

**$\mu$ -Oxo-bis[( $\eta^5$ -1,2-dicarbaundecaborato)bis(*N,N*-dimethylacetamidinato)-tantalum] dichloromethane hemisolvate**

Andrès E. Goeta, Andrew K. Hughes\* and John M. Malget

Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, England

Correspondence e-mail: a.k.hughes@durham.ac.uk

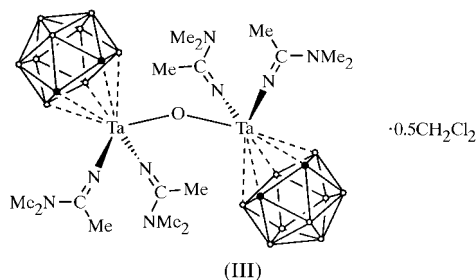
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The structure of the title compound, [Ta<sub>2</sub>O(C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>(C<sub>4</sub>H<sub>9</sub>N<sub>2</sub>)<sub>4</sub>].0.5CH<sub>2</sub>Cl<sub>2</sub>, contains two (C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)Ta[NC(Me)NMe<sub>2</sub>]<sub>2</sub> units bridged by a nearly linear [Ta—O—Ta 163.4 (4)°]  $\mu$ -oxo ligand. The dichloromethane molecule lies on a twofold axis.

**Comment**

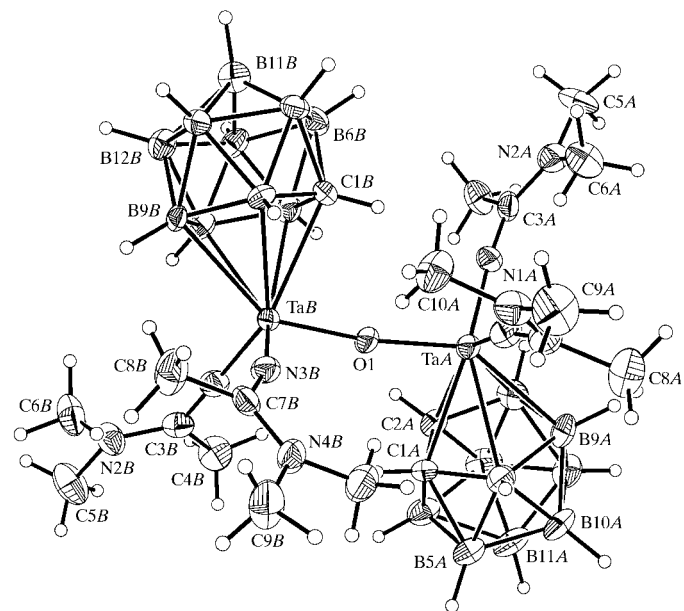
Treating tantalum-tris(*N,N*-dimethylamide)-1,2-dicarbaundecaborate, (C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)Ta(NMe<sub>2</sub>)<sub>3</sub>, (I), with MeCN results in insertion of the nitrile into the metal–amide bond to give mainly tantalum-tris(*N,N*-dimethylacetamidinato)-1,2-dicarbaundecaborate, (C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)Ta[NC(Me)NMe<sub>2</sub>]<sub>3</sub>, (II), whose structure has been described by Broder *et al.* (2000). The title complex, {(C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)Ta[NC(Me)NMe<sub>2</sub>]<sub>2</sub>}( $\mu$ -O), (III), was identified as a minor product and results from hydrolysis of (II) by adventitious water. Following recrystallization, the poor solubility of (III) in all common laboratory solvents hampered attempts to obtain supporting spectroscopic data, but the crystals proved suitable for a diffraction study.



The asymmetric unit of (III) comprises two Ta atoms, each ligated by two monodentate *N,N*-dimethylacetamidinato ligands, [NC(Me)NMe<sub>2</sub>], and tethered by a  $\mu$ -oxo bridge, plus a half-occupancy dichloromethane solvent molecule. The two Ta units are oriented mutually *trans* to each other to minimize the considerable steric interactions between the amidinato ligands. These factors are reflected in the almost linear

[163.4 (4)°] Ta—O—Ta bond. The *N,N*-dimethylacetamidinato ligands are close to being planar, with the mean deviations from planarity of the N—C—(C)NC<sub>2</sub> units varying from 0.011 (7) to 0.038 (7) Å. The Me<sub>2</sub>N—C(Me)N bonds in the amidinato are shorter than typical N—C single bonds. The Ta—N bonds [1.855 (6)–1.881 (6) Å] are intermediate between tantalum amido, Ta—NR<sub>2</sub> [Cambridge Structural Database (CSD; Allen & Kennard, 1993) mean 1.99 Å], and tantalum imido, Ta—NR (CSD mean 1.79 Å), distances.

These structural features reflect a delocalized  $\pi$ -bonding framework over the entire amidinato ligand and a balance between the tantalum amide and tantalum imide canonical



**Figure 1**  
The molecular structure of (III), with displacement ellipsoids drawn at the 40% probability level and H atoms shown as small spheres of arbitrary radii.

forms. The strong  $\pi$ -donation to the metal atom from the amidinato ligands results in a competitive weakening of the carborane to metal  $\pi$ -donation, and the C<sub>2</sub>B<sub>3</sub> ring-centroid–metal distances of 2.050 (8) Å to TaA and 2.037 (7) Å to TaB are intermediate between those of the parent amide complex, (I) [2.019 (6) and 2.003 (6) Å; Batsanov *et al.*, 1999], with moderate  $\pi$ -donor amide ligands, and of the tris(-acetamidinato), (II) [2.097 (5) Å]. There is often an orientational preference displayed by C<sub>2</sub>B<sub>9</sub>H<sub>11</sub> ligands with respect to other ligands, as previously noted in amido (Batsanov *et al.*, 1999, 2000), indenyl (Grädler *et al.*, 1996; Smith & Welch, 1986), pyrrolyl (Teixidor *et al.*, 1997; Gómez *et al.*, 1997) and carbonyl (Cowie *et al.*, 1990) complexes. This can be described as a strong *trans* influence of the C<sub>2</sub> unit of the dicarborollide, and arises from the non-equivalence of the two  $\pi$ -donor orbitals of the ligand. In the case of (III), the midpoint of the C—C bond of the dicarborollide is preferentially located approximately over the Ta—O vector, as quantified by the (C<sub>2</sub> midpoint)—(C<sub>2</sub>B<sub>3</sub> centroid)—Ta—O torsion angles, which are 11.4 (5)° for TaA and 4.6 (5)° to TaB.

## Experimental

MeCN containing a trace of water was added to a toluene solution of tantalum-tris(*N,N*-dimethylamide)-1,2-dicarbaundecaborate and the solution was brought to reflux, and heating was continued for 24 h. The resulting solution was cooled and layered with pentane. Interdiffusion of the two solvents over a period of two weeks afforded bright yellow crystals of (III).

### Crystal data

[Ta<sub>2</sub>O(C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>(C<sub>4</sub>H<sub>9</sub>N<sub>2</sub>)<sub>4</sub>]-  
0.5CH<sub>2</sub>Cl<sub>2</sub>  
*M<sub>r</sub>* = 1025.69  
Monoclinic, *P*2<sub>1</sub>  
*a* = 11.414 (3) Å  
*b* = 10.769 (3) Å  
*c* = 17.863 (5) Å  
*β* = 93.303 (6)°  
*V* = 2192.1 (11) Å<sup>3</sup>  
*Z* = 2

*D<sub>x</sub>* = 1.554 Mg m<sup>-3</sup>  
Mo *Kα* radiation  
Cell parameters from 616  
reflections  
*θ* = 13.7–19.1°  
*μ* = 5.08 mm<sup>-1</sup>  
*T* = 150 (2) K  
Rectangular prism, colourless  
0.22 × 0.12 × 0.08 mm

### Data collection

Bruker SMART CCD area-detector  
diffractometer  
*ω* scans  
Absorption correction: by integra-  
tion (*XPREP* in *SHELXTL-NT*;  
Bruker, 1998)  
*T<sub>min</sub>* = 0.381, *T<sub>max</sub>* = 0.690  
26 944 measured reflections

6464 independent reflections (plus  
4469 Friedel-related reflections)  
9396 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.042  
*θ<sub>max</sub>* = 30.4°  
*h* = -15 → 15  
*k* = -15 → 14  
*l* = -25 → 24

### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.035  
*wR* (*F*<sup>2</sup>) = 0.095  
*S* = 1.10  
10 933 reflections  
470 parameters  
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2 + 0.8328P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
(*Δ/σ*)<sub>max</sub> < 0.001  
*Δρ*<sub>max</sub> = 1.34 e Å<sup>-3</sup>  
*Δρ*<sub>min</sub> = -0.76 e Å<sup>-3</sup>  
Absolute structure: Flack (1983)  
Flack parameter = 0.41 (1)

H atoms were included as riding atoms, with B–H = 1.12 Å and C–H = 0.98–1.00 Å. The Flack parameter (Flack, 1983) indicates racemic twinning.

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1146). Services for accessing these data are described at the back of the journal.

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