Gerardo González-García*, Astrid Pérez, Jorge A. López, Esneyder Puello-Polo and Andrés González-García

Synthesis and structural characterization of neutral hexacoordinate silicon(IV) complexes containing salophen and thiocyanato-N ligands

Abstract: The reaction of the H$_2$salophen ligand, 2,2′-((1E,1′E)-(1,2-phenylenebis(azanylylidene))bis(methanylylidene))diphenol, with one molar equivalent of Si(NCS)$_2$, MeSi(NCS)$_3$ (13), or HMeSi(NCS)$_2$ afforded neutral hexacoordinate silicon complexes, which have an-NCS bi-functionality (complex 1) and mono-functionality (complex 14). The reaction of Si(NCS)$_4$ with the H$_2$salophen-type ligand1,1′-((1E,1′E)-(1,2-phenylenebis(azanylylidene)) bis(methanylylidene)) bis(naphthalen-2-ol) (H$_2$Noph), afforded the hexacoordinate silicon complex 15, which has an-NCS bi-functionality. Single-crystal X-ray structural and elemental analyses were used to characterize and confirm the structure of the starting material 13 and complexes 1, 14, and 15. The complexes were characterized in solution by $^1$H, $^{13}$C, and silicon-29 nuclear magnetic resonance ($^{29}$Si NMR) and in the solid state by $^{29}$Si cross-polarization/magic angle spinning (CP/MAS) NMR. Because of the poor solubility of complex 1, it was only possible to characterize it in the solid state by $^{13}$C and $^{29}$Si CP/MAS NMR and in solution by $^1$H NMR.

Keywords: $^{29}$Si NMR spectroscopy; coordination chemistry; crystal structure; hexacoordinate silicon; salophen ligand; thiocyanato-N ligands.

Introduction

Bi-functional hexacoordinate silicon compounds played an important role as a building block for the preparation of novel oligosilanes containing hexacoordinate silicon backbones (Mucha et al., 1998, 1999; González-García et al., 2009) and as an initiator for ring-opening polymerization of ε-caprolactone (Lee et al., 2003). On the other hand, Si(NCS)$_2$ and HMeSi(NCS)$_2$ have proved to be useful starting materials for hypercoordinate silicon containing salen (Seiler et al., 2005; González-García et al., 2008, 2009, 2015), Schiff base (Seiler et al., 2007), and β-diketone ligands (Seiler et al., 2003; González-García et al., 2012) without adding an auxiliary base, such as triethylamine, which acts as a proton acceptor. In this work, the synthesis, single-crystal structure, and nuclear magnetic resonance (NMR) spectroscopy characterization of hexacoordinate silicon complexes containing salophen (1 and 14) or Noph (15) ligands and thiocyanato-N functional groups are reported. Complex 1 was previously prepared (Puri et al., 2009) starting from di-ethoxy di-thiocyanato-N silane, (EtO)$_2$Si(NCS)$_2$, and a H$_2$salophen ligand (Scheme 1). However, the $^{29}$Si NMR chemical shift at ~132 ppm in a CDCl$_3$/DMSO-D$_6$ solution for complex 1 appears to correspond to a pentacoordinate silicon species rather than a hexacoordinate one. Indeed, complex 1 contains two-NCS functional groups of silicon, and it is well-known that the NCS ligand causes a large displacement to higher field signals in the silicon-29 ($^{29}$Si) NMR chemical shift (Seiler et al., 2003). No further studies were performed to confirm the solution $^{29}$Si NMR results, e.g. $^{29}$Si solid-state NMR study or single-crystal X-ray analysis.

In this context, it is well known that the $^{29}$Si NMR chemical shift is used as a tool to determine the silicon coordination number. Chart 1 shows selected examples of silicon compounds containing-NCS functionalities whose structure have been confirmed by a single-crystal X-ray diffraction analysis, and Table 1 shows the $^{29}$Si chemical shift and the coordinating framework in the silicon center.
Results and discussion

The starting material methyltri(thiocyanato-N)-silane, 13, was synthesized in 70% yield by treatment MeSiCl3 with three molar equivalents of NH4SCN by following a methodology reported (Voronkov and Dolgov, 1954), using toluene instead of benzene (Scheme 2).

The treatment of the H2salophen with one molar equivalent of Si(NCS)4, MeSi(NCS)3 or HMeSi(NCS)2 afforded complexes 1, (salophen)Si(NCS)2, and 14, (salophen)Si(NCS)6.
Silme(NCS), with 59.0%, 45.0%, and 34.5% yields, respectively (Scheme 3).

Complex 15, (Noph)Si(NCS)$_2$, was obtained analogously as complex 1 using 1,1'-(1E,1'E)-(1,2-phenylenebis(azanylylidene))bis(methanylylidene))bis(naphthalen-2-ol) (H$_2$Noph) (Abd-Elzaher, 2000) as the salophen-type ligand and Si(NCS)$_4$ as the starting material (yield 67%). The complexes 1 and 14 precipitated from the respective reaction mixture as yellow solids. A suitable crystal for the X-ray diffraction analysis of the starting material 13 was obtained by placing a neat sample at 10°C for 24 h. Figure 1 shows the asymmetric unit of the starting material 13 in crystal form. Selected bond lengths [Å] and angles [°]: Si-N1 1.6994(19), Si-N2 1.705(2), Si-N3 1.7014(18), Si-C4 1.819(2); N1-Si-N2 105.94(9), N1-Si-N3 105.75(9), N1-Si-C4 112.95(9).

Single crystals of complexes 1 and 14 were obtained by slow cooling in acetonitrile from 80°C to 20°C, while for complex 15, a single-crystal was obtained by placing a saturated solution in a Schlenk tube at 55°C in an oven for one night. Complexes 1 and 14 crystallized in a monoclinic system with the space groups $P2_1/c$ and $P2_1/n$, respectively, while complex 15 crystallized in a triclinic system with the $P1$ space group. The Si-coordination polyhedron for all complexes can be described as a distorted octahedron that maintains the NCS functional group in a trans position in the coordination sphere with two-NCS functional groups for complexes 1 and 15 and one for complex 14. In the asymmetric unit of the crystal structure of complex 1, two molecules of acetonitrile solvent were present after the crystallization, and one molecule of CH$_3$CN showed weak C-H···O intermolecular interactions (Figure 2), which can be best described as a larger type of electrostatic-based attractive force (Bakar).
The angle O1-Si-O2 in complex 1 (89.9°) is significantly smaller with respect to that in complexes 14 (91.0°) and 15 (93.6°), this can be due to the attractive electrostatic force of the C-H···O1 and C-H···O2 weak intermolecular interactions. Complex 6 showed a similar weakly electrostatic interaction with another acetonitrile molecule in the asymmetric unit of the crystal structure (González-García et al., 2015).

**Table 2:** Summary of the crystallographic data and structure refinement results for compounds 1, 13–15.

|   | 1       | 13     | 14     | 15       |
|---|---------|--------|--------|----------|
| Formula   | C_{26}H_{20}N_{6}O_{2}S_{2}Si | C_{4}H_{3}N_{3}S_{3}Si | C_{22}H_{17}N_{3}O_{2}SSi | C_{30}H_{18}N_{4}O_{2}S_{2}Si |
| Formula mass (g mol⁻¹) | 540.69 | 217.36 | 415.53 | 558.69 |
| Collection T (K) | 150(2) | 100(2) | 293(2) | 293(2) |
| λ (Mo Kα) (Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Triclinic |
| Space group | P_2_1/c | P_2_1/n | P_2_1/n | P'I |
| a (Å) | 8.7274 (7) | 7.6171(4) | 8.3676(5) | 8.7033(6) |
| b (Å) | 21.9312 (10) | 11.7556(6) | 17.9978(9) | 9.1667(9) |
| c (Å) | 16.3230 (14) | 10.5308(5) | 13.5450(7) | 17.4607(13) |
| α (deg) | 90 | 90 | 90 | 104.453(8) |
| β (deg) | 126.762 (13) | 101.078(5) | 103.461(5) | 90.933(6) |
| γ (deg) | 90 | 90 | 90 | 104.018(7) |
| V (Å³) | 2502.9 (3) | 925.39(8) | 1983.81(19) | 1304.39(19) |
| Z | 4 | 4 | 4 | 2 |
| ρ (calcld) (Mg m⁻³) | 1.435 | 1.560 | 1.391 | 1.422 |
| F(000) | 1120.0 | 440.0 | 864.0 | 576.0 |
| Crystal dimensions (mm) | 0.4 × 0.2 × 0.2 | 0.3 × 0.2 × 0.2 | 0.2 × 0.1 × 0.1 | 0.2 × 0.2 × 0.1 |
| 2θ range (deg) | 6.92–58.88° | 6.94–52.74° | 6.47–52.74° | 6.65–52.75 |
| No. of collected reflections | 11796 | 3952 | 9470 | 9684 |
| No. of independent reflections/parameter | 5787/336 | 1889/101 | 4052/263 | 5309/352 |
| R_{int} | 0.0305 | 0.0242 | 0.00251 | 0.0275 |
| R_{1}(F) | 0.0456 | 0.0340 | 0.00449 | 0.00568 |
| wR_{2}(F)² | 0.0995 | 0.00787 | 0.0160 | 0.1465 |
| S² | 1.043 | 1.076 | 1.034 | 1.051 |
| Max./min. residual electron density (e Å⁻³) | +0.35/-0.35 | 0.29/-0.031 | +0.28/-0.23 | +0.42/-0.29 |

* R_{1} = \sum ||\hat{F}_{o}|-|\hat{F}_{c}||/\sum |\hat{F}_{o}| for the observed reflections [F > 2σ(F)].
* wR_{2}(F)² = \sum [w\hat{F}_{o}² - \hat{F}_{c}²]²/\sum w\hat{F}_{o}².²
* S = [\sum |\hat{w}\hat{F}_{o}² - \hat{w}\hat{F}_{c}²|]/(n - p)²/²; (n = number of reflections, p = number of parameters).
As expected, for complex 14 (Figure 3), the Si-CH₃ and Si-NCS distances were significantly longer than the starting material 13. In all the hexacoordinated silicon compounds, the Si-NCS distances were significantly shorter than the Si-N dative bonds.

The salophen ligand adopted a bowl conformation in the equatorial plane, which was more remarkable for complex 15 (Figure 4).

Selected bonds lengths for complexes 1, 14, and 15 are given in their figure captions. The crystal data and experimental parameters used for the crystal structure analyses of compounds 1, and 13–15 are summarized in Table 2.

The ²⁹Si NMR chemical shift in the solid-state is at −200.4 ppm (Figure 5), and −177.1 and −202.3 ppm for complexes 1, 14, and 15, respectively, which are consistent with a hexacoordinate silicon compound with SiN₄O₂ (1 and 15) and SiN₃O₂C (14) coordinating frameworks containing a salen-type ligand (González-García et al., 2009, 2015). The ¹³C CP/MAS NMR spectrum of complex 1 (see online-only supporting information) showed six signals, four in the aromatic region between 110 and 140 ppm and two for the imine carbons at approximately 160 ppm. The signals of NCS and the acetonitrile solvent were not detected, probably due to the coupling of the quadrupolar nucleus ¹⁴N and the loss of acetonitrile molecule during the cross-polarization/magic angle spinning (CP/MAS) NMR rotor spinning, respectively.

In the solution, ²⁹Si NMR analysis, complexes 14 and 15 showed signals at −167.1 and −187.9 ppm, respectively, which are consistent with hexacoordinate silicon species (Figure 6). Thus, the silicon atom maintained the hexacoordination in the DMSO-D₆ solution for both complexes.

Because of poor solubility, it was only possible to study complex 1 in solution by ¹H NMR in DMSO-D₆ and acetone-D₆. Freshly prepared samples of complex 1 in DMSO-D₆ and acetone-D₆ are shown in Figure 6. In both solvents, the ¹H NMR spectrum showed the presence of two resonance signals for the imine proton of the salophen ligand, which suggest the presence of 1 in a possible mixture of trans- and cis-isomers with a ratio of 1.00:0.75 and 1.00:0.22 in DMSO-D₆ and acetone-D₆ solution. A similar behavior was observed for complexes 14 and 15 in a DMSO-D₆ solution. Nevertheless, decomposition was observed for all three complexes in the DMSO-D₆ solution in a few days, as shown by the ¹H NMR analysis. In this context, further experimental and computational studies are needed to understand more clearly the nature of the possible stereoisomerization and decomposition process.

Conclusions

In this work was confirmed that complexes 1, 14, and 15 are hexacoordinate silicon compounds containing two thiocyanato-N functional or methyl groups in the trans position, and the salophen ligand is located at the equatorial plane in the crystal structure. Nevertheless, complex 1 was poorly soluble, which made studying it by ²⁹Si NMR in the solution state impossible. The analogous complexes 13 and 15 had good solubility in DMSO-D₆, which allowed us to confirm that both complexes maintained the hexacoordination of the silicon atom in a DMSO-D₆ solution by ²⁹Si NMR spectroscopy. The synthetic potential of MeSi(NCS)₃ (13) as starting material for neutral hexacoordinate silicon
complex was demonstrated. Complexes 1, 14, and 15 have the potential to be used as starting materials for the preparation of new neutral hexacoordinate silicon(IV) complexes using a substitution or condensation reaction with thiocyanato-N functionalities.

Experimental

General procedures

The reaction and manipulations were carried out under an inert atmosphere of ultra-high-purity nitrogen (99.999% Infra, León, Guanajuato, Mexico) using standard Schlenk techniques. The organic solvents were dried and purified according to standard procedures and stored under nitrogen. Elemental analysis was carried out on PerkinElmer 2400 Series II CHNS/O Elemental Analyzer at the Chemistry Department of the Universidad de Guanajuato, Guanajuato, Mexico.

Nuclear magnetic resonance (NMR) analysis

The 1H, 13C, and 29Si NMR spectra were recorded at 25°C on a 400-MHz, 500-MHz NMR Bruker AdvanceIII (Karlsruhe, Germany) or 600 NMR Varian/Agilent NMR spectrometer (Oxford Instruments, Oxfordshire, UK). DMSO-D6 (99.9% D, Sigma-Aldrich, St Louis, MO, USA), CDCl3 (99.8% D, Sigma-Aldrich, St Louis, MO, USA) and acetone-D6 (99.9% D, Cambridge Isotope Laboratories, Inc., Tewksbury, MA, USA) were used as the solvents, and the chemical shifts (ppm) were determined relative to the internal residual signal of the solvent at 2.50, 7.26 and 2.05 ppm for 1H NMR and 39.05 and 70.0%. Anal. Calc. for C4H3N3S3Si (217.36): C 22.10 H 1.39 N 19.33 S 43.91. 1H NMR (400 MHz, DMSO-D6) δ 7.4 Hz, 1H), 7.12 (t, J = 8.0 Hz, 1H). 13C CP/MAS δ=143.91 (broad), 0.23. 29Si CP/MAS δ=−177.1.

Synthesis of complex 1

A 0.5-g (1.7 mmol) sample of H2salophen was added to a stirred suspension of 0.4 g (1.6 mmol) of Si(NCS)4 in acetonitrile (20 mL). The reaction mixture was stirred for 24 h at room temperature producing a yellow solid that was dissolved by the appropriated amount of acetonitrile, and the solution was heated to ca. 80°C to obtain a clear solution then filtered. By slowly cooling it to 20°C, the yellow crystals that formed were filtered off, washed with 20 mL of diethyl ether, and dried under vacuum (0.1 mmbar, 4 h). Yield: 0.5 g (0.9 mmol), 59.0%. M.p: decomposition over 270°C. Anal. Calc. C12H17N3O2SSi (560.49): C, 57.65; H, 3.73; N, 15.54; S, 11.86. Found: C, 57.85; H, 3.75; N, 15.58; S, 11.77%.

1H NMR (600 MHz, acetone-D6) δ 9.5 (s, 1H), 8.25 (dd, J = 6.2, 3.3 Hz, 1H), 7.84 (dd, J = 7.8, 1.7 Hz, 1H); 7.77–7.73 (m, 2H), 7.16–7.13 (m, 1H), 7.10 (d, J = 8.4 Hz, 1H); 1H NMR (500 MHz, DMSO-D6) δ 9.7 (s, 1H), 9.61 (s, 1H), 8.28–8.19 (m, 2H), 7.92 (dd, J = 7.7, 1.5 Hz, 1H), 7.84 (dt, J = 5.6, 2.8 Hz, 1H), 7.83–7.79 (m, 1H), 7.76 (dd, J = 8.1, 6.4 Hz, 3H), 7.26–7.21 (m, 2H), 7.17 (t, J = 7.4 Hz, 1H), 7.12 (t, J = 8.0 Hz, 1H). 13C CP/MAS δ=115.84, 121.66, 123.48, 138.93, 157.87, 160.26. 29Si CP/MAS δ=−200.4.

Synthesis of 13

Trichloro(methyl)silane (99%, Sigma-Aldrich, St Louis, MO, USA) 15.0 g (100 mmol) was added to ca. 80°C to a stirred suspension of ammonium thiocyanate (97.5%, Sigma-Aldrich, St Louis, MO, USA), 23.0 g (300 mmol) in 100 mL of toluene. The reaction was refluxed for 4 h; after that, the mixture was cooled to 20°C; the resulting precipitate was filtered off and discarded. The solvent was distilled at normal pressure, and the residue was distilled in vacuo to give a colorless liquid (b.p. 84°–86°C, 0.2 mbar). Yield: 15.2 g (70 mmol) 70.0%. Anal. Calc. for C12H17N3O2SSi (217.36): C 22.10 H 1.39 N 19.33 S 43.91. 1H NMR (600 MHz, DMSO-D6) δ 9.44 (s, 1H), 8.15 (s, 1H), 8.27 (s, 1H), 8.61 (dt, J = 7.8, 1.7 Hz, 1H), 7.83–7.79 (m, 1H), 7.74–7.68 (m, 2H), 7.17 (t, J = 8.0 Hz, 1H). 13C CP/MAS δ=124.39 (broad), 0.23. 29Si NMR (79 MHz, DMSO-D6) δ=−74.5 (broad).

Synthesis of complex 14

Synthesis (a) 1H NMR (600 MHz, DMSO-D6) δ 9.54 (s, 1H), 8.25 (dd, J = 6.2, 3.3 Hz, 1H), 7.84 (dd, J = 7.8, 1.7 Hz, 1H); 7.77–7.73 (m, 2H), 7.16–7.13 (m, 1H), 7.10 (d, J = 8.4 Hz, 1H); 1H NMR (500 MHz, DMSO-D6) δ 9.7 (s, 1H), 9.61 (s, 1H), 8.28–8.19 (m, 2H), 7.92 (dd, J = 7.7, 1.5 Hz, 1H), 7.84 (dt, J = 5.6, 2.8 Hz, 1H), 7.83–7.79 (m, 1H), 7.76 (dd, J = 8.1, 6.4 Hz, 3H), 7.26–7.21 (m, 2H), 7.17 (t, J = 7.4 Hz, 1H), 7.12 (t, J = 8.0 Hz, 1H). 13C CP/MAS δ=115.84, 121.66, 123.48, 138.93, 157.87, 160.26. 29Si CP/MAS δ=−200.4.

Synthesis (b) A 0.9-g (2.8 mmol) sample of H2salophen was added to a solution of 0.6 g (2.7 mmol) of MeSi(NCS)3 in acetonitrile (20 mL). The reaction mixture was left undisturbed at room temperature for 24 h to produce a yellow crystalline solid. The yellow crystals that formed were filtered off, washed with 20 mL of diethyl ether, and dried under vacuum (0.1 mmbar, 4 h). Yield: 0.7 g (1.4 mmol), 45.0%. M.p: decomposition over 190°C. Anal. Calc. C12H17N3O2SSi (415.54): C, 69.88; H, 4.10; N, 8.15; S, 6.22. Found: C, 69.92; H, 4.13; N, 8.27; S, 6.27%. 1H NMR (500 MHz, DMSO-D6) δ 9.44 (s, 2H), 8.20 (dd, J = 6.1, 3.4 Hz, 2H), 7.80 (d, J = 7.7 Hz, 2H), 7.71–7.65 (m, 4H), 7.08 (dd, J = 15.2, 7.8 Hz, 4H), -0.10 (s, 3H). 13C NMR (126 MHz, DMSO-D6) δ 160.37, 159.59, 138.72, 135.30, 134.19, 130.70, 130.19, 120.44, 119.86, 117.68, 117.66, 9.94. 29Si NMR (99 MHz, DMSO-D6) δ = −167.1. 31Si CP/MAS NMR δ = −177.1.

Synthesis (c) A 1.1-g (3.4 mmol) sample of H2salophen was added to a solution of 0.5 g (3.3 mmol) of HMeSi(NCS)3, in acetonitrile (20 mL). The reaction mixture was stirred for 24 h at room temperature to produce a yellow solid. The solution was heated to ca. 80°C and then filtered to obtain a clear solution. By slowly cooling it to 20°C, the yellow crystals
that formed were filtered off, washed with 20 mL of diethyl ether, and dried under vacuum (0.1 mbar, 4 h). Yield: 0.5 g (1.1 mmol), 34.5%.

Synthesis of complex 15

A 0.27 g (0.65 mmol) of H₂Noph was added to a stirred suspension of 0.16 g of Si(NCS)₂ (0.61 mmol) in 20 mL of acetonitrile. The reaction mixture was stirred for 24 h at room temperature to produce a solid orange precipitate, which was placed at 55°C inside an oven for one night. The orange crystals that formed were filtered off, washed with 10 mL of diethyl ether, and dried under vacuum (0.1 mbar, 4 h). Yield 0.23 g (0.41 mmol), 67%

Mp: decompose over 200°C. Anal. Calc. C₃₀H₁₈N₄O₂S₂Si (558.71): C, 64.49; H, 3.25; N, 10.03; S, 11.31%. Found: C, 64.33; H, 3.24; N, 10.12; S, 11.48. C/H/N/S.

H NMR (500 MHz, DMSO-D₆), mixture of trans- and cis-isomers. δ 9.71 (s, 1H), 9.37 (s, 1H), 8.55 (t, J = 12.2 Hz, 1H), 8.26 (t, J = 10.0 Hz, 1H), 8.02 (d, J = 27.2 Hz, 2H), 7.92 (t, J = 9.8 Hz, 1H), 7.88–7.80 (m, 1H), 7.67–7.52 (m, 2H), 7.51–7.42 (m, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.25–7.16 (m, 7H), 7.09 (d, J = 9.1 Hz, 1H), 6.83 (d, J = 8.9 Hz, 1H). ¹³C NMR (126 MHz, DMSO-D₆): δ 168.19, 163.12, 157.68, 152.02, 139.83, 138.39, 136.94, 133.63, 132.98, 131.74, 129.67, 129.26, 128.99, 128.76, 128.55, 128.42, 128.22, 127.51, 127.10, 126.93, 124.22, 124.01, 123.69, 121.70, 121.23, 120.70, 120.51, 119.83, 116.79, 109.20, 108.77. ²⁹Si CP/MAS NMR δ –187.29.

Supplementary data

Data from the X-ray crystallographic analyses of complexes 1, 14, 15 and the starting material 13, MeSi(NCS), are available in a crystallographic information file (CIF) under CCDC No: 1534652, 1584247, and 1862266, respectively. Online-only supplement: ¹H, ¹³C{¹H} and ²⁹Si NMR spectra of 13; H NMR in the solution state and ¹³C NMR in the solid-state CP/MAS spectra of 1.

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