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Crystallographic report

The crystal structure of bis-(3,3-dimethyl-3,4-dihydro-2*H*-1-thia-4a,9-diaza-3-sila-fluorene) silver nitrate

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The title compound is a silver nitrate complex with two molecules of 2-mercaptobenzimidazole derivative. The silver atom lies on an inversion centre of the crystal lattice; nitrogen of the nitrate anion is in another inversion centre. Bond length Ag(1)–N(7) is 2.087(3) Å. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: thiabenzimidazole; silver complex; crystal structure

COMMENT

Recent developments in the coordination chemistry of benzimidazole are of interest because of its property to make complexes with metal salts.[1–3] In the complex of imidazole with silver nitrate, the length of the Ag–N bond is 2.120 Å and the angle N–Ag–N is equal to 172°.[4,5] This report presents the X-ray structure of bis-(3,3-dimethyl-3,4-dihydro-2*H*-1-thia-4a,9-diaza-3-sila-fluorene) silver nitrate (**1**). Figure 1 shows the molecular structure of **1**. The compound crystallizes in structural class $P\overline{1}$, $Z = 1(\overline{1})$ of the triclinic crystallographic system. The silver atom lies on an inversion centre of the crystal lattice; nitrogen of the nitrate anion is in another inversion centre. Therefore, the valence angle N(7)–Ag(1)–N(7) is equal to 180°; bond length Ag(1)–N(7) is 2.087(3) Å. Thus, cations and anions are in special positions. However, the NO_3^- anion is not a centrosymmetric system; therefore, disorder occurs in the crystal structure.

The structure of **1** is similar to that of bis-(5,10-dihydro-benzimidazo(2,1-b) benzo(e)-1-thia-3-azacycloheptane) silver perchlorate reported in Ref. 1. In this structure, cations and anions also lie in a special position. However, the latter compound crystallizes in the trigonal system (space group $P\overline{3}c1$) and the silver atom lies on the second-order rotation axis (angle N–Ag–N is 170.2°). The perchlorate anions are in rotation axes of order 3 without structural disorder.

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Figure 2 shows the projection of the crystal structure **1** along the crystallographic *y* axis. There are stacking interactions in the crystal structure between the silver atom and the benzimidazole system. The distance from the silver atom to the plane defined by the atoms C(8), C(9), C(10), C(11), C(12) and C(13) is 3.321(4) Å.

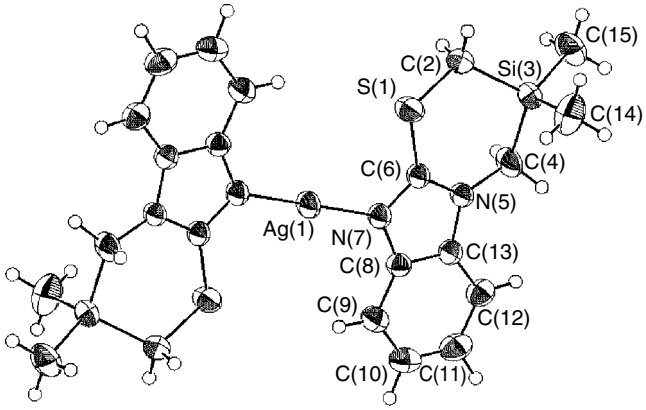

Figure 1. Molecular structure of **1**. Key geometric parameters: Ag(1)–N(7) 2.087(3), S(1)–C(6) 1.744(4), S(1)–C(2) 1.805(4), C(2)–Si(3) 1.873(5), Si(3)–C(4) 1.878(5), N(5)–C(6) 1.352(5), C(6)–N(7) 1.324(5), N(7)–C(8) 1.383(5) Å; C(6)–S(1)–C(2) 106.7(2), S(1)–C(2)–Si(3) 113.8(2), C(2)–Si(3)–C(4) 104.9(2), N(7)–C(6)–N(5) 112.5(3), N(7)–C(6)–S(1) 117.7(3), C(6)–N(7)–C(8) 106.0(3), C(6)–N(7)–Ag(1) 124.1(3), C(8)–N(7)–Ag(1) 129.8(3), N(7)–C(8)–C(13) 109.0(3)°.

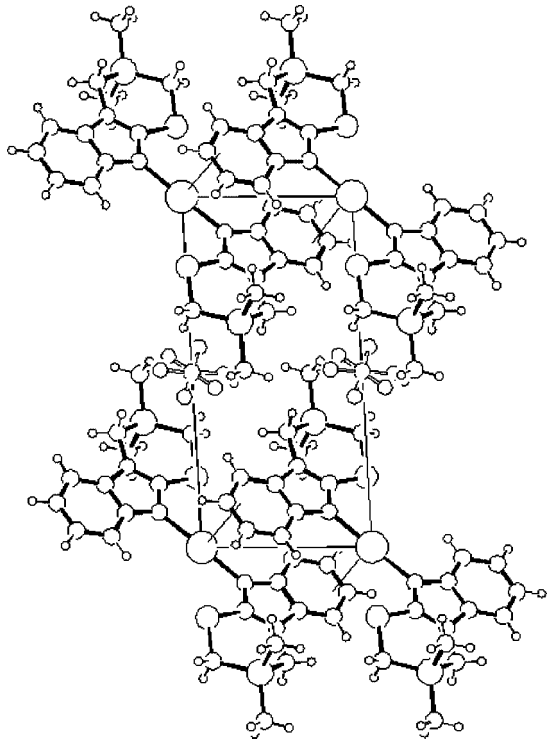

Figure 2. Projection of the crystal structure **1** along [010] direction.

EXPERIMENTAL

Synthesis of 3,3-dimethyl-3,4-dihydro-2*H*-1-thia-4a,9-diaza-3-sila-fluorene

Bis(chloromethyl)dimethylsilane (0.72 ml, 5 mmol) was added to a suspension of 2-mercaptobenzimidazole (0.75 g, 5 mmol), 18-crown-6 (0.13 g, 0.5 mmol), powdered KI (3.32 g, 20 mmol) and powdered K_2CO_3 (2.76 g, 20 mmol) in toluene (80 ml). The reaction mixture was stirred for 20 h at reflux. The resulting mixture was filtered, the toluene was removed under reduced pressure, and the crude product was purified on silica gel by column chromatography (eluent toluene/ethyl acetate 1 : 1) to give the desired product (1.08 g, 92%) as white crystals with m.p. 144–145 °C. ^{1}H NMR ($CDCL_3$/TMS) δ ppm 0.36 (s, 6H, $SiMe_2$), 2.20 (s, 2H, SCH_2), 3.51 (s, 2H, NCH_2), 7.21 and 7.61 (both m, 4H, benzimidazole protons). ^{13}C NMR δ ppm: −3.74 (Si–CH_3), 11.48 (SCH_2), 31.79 (NCH_2), 108.18, 118.23, 121.56, 122.12, 137.71, 142.67, 149.10. ^{29}Si NMR δ ppm: −5.43. MS, *m*/*z*: 234 (M^+, 100). Found: C, 56.37; H, 5.92; N, 11.70; S, 13.46. Calc. for $C_{11}H_{14}N_2SSi$: C, 56.37; H, 6.02; N, 11.95; S, 13.67%.

Synthesis of bis-(3,3-dimethyl-3,4-dihydro-2*H*-1-thia-4a,9-diaza-3-sila-fluorene) silver nitrate

A 5 ml aqueous solution of silver nitrate (2 mmol) and 4 mmol of 3,3-dimethyl-3,4-dihydro-2*H*-1-thia-4a,9-diaza-3-sila-fluorene in 10 ml of ethanol was stirred for 4 h. White precipitate was filtered off and washed with water. The silver complex (1.18 g, 91%) was recrystallized from methylene chloride, m.p. 224 °C. Anal. Found: C, 41.25; H, 4.36; N, 10.73; S, 10.14. Calc. for $(C_{22}H_{28}AgN_4S_2Si_2^+)(NO_3^-)$: C, 41.37; H, 4.42; N, 10.97; S, 10.04%. ^{1}H NMR (DMSO-d_6/HMDSO) δ ppm: 0.34 (s, 6H, Me), 2.48 (s, 2H, SCH_2), 3.75 (s, 2H, NCH_2), 7.29–7.67 (m, 4H, benzimidazole ring protons).

Crystallography

A single-crystal Nonius KappaCCD diffractometer with graphite-monochromated Mo Kα radiation was used for intensity data collection. A total of 5279 unique reflection intensities were collected at room temperature up to $2\theta = 55°$. The crystals of **1** are triclinic, space group $P\bar{1}$; the lattice parameters are as follows: $a = 6.5280(2)$, $b = 8.0670(2)$, $c = 13.1520(4)$ Å, $\alpha = 87.550(1)$, $\beta = 86.626(1)$, $\gamma = 77.061(1)°$; $V = 673.54(3)$ Å^3, $D_x = 1.575$ g cm^{-3}, $F(000) = 326$, $\mu = 1.026$ mm^{-1}, $Z = 1$. The crystal structure was solved by the direct method and refined by full-matrix least squares. All disodered oxygen atoms of the nitrate anion were located from difference synthesis and refined isotropically with occupancy factors $g = 0.5$. Positions of hydrogen atoms were calculated geometrically and refined using a riding model. The final *R*-factor is 0.050 for 3090 reflections with $I > 2\sigma(I)$; goodness of fit is 1.075. The calculations were carried out with the help of computer programs.[6,7] CCDC number: 222 242.

Acknowledgements

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