

## Di- $\mu$ -chlorido-bis[dichloridobis(methylamido- $\kappa$ N)bis(methylamine- $\kappa$ N)-titanium(IV)]

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The title compound,  $[\text{Ti}_2\text{Cl}_6(\text{C}_2\text{H}_6\text{N})_2(\text{C}_2\text{H}_7\text{N})_2]$ , is a binuclear octahedral complex lying about an inversion centre. There are four different chloride environments, two terminal  $[\text{Ti}-\text{Cl} = 2.2847(5)$  and  $2.3371(5) \text{ \AA}]$  and two bridging  $[\text{Ti}-\text{Cl} = 2.4414(5)$  and  $2.6759(5) \text{ \AA}]$ , with the  $\text{Ti}-\text{Cl}$  distances being strongly influenced by both the ligand *trans* to the chloride and whether or not the chloride anion is bridging between the two  $\text{Ti}^{\text{IV}}$  centres. The compound forms a two-dimensional network in the solid state, with weak intermolecular  $\text{C}-\text{H}\cdots\text{Cl}$  interactions giving rise to a planar network in the  $(10\bar{2})$  plane.

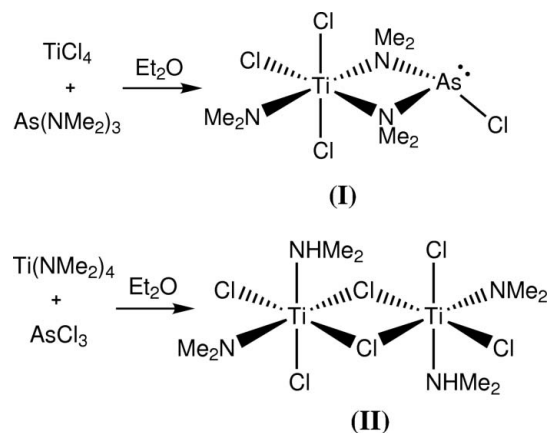
### Comment

Chemical vapour deposition (CVD) is a well used technique for depositing thin films of materials (Jones & Hitchman, 2009). Industrially, films of transition metal pnictide materials are deposited using volatile metal and pnictogen precursors, but these precursors are often toxic, flammable and generally difficult to handle. ‘Single-source’ precursors are compounds which contain a direct  $M-\text{Pn}$  bond ( $\text{Pn} = \text{pnictogen}$ ) and they are usually much less toxic and much easier to handle (Cowley & Jones, 1994; Carmalt & Basharat, 2007).

As part of recent work into the synthesis of molecular precursors for the deposition of transition metal pnictide thin films (Potts *et al.*, 2009; Thomas, Blackman *et al.*, 2010; Thomas *et al.*, 2011), we recently reported an unusual ligand-exchange reaction between  $\text{TiCl}_4$  and  $\text{As}(\text{NMe}_2)_3$  (Thomas, Pugh *et al.*, 2010). The reaction of one equivalent of  $\text{As}(\text{NMe}_2)_3$  with  $\text{TiCl}_4$  did not afford the 1:1 adduct  $[\text{TiCl}_4\{\text{As}(\text{NMe}_2)_3\}]$ . Instead, the compound  $[\text{TiCl}_3(\text{NMe}_2)(\mu\text{-NMe}_2)_2\text{AsCl}]$ , (I), was isolated as dark-green crystals. Structural characterization confirmed that an exchange of chloride and dimethylamide ligands had taken place.

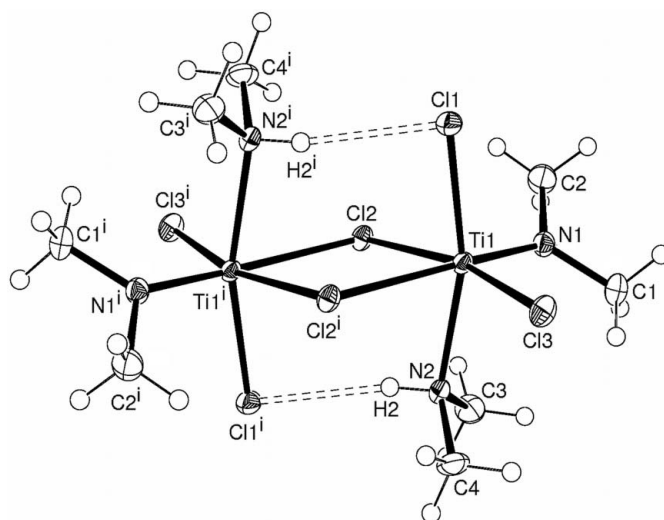
Despite the fact that (I) was largely unsuitable as a single-source precursor to thin films of TiAs (owing to the lack of a direct  $\text{Ti}-\text{As}$  bond), further investigations into this unusual

exchange were carried out. In an attempt to determine whether the exchange would still occur if the ligands on the metals were reversed, one equivalent of  $[\text{Ti}(\text{NMe}_2)_4]$  was reacted with  $\text{AsCl}_3$ . The title compound, (II), also a dark-green solid, was isolated from the reaction.



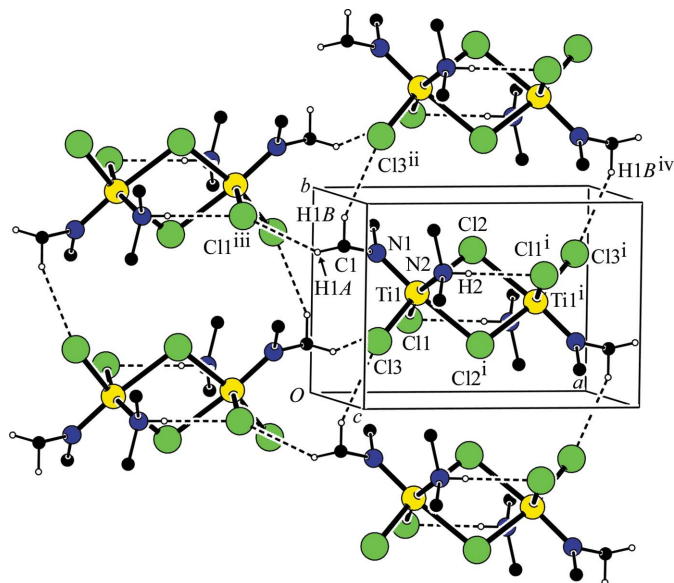
Compound (II) is a binuclear complex lying about an inversion centre, with each 14-electron  $\text{Ti}^{\text{IV}}$  centre distorted from ideal octahedral geometry. The bridging chloride ligand datively bonds *trans* to the dimethylamide group, with the four ligands *cis* to the dimethylamide group showing a slight repulsion from the strongly electronegative group (Fig. 1). The  $\text{Ti}_2\text{Cl}_2$  ring at the heart of the molecule is planar, with atom N1 departing from this plane by  $0.102(2) \text{ \AA}$ .

The  $\text{Ti}-\text{N}$  bond lengths in (II) give a strong indication of the presence of two different types of N-containing ligand within the complex (Table 1). The large difference between the  $\text{Ti}-\text{N1}$  and  $\text{Ti}-\text{N2}$  bond lengths is indicative of the presence of anionic amide and neutral amine ligands. In addition, the geometry at N2 and the presence of a peak in the difference Fourier map in the expected position for an amine



**Figure 1**

A view of (II), showing the atom-numbering scheme and the  $\text{N}-\text{H}\cdots\text{Cl}$  hydrogen bonds as dashed lines. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i)  $-x + 1, -y + 1, -z + 1$ ]



**Figure 2**  
A view of (II), showing the two-dimensional arrangement parallel to the  $(10\bar{2})$  plane. [Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $x, y + 1, z$ ; (iii)  $-x, y + \frac{1}{2}, -z + \frac{1}{2}$ ; (iv)  $-x + 1, -y + 2, -z + 1$ .]

H atom lead to the assignment of N2 to a neutral dimethylamine ligand.

The Ti—Cl bond distances are heavily influenced by the *trans* effect, with the longest found for the chloride ligand *trans* to the dimethylamide group (Table 1). However, the fact that this is the ‘bridging’ Ti—Cl<sup>2i</sup> bond [symmetry code: (i)  $-x + 1, -y + 1, -z + 1$ ] also has a strong influence on the bond length. This is confirmed by looking at the Ti—Cl bonds which are *trans* to each other: the Ti—Cl2 bond is longer than the Ti—Cl3 bond. This effect can only be a result of atom Cl2 being involved in bridging between the two Ti centres, because the immediate environment around the chloride ligands is otherwise identical. The other Ti—Cl distance demonstrates the difference in *trans* effect between chloride and amine ligands. The Ti—Cl3 distance is the shortest of the four Ti—Cl distances and is a result of atom Cl3 being *trans* to a bridging chloride ligand. Even though Cl1 is *trans* to a neutral amine ligand instead of an anionic chloride ligand, the stronger *trans* effect of the amine has the effect of lengthening the Ti—Cl1 bond.

These effects were also noted in other structurally characterized examples of  $[\text{TiCl}_3\text{L}_a\text{L}_n]_2$  species ( $L_a$  is an anionic amide donor and  $L_n$  is a neutral amine donor). Two types of these complexes have been reported in the Cambridge Structural Database (CSD, August 2010 update; Allen, 2002), both of which involve bidentate ligands. Two examples exist of 2-amidopyridine adducts, *viz.*  $[\text{Me}_3\text{SiN}(2\text{-py})\text{TiCl}_3]_2$  reported by Jones *et al.* (2003) and  $[\text{PhN}(2\text{-py})\text{TiCl}_3]_2$  reported by Talja *et al.* (2005). Also, two aminosilylamide adducts of  $\text{TiCl}_3$  have been reported, by Buheitel *et al.* (1996) and Rannabauer *et al.* (2002), where the donor atoms are linked through an  $\text{SiX}_2$  group ( $X = \text{Cl}$  or  $\text{Me}$ ). In each case, the geometry at the metal centre is very similar to that found in (II), with only the nature of the N-containing ligands differing. For example, in each

complex, the amide donor is *trans* to a bridging chloride ligand, resulting in a lengthening of that Ti—Cl bond.

Also present in (II) is an intramolecular hydrogen-bonding interaction between the N2—H2 group of the amine ligand and atom Cl1<sup>i</sup> (Fig. 1 and Table 2). Other weaker intermolecular methyl C—H...Cl interactions are also present in the crystal structure (see Table 2) and give rise to a two-dimensional network parallel to the  $(10\bar{2})$  plane, as shown in Fig. 2.

The lack of arsenic in (II) is notable compared with (I), where it was retained. This does rule out (II) as a potential single-source precursor to thin films of TiAs. However, it may prove to be a viable precursor to thin films of TiN, owing to the presence of two N-donor ligands attached to Ti.

## Experimental

A solution of  $\text{AsCl}_3$  (0.2 ml, 2.37 mmol) in diethyl ether (20 ml) was added dropwise to a solution of  $\text{Ti}(\text{NMe}_2)_4$  (0.6 ml, 2.53 mmol) in diethyl ether (20 ml). The reaction was stirred for 48 h and then the solvent was removed under vacuum, affording a dark-green solid (yield 93%). Crystallization occurred by layering a concentrated  $\text{CH}_2\text{Cl}_2$  solution of (II) with hexane.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 400 MHz, 298 K):  $\delta$  2.5 (s), 2.2 (s). Analysis calculated for  $\text{C}_4\text{H}_{13}\text{Cl}_3\text{N}_2\text{Ti}$ : C 19.74, H 5.38, N 11.51%; found: C 19.57, H 5.51, N 11.62%.

### Crystal data

$[\text{Ti}_2\text{Cl}_6(\text{C}_2\text{H}_6\text{N})_2(\text{C}_2\text{H}_7\text{N})_2]$	$V = 1010.16 (7) \text{ \AA}^3$
$M_r = 486.83$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 10.7088 (4) \text{ \AA}$	$\mu = 1.58 \text{ mm}^{-1}$
$b = 6.7143 (3) \text{ \AA}$	$T = 120 \text{ K}$
$c = 15.7006 (5) \text{ \AA}$	$0.16 \times 0.10 \times 0.08 \text{ mm}$
$\beta = 116.515 (2)^\circ$	

### Data collection

Bruker–Nonius APEXII diffractometer with a CCD camera on $\kappa$ -goniostat	9954 measured reflections 2317 independent reflections 2092 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 2007)	$R_{\text{int}} = 0.039$
$T_{\text{min}} = 0.786, T_{\text{max}} = 0.884$	

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$	95 parameters
$wR(F^2) = 0.062$	H-atom parameters constrained
$S = 1.12$	$\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$
2317 reflections	$\Delta\rho_{\text{min}} = -0.37 \text{ e \AA}^{-3}$

All H atoms were clearly visible in difference maps and were refined using a riding model. The methyl H atoms were constrained to an ideal geometry, with C—H = 0.98 Å and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ , but

**Table 1**

Selected geometric parameters (Å, °).

Ti1—N1	1.8576 (16)	Ti1—Cl1	2.3371 (5)
Ti1—N2	2.2358 (16)	Ti1—Cl2	2.4414 (5)
Ti1—Cl3	2.2847 (5)	Ti1—Cl2 <sup>i</sup>	2.6759 (5)
N2—Ti1—Cl1	164.09 (4)	N1—Ti1—Cl2 <sup>i</sup>	174.37 (5)
Cl3—Ti1—Cl2	165.80 (2)		

Symmetry code: (i)  $-x + 1, -y + 1, -z + 1$ .

**Table 2**

Hydrogen-bond and short-contact geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N2-H2 \cdots Cl1^i$	0.93	2.40	3.3282 (16)	175
$C1-H1B \cdots Cl3^{ii}$	0.98	2.92	3.822 (2)	153
$C1-H1A \cdots Cl1^{iii}$	0.98	2.83	3.661 (2)	143

 Symmetry codes: (i)  $-x+1, -y+1, -z+1$ ; (ii)  $x, y+1, z$ ; (iii)  $-x, y+\frac{1}{2}, -z+\frac{1}{2}$ .

were allowed to rotate freely about the adjacent C–N bonds. Atom H2 bonded to N2 was placed in a geometrically idealized position and constrained to ride, with  $N-H = 0.93 \text{ \AA}$  and  $U_{iso}(H) = 1.2U_{eq}(N)$ .

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *PLATON* (Spek, 2009), *WinGX* (Farrugia, 1999) and *enCIFer* (Allen *et al.*, 2004).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3220). Services for accessing these data are described at the back of the journal.

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