C_6D_6): $\delta = -103.3$ (s, 6 Si, *Si*OCHMe$_2$), -103.0 (s, 2 Si, *Si*OH); IR (KBr, Nujol): $\tilde{\nu} = 3411.3$ cm^{-1}; elemental analysis calcd for $C_{18}H_{44}O_{20}Si_8$: C 26.84, H 5.47, Si 27.93; found C 26.47, H 5.32, Si 27.85.

Received: July 23
Revised version: December 3 1998 [Z 12195 IE]
German version: *Angew. Chem.* **1999**, *111*, 702 – 705

Keywords: cage compounds · hydrogen bonds · silicon

[1] a) P. G. Harrisson, R. Kannengiesser, *Chem. Commun*. **1996**, 415; b) P. G. Harrisson, *J. Organomet. Chem.* **1997**, *542*, 141.
[2] a) P. A. Agaskar, *J. Chem Soc. Chem. Commun*. **1992**, 1024; b) P. A. Agaskar**,** *Inorg. Chem.* **1991,** *30*, 2707.
[3] a) D. Hoebbel, I. Pitsch, D. Heidermann, H. Jancke, W. Hiller, *Z. Anorg. Allg. Chem*. **1990**, *583*, 133; b) D. Hoebbel, K. Endres, T. Reinert, I. Pitsch, *J. Non-Cryst. Solids* **1994**, *176*, 179; c) M. Wiebcke, D. Hoebbel, *J. Chem. Soc. Dalton Trans.* **1992**, 2451.
[4] F. J. Feher, T. A. Budzichowski, *Polyhedron* **1995**, *14*, 3239.
[5] F. T. Edelmann, *Angew. Chem*. **1992**, *104*, 600; *Angew. Chem. Int. Ed. Engl*. **1992**, *31*, 586.
[6] A. Tsuchida, C. Bolln, F. G. Sernetz, H. Frey, R. Mülhaupt, *Macromolecules* **1997**, *30*, 2818.
[7] C. A. Fyfe, G. Fu, *J. Am. Chem. Soc.* **1995**, *117*, 9709.
[8] A. Firouzi, D. Kumar, L. M. Bull, T. Besier, P. Sieger, Q. Huo, S. A. Walker, J. A. Zasadzinski, C. Glinka, J. Nicol, D. Margolese, G. D. Stucky, B. F. Chmelka, *Science* **1995**, *267*, 1138.
[9] R. Murugavel, A. Voigt, M. G. Walawalkar, H. W. Roesky, *Chem. Rev*. **1996**, *96*, 2205.
[10] R. Murugavel, V. Chandrasekhar, H. W. Roesky, *Acc. Chem. Res.* **1996**, *29*, 183.
[11] a) K. Endo, T. Sawaki, M. Koyanagi, K. Kobayashi, H. Masuda, Y. Aoyama, *J. Am. Chem. Soc.* **1995**, *117*, 8341; b) K. Endo, T. Ezuhara, M. Koyanagi, H. Masuda, Y. Aoyama, *J. Am. Chem. Soc.* **1997**, *119*, 499.
[12] a) M. J. Zaworotko, *Chem. Soc. Rev.* **1994**, *23*, 283; b) G. R. Desiraju, *Chem. Commun*. **1997**, 1475.
[13] F. J. Feher, T. A. Budzichowski, *J. Organomet. Chem*. **1989**, *379*, 33.
[14] A. R. Bassindale, T. E. Gentle, *J. Mater. Chem.* **1993**, *3*, 1319.
[15] F. J. Feher, K. D. Wyndham, *Chem. Commun*. **1998**, 323.
[16] I. Ojima *The Chemistry of Organic Silicon Compounds, part 2* (Eds.: S. Patai, Z. Rappoport), Wiley, New York, **1989**, pp. 1479 – 1526, and references therein.
[17] a) J. D. Lichtenhan in *Silsesquioxane-Based Polymers* (Ed.: J. C. Salamone), Wiley, New York, **1996**; b) J. D. Lichtenhan, Y. A. Otonari, M. J. Carr, *Macromolecules* **1995**, *28*, 8435; c) J. D. Lichtenhan, *Comments Inorg. Chem*. **1995**, *5*, 93.
[18] C. Bonhomme, P. Tolédano, J. Maquet, J. Livage, L. Bonhomme-Coury, *J. Chem. Soc. Dalton. Trans.* **1997**, 1617.
[19] G. Calzaferri, R. Imhof, K. W. Törnroos *J. Chem. Soc. Dalton. Trans.* **1994**, 3123.
[20] G. Koellner, U. Müller, *Acta Crystallogr. Sect. C* **1989**, *45*, 1106.
[21] a) Crystal structure analysis of **1** · THF · 2 H$_2$O: $C_{44}H_{100}O_{23}Si_8$, $M_r = 1221.96$, triclinic, space group $P\bar{1}$, $a = 11.865(2)$, $b = 12.251(2)$, $c = 12.322(2)$ Å, $\alpha = 70.471(0)$, $\beta = 74.136$ (13), $\gamma = 81.244(8)^\circ$, $V = 1.6201(5)$ nm^3, $Z = 1$, $\rho_{calcd} = 1.252$ Mg m^{-3}, $\mu = 0.234$ mm^{-1}, $F(000) = 660$; total number of reflections measured 6191, of which 5723 were unique ($R_{int} = 0.0307$)and 5714 observed, 1 restraint, 341 parameters. Data collection range: $3.54 \le 2\theta \le 25.08^\circ$. Final R indices: $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.0428$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w F_o^4]^{1/2} = 0.1174$ for data with $I > 2\sigma(I)$ and $R1 = 0.0470$, $wR2 = 0.1263$ for all data; GOF $= [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma(n-p)]^{1/2} = 1.071$; max./min. residual electron density 933/ – 690 e nm^{-3}. b) Crystal structure analysis of **2**: $C_{24}H_{56}O_{20}Si_8$, $M_r = 889.41$, rhombohedral, space group $R\bar{3}$, $a = 15.444(2)$, $b = 15.444(2)$, $c = 16.749(3)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 120^\circ$, $V = 3.459.8(10)$ nm^3, $Z = 3$, $\rho_{calcd} = 1.281$ Mg m^{-3}, $\mu = 0.298$ mm^{-1}, $F(000) = 1416$; total number of reflections measured 1926, of which 711 were unique ($R_{int} = 0.0617$) and 709 observed, 0 restraints, 76 parameters. Data collection range: $3.65 \le 2\theta \le 19.94^\circ$. Final R indices: $R1 = 0.1014$, $wR2 = 0.2790$ for data with $I > 2\sigma(I)$ and $R1 = 0.1234$, $wR2 = 0.3502$ for all data; GOF $= 1.022$; max/min. residual electron density 645/ – 455 e nm^{-3}. c) Colorless single crystals suitable for X-ray diffraction studies were grown from tetrahydrofuran and *n*-hexane for **1** and *n*-hexane for **2**. A suitable crystal of each compound was mounted on a glass fiber and coated with paraffin oil. Diffraction data were collected on a Siemens – Stoe AED2 four-circle instrument (at $-150\,^\circ$C for both compounds), with graphite-monochromated $Mo_{K\alpha}$ radiation (0.71073 Å). The structures were solved by direct methods with SHELXS-90[22] and refined against F^2 on all data by full-matrix least-squares with SHELXL-93.[23] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically calculated positions and refined using a riding model. 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-102246 and 102247. 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).
[22] G. M. Sheldrick, *Acta Crystallogr. Sec. A* **1990**, *46*, 467.
[23] G. M. Sheldrick, SHELXL-93, *program for crystal structure refinement*, University of Göttingen Germany, **1993**.

$[Zn_2(thf)_2(EtZn)_6Zn_4(\mu_4\text{-}O)(t\text{BuPO}_3)_8]$: A Dodecanuclear Zincophosphonate Aggregate with a $Zn_4(\mu_4\text{-}O)$ Core**

Yu Yang, Jiri Pinkas, Mathias Noltemeyer, Hans-Georg Schmidt, and Herbert W. Roesky*

Dedicated to Professor Helmut Werner on the occasion of his 65th birthday

Zincophosphates and phosphonates are among the targets of current vigorous research activity aimed at the preparation of novel types of porous structures. These materials could serve as molecular sieves, size/shape selective catalysts, adsorbents, ion exchangers, and matrices for electronic and optical devices. Zincophosphates display a large structural variety and in most cases, they form three-dimensional networks.[1] Importantly, chiral structures[2] and large-pore structures with low densities[3] have also been demonstrated in zincophosphates. Recently, a new family of $M_3Zn_4O(PO_4)_3$ phases (M = alkali metal) that feature $Zn_4(\mu_4\text{-}O)$ centers was reported.[4] Layered,[5] chain-like,[3d, 5a,b, 6] and, in rare cases, even molecular species are also known. Of the two molecular zincophosphates known one features an eight-membered

[*] Prof. Dr. H. W. Roesky, Y. Yang, Dr. J. Pinkas, Dr. M. Noltemeyer, H.-G. Schmidt
Institut für Anorganische Chemie der Universität
Tammannstrasse 4, D-37077 Göttingen (Germany)
Fax: (+49) 551-393-373
E-mail: hroesky@gwdg.de

[**] This work was supported by the Deutsche Forschungsgemeinschaft. J.P. thanks the Alexander von Humboldt-Stiftung for a research fellowship.

  1433-7851/99/3805-0664 $ 17.50+.50/0

$[\{Zn(\mu_2\text{-}O)_2PO_2\}_2]$ ring[3b] while the other possesses a $[Zn_4(\mu_4\text{-}O)\{(\mu_2\text{-}O)_2PO_2\}_4]$ moiety.[6b]

The majority of zincophosphonates, on the other hand, have layered structures into which various organic species can intercalate.[7, 8] However, the dimensionality of the resulting network can be controlled by changing the functionality and steric bulk of the phosphonate R group and through this three-dimensional and chain compounds have been synthesized.[9]

Oligonuclear zinc complexes have been studied as polymerization catalysts, reagents in organic synthesis, precursors to ZnO-based materials,[10] and models of active sites in zinc enzymes. The most prevalent species are tetranuclear clusters with an oxygen-centered tetrahedral Zn_4O core.[11] Other structural types involve Zn_4O_4 cubanes,[12] a linear Zn_4O_6 chain,[13] and an eight-membered Zn_4O_4 ring.[14] However, only a handful of high-nuclearity aggregates have been structurally characterized. The sole example of a hexanuclear aggregate is a drum-like Zn_6O_9 species.[15] Heptanuclear arrays feature dicubane Zn_7O_8 units,[16] a Zn_7O_2 double tetrahedron,[17] and a $Zn_7O_{12}N_{12}$ aggregate in the form of a six-point star.[18]

Herein we report on the synthesis and the structural and spectroscopic characterization of a large dodecanuclear zincophosphonate aggregate **1** that possesses a $Zn_4(\mu_4\text{-}O)$ core. Reaction of *tert*-butylphosphonic acid in THF with

$[Zn_2(thf)_2(EtZn)_6Zn_4(\mu_4\text{-}O)(t\text{BuPO}_3)_8]$ **1**

$ZnEt_2$ in toluene (in a 1:1.5 ratio) provided compound **1** as colorless crystals in 27 % yield. The ^{31}P NMR spectrum of the reaction mixture displayed signals of several products, with **1** being the major species as shown by four signals of the same intensity in the ^{31}P NMR spectrum (Figure 1).

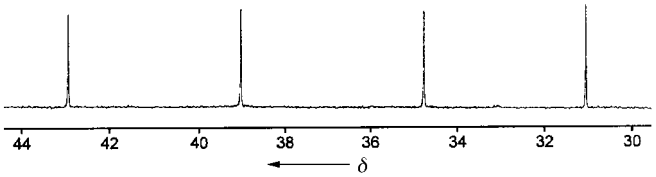

Figure 1. ^{31}P NMR spectrum of **1**.

The four types of chemically inequivalent phosphorus atoms present in the aggregate **1** in solution are also evident in the solid state structure of **1**, which was established by single crystal X-ray diffraction (Figure 2).[19] The dodecanuclear aggregate consists of a central $Zn_4(\mu_4\text{-}O)$ core and a zincophosphonate "shell". The molecule **1** has approximate C_2 symmetry with a pseudo-C_2 axis that passes through the μ_4-O3 atom in the central moiety. There are four pairs of equivalent phosphonate $t\text{BuPO}_3$ groups and six pairs of chemically quite diverse zinc centers. Half of the zinc atoms retained one ethyl group while the other half lost the alkyl substituents completely. Four of these zinc atoms surround the central oxide in a tetrahedral fashion whereas the remaining two complete their coordination sphere by accepting an oxygen atom from the THF ligands. Two zinc atoms reside in a five-coordinate environment and the rest are four coordinate.

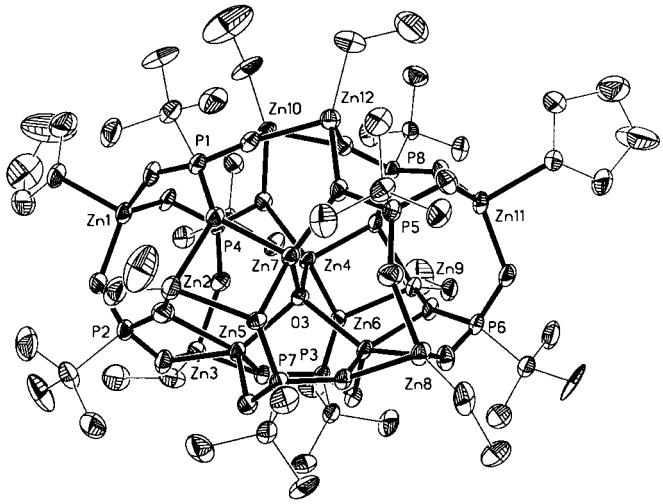

Figure 2. Molecular structure of **1**. Selected bond lengths [Å]: O3 – Zn4 1.948(4), O3 – Zn5 2.073(4), O3 – Zn6 2.072(4), O3 – Zn7 1.958(4).

Interestingly, the Zn:P ratio in **1** is the same as in the starting reaction mixture (Zn:P = 1.5:1). Thus, **1** contains an excess of zinc with respect to the usual 1:1 ratio that is found in divalent metal phosphonates. This is in turn reflected in the presence of the Zn-O-Zn bonds and, consequently, also of μ_3- and μ_4-bridging oxygen atoms.[20] The bond distances between the phosphorus and μ_2-O atoms (1.499(5) – 1.527(5) Å) and μ_3-O (1.531(5) – 1.569(5) Å) fall in a narrow range, while the corresponding distances with zinc display a wider spread: Zn-μ_2-O 1.891(5) – 1.990(5) Å, Zn-μ_3-O 1.971(4) – 2.291(5) Å, and Zn-μ_4-O 1.948(4) – 2.073(4) Å. The presence of the μ_4-O atom cannot be attributed to adventitious moisture because of the relatively high yield of **1**. We speculate that its origin can be ascribed to the induced dehydration of phosphonic acid by $ZnEt_2$, which resulted in the formation of the phosphonic anhydride $(t\text{BuPO}_2)_3$. A signal observed in the ^{31}P NMR spectrum of the crude reaction mixture at $\delta = 31.18$ supports this notion as it agrees well with the reported value for $(t\text{BuPO}_2)_3$.[21]

In summary, we have presented the largest zinc oligonuclear aggregate **1** to date, which features several interesting structural motifs that are closely related to zincophosphate and phosphonate frameworks, namely the Zn-O-Zn bonds, three- and four-coordinate oxygen atoms, and a Zn:P ratio of 1.5:1. Moreover, this molecule contains several reactive centers, which may be potentially utilized for the transformation of this precursor into porous materials.

Experimental Section

1: A solution of *tert*-butylphosphonic acid (0.44 g, 3.2 mmol) in THF (10 mL) was added dropwise to a solution of $ZnEt_2$ (4.3 mL, 1.1 M in toluene) in toluene (10 mL) at −78 °C. The resulting solution was slowly warmed to room temperature and stirred for 6 h, and then concentrated to 5 mL. A white precipitate formed overnight and was removed by filtration. The clear solution was allowed to stand at room temperature for two months. Colorless crystals of **1** (0.22 g, 27 %) suitable for single crystal X-ray diffraction experiments were formed. M.p. > 270 °C decomp; ^1H NMR (250.1 MHz, $C_6D_6/[D_8]$THF 1:3): $\delta = 0.15$ (m; $ZnCH_2$), 0.75 (m; CH_3), 1.14 (m; *t*BuP) 1.55 (m; THF), 2.14 (s; $CH_3C_6H_5$), 3.44 (m; THF), 7.0 (m; $CH_3C_6H_5$); ^{31}P NMR (101.3 MHz, $C_6D_6/[D_8]$THF 1:3): $\delta = 42.94$, 39.04, 34.75, 31.04 (s, 1:1:1:1); IR (nujol): $\tilde{\nu}$ = 1603 vw, 1496 w, 1476 s, 1394 m, 1262

  1433-7851/99/3805-0665 $ 17.50+.50/0

m, 1232 m, 1171 vs, 1139 vs, 1093 vs, 1055 s, 1021 m, 982 s, 955 vs, 921 m, 881 m, 834 s, 802 w, 734 m, 675 vs, 615 s, 586 m, 529 m, 509 m, 465 w, 454 w cm^{-1}; elemental analyses (THF and toluene were removed by drying **1** under vacuum) calcd for $C_{44}H_{102}O_{25}P_8Zn_{12}$ (2063.51): C 25.61, H 4.98; found: C 25.86, H 5.25.

Received: August 5, 1998 [Z12251IE]
German version: *Angew. Chem.* **1999**, *111*, 706 – 708

Keywords: cage compounds · phosphonate complexes · zinc

[1] a) X. Bu, P. Feng, T. E. Gier, G. D. Stucky, *J. Solid State Chem.* **1998**, *136*, 210; b) P. Feng, X. Bu, G. D. Stucky, *Angew. Chem.* **1995**, *107*, 1911; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1745; c) T. E. Gier, G. D. Stucky, *Nature* **1991**, *349*, 508; d) T. M. Nenoff, W. T. A. Harrison, T. E. Gier, G. D. Stucky, *J. Am. Chem. Soc.* **1991**, *113*, 378; e) W. T. A. Harrison, T. E. Gier, K. L. Moran, J. M. Nicol, H. Eckert, G. D. Stucky, *Chem. Mater.* **1991**, *3*, 27; f) T. Song, J. Xu, Y. Zhao, Y. Yue, Y. Xu, R. Xu, N. Hu, G. Wei, H. Jia, *J. Chem. Soc. Chem. Commun.* **1994**, 1171.

[2] W. T. A. Harrison, T. E. Gier, G. D. Stucky, R. W. Broach, R. A. Bedard, *Chem. Mater.* **1996**, *8*, 145.

[3] a) W. T. A. Harrison, L. Hannooman, *Angew. Chem.* **1997**, *109*, 663; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 640; b) W. T. A. Harrison, L. Hannooman, *J. Solid State Chem.* **1997**, *131*, 363; c) W. T. A. Harrison, M. L. F. Phillips, *Chem. Commun.* **1996**, 2771; d) W. T. A. Harrison, M. L. F. Phillips, *Chem. Mater.* **1997**, *9*, 1837.

[4] W. T. A. Harrison, R. W. Broach, R. A. Bedard, T. E. Gier, X. Bu, G. D. Stucky, *Chem. Mater.* **1996**, *8*, 691.

[5] a) W. T. A. Harrison, Z. Bircsak, L. Hannooman, *J. Solid State Chem.* **1997**, *134*, 148; b) W. T. A. Harrison, Z. Bircsak, L. Hannooman, Z. Zhang, *J. Solid State Chem.* **1998**, *136*, 93; c) Y. Ortiz-Avila, P. R. Rudolf, A. Clearfield, *Inorg. Chem.* **1989**, *28*, 2137; d) S. Natarajan, M. P. Attfield, A. K. Cheetham, *J. Solid State Chem.* **1997**, *132*, 229.

[6] a) W. T. A. Harrison, T. M. Nenoff, T. E. Gier, G. D. Stucky, *Inorg. Chem.* **1992**, *31*, 5395; b) C. G. Lugmair, T. D. Tilley, A. L. Rheingold, *Chem. Mater.* **1997**, *9*, 339; c) P. Reinert, N. Z. Logar, J. Patarin, V. Kaucic, *Eur. J. Solid State Inorg. Chem.* **1998**, *35*, 373.

[7] a) K. J. Martin, P. J. Squattrito, A. Clearfield, *Inorg. Chim. Acta* **1989**, *155*, 7; b) K. J. Frink, R.-C. Wang, J. L. Colon, A. Clearfield, *Inorg. Chem.* **1991**, *30*, 1438; c) D. M. Poojary, A. Clearfield, *J. Am. Chem. Soc.* **1995**, *117*, 11278.

[8] a) G. Cao, H. Lee, V. M. Lynch, T. E. Mallouk, *Inorg. Chem.* **1988**, *27*, 2781; b) G. Cao, T. E. Mallouk, *Inorg. Chem.* **1991**, *30*, 1434.

[9] a) S. Drumel, P. Janvier, P. Barboux, M. Bujoli-Doeuff, B. Bujoli, *Inorg. Chem.* **1995**, *34*, 148; b) S. Drumel, P. Janvier, D. Deniaud, B. Bujoli, *J. Chem. Soc. Chem. Commun.* **1995**, 1051; c) F. Fredoueil, V. Penicaud, M. Bujoli-Doeuff, B. Bujoli, *Inorg. Chem.* **1997**, *36*, 4702.

[10] a) S. Jain, T. T. Kodas, M. Hampden-Smith, *Chem. Vap. Deposition* **1998**, *4*, 51; b) J. Auld, D. J. Houlton, A. C. Jones, S. A. Rushworth, M. A. Malik, P. O'Brien, G. W. Critchlow, *J. Mater. Chem.* **1994**, *4*, 1249.

[11] F. A. Cotton, L. M. Daniels, L. R. Falvello, J. H. Matonic, C. A. Murillo, X. Wang, H. Zhou, *Inorg. Chim. Acta* **1997**, *266*, 91.

[12] a) H. M. M. Shearer, C. B. Spencer, *Acta Crystallogr. Sect. B* **1980**, *36*, 2046; b) M. M. Olmstead, P. P. Power, S. C. Shoner, *J. Am. Chem. Soc.* **1991**, *113*, 3379.

[13] Y. Kai, M. Morita, N. Yasuoka, N. Kasai, *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1631.

[14] F. H. van der Steen, J. Boersma, A. L. Spek, G. van Koten, *Organometallics* **1991**, *10*, 2467.

[15] S. Uhlenbrock, R. Wegner, B. Krebs, *J. Chem. Soc. Dalton Trans.* **1996**, 3731.

[16] a) M. L. Ziegler, J. Weiss, *Angew. Chem.* **1970**, *82*, 931; *Angew. Chem. Int. Ed. Engl.* **1970**, *9*, 905; b) M. Ishimori, T. Hagiwara, T. Tsuruta, Y. Kai, N. Yasuoka, N. Kasai, *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1165.

[17] a) D. Attanasio, G. Dessy, V. Fares, *J. Chem. Soc. Dalton Trans.* **1979**, 28; b) N. Lalioti, C. P. Raptopoulou, A. Terzis, A. E. Aliev, S. P. Perlepes, I. P. Gerothanassis, E. Manessi-Zoupa, *Chem. Commun.* **1998**, 1513.

[18] M. Tesmer, B. Mueller, H. Vahrenkamp, *Chem. Commun.* **1997**, 721.

[19] Crystal data for **1**: $C_{62.5}H_{130}O_{27}P_8Zn_{12}$ ($\mathbf{1}\cdot 1.5\,C_7H_8$), $M_r = 2345.86$, triclinic, space group $P\bar{1}$, $a = 15.049(10)$, $b = 15.178(10)$, $c = 24.89(2)$ Å, $\alpha = 72.89(2)$, $\beta = 75.54(3)$, $\gamma = 62.51(4)^\circ$, $V = 4777(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.631$ g cm^{-3}, $F(000) = 2402$, $\lambda = 0.71073$ Å, $T = 150$ K, $\mu(Mo_{K\alpha}) = 31.51$ cm^{-1}, min./max transmission 0.1871/0.3654, crystal dimensions $0.80 \times 0.50 \times 0.40$ mm, $3.59 < \Theta < 25.13^\circ$; 16331 data were collected of which 13156 were independent ($R_{int} = 0.0753$). For the final refinement of 1023 parameters no restraints were used. The R values were: $R1 = \Sigma\,|F_o - F_c|\,/\Sigma F_o = 0.0467$ for $I > 2\sigma(I)$, and $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w F_o^4]^{1/2} = 0.1292$ for all data; max/min. residual electron density: 0.990/ − 0.782 e Å^{-3}. The unit cell contains two molecules of **1** and three molecules of toluene of crystallization, one of them disordered about the inversion center. Intensity data of **1** were collected on a Siemens – Stoe AED-2 four-circle diffractometer. The crystal was transferred in an inert oil and then flash-cooled in a nitrogen stream.[22] The structure of **1** was solved with direct methods (SHELXS-97)[23] and was refined against F^2.[24] An empirical absorption correction was employed.[25] All non-hydrogen atoms were refined anisotropically and the riding model was used for the hydrogen atoms. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102564. 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).

[20] a) T. Song, M. B. Hursthouse, J. Chen, J. Xu, K. M. A. Malik, R. H. Jones, R. Xu, J. M. Thomas, *Adv. Mater.* **1994**, *6*, 679; b) X. Bu, P. Feng, G. D. Stucky, *J. Solid State Chem.* **1996**, *125*, 243.

[21] S. Fuchs, H. Schmidbaur, *Z. Naturforsch. B* **1995**, *50*, 855. However, an AB_2 spin system has also been reported for $(t\mathrm{BuPO_2})_3$, see K. Diemert, W. Kuchen, W. Poll, F. Sandt, *Eur. J. Inorg. Chem.* **1998**, *1*, 361.

[22] T. Kottke, D. Stalke, *J. Appl. Crystallogr.* **1993**, *26*, 615.

[23] G. M. Sheldrick, SHELXS-97, *Program for Structure Solution*, *Acta Crystallogr. Sect A* **1990**, *46*, 467.

[24] G. M. Sheldrick, SHELXL-97, *Program for Structure Refinement*, Universität Göttingen, **1997**.

[25] S. Parkin, B. Moezzi, H. Hope, *J. Appl. Crystallogr.* **1995**, *28*, 53.

Hydrogen-Bonding Cavities about Metal Ions: A Redox Pair of Coordinatively Unsaturated Paramagnetic Co – OH Complexes**

Brian S. Hammes, Victor G. Young, Jr, and Andrew S. Borovik*

Described herein is a synthetic system that uses hydrogen bonds to regulate the chemistry at a coordinatively unsaturated metal center. These regulatory properties are illustrated by the isolation and characterization of monomeric Co – OH complexes, including a five-coordinate paramagnetic Co^{III} – OH complex which, to our knowledge, has not been observed

[*] Prof. A. S. Borovik, Dr. B. S. Hammes
Department of Chemistry
University of Kansas
Lawrence, KS 66045 (USA)
Fax: (+1) 785-864-5396
E-mail: aborovik@caco3.chem.ukans.edu
Dr. V. G. Young, Jr.
Department of Chemistry, University of Minnesota (USA)

[**] The NIH (GM50781 to A.S.B.) is acknowledged for financial support of this research.

  1433-7851/99/3805-0666 $ 17.50+.50/0