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#### Key indicators

Single-crystal X-ray study  
 T = 120 K  
 Mean  $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$   
 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>.

## Di- $\mu$ -pyridyl-1:2 $\kappa^2\text{N}:\text{C}^2$ ;2:1 $\kappa^2\text{N}:\text{C}^2$ - $\mu$ -tetrahydrofuran- $\kappa^2\text{O}:\text{O}$ -bis[bromo(tetrahydrofuran)-magnesium(II)] tetrahydrofuran hemisolvate

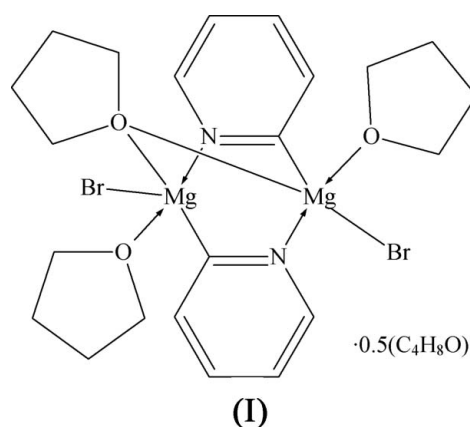
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The title compound,  $[\text{Mg}_2\text{Br}_2(\text{C}_5\text{H}_4\text{N})_2(\text{C}_4\text{H}_8\text{O})_3] \cdot 0.5\text{C}_4\text{H}_8\text{O}$ , contains dimeric associations of Mg atoms bridged by tetrahydrofuran (THF) molecules. The coordination polyhedron of the Mg atom is a slightly distorted  $\text{MgCNO}_2\text{Br}$  trigonal bipyramid with two THF molecules in the axial positions. One O atom occupies a site with symmetry 2.

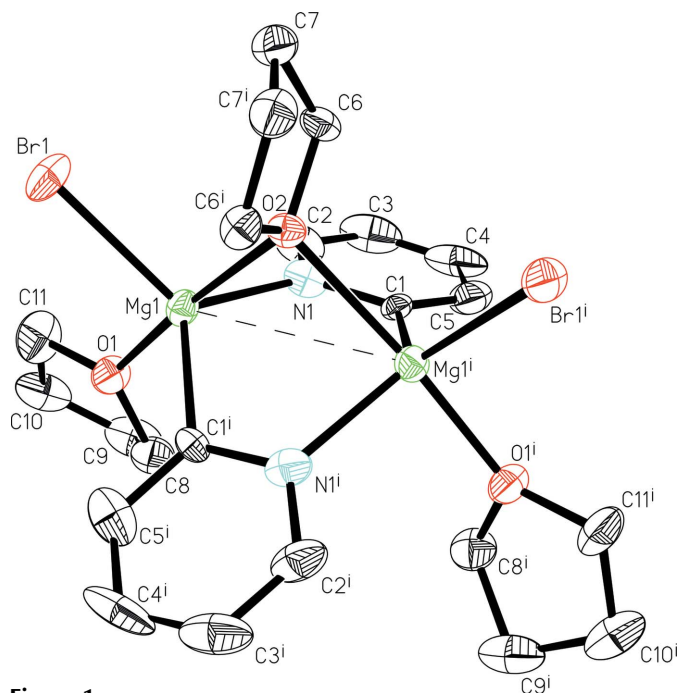
#### Comment

The main molecule of the title Grignard reagent,  $(\mu\text{-C}_4\text{H}_8\text{O})\text{-}[\text{Br}(\text{C}_4\text{H}_8\text{O})(\mu\text{-}\eta^2\text{-C,N-C}_5\text{H}_4\text{N-2})\text{Mg}]_2$ , (I) (Fig. 1), is dimeric  $[\text{Mg}1 \cdots \text{Mg}1^i = 3.3237 (18) \text{ \AA}$ ; 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  $\text{MgCNO}_2\text{Br}$  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  $115.52 (11)$ – $121.74 (8)^\circ$  and the ax–Mg1–eq angles are close to  $90^\circ$  [ $83.16 (8)$ – $95.07 (10)^\circ$ ].



This coordination environment of Mg is rather characteristic for adducts of Grignard reagents with THF, as was observed for  $\text{MeMgBr}$  (Vallino, 1969) and  $\text{EtMgCl}$  (Toney & Stucky, 1971). The  $\text{Mg}1\text{--Br}1$ ,  $\text{Mg}1\text{--O}1$  and  $\text{Mg}1\text{--C}1$  bond lengths are normal and consistent with related structures (Cambridge Structural Database; Version 5.27 of January 2006; Allen, 2002). The  $\text{Mg}1\text{--N}1$  distance in (I) is close to that found previously for pyridyl substituted alkylmagnesiumbromide [ $2.122 (4) \text{ \AA}$ ; Al-Juaid *et al.*, 2001].

The sum of valence angles around O1,  $358.0^\circ$ , corresponds to  $sp^2$ -hybridization. Analysis of data in the CSD showed that the latter is common for structures with  $\text{Hal-Mg(C)-O(THF, terminal)}$  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  $\text{Mg1}-\text{O2}-\text{Mg1}^i$  angle is 88.86 (10)° [symmetry code: (i)  $-y, -x, \frac{1}{2} - z$ ]. As expected, the  $\text{Mg}-\text{O2}$  bond length is much longer than  $\text{Mg}-\text{O1}$ .

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  $[(\text{THF})(\eta^2\text{-PhNCNPh})_2\text{Mg}_2(\mu\text{-Cl})_2(\mu\text{-THF})]$ , (II), was structurally investigated (Cotton *et al.*, 1997); for comparison, the  $\text{Mg}-\text{O}(\mu\text{-THF})$  distances in (II) are 2.322 (6) and 2.357 (6) Å, while the  $\text{Mg}-\text{O}-\text{Mg}$  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 ( $\mu\text{-C}, N$ -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  $[\text{Mg}_2(\mu\text{-Hal})_2]$  fragments (16 entries).

Previously, the synthesis of closely related Grignard reagents (2-pyridyl) $\text{MgX}\cdot 2\text{THF}$  ( $X = \text{Br}$  and  $\text{I}$ ) 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

$[\text{Mg}_2\text{Br}_2(\text{C}_5\text{H}_4\text{N})_2(\text{C}_4\text{H}_8\text{O})_3] \cdot 0.5\text{C}_4\text{H}_8\text{O}$   
 $M_r = 616.99$   
 Tetragonal,  $P4/ncc$   
 $a = 17.3368$  (3) Å  
 $c = 18.8696$  (4) Å  
 $V = 5671.53$  (18) Å<sup>3</sup>

$Z = 8$   
 $D_x = 1.445$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 $\mu = 2.93$  mm<sup>-1</sup>  
 $T = 120$  (2) K  
 Block, colourless  
 $0.30 \times 0.20 \times 0.10$  mm

### Data collection

Bruker SMART 1K diffractometer  
 $\omega$  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  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.093$   
 $\theta_{\text{max}} = 27.0^\circ$

### 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  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.47$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.36$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

$\text{Mg1}-\text{Br1}$	2.4887 (9)	$\text{Mg1}-\text{C1}^i$	2.149 (3)
$\text{Mg1}-\text{O1}$	2.089 (2)	$\text{Mg1}-\text{O2}$	2.374 (2)
$\text{Mg1}-\text{N1}$	2.129 (3)		
$\text{O1}-\text{Mg1}-\text{N1}$	93.15 (9)	$\text{C1}^i-\text{Mg1}-\text{Br1}$	120.98 (8)
$\text{O1}-\text{Mg1}-\text{C1}^i$	95.07 (10)	$\text{O2}-\text{Mg1}-\text{Br1}$	89.57 (5)
$\text{N1}-\text{Mg1}-\text{C1}^i$	115.52 (11)	$\text{C6}-\text{O2}-\text{C6}^i$	108.2 (3)
$\text{O1}-\text{Mg1}-\text{O2}$	175.18 (8)	$\text{C6}-\text{O2}-\text{Mg1}^i$	115.36 (12)
$\text{N1}-\text{Mg1}-\text{O2}$	83.16 (8)	$\text{C6}^i-\text{O2}-\text{Mg1}^i$	114.16 (12)
$\text{C1}^i-\text{Mg1}-\text{O2}$	83.78 (8)	$\text{C6}-\text{O2}-\text{Mg1}$	114.16 (12)
$\text{O1}-\text{Mg1}-\text{Br1}$	95.02 (6)	$\text{C6}^i-\text{O2}-\text{Mg1}$	115.36 (12)
$\text{N1}-\text{Mg1}-\text{Br1}$	121.74 (8)	$\text{Mg1}^i-\text{O2}-\text{Mg1}$	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  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$ .

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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