C4—B8—C2	51.9 (7)	51.6 (7)
C4—B8—B11	103.7 (9)	103.2 (11)
C2—B8—B11	107.0 (10)	106.9 (11)
C4—B8—B10	56.9 (8)	56.2 (8)
C2—B8—B10	99.9 (9)	100.0 (10)
C4—B8—B5	94.7 (9)	93.3 (10)
C2—B8—B5	55.8 (7)	55.1 (8)
B10—B8—B5	102.6 (10)	103.4 (12)
C4—B10—B11	104.8 (11)	103.5 (10)
C4—B10—B9	113.4 (11)	114.1 (11)
B11—B10—B7	104.4 (11)	103.8 (10)

The title structure was solved by the Patterson method and refined by full-matrix least-squares techniques. The non-H atoms were refined anisotropically to convergence. The methyl H atoms were treated using a riding model. Neither the borane H atoms nor the hydride ligand were included in the model.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1994). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*.

The authors thank the National Science Foundation, The Missouri Research Board, a UM–St. Louis Research Incentive Award and the University of Missouri–St. Louis for the financial support of this work, NSF and the DOE (through the UM–St. Louis Center for Molecular Electronics) for funds for the purchase of the XRD equipment and the Johnson–Matthey Company for a loan of $IrCl_3.3H_2O$.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BK1240). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 419–422

Bis{μ-[1-(*N*-methylsulfonimidoyl)-2,2-diphenylethene]}-1κ^2C^1,*N*:2κO;1κO:-2κ^2C^1,*N*-bis[(tetrahydrofuran-*O*)lithium] Tetrahydrofuran Solvate and 1-(*N*-Methylphenylsulfonimidoyl)-2,2-diphenylethene

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(*Received 24 July 1996; accepted 21 November 1996*)

Abstract

The crystal structure of the THF (C_4H_8O) solvate of $[Li_2(C_{21}H_{19}NOS)_2(C_4H_8O)_2]$, (1), prepared by the addition of *n*-BuLi to 1-(*N*-methylphenylsulfonimidoyl)-2,2-diphenylethene, $C_{21}H_{19}NOS$, (2), at low temperature in THF, shows a centrosymmetric dimeric aggregate featuring an eight-membered ring with the atomic sequence $(Li—C—S—O)_2$. The O atom of one tetrahydrofuran molecule, the sulfoximine O and N atoms, and the C_α atom are coordinated to the lithium cation in a distorted tetrahedral arrangement. A comparison with the molecular structure of the precursor (2) is drawn.

Comment

In recent years, sulfoximines and their derivatives have become increasingly important in asymmetric synthesis (Johnson, 1985). The stabilization of carbanionic sites adjacent to the sulfonimidoyl moiety has allowed the use of such lithiated derivatives for the transfer of chiral information (Gais, Erdelmeier & Lindner, 1986). Despite their widespread synthetic use, remarkably little is known about the structures of such lithio derivatives and no solid-state data exist for the synthetically important lithiovinyl carbanions (Gais, Erdelmeier, Lindner & Vollhardt, 1986; Chassaing & Marquet, 1978). Such data are required for a detailed understanding of the mechanism in stereoselective C—C bond formation reactions. In principle, three chelating lithium-binding modes are possible in lithiovinylsulfoximines, resulting in *N*,*C*-, *O*,*C*- or *O*,*N*-chelates. In this paper, we describe the

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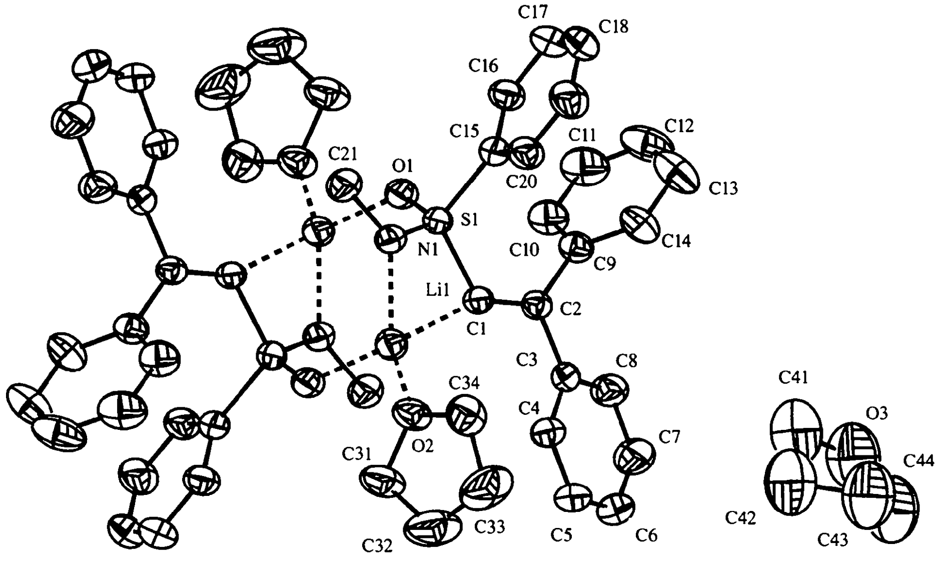
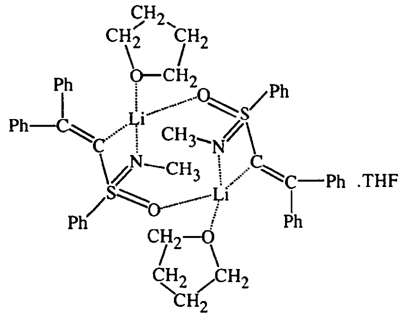


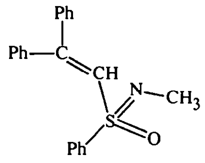
Fig. 1. The molecular structure of (1).THF, with ellipsoids drawn at the 30% probability level using the program *SNOOPI* (Davies *et al.*, 1989). H atoms have been omitted for clarity.

synthesis and structural characterization of such a compound, (I).THF.



(1).THF

The lithiosulfoximine (1) was prepared by the addition of *n*-BuLi to a tetrahydrofuran solution of racemic 1-(*N*-methylphenylsulfonimidoyl)-2,2-diphenyl-ethene, (2), which is readily prepared from benzophenone by an addition–elimination sequence (Gais, Erdelmeier & Lindner, 1986). Recrystallization of the resultant yellow precipitate from tetrahydrofuran afforded air- and moisture-sensitive crystals of (1).THF. The molecular structure of the dinuclear lithium complex is shown in Fig. 1 and the neutral starting material, (2), is shown in Fig. 2.



(2)

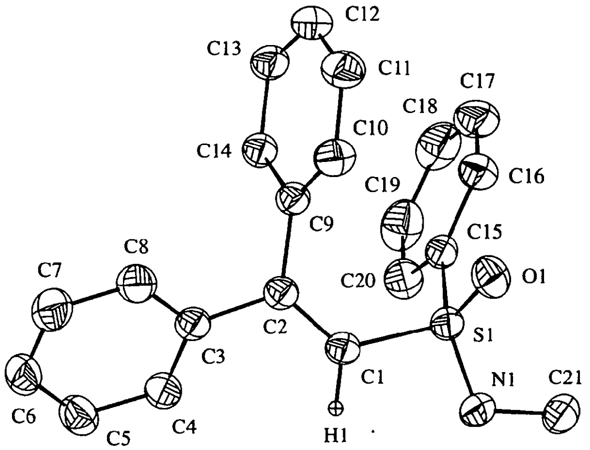


Fig. 2. The molecular structure of (2), with ellipsoids drawn at the 30% probability level using the program *SNOOPI* (Davies *et al.*, 1989). H atoms, with exception of the H1 atom, have been omitted for clarity.

The dimeric aggregate (1) is bridged through the C, N and O atoms of the sulfoximine ligands, forming two eight-membered rings with the different atomic sequences $(Li—O—S—N)_2$ and $(Li—C—S—O)_2$. The two halves of the molecule are related by a crystallographic centre of symmetry. Remarkably, the Li1—C contact, with a distance of 2.210 (5) Å, together with the lithium coordination to the sulfoximine N atom leads to an *N*,*C*-chelate. In this respect, complex (1) differs both from lithiovinylsulfones and lithioallylsulfoximines, which do not show Li—C bonds, and also from more highly associated lithioalkylsulfoximines, which characteristically show *N,C*- and *O,C*-chelation (Müller, Neuburger & Zehnder, 1995; Boche, 1989). The distorted tetrahedral coordination of the lithium cation is completed by coordination to an O atom of a tetrahydrofuran molecule. This arrangement could serve as a good model for the structure solution of such α-lithiosulfoximines.

The S—C$_\alpha$ bond is slightly shortened from 1.753 (2) Å in compound (2) to 1.734 (3) Å in (1). Even if these values are not grossly different in terms of their standard deviations, the observed trend is in good agreement with the observed bond shortening in our previously reported *ab initio* calculations (Müller, Batra, Spingler & Zehnder, 1996). Compared with lithiovinylsulfones, however, this shortening is small and reveals the minor stabilizing abilities of the sulfonimidoyl group.

No significant change in the C1—C2 bond length after the lithiation is observed [1.336 (4) in (1) *versus* 1.330 (2) Å in (2)]. The magnitudes of the torsion angles Li—C1—C2—C3 and S1—C1—C2—C3 in (1) are 0.7 (7) and 175.6 (2)°, respectively, indicating a near planar geometry at the anionic C atom. In order to get a deeper insight into the mechanistic implications and the dynamics of these lithio compounds, further investigations to determine the solution structures are currently under way.

Experimental

For the preparation of (1), a 1.43 *M* solution of *n*-butyllithium in hexane (0.44 ml, 0.63 mmol) was slowly added at 195 K to a solution of compound (2) (205 mg, 0.62 mmol) in a mixture of 2 ml THF, 0.5 ml TMEDA and 1 ml hexane. After precipitation of a yellow precipitate, the supernatant solution was decanted. Recrystallization of the solid residue from 2 ml THF afforded yellow moisture-sensitive crystals of (1).THF, which were sealed in a glass capillary under nitrogen (yield 142 mg, 56%). As the crystals of (1).THF had been sealed in glass capillaries to prevent decomposition, there was no possibility of cutting the needles to a usual size. A 1.3 mm collimator was used to carry out the data collection.

Compound (1)

Crystal data

$[Li_2(C_{21}H_{19}NOS)_2(C_4H_8O)_2].C_4H_8O$
$M_r = 895.08$
Monoclinic
$P2_1/n$
$a = 13.853$ (1) Å
$b = 10.988$ (2) Å
$c = 16.678$ (2) Å
$\beta = 98.703$ (7)°
$V = 2509.5$ (6) Å^3
$Z = 2$
$D_x = 1.18$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 21$–42°
$\mu = 1.29$ mm^{-1}
$T = 293$ K
Needle
1.10 × 0.30 × 0.30 mm
Pale yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$2\theta/\omega$ scans
Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.543$, $T_{max} = 0.679$
4683 measured reflections
4379 independent reflections

3337 reflections with $I > 3\sigma(I)$
$R_{int} = 0.02$
$\theta_{max} = 74.33°$
$h = -17 \rightarrow 0$
$k = 0 \rightarrow 13$
$l = -20 \rightarrow 20$
3 standard reflections
frequency: 120 min
intensity decay: 3.11%

Refinement

Refinement on F
$R = 0.0623$
$wR = 0.0702$
$S = 0.970$
3337 reflections
317 parameters
H atoms placed geometrically after each cycle
Chebychev polynomial (Carruthers & Watkin, 1979)

$(\Delta/\sigma)_{max} = 0.021$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.65$ e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 132 (18)
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

Li1—N1	2.035 (6)	S1—C1	1.734 (3)
Li1—O1^i	1.932 (5)	S1—C15	1.792 (3)
Li1—O2	1.968 (5)	C1—C2	1.336 (4)
Li1—C1	2.210 (5)	C2—C3	1.503 (4)
S1—N1	1.539 (2)	C2—C9	1.500 (4)
S1—O1	1.477 (2)		
N1—Li1—O1^i	115.2 (2)	O1—S1—C1	113.1 (1)
N1—Li1—O2	126.5 (3)	N1—S1—C15	107.9 (1)
O1^i—Li1—O2	102.3 (2)	O1—S1—C15	103.5 (1)
N1—Li1—C1	72.1 (2)	C1—S1—C15	116.2 (1)
O1^i—Li1—C1	120.4 (3)	S1—C1—C2	120.6 (2)
O2—Li1—C1	119.9 (2)	C1—C2—C3	117.8 (2)
N1—S1—O1	117.1 (1)	C1—C2—C9	127.7 (2)
N1—S1—C1	99.5 (1)	C3—C2—C9	114.5 (2)

Symmetry code: (i) $-x, -y, -z$.

Compound (2)

Crystal data

$C_{21}H_{19}NOS$
$M_r = 333.45$
Triclinic
$P\bar{1}$
$a = 6.0861$ (4) Å
$b = 11.9803$ (7) Å
$c = 12.4121$ (7) Å
$\alpha = 97.170$ (4)°
$\beta = 90.662$ (5)°
$\gamma = 99.241$ (5)°
$V = 885.82$ (9) Å^3
$Z = 2$
$D_x = 1.25$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 23$–46°
$\mu = 1.62$ mm^{-1}
$T = 293$ K
Needle
0.75 × 0.45 × 0.20 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$2\theta/\omega$ scans

3066 reflections with $I > 3\sigma(I)$
$R_{int} = 0.01$

Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.535$, $T_{max} = 0.723$
3797 measured reflections
3464 independent reflections
$\theta_{max} = 77.50°$
$h = 0 \rightarrow 7$
$k = -15 \rightarrow 14$
$l = -15 \rightarrow 15$
3 standard reflections
frequency: 120 min
intensity decay: 3.52%

Refinement

Refinement on F
$R = 0.0394$
$wR = 0.0473$
$S = 1.03$
3066 reflections
222 parameters
H atoms placed geometrically after each cycle
Chebychev polynomial (Carruthers & Watkin, 1979)
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 28 (2)
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 2. *Selected geometric parameters (Å, °) for (2)*

S1—N1	1.520 (1)	C1—C2	1.330 (2)
S1—O1	1.452 (1)	C2—C3	1.488 (2)
S1—C1	1.753 (2)	C2—C9	1.491 (2)
S1—C15	1.784 (2)		
N1—S1—O1	121.26 (8)	C1—S1—C15	105.86 (7)
N1—S1—C1	99.85 (8)	S1—C1—C2	125.9 (1)
O1—S1—C1	113.35 (8)	C1—C2—C3	119.8 (1)
N1—S1—C15	110.92 (8)	C1—C2—C9	123.9 (1)
O1—S1—C15	104.82 (8)	C3—C2—C9	116.3 (1)

The structure of (1) contains a disordered tetrahydrofuran molecule which is situated on a centre of symmetry. It was refined restraining the C—O and C—C bond lengths to their common mean. Displacement parameters were restrained to meet a null-motion criterion. Except for the H1 atom in compound (2), all H atoms (including solvent H atoms) are in calculated positions. The H1 atom in structure (2) was located in the difference map and refined isotropically restraining the C1—H1 bond length to 0.96 Å. The e.s.d.'s of the U_{eq} values were calculated using the method described by Schomaker & Marsh (1983).

For both compounds, data collection: *CAD*-4 *Express* (Enraf–Nonius, 1992); program(s) used to solve structures: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structures: *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985); molecular graphics: *SNOOPI* (Davies, Braid, Foxman & Powell, 1989).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: JZ1153). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 422–425

Metal–α,ω-Dicarboxylate Complexes. II. *catena*-Poly[bis(imidazole-N^3)copper(II)-di-μ-adipato(1−)-O^1:O^6;O^6:O^1]

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(*Received 11 July 1996; accepted 11 November 1996*)

Abstract

The structure of the title compound, $[Cu(C_6H_9O_4)_2(C_3H_4N_2)_2]_n$, is polymeric, joining two Cu^{II}–*trans*-(imidazole)$_2$ units by two extended adipate monoanions. The metal ion at the centre of symmetry has a highly distorted octahedral coordination; the two longer bonds are formed to the protonated carboxylate O atoms [Cu1—O3 2.499 (2) Å] and the octahedron is completed by bonds to two imidazole N atoms and two deprotonated carboxylate groups. The 'building block' of the polymer is an 18-membered ring of maximum dimensions 10.61 and 5.61 Å. Their molecular packing in space group *C*2/*c*, however, prevents channel formation of this size. The polymeric chains of the acid form very strong intramolecular hydrogen bonds *via* O3—H···O2 across the metal centre.

Acta Crystallographica Section C
ISSN 0108-2701 © 1997