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References

- Bailey, P. S. (1978). *Ozonation in Organic Chemistry*, pp. 1, 9–52. New York: Academic Press.
- Bailey, P. S. & Ferrel, T. M. (1978). *J. Am. Chem. Soc.* **100**, 899–905.
- Choe, J.-I., Choi, H.-S. & Kuczkowski, R. L. (1986). *Magn. Reson. Chem.* **24**, 1044–1047.
- Criegee, R. & Korber, H. (1971). *Chem. Ber.* **104**, 1807–1815.
- Criegee, R. & Wenner, G. (1949). *Justus Liebigs Ann. Chem.* **561**, 9–16.
- Griesbaum, K., Ball, V., Beck, J. & McCullough, K. (1995). *Liebigs Ann.* pp. 1993–1995.
- Griesbaum, K., Krieger-Beck, P. & Beck, J. (1991). *J. Org. Chem.* **56**, 4005–4008.
- Griesbaum, K., Övez, B., Huh, T. S. & Dong, Y. (1995). *Liebigs Ann.* pp. 1571–1574.
- Johnson, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Jung, I., Yun, H. & Huh, T. S. (1996). *Bull. Korean Chem. Soc.* **17**, 307–308.
- Kuczkowski, R. L., Gillies, C. W. & Gallaher, K. L. (1993). *J. Mol. Spectrosc.* **64**, 361–365.
- Lattimer, P. R., Kuczkowski, R. L. & Gillies, C. W. (1974). *J. Am. Chem. Soc.* **96**, 348–358.
- Loan, L. D., Murray, R. W. & Story, P. R. (1965). *J. Am. Chem. Soc.* **87**, 737–741.
- Mac Science Corporation (1994). *MXC Diffractometer Control Software*. Mac Science Corporation, Tokyo, Japan.
- Mazur, W. & Kuczkowski, R. L. (1977). *J. Mol. Spectrosc.* **65**, 84–88.
- Murray, R. W., Youssefeyeh, R. D. & Story, P. R. (1967). *J. Am. Chem. Soc.* **89**, 2429–2434.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

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N,N'-Bis(2-hydroxybenzyl)-1,4-butanedi-ammonium Dinitrate

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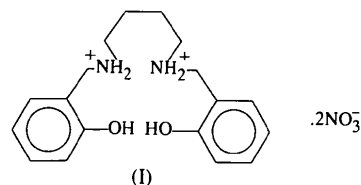
Abstract

In the title compound, $C_{18}H_{26}N_2O_2^{2+} \cdot 2NO_3^-$, both N atoms of the cationic moiety are protonated and linked to two NO_3^- anions by intermolecular hydrogen bonding. Intramolecular hydrogen bonding also exists be-

tween the amine H and phenol O atoms. The compound displays a centrosymmetric structure with the two aromatic rings parallel to each other.

Comment

Tetradentate 2N2O amine–phenols have a high coordinating affinity towards transition metals and are commonly used as chelate agents. Although many crystal structures of amine–phenol metals have been determined (Pillai, John, Lo, Schlemper & Troutner, 1990; Pillai, Barnes, John, Troutner & Schlemper, 1993; Pillai, Barnes & Schlemper, 1993, 1994; Pillai & Schlemper, 1994), none of the free ligands has been reported so far. We describe here the title compound, (I), in order to detect its structural variations upon coordination and to provide some insight into the coordination behaviour of this type of ligand.



Under the conditions of preparation (pH 5), both N atoms of *N,N'*-bis(2-hydroxybenzyl)-1,4-butanedi-ammonium (*L*) are protonated resulting in $-NH_2^+$ -moieties. The asymmetric unit contains one anion, NO_3^- , and half of a doubly charged cation, H_2L^{2+} . In order to coordinate tetradentate amine–phenol ligands to metal ions, alkaline conditions are required to prevent protonation of the amine N atoms and to facilitate deprotonation of the phenol groups.

The title compound, (I), is centrosymmetric, the inversion center being located at the midpoint of the C9—C9ⁱ bond [symmetry code: (i) $-x, -y, -z$]. The O—H_n1 distance of 2.50 Å is clearly indicative of intramolecular hydrogen bonding. In addition, both strong and weak intermolecular hydrogen bonds involving O1···H_n1, O1···H_n2, O2···H, O2···H_n1 and O3···H_n2 distances of 2.64, 2.41, 1.85, 2.04 and 1.96 Å, respectively, contribute to the extreme stability of this compound.

The conformation of the amine–phenol ligand is of particular interest in interpretation of its coordination with a metal. The torsion angles C7—N1—C8—C9 and N1—C8—C9—C9ⁱ are 65.6(3) and 59.5(3)°, respectively. As a result, the title compound has a planar structure with the two aromatic rings parallel to each other. The intramolecular O···Oⁱ distance of 7.624(1) Å is much larger than that found when the ligand is coordinated to a metal. For example, the corresponding distance is reduced to 2.630 Å when the H-substituted ligand is coordinated to Pd^{II} (Pillai & Schlemper, 1994), and to 2.412 and 2.428 Å when coordinated to Tc^V (Pillai, John, Lo, Schlemper & Troutner, 1990). The

extended conformation of the free ligand is therefore significantly distinct from the folded one which occurs upon coordination.

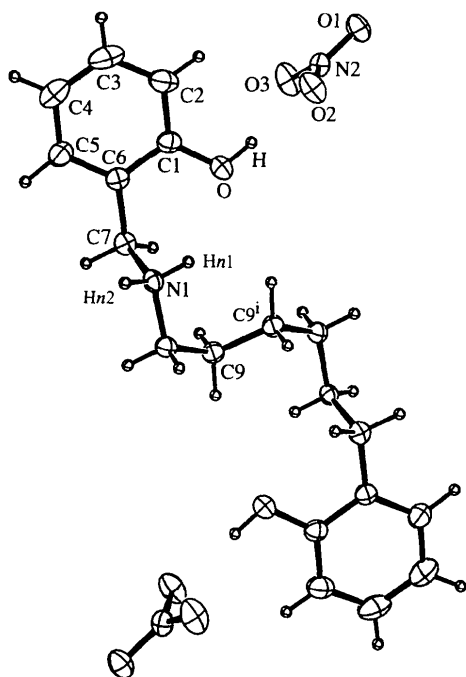


Fig. 1. A perspective view of the title molecule with the atom-numbering scheme. The displacement ellipsoids are drawn at the 30% probability level (Johnson, 1976).

Experimental

Synthesis of 1,4-bis(2-hydroxybenzylimino)butane was carried out by reaction of salicylaldehyde and 1,4-diaminobutane (molar ratio 2:1) in ethanol solution for 2 h at 298 K. 1,4-Bis(2-hydroxybenzylamino)butane was prepared by mixing 1,4-bis(2-hydroxybenzylimino)butane and $NaBH_4$ (molar ratio 1:2) in ethanol solution for 1 h at 333 K. The title compound was obtained by mixing copper(II) nitrate trihydrate and 1,4-bis(2-hydroxybenzylamino)butane in ethanol (molar ratio 2:1) and stirring at 298 K for 1 h. Recrystallization was from ethanol.

Crystal data

$C_{18}H_{26}N_2O_2^{2+} \cdot 2NO_3^-$

$M_r = 426.42$

Monoclinic

$P2_1/c$

$a = 8.6351(8) \text{ \AA}$

$b = 15.6177(10) \text{ \AA}$

$c = 8.8929(15) \text{ \AA}$

$\beta = 115.486(8)^\circ$

$V = 1082.6(2) \text{ \AA}^3$

$Z = 2$

$D_x = 1.308 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.7107 \text{ \AA}$

Cell parameters from 21

reflections

$\theta = 5.79\text{--}12.08^\circ$

$\mu = 0.10 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Pillar

$0.26 \times 0.14 \times 0.13 \text{ mm}$

Light brown

Data collection

Nonius CAD-4 diffractometer

$\theta/2\theta$ scans

Absorption correction: none

2038 measured reflections

1908 independent reflections

1329 reflections with

$I_{net} > \sigma(I_{net})$

$R_{int} = 0.013$

$\theta_{max} = 24.92^\circ$

$h = -10 \rightarrow 9$

$k = 0 \rightarrow 18$

$l = 0 \rightarrow 10$

3 standard reflections

frequency: 60 min

intensity decay: 1.0%

Refinement

Refinement on F

$R = 0.042$

$wR = 0.048$

$S = 1.21$

1324 reflections

137 parameters

H atoms: see below

$w = 1/[\sigma^2(F) + 0.0005F^2]$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.16 \text{ e \AA}^{-3}$

$\Delta\rho_{min} = -0.15 \text{ e \AA}^{-3}$

Extinction correction:

Larson (1970)

Extinction coefficient:

0.80 (19)

Scattering factors from *International Tables for X-ray*

Crystallography (Vol. IV)

Table 1. Selected geometric parameters (\AA , $^\circ$)

O1—N2	1.227 (3)	O—C1	1.357 (3)
O2—N2	1.258 (2)	N1—C7	1.498 (3)
O3—N2	1.238 (3)	N1—C8	1.492 (3)
C7—N1—C8	115.28 (16)	O—C1—C2	123.5 (2)
O1—N2—O2	119.56 (18)	O—C1—C6	116.5 (2)
O1—N2—O3	120.79 (18)	N1—C7—C6	110.14 (17)
O2—N2—O3	119.66 (19)	N1—C8—C9	113.66 (17)

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O—H \cdots O2	0.88	1.85	2.728 (2)	174
N1—Hn1 \cdots O	0.91	2.50	3.038 (2)	118
N1—Hn1 \cdots O1 ⁱ	0.91	2.64	2.996 (2)	104
N1—Hn1 \cdots O2 ⁱ	0.91	2.04	2.894 (3)	156
N1—Hn2 \cdots O1 ⁱⁱ	0.95	2.41	3.046 (2)	125
N1—Hn2 \cdots O3 ⁱⁱ	0.95	1.96	2.910 (2)	172

Symmetry codes: (i) $1 - x, -y, -z$; (ii) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$.

H atoms were located from a difference Fourier map and their positions and displacement parameters were held fixed. Refinement was by full-matrix least-squares techniques for all non-H atoms. Five reflections considered to be outliers were excluded from the refinement.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *NRCVAX DATRD2* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX SOLVER*. Program(s) used to refine structure: *NRCVAX LSTSQ*. Molecular graphics: *ORTEPII* (Johnson, 1976) in *NRCVAX*. Software used to prepare material for publication: *NRCVAX TABLES* (Version of January 1994).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1002). Services for accessing these data are described at the back of the journal.

References

- Enraf-Nonius (1989). *CAD-4 Software*. Version 5.0. 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.
- Johnson, C. K. (1976). *ORTEP II*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.
- Pillai, M. R. A., Barnes, C. L., John, C. S., Troutner D. E. & Schlemper, E. O. (1993). *J. Crystallogr. Spectrosc. Res.* **23**, 949–953.
- Pillai, M. R. A., Barnes, C. L. & Schlemper, E. O. (1993). *J. Crystallogr. Spectrosc. Res.* **23**, 719–723.
- Pillai, M. R. A., Barnes, C. L. & Schlemper, E. O. (1994). *Polyhedron*, **13**, 701–708.
- Pillai, M. R. A., John, C. S., Lo, J. M., Schlemper, E. O. & Troutner, D. E. (1990). *Inorg. Chem.* **29**, 1850–1856.
- Pillai, M. R. A. & Schlemper, E. O. (1994). *J. Chem. Cryst.* **24**, 129–132.

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1,2,4,5-Tetrakis(trimethylsilylmethyl)-benzene at 150 K

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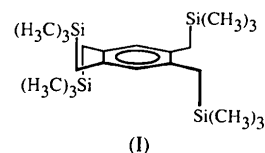
Abstract

The title compound, $C_{22}H_{46}Si_4$, crystallizes in space group *Fddd* with crystallographic symmetry 222. Steric overcrowding by the bulky ligands is avoided by arranging the trimethylsilyl groups alternately above and below the benzene plane in skeletal D_2 symmetry.

Comment

Molecular state properties of organosilicon compounds are strongly influenced by substituent effects (Bock, 1989). It is well documented in the literature that π -hydrocarbons substituted by trimethylsilyl groups, $-Si(CH_3)_3$, e.g. 1,2,4,5-tetrakis(trimethylsilyl)benzene (Bock, Ansari, Nagel & Havlas, 1995; Sekiguchi, Ebata, Kabuto & Sakurai, 1991a), hexakis(trimethylsilyl)benzene (Sakurai, Ebata, Kabuto & Sekiguchi, 1990; Sekiguchi, Ebata, Kabuto & Sakurai, 1991b; Podlogar, Glauser, Rodriguez & Raber, 1988) 9,10-bis(trimethylsilyl)anthracene (Bock, Ansari, Nagel & Claridge, 1995) or 9,10-bis(diisopropylsilyl)anthracene (Bock, Ansari, Nagel & Claridge, 1996), easily form

radical anions on one-electron reduction at lithium or sodium metal mirrors. In contrast, substitution by trimethylsilylmethyl groups, $-CH_2Si(CH_3)_3$, facilitates the one-electron oxidation to radical cations (Bock & Kaim, 1978; Bock, Meuret & Ruppert, 1993). The rather low first ionization energy of 1,2,4,5-tetrakis(trimethylsilylmethyl)benzene ($IE_1^V = 7.10$ eV) allows its oxidation with $AlCl_3$ in CH_2Cl_2 and the radical cation generated has been characterized by its ESR spectrum (Bock & Kaim, 1978). So far, however, no suitable single crystals of the oxidation product have been grown and, therefore, only the crystal structure of the neutral compound (I) is presented.



1,2,4,5-Tetrakis(trimethylsilylmethyl)benzene, (I), crystallizes in space group *Fddd* (No. 70) with a quarter of a molecule inside the asymmetric unit. The molecule is located around the intersection of three crystallographic twofold axes (Fig. 1) [Wyckoff position 222 (*a*); origin at -1 at *ddd*, at $\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$ from 222 (choice 2); Hahn, 1983]. The four trimethylsilylmethyl groups are oriented alternately above and below the six-membered ring plane with $\omega(C1-C2-C10-Si1) = 82.40(14)^\circ$ and the methylene centres are twisted out of plane by $\pm 0.07(2)$ Å, each towards the attached trimethylsilyl group. The conformational arrangement with alternating trimethylsilyl groups around the ring corresponds to that of hexakis(trimethylsilylmethyl)benzene, which in the crystal adopts S_3 symmetry and is located around a centre of inversion on a threefold axis (Bock, Meuret & Ruppert, 1993). Bond lengths and angles of both compounds are very similar and within the usual range of organosilicon compounds (Orpen, Brammer, Allen, Kennard, Watson & Taylor, 1994). In the crystal structure, all phenyl rings are oriented paral-

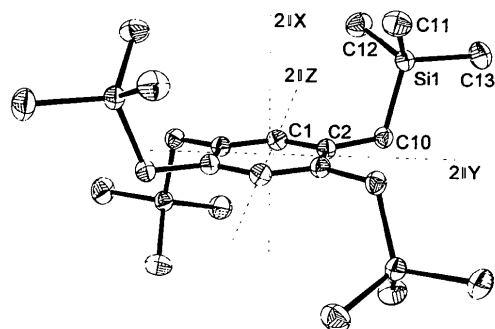


Fig. 1. A view of the title compound with anisotropic displacement ellipsoids for C and Si atoms at the 50% probability level, crystallographic symmetry elements intersecting the molecule and our numbering scheme of the asymmetric unit.