DALTON COMMUNICATION

$[(thf)_6Ba_6(dmpz)_8\{(OSiMe_2)_2O\}_2]$ (dmpz = 3,5-dimethylpyrazolate): a molecule with six barium cations in a plane capped by two siloxane dianions and framed by eight dmpz anions †

Alexander Steiner,[a] Gavin T. Lawson,[a] Bernhard Walfort,[b] Dirk Leusser[b] and Dietmar Stalke*[b]

[a] *Department of Chemistry, University of Liverpool, Crown Street, Liverpool, UK L69 7ZD*
[b] *Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany. E-mail: dstalke@chemie.uni-wuerzburg.de*

Received 14th November 2000, Accepted 20th December 2000
First published as an Advance Article on the web 12th January 2001

In the synthesis of barium 3,5-dimethylpyrazolate, silicone joint grease and *cyclo*-$(Me_2SiO)_4$ are cleaved and two $O(SiMe_2O)_2^{2-}$ bidentate chelating siloxane anions are coordinated above and below an unprecedented Ba_6^{12-} layer framed by eight σ/π coordinated pyrazolate anions.

The s block metal amides and alkoxides are targets in organic and organometallic synthesis and in new materials. While the first application is clearly dominated by alkali metal amides,[1] materials scientists predominantly focus on alkaline earth metal alkoxides.[2] The first class of compounds has been systematically studied and rationalised by Snaith and co-workers.[3,4] The ring-laddering and ring-stacking principles explain the solid state architectures of lithium amides[3] and, more recently, their impact on the reaction pathways of chiral lithium amides.[4] Compared to such systematic knowledge, the alkaline earth metal amides and alkoxides represent a less elaborated class of compounds like, for example, the alkaline earth organometallics.[5]

In this paper we present a mixed barium amide–siloxane made up from six barium dications arranged in a plane. This plane is capped both above and below by a $-O-(SiMe_2)-O-(SiMe_2)-O-$ siloxane dianion and framed by eight 3,5-dimethylpyrazolyl amide anions. The six coordinating thf molecules are located at the periphery of the Ba_6 plane. Originally made and isolated by pure serendipity from the reaction of barium 3,5-dimethylpyrazolate and silicone joint grease the syntheses could be reproduced in a more planned approach *via* reaction with octamethylcyclotetrasiloxane.

Elemental barium reacts with pyrazole in a different way to alkali metals or alkali metal hydrides, *i.e.* very slowly.[6] It takes 20 h in boiling thf to deprotonate two equivalents of 3,5-dimethylpyrazole using 1 g of freshly grated barium. During the whole period the shiny surface of the substrate is maintained, enhancing the probability of chemical attacks by other reactants. At the end of the reaction the solution was decanted. Within one day, colourless crystals of the composition $[(thf)_6Ba_6(dmpz)_8\{(OSiMe_2)_2O\}_2]$ (dmpz = 3,5-dimethylpyrazolate) **1** were obtained.‡

Obviously the boiling thf dissolved the silicone grease partly out of the joints of the glass apparatus so it could take part in the overall reaction.[7] Thereupon the reaction was repeated twice in a grease-free apparatus. In the first reaction silicone joint grease was added as a starting material, in the second octamethylcyclotetrasiloxane was used. In both reactions **1** was isolated. Apparently the reaction described above is able to cleave cyclic as well as acyclic polymeric siloxanes like $[-Me_2Si-O-]_n$. In all cases defined fragments ($-O-SiMe_2-O-SiMe_2-O-$) were cut out of the siloxane chains.[8]

† In memoriam to Ron Snaith, a wonderful character and charismatic scholar.

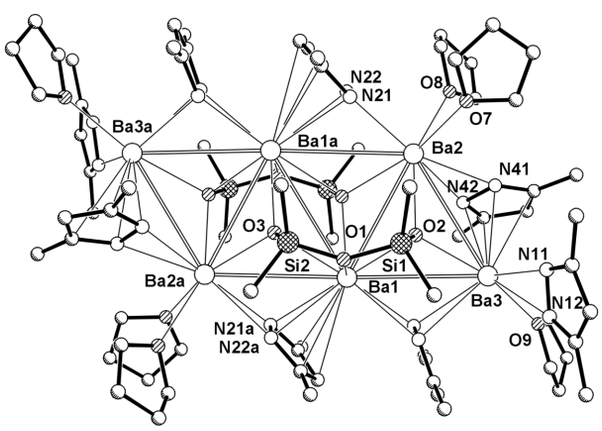

Fig. 1 The structure of $[(thf)_6Ba_6(dmpz)_8\{(OSiMe_2)_2O\}_2]$ (**1**) in the solid state. Selected bond lengths [pm] and angles [°]: Ba1–O1 289.7(6), Ba1–O3 285.4(5), Ba1–O2 274.0(6), Ba1a–O3 261.9(6), Ba2–O2 270.5(5), Ba2–O3a 271.6(6), Ba3–O2 274.1(5), Ba1–N31 279.2(7), Ba1–N32 284.3(8), Ba1–N21a 298.4(8), Ba1–N22a 292.1(7), Ba2–N21 280.9(7), Ba2–N22 275.8(7), Ba2–N41 278.4(7), Ba2–N42 275.5(7), Ba3–N11 266.5(9), Ba3–N12 269.4(8), Ba3–N31 300.7(8), Ba3–N32 281.3(8), Ba3–N41 287.7(7), Ba3–N42 293.2(7), Si1–O1 167.7(7), Si1–O2 160.4(6), Si2–O1 163.9(6), Si2–O3 160.5(6); Si2–O1–Si1 146.9(4), O1–Si1–O2 107.4(3), O3–Si2–O1 108.0(3).

Fig. 1 illustrates the result of the single crystal X-ray structure analysis of **1**.§ A molecular rhomboid layer is formed of six barium dications *via* four adjacent almost equilateral triangles (av. Ba···Ba 427.8; from 422.00(10) to 446.80(9) pm). These Ba···Ba distances are considerably longer than in $[(thf)Ba_3(OSiPh_3)_6]$[9] (393.3 pm) or in $[(thf)_3Ba_6Li_3O_2(OBu^t)_{11}]$[10] (381 pm) but close to interatomic distances in elemental barium (435 and 502 pm in the body-centred cubic metal).[11] The Ba_6 layer in **1** is capped above as well as below by a siloxane fragment. The terminal oxygen atoms of this fragment are μ_3-capping the barium triangles. The Ba–O distances (av. 273 pm) are comparable with those found in $[(thf)Ba_3(OSiPh_3)_6]$[9] in which a barium triangle is μ_3-bicapped by a siloxane anion (Ba–O = 269 pm). In $[(thf)_3Ba_6Li_3O_2(OBu^t)_{11}]$ an O^{2-} filled Ba_6 octahedron with a fused Ba_3Li_3 and O^{2-} filled prism is formed. Seven of the eight Ba_3 triangles are capped by the OBu^t groups and the Ba–O distances vary from 264 to 278 pm.[10] The central oxygen atoms of the siloxane fragments in **1** are coordinated to only one barium atom each. The resulting Ba1–O1 and Ba1a–O1a distances are longer (289.7(6) pm) than the others. The Ba_6 layer is framed by eight 3,5-dimethylpyrazolyl anions and six tetrahydrofuran donor molecules limiting the barium unit to the edges. All 3,5-dimethylpyrazolate substituents are η^2-coordinated by their two nitrogen atoms to at least one barium atom. Three groups of differently coordinated 3,5-dimethylpyrazolate ligands are present in **1**: two 3,5-dimethylpyrazolate ligands are

DOI: 10.1039/b009121i

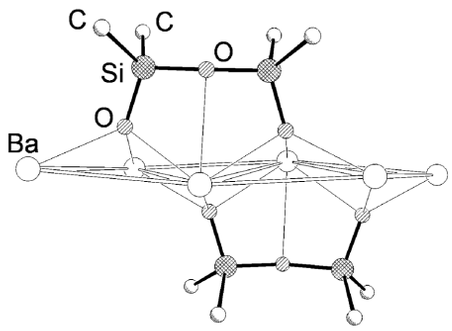

Fig. 2 Coordination of a single siloxane fragment on the cationic barium surface in **1**.

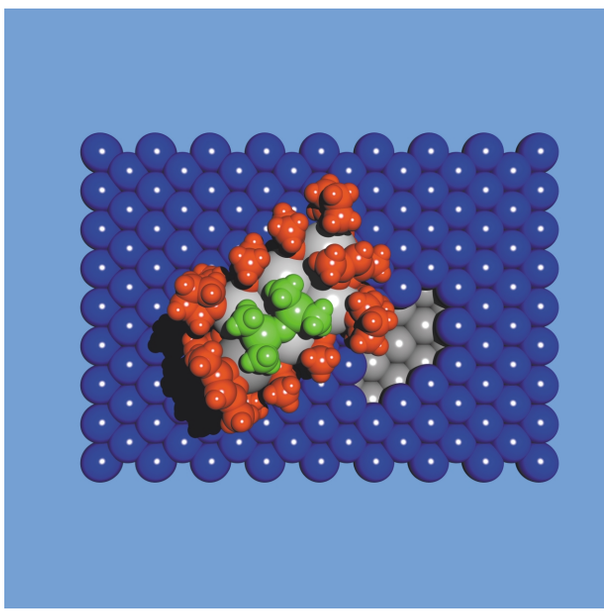

Fig. 3 View perpendicular to the (110) layer of metallic barium in the background (blue). The Ba_6 layer of **1** is almost identical to a Ba_6 section from the blue layer (next layer of atoms coloured in grey). It is framed by eight dmpz and six thf molecules coloured in red and capped by a $O(SiMe_2O)_2^{2-}$ bidentate chelating anion coloured in green.

terminally η^2-coordinated to one barium atom each (N11–N12, N11a–N12a; Ba3–N11 266.5(9) and Ba3–N12 269.4(8) pm) while two are η^2-μ-bridging two barium atoms (N31–N32, N31a–N32a; Ba–N from 279.2(7) to 300.7(8) pm). The remaining four 3,5-dimethylpyrazolate ligands coordinate one barium atom each, η^2 through their nitrogen atoms, and a second each through their π-electron system (N21–N22, N21a–N22a, N41–N42, N41a–N42a; Ba–N from 275.5(7) to 298.4(8); Ba–C from 315.7(9) to 338.5(9) pm). The η^2-coordination mode is already known in pyrazolyl derivatives of lanthanides and actinides,[12] but there is only one example of an alkaline earth compound. In $[Ba\{(dmpz)_3Ge\}_2]$[13] two of the 3,5-dimethylpyrazolate rings are η^2-coordinated to the barium cation (Ba–N 292.7 and 296.7 pm) while four are σ-coordinated to the barium (av. Ba–N 280.3 pm). The Ba–C distances of 327.5 and 339.3 pm in $[Ba\{(dmpz)_3Ge\}_2]$ are marginally longer than in **1**. The structure of $[Ba_2\{CyNC(Me)CHC(Me)NCy\}_3\{N(SiMe_3)_2\}]$[14] (Cy = cyclohexyl) in which the three diazapentadienide anions are present in three different coordination modes best fits the geometrical features found in **1**.

Fig. 2 depicts the coordination of the siloxane fragment on the Ba_6 surface. The nearly hexagonal monomolecular layer is very similar to the (110) layer in cubic body-centred metallic barium (see Fig. 3). Known multinuclear barium Ba_n ($n > 3$) derivatives form three-dimensional metal skeletons.[15] To our knowledge **1** is the first example of a two-dimensional molecular monolayer which is so highly aggregated. The 3,5-dimethylpyrazolyl anions and thf molecules act as a "mirror frame" stabilising the cationic layer along the edges. Similar to the features found in **1** metal surfaces are structurally flexible and fit the coating of adsorbed atoms or molecules. As a consequence, the local symmetry of the surface is changed relative to that in the inner metal core.[16] The barium metal adopts a cubic body-centred structure. The coordination of the siloxane fragments to the surface induces hexagonal symmetry. Therefore, the Ba_6 unit in **1** is similar to a section of the (110) layer of metallic barium. The coordinated siloxane differs marginally from the starting material. In **1** the O–Si–O bond angle is on average 5° more acute while the angle at the central oxygen atom is 5° wider than the related angles in octamethylcyclotetrasiloxane.[17] The $O(SiMe_2O)_2^{2-}$ bidentate chelating anion functions as a molecular staple to two alternate Ba_3 triangles each (above and below) and favours the layer arrangement rather than the three-dimensional cluster. The σ/π coordination flexibility of the 3,5-dimethylpyrazolyl anions terminates the layer at the edges.

Acknowledgements

We gratefully acknowledge the continued financial support of the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the DAAD (German/British exchange program).

Notes and references

‡ All manipulations were performed under a dry N_2 inert gas atmosphere with Schlenk techniques or in an argon glove box. All solvents were dried over Na/K alloy and distilled prior to use. NMR spectra were obtained in d_8-thf as solvent with $SiMe_4$ or $SnMe_4$ as external reference on a Bruker AM 250. IR spectra were recorded on Bio-Rad FTS or Perkin-Elmer 180, 325, 735 B spectrometers as Nujol mulls between KBr plates. Elemental analyses were performed by the Analytisches Laboratorium des Instituts für Anorganische Chemie der Universität Göttingen.

$Ba(dmpz)_2$: A mixture of 6.0 g (45 mmol) freshly cut barium metal and 8.6 g (90 mmol) 3,5-dimethylpyrazole was refluxed for 2 d in 100 mL thf. After cooling the solution to room temperature the colorless precipitate was washed twice with 50 mL thf and dried in a vacuum at 60 °C. Yield: 14.0 g (95%). IR (KBr/Nujol): ν(cm^{-1}) 1510 (s), 1406 (s), 1315 (m), 1040 (m), 1007 (s), 787 (s), 750 (m), 730 (m), 416 (m); Anal. calc. (found): C, 36.66 (36.42); H, 4.31 (4.35); N 17.11 (16.90)%.

$[(thf)_6Ba_6(dmpz)_8\{(OSiMe_2)_2O\}_2]$ (**1**): 1.00 g (7.3 mmol) of freshly grated barium, 1.05 g (14.6 mmol) 3,5-dimethylpyrazole and 0.72 g (2.4 mmol) octamethylcyclotetrasiloxane were refluxed in 50 mL thf and stirred intensely until all of the metal had reacted (*ca.* 20 h). The white precipitate was allowed to settle and the reaction solution was decanted. Within one day colourless crystals were obtained. Yield: 0.47 g (15% relative to reacted barium, first batch, not optimised); Anal. calc. (found): C, 36.85 (36.18); H, 5.55 (5.24); N, 9.55 (9.83)%; ^{1}H NMR (C_6D_6, 25 °C): δ = 0.29 (s, $SiMe_2$), 1.11 and 3.25 (thf), 1.98 (broad signal, $Me_2C_3H_3N_2$), 5.67 (broad signal, $Me_2C_3H_3N_2$). Due to the insolubility of **1** and low concentration neither ^{13}C-, ^{15}N- nor ^{29}Si-NMR spectra could be obtained, however, MAS-NMR experiments are planned to assign the chemically different dmpz sites.

§ Crystal data for **1**: $C_{72}H_{128}Ba_6N_{16}O_{12}Si_4$: M = 2346.30, orthorhombic, space group *Pbca*, a = 2141.6(3), b = 1394.4(2), c = 3231.7(4) pm, V = 9.651(2) nm^3, Z = 4, $\rho_{cal.}$ = 1.615 Mg m^{-3}, $F(000)$ = 4640, λ = 71.073 pm, T = –120 °C, μ(Mo-Kα) = 2.518 mm^{-1}. Intensities were collected on a Stoe-Siemens-AED-diffractometer from a shock-cooled crystal in an oil drop[18] of the dimensions 0.5 × 0.4 × 0.4 mm in the region of $8° \le 2\theta \le 45°$. Of the 6384 collected reflections 6312 were unique and 6306 were employed in the structure refinement. All data were semi-empirical absorption corrected. The R-values are $R1 = \Sigma|F_o - F_c|/\Sigma F_o = 0.047$ ($F > 4\sigma F$) and $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{\ddagger} = 0.110$ (all data) with $w^{-1} = \sigma^2(F_o^2) + (g_1P)^2 + g_2P$ with $P = (F_o^2 + 2F_c^2)/3$ and $g_1 = 0.0273$ and $g_2 = 91.0317$. The structure was solved by direct methods (SHELXS-90)[19] and refined by full-matrix least-squares on F^2 with all data (SHELXL-97).[20] All non-hydrogen atoms were assigned idealised positions and refined anisotropically using a riding model. The hydrogen atoms were placed in geometrically idealised positions in the refinement. CCDC reference number 152863. See http://www.rsc.org/suppdata/dt/b0/b009121i/ for crystallographic data in CIF or other electronic format.

1 (*a*) M. F. Lappert, P. P. Power, A. R. Sanger and R. C. Srivastava, *Metal and Metalloid Amides*, Wiley, New York, 1980; (*b*) R. Snaith,

D. S. Wright, F. Pauer and P. P. Power, in *Lithium Chemistry: A theoretical and Experimental Overview*, eds. A.-M. Sapse and P. v. R. Schleyer; John Wiley & Sons, New York, 1994, Ch. 8 and 9.
2 (*a*) O. B. Koper, I. Lagadic, A. Volodin and K. J. Klabunde, *Chem. Mater.*, 1997, **9**, 2468; (*b*) M. Tada, S. Fujihara and T. Kimura, *J. Mater. Res.*, 1999, **14**, 1610; (*c*) D. Y. Jun, E. S. Kim, K. H. Jo and D. A. Payne, *Mol. Cryst.*, *Liq. Cryst.*, 2000, **339**, 11; (*d*) N. I. Al-Salim, S. A. Bagshaw, A. Bittar, T. Kemmitt, A. J. McQuillan, A. M. Mills and M. J. Ryan, *J. Mater. Chem.*, 2000, **10**, 2358.
3 (*a*) D. R. Armstrong, D. Barr, W. Clegg, R. E. Mulvey, D. Reed, R. Snaith and K. Wade, *J. Chem. Soc.*, *Chem. Commun.*, 1989, 869; (*b*) K. Gregory, P. v. R. Schleyer and R. Snaith, *Adv. Inorg. Chem.*, 1991, **37**, 47; (*c*) R. E. Mulvey, *Chem. Soc. Rev.* 1991, **20**, 167; (*d*) R. E. Mulvey, *Chem. Soc. Rev.*, 1999, **27**, 339.
4 D. R. Armstrong, K. W. Henderson, A. R. Kennedy, W. J. Kerr, F. S. Mair, J. H. Moir, P. H. Moran and R. Snaith, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 4063.
5 (*a*) M. J. Harvey, T. P. Hanusa and V. G. Young Jr., *Angew. Chem.*, 1999, **111**, 241; M. J. Harvey, T. P. Hanusa and V. G. Young Jr., *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 217; (*b*) D. Stalke, *Angew. Chem.*, 1994, **106**, 2256; D. Stalke, *Angew. Chem.*, *Int. Ed. Engl.*, 1994, **33**, 2168; (*c*) T. P. Hanusa, *Chem. Rev.*, 1993, **93**, 1023.
6 A. Steiner and D. Stalke, *J. Chem. Soc.*, *Chem. Commun.*, 1993, 1702.
7 Another example: M. R. Churchill, C. H. Lake, S.-H. L. Chao and O. T. Beachley Jr., *J. Chem. Soc.*, *Chem. Commun*., 1993, 1577.
8 The selective cleavage of silicone is not unprecedented and not limited to Ba: *e.g.* **Tl**: (*a*) S. Harvey, M. F. Lappert, C. L. Raston, B. W. Skelton, G. Srivastava and A. H. White, *J. Chem. Soc.*, *Chem. Commun.*, 1988, 1216; (*b*) **Sm**: W. J. Evans, T. A. Ulibarri and J. W. Ziller, *Organometallics*, 1991, **10**, 134; **Ba/Y**: J. D. Foulon, P. Miele and N. Hovnanian, *Z. Kristallogr.*, 1994, **209**, 282; **Ag**: D. A. Edwards, R. M. Harker, M. F. Mahon and K. C. Molloy, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 3509; **Pt**: P. Gomez-Elipe, R. Resendes, P. M. McDonald and I. Manners, *J. Am. Chem. Soc.*, 1998, **120**, 8348; (*c*) **Al**: C. N. McMahon, S. G. Bott, L. B. Alemany, H. W. Roesky and A. R. Barron, *Organometallics*, 1999, **18**, 5395.
9 K. G. Caulton, M. H. Chisholm, S. R. Drake and W. E. Streib, *Angew. Chem.*, 1990, **102**, 1492; K. G. Caulton, M. H. Chisholm, S. R. Drake and W. E. Streib, *Angew. Chem.*, *Int. Ed. Engl.*, 1990, **29**, 1483.
10 H. Bock, T. Hauck, C. Näther, N. Rösch, M. Staufer and O. D. Häberlen, *Angew. Chem.*, 1995, **107**, 1439; H. Bock, T. Hauck, C. Näther, N. Rösch, M. Staufer and O. D. Häberlen, *Angew. Chem.*, *Int. Ed. Engl.*, 1995, **34**, 1353.
11 A. F. Wells, *Structural Inorganic Chemistry*, 5th edition, Oxford University Press, Oxford, 1984.
12 (*a*) C. W. Eigenbrot, Jr. and K. N. Raymond, *Inorg. Chem.*, 1981, **20**, 1553 and 1982, **21**, 2653; (*b*) J. E. Cosgriff, G. B. Deacon, B. M. Gatehouse, H. Hemling and H. Schumann, *Angew. Chem.*, 1993, **105**, 906; J. E. Cosgriff, G. B. Deacon, B. M. Gatehouse, H. Hemling and H. Schumann, *Angew. Chem.*, *Int. Ed. Engl.*, 1993, **32**, 874.
13 A. Steiner and D. Stalke, *Inorg. Chem.*, 1995, **34**, 4846.
14 W. Clegg, S. J. Coles, E. K. Cope and F. S. Mair, *Angew. Chem.*, 1998, **110**, 841; W. Clegg, S. J. Coles, E. K. Cope and F. S. Mair, *Angew. Chem.*, *Int. Ed. Engl.*, 1993, **37**, 796.
15 (*a*) K. G. Caulton, M. H. Chisholm, S. R. Drake and K. Folting, *J. Chem. Soc.*, *Chem. Commun.*, 1990, 1349; (*b*) K. G. Caulton, M. H. Chisholm, S. R. Drake and K. Folting, *J. Chem. Soc.*, *Chem. Commun.*, 1990, 1498; (*c*) S. K. Pandey, A. Steiner, H. W. Roesky and D. Stalke, *Angew. Chem.*, 1993, **105**, 625; S. K. Pandey, A. Steiner, H. W. Roesky and D. Stalke, *Angew. Chem.*, *Int. Ed. Engl.*, 1993, **32**, 596.
16 G. A. Somorjai, *Langmuir*, 1991, **7**, 3176.
17 (*a*) H. Stenfink, B. Post and I. Fankuchen, *Acta Crystallogr.*, 1955, **8**, 420; (*b*) T. Kottke and D. Stalke, *Organometallics*, 1996, **21**, 4553.
18 D. Stalke, *Chem. Soc. Rev.*, 1998, **27**, 171.
19 G. M. Sheldrick, *Acta Crystallogr.*, *Sect. A*, 1990, **46**, 467.
20 G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, 1997.