

(Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai & Pritzkow, 1996). Software used to prepare material for publication: *SHELXL93*.

The author thanks the University of Malaya (F102/66, F677/96) for supporting this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KH1135). Services for accessing these data are described at the back of the journal.

## References

- Enraf–Nonius (1988). *CAD-4 VAX/PC Fortran System. Operator's Guide to the Enraf–Nonius CAD-4 Diffractometer Hardware, its Software and the Operating System*. Enraf–Nonius, Delft, The Netherlands.
- Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
- Ng, S. W. & Kumar Das, V. G. (1995). *J. Organomet. Chem.* **513**, 105–108.
- Ng, S. W., Kumar Das, V. G. & Kennard, C. H. L. (1996). *Main Group Met. Chem.* **19**, 107–111.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sheldrick, G. M. (1990). *SHELXTL/PC Users Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Zsolnai, L. & Pritzkow, H. (1996). *ZORTEP. Interactive Graphics Program*. University of Heidelberg, Germany.

*Acta Cryst.* (1997). **C53**, 1061–1063

## Pentakis(tetrahydrofuran)barium Bis-(carbazolate) Tetrahydrofuran Solvate

CHRISTIAN NÄTHER, TIM HAUCK AND HANS BOCK

*Institut für Anorganische Chemie der Universität Frankfurt, Marie-Curie-Strasse 11, 60439 Frankfurt/Main, Germany.*  
E-mail: bock@bock.anorg.chemie.uni-frankfurt.de

(Received 1 October 1996; accepted 26 February 1997)

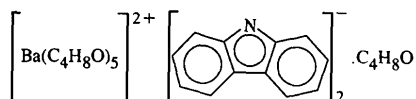
### Abstract

Reaction of carbazole with barium metal in dry tetrahydrofuran yields colourless blocks of the title compound,  $[\text{Ba}(\text{C}_4\text{H}_8\text{O})_5](\text{C}_{12}\text{H}_8\text{N})_2\cdot\text{C}_4\text{H}_8\text{O}$ . The structure contains sevenfold-coordinated barium counter cations, which are surrounded by two carbazole monoanions and five tetrahydrofuran molecules in a  $C_2$  symmetric environment.

### Comment

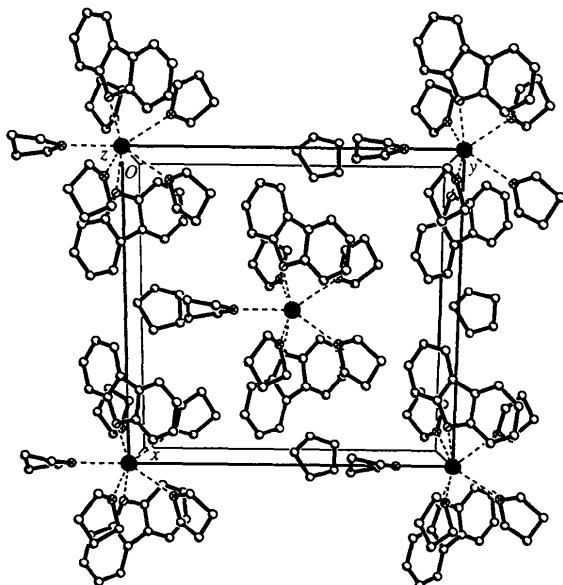
Numerous structures of alkaline and alkaline earth organometallic compounds have contributed to the rationalization of their chemical and physical properties. The effects of metal cation solvation on the structure of the complexes are well known, especially for the respective sodium complexes (Bock, Näther, Havlas, John & Arad, 1994; Bock *et al.*, 1992; Schade & Schleyer, 1987), whereas analogous investigations for the heavier alkaline and the doubly charged alkaline earth ions are still missing. The structure of the title compound was determined as part of a study of both solvent and counter cation effects in carbazolate anion salts. In the presence of strong solvating agents like tetraglyme, crown ethers or cryptands, alkali metal ions form monomers (Bock, Arad, Näther & Havlas, 1997; Bock, Arad & Näther, 1997), contrary to the otherwise crystallizing dimers. According to their structures, in the dimers, the nitrogen centre of one anion is  $\sigma$ -coordinated to the alkali metal ion, whereas the coordination of the second anion depends predominantly on the cation size. Small cations such as lithium are  $\sigma$ -coordinated, medium-sized ones such as sodium exhibit mixed  $\pi$ - $\sigma$  contacts, and the rather large caesium cation is  $\pi$ -coordinated to the other carbazole anion (Bock, Arad, Näther & Havlas, 1997; Gregory, Bremer, Schleyer, Klusener & Brandsma, 1989; Hacker, Kaufmann, Schleyer, Mahdi & Dietrich, 1987). In carbazole–barium–tris(dimethoxyethane), the only structurally characterized barium carbazolate to date, the barium dication is only  $\sigma$ -coordinated to both carbazolate anions (Mösges, Hampel, Kaupp & Schleyer, 1992).

The crystal structure of the title compound, (I), shows the metal complex to be located around a twofold axis, which passes through the barium dication and the O atom of one tetrahydrofuran ligand. In the selected setting for the non-centrosymmetric space group, this solvent molecule is oriented into the direction of the negative  $b$  axis. Of the four crystallographically independent solvent molecules, one is not connected to the barium counter dication and found disordered around the twofold axis in holes of the crystal packing. Its shortest intermolecular C—C distances to a neighbouring molecule amounts to 3.7 Å. The barium dication exhibits a coordination number of seven and is surrounded by two carbazole anions and five tetrahydrofuran molecules in an asymmetric environment. The coordination polyhedron around Ba1 can be described as a strongly distorted pentagonal bipyramid with the oxygen centres in the pentagonal plane and the nitrogen centres at both peaks. The Ba1—N1 distances amount to 2.772 (2) Å and the Ba—O distances to 2.773 (2) (two contacts), 2.790 (2) (two contacts) and 2.785 (2) Å. The barium dication is located 1.475 (4) Å above the carbazole plane. The angle between Ba1, N1 and the centroid of the five-membered ring amounts to 146.7 (1)°.

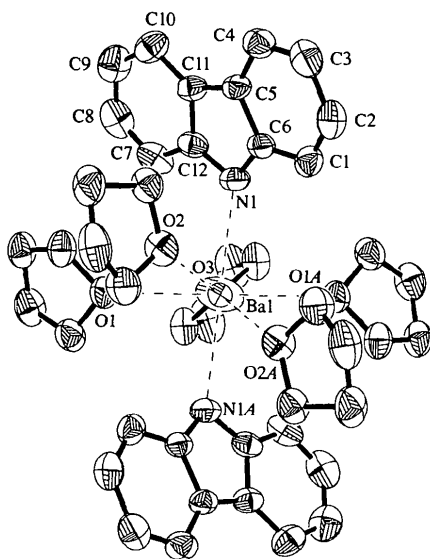


(I)

The carbazolate anion is planar within experimental error, with largest deviations of the individual centres from its mean plane of 0.068 (3) Å. All structural parameters of the anion are comparable to those in other carbazolate anion salts.



(a)



(b)

Fig. 1. (a) The crystal structure of the title compound viewed along the *c* axis, and (b) barium coordination with labelling. Displacement ellipsoids are drawn at the 50% probability level.

In summary, in barium carbazolates, neither dimer formation with weakly solvating tetrahydrofuran ligands nor multi-hapto interactions with large counter cations such as in fluorene–barium–tetrakis(ammonia) (Mösges, Hampel & Schleyer, 1992) are observed, presumably due to sterical reasons. Obviously in the complex investigated,  $\sigma$ -coordination to the negatively charged carbazole nitrogen centre is preferred.

## Experimental

Carbazole is commercially available. Carefully decaerated barium (150 mg, 1.1 mmol) was distilled at  $10^{-6}$  mbar and 700 K onto the wall of a quartz Schlenk trap under argon, and carbazole (334 mg, 2 mmol) and 10 ml THF (dried over Na/K alloy) were added. The solution was covered three times with a layer of 5 ml *n*-hexane (dried over Na/K alloy) and within one week colourless crystals had grown.

### Crystal data

[Ba(C<sub>4</sub>H<sub>8</sub>O)<sub>5</sub>](C<sub>12</sub>H<sub>8</sub>N)<sub>2</sub>·  
C<sub>4</sub>H<sub>8</sub>O  
*M<sub>r</sub>* = 902.35  
Monoclinic  
*C*2  
*a* = 15.7566 (9) Å  
*b* = 15.9146 (9) Å  
*c* = 9.5363 (7) Å  
 $\beta$  = 106.854 (5)°  
*V* = 2288.6 (2) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 1.309 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

Mo *K*α radiation  
 $\lambda$  = 0.71073 Å  
Cell parameters from 100 reflections  
 $\theta$  = 10.5–18.5°  
 $\mu$  = 0.916 mm<sup>-1</sup>  
*T* = 200 (2) K  
Block  
0.6 × 0.4 × 0.4 mm  
Colourless

### Data collection

Stoe AED-II diffractometer  
 $\omega$ -2 $\theta$  scan  
Absorption correction:  
empirical via  $\psi$  scans  
(Siemens, 1990)  
*T<sub>min</sub>* = 0.588, *T<sub>max</sub>* = 0.693  
5628 measured reflections  
4579 independent reflections  
4578 reflections with  
*I* > 2 $\sigma$ (*I*)

*R<sub>int</sub>* = 0.0059  
 $\theta_{\text{max}}$  = 32.02°  
*h* = -23 → 22  
*k* = -6 → 20  
*l* = 0 → 14  
4 standard reflections  
frequency: 120 min  
intensity decay: none

### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.023  
*wR*(*F*<sup>2</sup>) = 0.056  
*S* = 1.148  
4579 reflections  
259 parameters  
H atoms: see below  
*w* = 1/[ $\sigma^2(F_o^2) + (0.0442P)^2$ ]  
where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3  
( $\Delta/\sigma$ )<sub>max</sub> < 0.001  
 $\Delta\rho_{\text{max}}$  = 0.748 e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}}$  = -0.596 e Å<sup>-3</sup>

Extinction correction:  
*SHELXL93* (Sheldrick,  
1993)  
Extinction coefficient:  
0.0072 (4)  
Scattering factors from  
*International Tables for  
Crystallography* (Vol. C)  
Absolute configuration:  
Flack (1983)  
Flack parameter = 0.012 (11)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )
$$U_{eq} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

|        | x            | y            | z           | $U_{eq}$    |
|--------|--------------|--------------|-------------|-------------|
| N1     | 0.13719 (13) | -0.0266 (2)  | -0.1227 (2) | 0.0457 (4)  |
| C1     | 0.0930 (2)   | 0.0900 (2)   | -0.3039 (3) | 0.0497 (6)  |
| C2     | 0.1231 (2)   | 0.1527 (2)   | -0.3765 (3) | 0.0570 (7)  |
| C3     | 0.2148 (3)   | 0.1630 (2)   | -0.3604 (3) | 0.0587 (7)  |
| C4     | 0.2758 (2)   | 0.1099 (2)   | -0.2693 (3) | 0.0509 (6)  |
| C5     | 0.24701 (14) | 0.0466 (2)   | -0.1915 (2) | 0.0402 (5)  |
| C6     | 0.15405 (13) | 0.0359 (2)   | -0.2087 (2) | 0.0404 (4)  |
| C7     | 0.2405 (3)   | -0.1201 (2)  | 0.0589 (4)  | 0.0619 (8)  |
| C8     | 0.3290 (3)   | -0.1390 (3)  | 0.1258 (4)  | 0.0718 (10) |
| C9     | 0.3979 (3)   | -0.0968 (3)  | 0.0883 (5)  | 0.0697 (10) |
| C10    | 0.3786 (2)   | -0.0350 (3)  | -0.0171 (4) | 0.0570 (6)  |
| C11    | 0.28934 (14) | -0.0145 (2)  | -0.0856 (3) | 0.0419 (9)  |
| C12    | 0.2197 (2)   | -0.0569 (2)  | -0.0470 (3) | 0.0447 (5)  |
| Ba1    | 0            | 0            | 0           | 0.03057 (4) |
| O1     | 0.10277 (13) | -0.0366 (2)  | 0.2848 (2)  | 0.0545 (5)  |
| C21    | 0.0768 (2)   | -0.0700 (3)  | 0.4035 (3)  | 0.0607 (8)  |
| C22    | 0.1519 (3)   | -0.1236 (3)  | 0.4924 (4)  | 0.0681 (9)  |
| C23    | 0.2319 (2)   | -0.0841 (3)  | 0.4612 (4)  | 0.0614 (8)  |
| C24    | 0.1941 (2)   | -0.0143 (2)  | 0.3513 (3)  | 0.0560 (11) |
| O2     | 0.1039 (2)   | 0.1404 (2)   | 0.1011 (2)  | 0.0538 (5)  |
| C31    | 0.1906 (2)   | 0.1606 (2)   | 0.0892 (3)  | 0.0543 (6)  |
| C32    | 0.2309 (3)   | 0.2203 (3)   | 0.2152 (4)  | 0.0682 (10) |
| C33    | 0.1511 (3)   | 0.2633 (2)   | 0.2398 (4)  | 0.0685 (10) |
| C34†   | 0.0876 (4)   | 0.1939 (4)   | 0.2097 (6)  | 0.0625 (12) |
| C34'‡  | 0.0643 (6)   | 0.2208 (7)   | 0.1355 (11) | 0.047 (2)   |
| O3     | 0            | -0.1750 (3)  | 0           | 0.0861 (15) |
| C41    | -0.0269 (5)  | -0.3134 (3)  | 0.0565 (6)  | 0.091 (2)   |
| C42§   | -0.0120 (4)  | -0.2265 (3)  | 0.1207 (5)  | 0.0608 (10) |
| C42'¶  | -0.0621 (11) | -0.2361 (13) | 0.032 (2)   | 0.071 (4)   |
| O4     | 1/2          | -0.003 (2)   | 1/2         | 0.355 (10)  |
| C51    | 0.4259 (12)  | 0.0623 (10)  | 0.4405 (18) | 0.215 (7)   |
| C52††  | 0.4566 (10)  | 0.1503 (14)  | 0.442 (2)   | 0.146 (7)   |
| C52'†† | 0.464 (2)    | 0.136 (2)    | 0.542 (4)   | 0.259 (19)  |

† Site occupancy = 0.70. ‡ Site occupancy = 0.30. § Site occupancy = 0.75. ¶ Site occupancy = 0.25. †† Site occupancy = 0.50.

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

|           |           |             |           |
|-----------|-----------|-------------|-----------|
| N1—Ba1    | 2.772 (2) | Ba1—O3      | 2.785 (4) |
| Ba1—N1'   | 2.772 (2) | Ba1—O1'     | 2.790 (2) |
| Ba1—O2    | 2.773 (2) | Ba1—O1      | 2.790 (2) |
| Ba1—O2'   | 2.773 (2) |             |           |
| C2—C1—C6  | 119.8 (3) | C8—C7—C12   | 118.8 (3) |
| C1—C2—C3  | 121.3 (3) | C7—C8—C9    | 121.7 (4) |
| C4—C3—C2  | 119.9 (3) | C10—C9—C8   | 120.3 (3) |
| C3—C4—C5  | 120.0 (3) | C9—C10—C11  | 118.9 (3) |
| C4—C5—C11 | 135.2 (2) | C10—C11—C5  | 133.5 (2) |
| C4—C5—C6  | 120.1 (3) | C10—C11—C12 | 120.8 (3) |
| C11—C5—C6 | 104.6 (2) | C5—C11—C12  | 105.7 (2) |
| N1—C6—C1  | 128.2 (2) | N1—C12—C7   | 128.2 (3) |
| N1—C6—C5  | 112.9 (2) | N1—C12—C11  | 112.3 (2) |
| C1—C6—C5  | 118.9 (3) | C7—C12—C11  | 119.5 (3) |

Symmetry code: (i)  $-x, y, -z$ .

H atoms were positioned in idealized geometry and refined with fixed individual isotropic displacement parameters [ $U_{iso} = 1.2U_{eq}(\text{C}_{aromatic}/\text{C}_{methylene})$ ] using a riding model with parameters C—H (aromatic) 0.95 and C—H (methylene) 0.99  $\text{\AA}$ . Three of the four crystallographically independent tetrahydro-

furan molecules were disordered and were refined using a split model. The absolute structure was determined using the Flack test (Flack, 1983) in *SHELXL93* (Sheldrick, 1993) and is in agreement with the selected setting. The Flack absolute structure parameter refined to 0.012 (11). In addition, inversion of the structure leads to significantly different *R* values of 0.0306 and 0.0799 (*wR2*).

Data collection: *DIF4* (Stoe & Cie, 1992a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1992b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93*. Molecular graphics: *SHELXTL/PC* (Siemens, 1990). Software used to prepare material for publication: *SHELXL93 CIFTAB*.

This project is supported by the Deutsche Forschungsgemeinschaft, the State of Hessen, the Fonds der Chemischen Industrie and the A. Messer Foundation.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1064). Services for accessing these data are described at the back of the journal.

## References

- Bock, H., Arad, C. & Näther, C. (1997). *Helv. Chim. Acta*. In the press.
- Bock, H., Arad, C., Näther, C. & Havlas, Z. (1997). *Organometallics*. Submitted.
- Bock, H., Näther, C., Havlas, Z., John, A. & Arad, C. (1994). *Angew. Chem.* **106**, 931–934; *Angew. Chem. Int. Ed. Engl.* **33**, 875–878.
- Bock, H., Ruppert, K., Näther, C., Havlas, Z., Hermann, H.-F., Arad, C., Göbel, I., John, A., Meuret, J., Nick, S., Rauschenbach, A., Seitz, W., Vaupel, T. & Solouki, B. (1992). *Angew. Chem.* **104**, 564–595; *Angew. Chem. Int. Ed. Engl.* **31**, 550–581.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Gregory, K., Bremer, M., Schleyer, P. v. R., Klusener, P. A. A. & Brandsma, L. (1989). *Angew. Chem.* **101**, 1261–1264; *Angew. Chem. Int. Ed. Engl.* **28**, 1224–1227.
- Hacker, R., Kaufmann, E., Schleyer, P. v. R., Mahdi, W. & Dietrich, H. (1987). *Chem. Ber.* **120**, 1533–1538.
- Mösger, G., Hampel, H., Kaupp, M. & Schleyer, P. v. R. (1992). *J. Am. Chem. Soc.* **114**, 10880–10881.
- Mösger, G., Hampel, F. & Schleyer, P. v. R. (1992). *Organometallics*, **11**, 1769–1773.
- Schade, C. & Schleyer, P. v. R. (1987). *Adv. Organomet. Chem.* **27**, 169–278.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Siemens (1990). *SHELXTL/PC*. Version 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Stoe & Cie (1992a). *DIF4. Diffractometer Control Program*. Version 7.09/DOS. Stoe & Cie, Darmstadt, Germany.
- Stoe & Cie (1992b). *REDU4. Data Reduction Program*. Version 7.03. Stoe & Cie, Darmstadt, Germany.