Bis[N,N′-bis(trimethylsilyl)ferrocene-1,1′-diaminato]uranium(IV)

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The title compound, [U{Fe(C$_8$H$_{13}$NSi)$_2$}$_2$] or [Fe$_2$U(C$_8$H$_{13}$NSi)$_4$], possessess twofold symmetry in the crystal structure, with the U atom lying on the rotation axis; a distorted UN$_4$ tetrahedron results.

Comment

Ferrocene-containing ligands have been extensively employed in coordination chemistry (Togni & Hayashi, 1995). Previously reported work in our laboratory has focused on the development of early transition metal complexes supported by both bidentate (Shafir *et al.*, 2003) and tetradentate (Shafir *et al.*, 2002) dianionic ligands derived from 1,1′-diaminoferrocene. More recently, our research has explored the preparation of related complexes of the actinide (*An*) metals. Our attempts to prepare complexes of the form *LAnX*$_2$, where *L* is a dianionic diaminoferrocene ligand and *X* is an ancillary (*e.g.* chloride, iodide) were unsuccessful. However, metathesis of the magnesium salt of an N,N′-functionalized diaminoferrocene, (I), with uranium(IV) chloride gave the title compound, (II), in which uranium is coordinated by a pair of diaminoferrocene ligands. Since we were unable to isolate the mono-substituted complex *L*UCl$_2$, in spite of modifications to reaction conditions and stoichiometry, we presume that this species disproportionates to (II) in solution. We further speculate that complexes of the desired form *LAnX*$_2$ will be accessible where substituents bulkier than trimethylsilyl are employed on the diaminoferrocene unit.
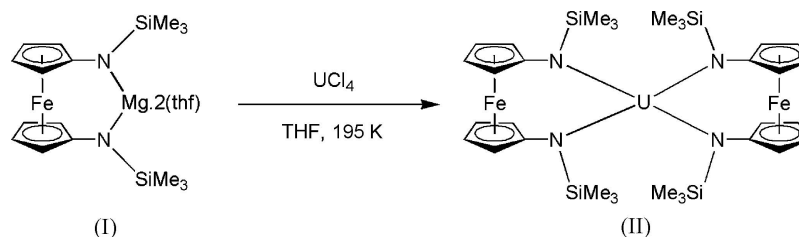
The central U atom in (II) is coordinated by a pair of bidentate N,N′-bis(trimethylsilyl)ferrocene-1,1′-diaminate ligands (Fig. 1). The complete molecule is generated by twofold symmetry, with the U atom lying on the rotation axis. The resulting geometry at the four-coordinate U atom (Table 1) is considerably distorted from tetrahedral, the ligand bite angle of 131.81 (8)° for N1—U1—N2 being significantly greater than the tetrahedral angle of 109.47°. The N1—U1—N1^i and N2—U1—N2^i (see Table 1 for symmetry code) angles between the ligands are not equal, being 98.8 (1)° and 93.7 (1)°, respectively. This discrepancy results from the alignment of the two ligands with respect to the twofold

rotation axis. The complementary angles $N1-U1-N2^i$ and $N2-U1-N1^i$ are constrained to be equal by symmetry at $102.92 (9)°$.

The four U—N bond lengths in (II), which fall within the narrow range 2.25–2.27 Å, are comparable with those in related compounds (Diaconescu *et al.*, 2000). The Fe—C distances within the ferrocene system and the N—Si bond lengths between the trimethylsilyl Si atom and the N atom of the diaminoferrocene unit are also comparable with literature values (Allen *et al.*, 1987). The dihedral angle between the C1—C5 and C9—C13 cyclopentadienyl ring planes is $13.3 (2)°$.

Experimental

Under an inert atmosphere, a suspension of UCl_4 (135 mg, 0.36 mmol) in tetrahydrofuran (10 ml) was cooled to 195 K. To this was added a solution of [*N,N*′-(trimethylsilyl)-1,1′-diaminoferrocen-yl]magnesium tetrahydrofuran disolvate (400 mg, 0.71 mmol) in tetrahydrofuran (10 ml) dropwise with stirring. The resulting black mixture was allowed to warm to room temperature and stirring was continued for 15 h. The solution was filtered and the black filtrate concentrated under reduced pressure. This material was extracted with pentane (2 × 10 ml), and the combined extracts concentrated and cooled to 233 K to afford single crystals of (II) as black prisms.

Crystal data

$[Fe_2U(C_8H_{13}NSi)_4]$	$Z = 4$
$M_r = 954.86$	$D_x = 1.652$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 18.987 (1)$ Å	$\mu = 5.11$ mm^{-1}
$b = 11.5384 (7)$ Å	$T = 148.2$ K
$c = 19.468 (1)$ Å	Prism, black
$\beta = 115.807 (1)°$	$0.30 \times 0.26 \times 0.20$ mm
$V = 3839.6 (4)$ Å^3	

Data collection

Bruker SMART 1000 CCD diffractometer	8606 measured reflections
	3231 independent reflections
ω scans	2925 reflections with $F^2 > 3\sigma(F^2)$
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)	$R_{int} = 0.018$
$T_{min} = 0.259$, $T_{max} = 0.360$	$\theta_{max} = 24.7°$

Refinement

Refinement on F	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.017$	$w = 1/[\sigma^2(F_o) + 0.00022|F_o|^2]$
$wR(F^2) = 0.023$	$(\Delta/\sigma)_{max} = 0.015$
$S = 1.05$	$\Delta\rho_{max} = 0.88$ e Å^{-3}
2925 reflections	$\Delta\rho_{min} = -0.56$ e Å^{-3}
195 parameters	

Table 1
Selected geometric parameters (Å, °).

U1—N1	2.272 (2)	U1—N2	2.257 (2)
$N1-U1-N1^i$	98.8 (1)	$N1-U1-N2^i$	102.92 (9)
N1—U1—N2	131.81 (8)	$N2-U1-N2^i$	93.7 (1)

Symmetry code: (i) $-x, y, -z + \frac{1}{2}$.
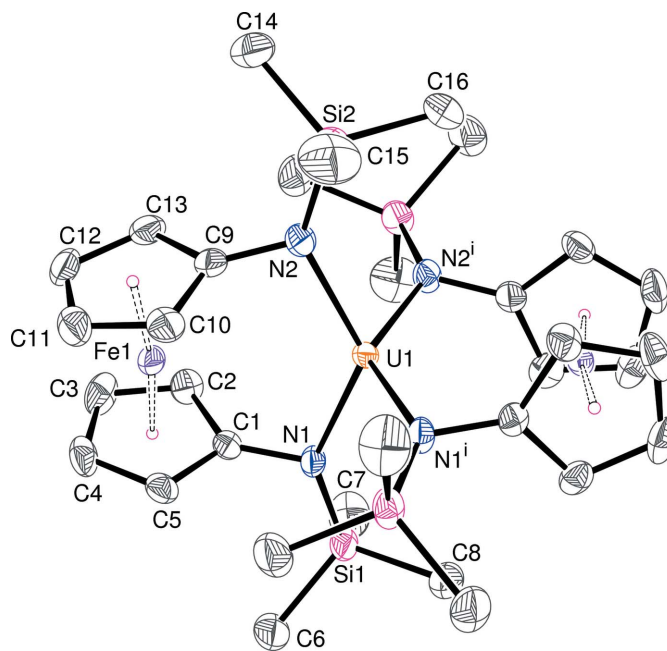
Figure 1
View of the molecular structure of (II), with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity. [Symmetry code: (i) $-x, y, \frac{1}{2} - z$.]

H atoms were included in the riding-model approximation, with C—H = 0.94–0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation & Rigaku, 1998); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *TEXSAN*.

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