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The first amidozirconium(IV)–porphyrin complex: *cis*-[bis(trimethylsilyl)amido]-chloro(tetraphenylporphyrinato)-zirconium(IV)

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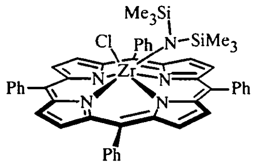
Abstract

The title compound, [ZrCl($C_{44}H_{28}N_4$)($C_6H_{18}NSi_2$)], is the first amidozirconium(IV)–porphyrin complex and it adopts an out-of-plane *cis* structure with the Zr atom in a distorted trigonal prismatic coordination geometry.

Comment

Organometallic early transition metal porphyrin complexes have attracted much attention in recent years due to their unusual structures and reactivities (Brand & Arnold, 1995). In the course of our ongoing research on organometallic zirconium–porphyrin complexes (Kim *et al.*, 1993, 1997, 1999), we have synthesized the title complex, *cis*-[bis(trimethylsilyl)amido]chloro(tetraphenylporphyrinato)zirconium(IV), (I), and determined its crystal structure. To our knowledge, complex (I) is the first example of an amidozirconium(IV)–porphyrin complex.



(I)

Complex (I) adopts an out-of-plane *cis* structure in which the Zr atom is displaced by 1.0264 (7) Å from the mean N_4 plane of the porphyrin ligand and the Cl—Zr—N5 angle is 81.33 (4)°. The coordination geometry of the Zr centre is best described as a distorted trigonal prism. The plane defined by atoms Cl, N5 and Zr bisects two of the N—Zr—N angles (N1—Zr—N4 and N2—Zr—N4). The distance between the Zr and amide N atoms [Zr—N5 2.1009 (15) Å] is similar to the average value of 2.112 Å found in *cis*-[$(NMe_2)_2$Zr(Me_4taen)] (Me_4taen is the 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenate dianion; Black *et al.*, 1995). As observed in *cis*-[$(NMe_2)_2$Zr(Me_4taen)], the amide N atom is nearly flat (the sum of the angles around N5 is 356.28°), which indicates the presence of π-bonding between the Zr and amide N atoms. The steric bulk around N5 may also contribute to its planarity. The Zr—Cl distance of 2.5112 (5) Å is significantly longer than those in *cis*-[Cl_2(thf)Zr(tpp)] [2.473 (1) and 2.499 (2) Å; thf is tetrahydrofuran and tpp is the 5,10,15,20-tetraphenylporphyrinate dianion; Kim *et al.*, 1993] or those in *cis*-[Cl_2Zr(oep)] [2.473 (1) and 2.459 (1) Å; oep is the 2,3,7,8,12,13,17,18-octaethylporphyrinate dianion; Brand & Arnold, 1993]. The Zr—$N_{\mathrm{porphyrin}}$ distances range from 2.2465 (14) to 2.2948 (15) Å, with an average value of 2.266 (3) Å. Interestingly, at 2.2948 (15) Å the Zr—N2 bond is considerably longer than the others, which may be due in part to the *trans* influence of the amide ligand, although the Zr—N2 bond is not perfectly *trans* to the Zr—N5 bond [N2—Zr—N5 140.12 (6)°].

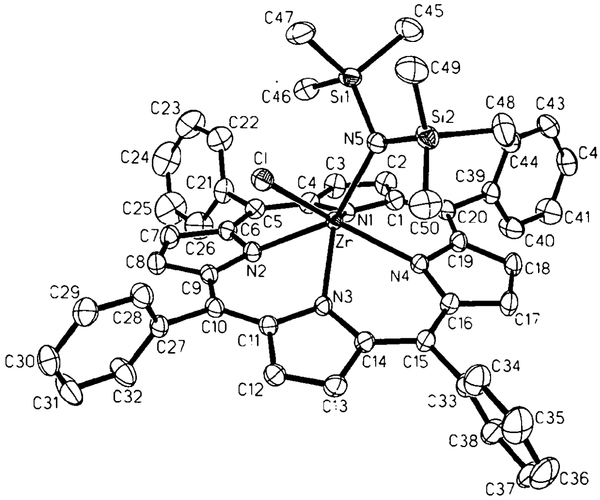


Fig. 1. The molecular structure of (I). Displacement ellipsoids are shown at the 50% probability level and H atoms have been omitted for clarity.

Experimental

For the preparation of (I), a toluene solution (*ca* 2 ml) of LiN$(SiMe_3)_2$ (75 mg, 0.43 mmol) was added slowly to a suspension of *cis*-[Cl_2Zr(tpp)] (263 mg, 0.272 mmol) in toluene (*ca* 20 ml). The reaction mixture was stirred at room temperature for 12 h and then filtered. The filtrate was concentrated under reduced pressure and pentane was layered over the solution to give (I) as dark purple X-ray quality crystals in 95% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.99 (*s*, 8H, H_{pyrrole}), 8.65 (*bs*, 4H, *o*-Ph), 7.83–7.71 (*br*, *m*, 16H, Ph), −1.51 (*s*, 18H, CH_3); ^{13}C NMR ($CDCl_3$): δ 152.1, 141.9, 134.7, 134.1, 132.3, 128.7, 127.4, 126.8, 3.06.

Crystal data

[ZrCl($C_{44}H_{28}N_4$)($C_6H_{18}NSi_2$)]	Mo $K\alpha$ radiation
M_r = 899.77	λ = 0.71073 Å

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Triclinic
$P\bar{1}$
$a = 11.9557\,(7)$ Å
$b = 12.1110\,(7)$ Å
$c = 17.931\,(1)$ Å
$\alpha = 99.790\,(1)^\circ$
$\beta = 98.943\,(1)^\circ$
$\gamma = 114.365\,(1)^\circ$
$V = 2255.9\,(2)$ Å^3
$Z = 2$
$D_x = 1.325$ Mg m^{-3}
D_m not measured

Cell parameters from 5599 reflections
$\theta = 2.6$–28.3°
$\mu = 0.396$ mm^{-1}
$T = 188\,(2)$ K
Block
0.4 × 0.3 × 0.3 mm
Purple

Data collection

Siemens SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997*a*)
$T_{\min} = 0.873$, $T_{\max} = 0.976$
14 640 measured reflections
10 520 independent reflections

9504 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.016$
$\theta_{\max} = 28.33^\circ$
$h = -15 \rightarrow 15$
$k = -13 \rightarrow 16$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.081$
$S = 1.104$
10 520 reflections
532 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0227P)^2 + 1.9648P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.04$
$\Delta\rho_{\max} = 0.40$ e Å^{-3}
$\Delta\rho_{\min} = -0.47$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Zr—Cl	2.5112 (5)	Zr—N3	2.2631 (15)
Zr—N1	2.2465 (14)	Zr—N4	2.2608 (15)
Zr—N2	2.2948 (15)	Zr—N5	2.1009 (15)
Cl—Zr—N1	135.15 (4)	N2—Zr—N3	79.25 (5)
Cl—Zr—N2	79.27 (4)	N2—Zr—N4	125.85 (5)
Cl—Zr—N3	84.21 (4)	N2—Zr—N5	140.12 (6)
Cl—Zr—N4	143.71 (4)	N3—Zr—N4	76.87 (5)
Cl—Zr—N5	81.33 (4)	N3—Zr—N5	132.77 (6)
N1—Zr—N2	76.37 (5)	N4—Zr—N5	89.13 (6)
N1—Zr—N3	126.41 (5)	Si1—N5—Si2	114.59 (9)
N1—Zr—N4	80.15 (5)	Si1—N5—Zr	122.04 (8)
N1—Zr—N5	94.06 (6)	Si2—N5—Zr	119.65 (8)

The crystal showed no significant decay and thus no correction was applied for decay. The structure was solved by direct methods. H atoms were added at calculated positions and refined using a riding model with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997*b*). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1353). Services for accessing these data are described at the back of the journal.

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Tetraaqua(1,10-phenanthroline)zinc(II) sulfate dihydrate

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Abstract

A novel monomeric phenanthroline (phen) zinc complex, $[{\rm Zn}({\rm C}_{12}{\rm H}_8{\rm N}_2)({\rm H}_2{\rm O})_4]{\rm SO}_4\cdot 2{\rm H}_2{\rm O}$, has been characterized by X-ray analysis. The Zn atom is coordinated in a slightly distorted octahedral geometry by two N atoms from 1,10-phenanthroline and four O atoms from water ligands. The Zn—N bond lengths are in the range 2.136 (3)–2.156 (2) Å and the Zn—O bond lengths are in the range 2.083 (2)–2.130 (2) Å. Hydrogen bonds stabilize the structure.

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