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Di-μ-pyridyl-1:2κ^2N:C^2;2:1κ^2N:C^2-μ-tetrahydrofuran-κ^2O:O-bis[bromo(tetrahydrofuran)magnesium(II)] tetrahydrofuran hemisolvate

Andrei V. Churakov,[a]* Dmitry P. Krut'ko,[b] Maxim V. Borzov,[b] Roman S. Kirsanov,[b] Sergei A. Belov[b] and Judith A. K. Howard[c]

[a]N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Science, 31 Leninskii Prospect, Moscow 119991, Russian Federation, [b]Department of Chemistry, Moscow State University, Leninskie Gory, Moscow 119992, Russian Federation, and [c]Department of Chemistry, University of Durham, Science Laboratories, South Road, Durham DH1 3LE, England

Correspondence e-mail: churakov@igic.ras.ru

Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.005 Å
Disorder in solvent or counterion
R factor = 0.039
wR factor = 0.085
Data-to-parameter ratio = 19.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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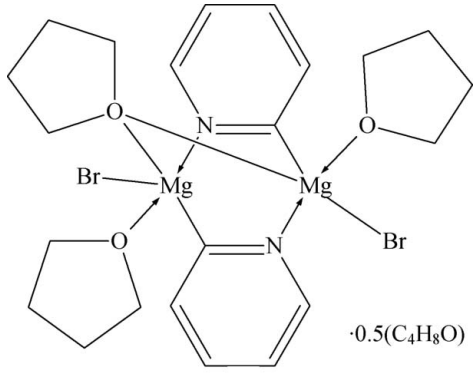
The title compound, $[Mg_2Br_2(C_5H_4N)_2(C_4H_8O)_3]\cdot0.5C_4H_8O$, contains dimeric associations of Mg atoms bridged by tetrahydrofuran (THF) molecules. The coordination polyhedron of the Mg atom is a slightly distorted $MgCNO_2Br$ trigonal bipyramid with two THF molecules in the axial positions. One O atom occupies a site with symmetry 2.

Comment

The main molecule of the title Grignard reagent, (μ-C_4H_8O)-[$Br(C_4H_8O)(\mu$-η^2-C,N—C_5H_4N-2)$Mg]_2$, (I) (Fig. 1), is dimeric [$Mg1\cdots Mg1^i = 3.3237$ (18) Å; symmetry code: (i) $-y, -x, \frac{1}{2}-z$] and is generated by twofold symmetry with O2 lying on a twofold rotation axis. The coordination polyhedron of the Mg atom is a slightly distorted $MgCNO_2Br$ trigonal bipyramid (Table 1) with two tetrahydrofuran (THF) molecules in the axial (ax) positions. Bromine, pyridyl N and C atoms occupy equatorial (eq) sites. The eq—Mg1—eq angles lie within the range 115.52 (11)–121.74 (8)° and the ax—Mg1—eq angles are close to 90° [83.16 (8)–95.07 (10)°].



(I)

This coordination environment of Mg is rather characteristic for adducts of Grignard reagents with THF, as was observed for MeMgBr (Vallino, 1969) and EtMgCl (Toney & Stucky, 1971). The Mg1—Br1, Mg1—O1 and Mg1—C1 bond lengths are normal and consistent with related structures (Cambridge Structural Database; Version 5.27 of January 2006; Allen, 2002). The Mg1—N1 distance in (I) is close to that found previously for pyridyl substituted alkylmagnesiumbromide [2.122 (4) Å; Al-Juaid *et al.*, 2001].

The sum of valence angles around O1, 358.0°, corresponds to sp^2-hybridization. Analysis of data in the CSD showed that the latter is common for structures with Hal—Mg(C)—O(THF, terminal) fragments where the sum of angles varies

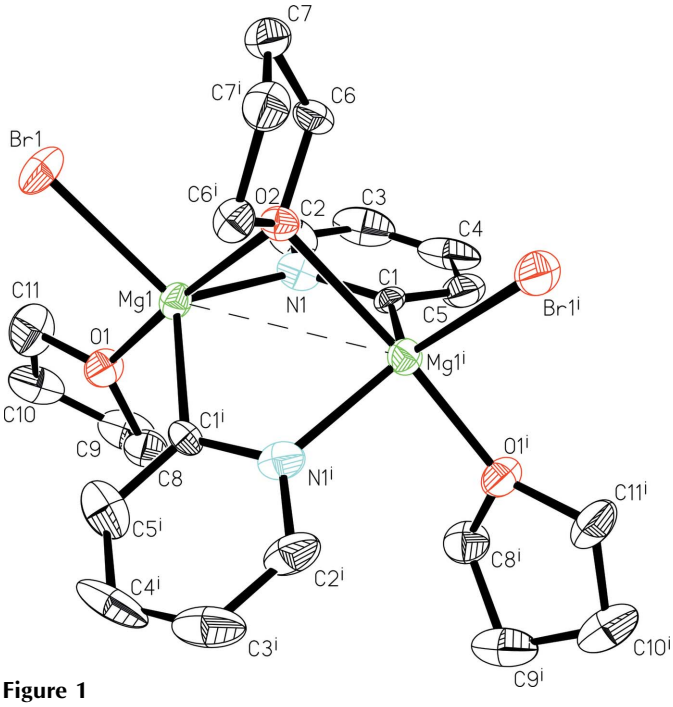


Figure 1
Molecular structure of the main molecule of (I), showing 50% probability displacement ellipsoids with H atoms omitted for clarity. [Symmetry code: (i) $-y, -x, \frac{1}{2}-z$.]

from 351.8 to 360.0°. The second (O2) THF molecule is bridging and the Mg1—O2—Mg1^{i} angle is 88.86 (10)° [symmetry code: (i) $-y, -x, \frac{1}{2}-z$]. As expected, the Mg—O2 bond length is much longer than Mg—O1.

To the best of our knowledge, (I) is only the second example of an Mg complex with a bridging THF molecule. Previously, the dinuclear complex [(THF)(η^2-PhNCNPh)]$_2$Mg$_2$(μ-Cl)$_2$(μ-THF), (II), was structurally investigated (Cotton *et al.*, 1997); for comparison, the Mg—O(μ-THF) distances in (II) are 2.322 (6) and 2.357 (6) Å, while the Mg—O—Mg angle is 84.3 (2)°. However, the bridging THF ligand is well known in the structures of alkali and rare earth metals complexes; there are 70 entries in the CSD, of which 29 are Li derivatives.

Compound (I) is the first structurally characterized example of an Mg complex with bridging (μ-C,*N*-pyridyl-2) ligands. However, this bridging ligand is common for di- and polynuclear complexes of other metals (110 entries in the CSD, of which 85 are compounds of 8B group metals).

In the dimeric structure of (I), the Br atoms are terminal. In contrast, an analysis of the CSD demonstrates that in all previously investigated di- and polymeric structures of Grignard reagents, the halogen atoms serve as bridges forming [Mg$_2$(μ-Hal)$_2$] fragments (16 entries).

Previously, the synthesis of closely related Grignard reagents (2-pyridyl)Mg*X*·2THF (*X* = Br and I) was reported and their unit-cell parameters were determined (Paradies, 1974). However, no information on their molecular structures was published.

The crystals of (I) contain disordered solvent THF molecules lying on a fourfold axis. These THF molecules occupy the cavities between the main molecules.

Experimental

The synthetic procedure for (I) reported by Paradies & Görbing (1969) was found to be non-reproducible. This fact was mentioned by Furukava *et al.* (1987). Compound (I) was prepared by treatment of *i*-PrMgBr with 2-brompyridine (Trécourt *et al.*, 1999) and for the first time isolated in pure form (yield 58%). The crystals of (I) decompose rapidly in open air.

Crystal data

[Mg$_2$Br$_2$(C$_5$H$_4$N)$_2$(C$_4$H$_8$O)$_3$]·0.5C$_4$H$_8$O
M_r = 616.99
Tetragonal, $P4/ncc$
a = 17.3368 (3) Å
c = 18.8696 (4) Å
V = 5671.53 (18) Å^3
Z = 8
D_x = 1.445 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 2.93 mm^{-1}
T = 120 (2) K
Block, colourless
0.30 × 0.20 × 0.10 mm

Data collection

Bruker SMART 1K diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
T_{min} = 0.473, T_{max} = 0.758
30363 measured reflections
3108 independent reflections
2022 reflections with $I > 2\sigma(I)$
R_{int} = 0.093
θ_{max} = 27.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.085
S = 1.00
3108 reflections
161 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0384P)^2 + 1.9833P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.47 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mg1—Br1	2.4887 (9)	Mg1—C1^{i}	2.149 (3)
Mg1—O1	2.089 (2)	Mg1—O2	2.374 (2)
Mg1—N1	2.129 (3)		
O1—Mg1—N1	93.15 (9)	C1^{i}—Mg1—Br1	120.98 (8)
O1—Mg1—C1^{i}	95.07 (10)	O2—Mg1—Br1	89.57 (5)
N1—Mg1—C1^{i}	115.52 (11)	C6—O2—C6^{i}	108.2 (3)
O1—Mg1—O2	175.18 (8)	C6—O2—Mg1^{i}	115.36 (12)
N1—Mg1—O2	83.16 (8)	C6^{i}—O2—Mg1^{i}	114.16 (12)
C1^{i}—Mg1—O2	83.78 (8)	C6—O2—Mg1	114.16 (12)
O1—Mg1—Br1	95.02 (6)	C6^{i}—O2—Mg1	115.36 (12)
N1—Mg1—Br1	121.74 (8)	Mg1^{i}—O2—Mg1	88.86 (10)

Symmetry code: (i) $-y, -x, -z+\frac{1}{2}$.

The possibility of partial positional disorder of C1 and N1 was checked; no evidence for such disorder was found. The disordered solvent (THF) molecule was refined isotropically with restrained C—C and C—O distances. The position of the O atom in the five-membered ring of the solvent THF molecule was assigned by analysis of isotropic displacement parameters and confirmed by the fact that the methylene group could not be placed in the O22 site without forming unusually short intermolecular H···H contacts (1.90–1.94 Å). All H atoms were placed in calculated positions (C—H = 0.95–0.99 Å) and refined using a riding model with U_{iso}(H) = 1.2U_{eq}(carrier)

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

SHELXTL-Plus (Bruker, 2000); software used to prepare material for publication: *SHELXTL-Plus*.

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