8, H 6.64, N 1.97; IR (KBr, 400–1600 cm^{-1}): $\tilde{\nu} = 424$ (s), 464 (m) 573 (m), 967 (s), 976 (s) 1033 (s), 1069 (m), 1098 (w), 1446 (s), 1471 (s), 1523 cm^{-1} (vs, br).

3: The synthesis of the potassium salt was analogous to that of the compound **2**, with a stoichiometric amount of potassium hydroxide instead of tetra-*n*-butylammonium hydroxide. Green crystals were isolated by filtering immediately after cooling the autoclave to room temperature. Yield (based on the solvent free compound): 0.36 g (0.084 mmol), 41 %. Elemental analysis calcd (%, based on the solvent free compound) for $K_8C_{80}H_{96}O_{104}V_{24}$ ($M = 4256.9\ \mathrm{g\,mol^{-1}}$): C 22.6, H 2.27; found: C 21.5, H 2.32; IR (KBr, 400–1600 cm^{-1}): $\tilde{\nu} = 427$ (s), 471 (m) 576 (m), 959 (s, br), 1013 (s, br),1058 (m), 1099 (w), 1443 (s), 1483 (vs), 1521 cm^{-1} (vs, br).

Received: April 24, 2001
Revised: July 25, 2001 [Z 16992]

---

[1] P. Gouzerh, A. Proust, *Chem. Rev.* **1998**, *98*, 77–111.

[2] a) D. E. Katsoulis, *Chem. Rev.* **1998**, *98*, 359–388; b) J. Spandl, I. Brüdgam, R. Friese, H. Hartl, *Z. Kristallogr. Suppl.* **2000**, *17*, 136.

[3] M. I. Khan, J. Zubieta, *Prog. Inorg. Chem.* **1995**, *43*, 1–149.

[4] A. Müller, R. Rohlfing, E. Krickemeyer, H. Bögge, *Angew. Chem.* **1993**, *104*, 916–918; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 909–912.

[5] M. J. Khan, Y.-D. Chang, Q. Chen, J. Salta, Y. S. Lee, C. J. O'Connor, J. Zubieta, *Inorg. Chem.* **1994**, *33*, 6340–6350.

[6] M. Hilbers, M. Meiwald, R. Mattes, *Z. Naturforsch. B* **1996**, *51*, 57–67.

[7] K.-J. Lin, K.-H. Lii, *Angew. Chem.* **1997**, *109*, 2166–2167; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2076–2077.

[8] J. Spandl, I. Brüdgam, H. Hartl, *Z. Anorg. Allg. Chem.* **2000**, *626*, 2125–2132.

[9] W. Prandtl, L. Hess, *Z. Anorg. Allg. Chem.* **1913**, *82*, 103–129.

[10] Crystal structure analysis of **2**: Bruker XPS diffractometer (CCD area detector, $\mathrm{Mo_{K\alpha}}$ radiation, $\lambda = 0.71073$ Å), graphite monochromator, empirical absorption correction using symmetry-equivalent reflections (SADABS, Area-Detector-Absorbsion Correction, Siemens Industrial Automation Inc., Madison, WI, **1996**); the structures were solved by direct methods; the initial structures were refined against F^2 (Bruker-SHELXTL, version 5.1, **1998**). The hydrogen atoms were calculated in geometrically idealized positions. Crystal size $0.40 \times 0.38 \times 0.24$ mm, $T = 133$ K, triclinic, space group $P\bar{1}$, $a = 20.277(2)$, $b = 20.605(2)$, $c = 20.631(2)$ Å, $\alpha = 115.07(1)$, $\beta = 94.39(1)$, $\gamma = 91.88(1)^\circ$, $V = 7764.0(15)$ Å^3, $Z = 2$, $\rho_{\mathrm{calcd}} = 1.258\ \mathrm{g\,cm^{-3}}$, $2\theta_{\max} = 47^\circ$, 54 859 collected reflections, 22 361 unique reflections, 1042 parameters, $\mu = 0.76\ \mathrm{mm^{-1}}$, absorption correction, effective transmission max./min. = 0.7456/0.3775. R_1 $(I > 2\sigma(I)) = 0.0718$, wR_2 $(I > 2\sigma(I)) = 0.1964$, R_1 (all data) = 0.1149, wR_2 (all data) = 0.2166, largest difference peak and hole +/− = 1.767/0.743 e Å^{-3}. The crystals were picked directly out of the mother liquor under a cold nitrogen stream. Because of the loss of the enclosed solvent methanol even at low temperatures, it was not possible to determine the number and exact positions of the remaining methanol molecules. Therefore, a solvent-free data set was generated with the computer program SQUEEZE (T. Spek, PLATON, **1999**). This data set was used for the crystal structure refinement.[12]

[11] Crystal structure analysis of **3** (carried out analogously to details in reference [10]): tetragonal, *P*4/*ncc*, $a = 26.356(3)$, $b = 26.356(3)$, $c = 31.290(5)$ Å, $V = 21\,731.6$ Å^3, $T = 143$ K.[12]

[12] 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-162386 (**2**) and CCDC-169184 (anion substructure of **3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

1,6-Methano[10]annulene has a Delocalized Structure in S_0 and S_1: High-Resolution Spectroscopy in a Supersonic Jet[**]

Reinhold Seiler and Bernhard Dick[*]

Aromatic molecules substantially differ from olefins in terms of their reactivity and spectroscopic properties. A common characteristic and necessary structural element of aromatic molecules is a planar, cyclically conjugated system of $4n+2$ π electrons, without bond-length alternation. The Hückel rule predicts that such systems are more stable than theoretical systems with alternating bond lengths.[1] This rule emerges from a molecular orbital (MO) description of the wavefunction of the π electrons, and has been verified by ab initio calculations for benzene and a number of other polycyclic arenes. For some species, however, calculations on the electron-delocalized structure found it to be a transition state between two electron-localized structures. A noted example of this effect is 1,6-methano[10]annulene (MA): The semiempirical MNDO, AM1, and PM3 methods obtained a localized structure while ab initio calculations at the SCF level with a simple STO-3G basis set favored delocalized

---

[*] Prof. Dr. B. Dick, Dipl.-Chem. R. Seiler
Institut für Physikalische und Theoretische Chemie
Universität Regensburg
93040 Regensburg (Germany)
Fax: (+49) 941-943-4488
E-mail: Bernhard.Dick@chemie.uni-regensburg.de

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