PERGAMON

Available online at www.sciencedirect.com
SCIENCE DIRECT®

Polyhedron 22 (2003) 2731–2737

POLYHEDRON

www.elsevier.com/locate/poly

Tantalum chloride species incorporating anionic and cationic guanidine components

Delia B. Soria [1], Joanna Grundy, Martyn P. Coles *, Peter B. Hitchcock

Department of Chemistry, University of Sussex, Falmer, Brighton BN1 9QJ, UK

Received 4 April 2003; accepted 27 May 2003

Abstract

Attempted preparation of tantalum complexes incorporating the anionic guanidinate ligand derived from 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine (hppH) are reported. Reaction of (hpp)$SiMe_3$ and $TaCl_5$ in a 1:1 ratio gave the bis-guanidinate compound rather than the expected mono-ligand species. Reaction of 2 equiv. of (hpp)$SiMe_3$ or in situ generated [hpp]Li with $TaCl_5$ afforded a solid which analysed correctly for the compound $(hpp)_2TaCl_3$. X-ray structural analysis of the crystallised product identified the coordination isomer $[Ta(hpp)_4][TaCl_6]$, with a distorted dodecahedral cation and a regular octahedral anion. During the course of this study, two closely related hydrolysis products, $[(hppH_2)]_2[\{TaCl_6\}\{Cl\}]$ and $[(hppH_2)]_3[\{TaCl_6\}_2\{Cl\}]\cdot MeCN$ were isolated and structurally characterised, each containing $[hppH_2]^+$ cations and $[Cl]^-$ and $[TaCl_6]^-$ anions in extended arrays, linked by intermolecular hydrogen bonds.

Keywords: Tantalum; Bicyclic guanidinate; Intermolecular hydrogen bonds; Coordination isomer; Dodecahedral geometry

1. Introduction

Amidinate anions, $[RC\{NR'\}_2]^-$, have been extensively used as a supporting ligand in a large range of coordination compounds that extend across the elements of the periodic table [1]. In particular, the benzamidinate ligand ($R = Ph$ and $R' = SiMe_3$) has found application in this field due to its facile synthesis from the reaction between benzonitrile and lithium bis(trimethylsilyl)amide and the ease of derivatisation at the phenyl substituent of the central carbon atom [2]. Extension to closely related guanidinates ($R = NR'_2$) has allowed further developments in the coordination chemistry of this type of ligand [3], the principle difference being the potential for delocalisation of the amide lone pair into the core of the ligand, contributing an additional 'zwitterionic' resonance form to the overall bonding situation (**I**, Fig. 1). This has been exploited in the synthesis of early transition metal complexes in high oxidation states, where the increased donation of electron density is predicted to stabilise electron deficient metal centres.

It was found that the nature of the nitrogen substituents within the guanidinate anion strongly affected the extent to which resonance form **I** was able to contribute to the bonding, primarily as a result of steric interactions preventing the parallel alignment of the p-orbital of the central sp^2-carbon atom and the N_{amide} lone-pair necessary for delocalisation of electron density [4]. A method by which ourselves [5], and others [6], have maximised this effect is to employ a bicyclic guanidinate framework based on the neutral 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine (hppH, Fig. 2), where the $-(CH_2)_3-$ alkyl chains constrain the molecule in the necessary configuration for the promotion of orbital overlap.

The use of guanidinates, $[\{R'_2N\}C\{NR'\}_2]^-$, as ligands in Group 5 chemistry has not been as straightforward as with other groups in the periodic table. Studies have demonstrated that a number of established

---

* Corresponding author. Tel.: +44-1273-877-339; fax: +44-1273-677-196.

E-mail address: m.p.coles@sussex.ac.uk (M.P. Coles).

[1] Member of research Career of CONICET, Consejo Nacional de Investigaciones Científicas y Técnicas, on leave from CEQUINOR, Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, C.C. 962, 1900 La Plata, R. Argentina.

doi:10.1016/S0277-5387(03)00364-4

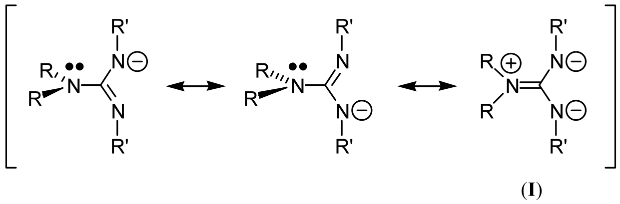

Fig. 1. Resonance structures for the guanidinate anion, where **I** = the ‘zwitterionic’ component.

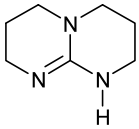

Fig. 2. 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine (hppH).

procedures for the synthesis of metal guanidinate compounds are not always viable routes to compounds of the heavier Group 5 metals. For example, protonolysis of $M(NMe_2)_5$ [M = Ta, Nb] with tricyclohexyl- or triisopropylguanidine affords complexes incorporating the *dianionic* ligand, $[(RN=)C(NR)_2]^{2-}$ [7,8]. Attempts at hydrogen halide elimination from $TaCl_5$ with triisopropylguanidine afforded the complex $[Ta(\{H^iPrN\}C\{N^iPr\}_2)_2(N^iPr)Cl]$ which incorporates the desired monoanionic ligand, but also contains the imido group $[N^iPr]^{2-}$ as a result of degradation of the guanidine starting material [9]. A similar fragmentation was observed while attempting lithium halide elimination using in situ generated $Li[\{H^iPrN\}C\{N^iPr\}_2]$ [9], although the salt metathesis using $Li[\{(Me_3Si)_2N\}C\{NCy\}_2]$ and $TaCl_5$ or $Ta(NEt_2)_2Cl_3$ proceed smoothly, highlighting the sensitivity of the reaction to the substituents on the ligand precursor. We believed that the $[hpp]^-$ anion would provide a robust framework that would be unlikely to fragment and report here our preliminary findings on the synthesis of tantalum complexes incorporating this ligand.

2. Experimental

All manipulations were carried out under dry nitrogen using standard Schlenk and cannula techniques, or in a conventional nitrogen-filled glovebox. Solvents were dried over appropriate drying agent and degassed prior to use. hppH (Fluka), ^{n}BuLi (2.5 M solution in hexanes, Acros) and $TaCl_5$ (Aldrich) were purchased from commercial sources and used as received. Chlorotrimethylsilane was distilled under a nitrogen atmosphere and stored over molecular sieves. Elemental analyses were performed by S. Boyer at London Metropolitan University.

2.1. *$[(hppH_2)]_2[\{TaCl_6\}\{Cl\}]$ (**1**)*

A solution of $(hpp)SiMe_3$ (0.76 g, 3.59 mmol) in dichloromethane (approximately 30 ml) was added to a slurry of tantalum(V) chloride (1.28 g, 3.59 mmol) in toluene (approximately 30 ml) at −78 °C, resulting in the immediate formation of a red solution and an orange precipitate. The mixture was allowed to warm to ambient temperature and stirred for 20 h. The volatile components were removed in vacuo and an attempt at extraction of the product was made using CH_2Cl_2, affording a red solution. No product was isolated from dichloromethane and crystallisation was attempted from THF at −30 °C. A small number of colourless crystals of **1** were recovered from the reaction mixture and analysed by X-ray crystallography. No other pure product was obtained.

2.2. *$[(hppH_2)]_3[\{TaCl_6\}_2\{Cl\}]\cdot MeCN$ (**2**)*

The reaction was repeated as outlined above using the same quantities of material. Attempted crystallisation of the crude material from MeCN afforded a small number of colourless crystals of **2** which were analysed by X-ray crystallography. No other pure product was obtained.

2.3. *$Ta(hpp)_2Cl_3$ (**3**)/$[Ta(hpp)_4][TaCl_6]$ (**4**)*

^{n}BuLi (1.6 ml, 3.59 mmol) was added to a solution of hppH (0.50 g, 3.59 mmol) in THF (approximately 30 ml) at 0 °C and the solution was allowed to warm to room temperature (r.t.) and stirred for 1 h. The volatiles were removed and the resultant white solid was dissolved in toluene and added to a suspension of tantalum(V) chloride (0.68 g, 1.79 mmol) in toluene (approximately 30 ml) at −78 °C, resulting in the formation of an orange precipitate. The mixture was allowed to warm to r.t. and stirred for 20 h. The volatiles were removed in vacuo and the crude solid was analysed by mass spec indicating formation of the bis-ligand product $Ta(hpp)_2Cl_3$ (**3**). Crystallisation by layering a concentrated solution of the solid in dichloromethane with hexane at r.t. resulted in isolation of orange crystals of $[Ta(hpp)_4][TaCl_6]$ (**4**). Yield: 0.27 g, 27%.

Mass Spec. (EI^+, *m/z*): 562 $[M]^+$, and 527 $[M-Cl]^+$ (where $M = Ta(hpp)_2Cl_3$). *Anal.* Calc. for $C_{14}H_{24}Cl_3N_6Ta$: C, 29.93; H, 4.29; N, 14.91. Found: C, 29.64; H, 4.19; N, 14.69%.

3. Crystallography

Details of the crystal data, intensity collection and refinement for complexes **1**, **2** and **4** are listed in Table 1. Crystals were covered in oil and suitable single crystals were selected under a microscope and mounted on a

Table 1
Crystal structure and refinement data for **1**, **2** and **4**

	1	**2**	**4**
Formula	$C_{14}H_{28}Cl_7N_6Ta$	$C_{23}H_{45}Cl_{13}N_{10}Ta_2$	$C_{28}H_{48}Cl_6N_{12}Ta_2$
Formula weight	709.52	1284.44	1127.38
Temperature (K)	173(2)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	tetragonal	monoclinic	tetragonal
Space group	$P4/n$ (No. 85)	$P2_1$ (No. 4)	$P4/n$ (No. 85)
a (Å)	13.3502(3)	8.0314(2)	14.2101(2)
b (Å)	13.3502(3)	13.8840(4)	14.2101(2)
c (Å)	8.0840(2)	19.4855(4)	9.5144(2)
β (°)	90	95.512(2)	90
V (Å^3)	1440.79(6)	2162.74(9)	1921.21(6)
Z	2	2	2
D_{calc} (Mg m^{-3})	1.64	1.97	1.95
Crystal size (mm)	0.10 × 0.02 × 0.02	0.30 × 0.10 × 0.10	0.40 × 0.05 × 0.02
Absorption coefficient (mm^{-1})	4.48	5.89	6.15
θ Range for data collection (°)	3.96–22.98	3.75–23.05	3.86–27.88
Reflections collected	10 907	17 986	17 230
Independent reflections	1004 [$R_{int} = 0.067$]	5930 [$R_{int} = 0.090$]	2304 [$R_{int} = 0.056$]
Reflections with $I > 2\sigma(I)$	950	5471	2031
Data/restraints/parameters	1004/6/41	5930/0/432	2304/0/111
Goodness-of-fit on F^2	1.094	1.039	1.087
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.073$, $wR_2 = 0.194$	$R_1 = 0.047$, $wR_2 = 0.112$	$R_1 = 0.029$, $wR_2 = 0.056$
R indices (all data)	$R_1 = 0.077$, $wR_2 = 0.198$	$R_1 = 0.052$, $wR_2 = 0.115$	$R_1 = 0.036$, $wR_2 = 0.059$
Largest difference peak and hole (e Å^{-3})	3.146 and −1.238	1.86 and −1.84 (close to Ta)	1.57 and −1.48 (close to Ta)

Kappa CCD diffractometer. The structures were refined with SHELXL-97 [10]. Additional features of note are described below.

3.1. *[(hppH$_2$)]$_2$[{TaCl$_6$}{Cl}]* (*1*)

The $[TaCl_6]^-$ anion is on a site of symmetry 4, and is well defined. The $[hppH_2]^+$ cations are disordered across inversion centres and have unresolved C/N overlap; they were refined with distance constraints (SADI). There is residual density near the cation atoms and also near an isolated site of bar-4 symmetry. The latter density probably representing very disordered unidentified solvate.

3.2. *[(hppH$_2$)]$_3$[{TaCl$_6$}$_2${Cl}]·MeCN* (*2*)

Atoms C(3) and C(7) were disordered (occupancies: *a* 0.46, *b* 0.54, *c* 0.59, *d* 0.41). Hydrogen atoms for the MeCN solvate molecule could not be located.

3.3. *[Ta(hpp)$_4$][TaCl$_6$]* (*4*)

The $[Ta(hpp)_4]^+$ cation lies on a site of bar-4 symmetry. The $[TaCl_6]^-$ anion lies on a site of 4 symmetry.

4. Results and discussion

Different synthetic methodologies have been investigated for the introduction of the $[hpp]^-$ anion at a tantalum centre, which have met with limited success. Initial attempts focused on reactions involving silylated-hpp with tantalum pentachloride, where it was anticipated that reaction would proceed by elimination of Me_3SiCl as observed in the synthesis of the titanium(IV) complex, $[(hpp)TiCl_3]_2$ [5]. The ligand precursor, hpp(SiMe$_3$), was synthesised by quenching the in situ generated lithium salt with Me_3SiCl, and reacted without further purification [11].

The 1:1 reaction between hpp(SiMe$_3$) and $TaCl_5$ in CH_2CL_2 generated an immediate red coloured solution upon mixing at −78 °C, suggesting a rapid reaction was occurring at low temperature. A molecular ion fragment corresponding to $[(hpp)_2TaCl_2]^+$, arising from loss of a chloride ion from the *bis-ligand* species, was identified by mass spectral analysis of the crude solid material obtained by removal of the volatile components. This is in contrast to formation of the mono-ligand species predicted from the stoichiometry of the reaction. All attempts at crystallisation (CH_2Cl_2, toluene, Et_2O) failed to separate a pure product from the mixture. However, a small quantity of colourless crystals were isolated from a THF solution, corresponding to the product $[(hppH_2)]_2[\{TaCl_6\}\{Cl\}]$ (**1**), presumably generated as a result of the introduction of adventitious moisture to the reaction and generation of HCl through reaction with $TaCl_5$. The high moisture sensitivity of the compounds formed in this reaction and propensity to form ionic species was further high-lighted in a separate reaction carried out in CH_2Cl_2 at −78 °C, with attempted crystallisation of the product from MeCN. This afforded colourless crystals of the closely related hydrolysis product, $[(\mathrm{hppH}_2)]_3[\{TaCl_6\}_2\{Cl\}]\cdot\mathrm{MeCN}$ (**2**). Neither compound was isolated in sufficient quantity to obtain full characterising data; however, X-ray structural analysis of **1** and **2** were performed to help understand the course of the reactivity observed during these reactions and the nature of the products formed. Key features of the molecular structures of **1** and **2** are illustrated in Figs. 3–5. Crystal data is summarised in Table 1 and selected bond lengths and angles for **2** are collected in Tables 2 and 3.

Disorder of the $[\mathrm{hppH}_2]^+$ cation about an inversion centre in **1** causes unresolved overlap for the position of the carbon and nitrogen atoms, and hence the bond lengths and angles within the cationic component are unreliable. Solution of the structure does however accurately show the position of the atoms within the anionic components, which are arranged in alternating $[TaCl_6]^-$ and $[Cl]^-$ rows repeated in an $\cdots$**A**–**B**–**A**$\cdots$ pattern, where **A** = $\cdots\{Cl\}\{TaCl_6\}\{Cl\}\{TaCl_6\}\cdots$ and **B** = $\cdots\{TaCl_6\}\{Cl\}\{TaCl_6\}\{Cl\}\cdots$ (Fig. 3). The $[\mathrm{hppH}_2]^+$ ions interdigitate in this anionic framework, with an indication of intermolecular stabilisation by N*H*$\cdots[Cl]^-$ interactions.

X-ray data for **2** reveals an unit cell comprised of three $[\mathrm{hppH}_2]^+$ cations, two $[TaCl_6]^-$ and a $[Cl]^-$ anion, with a molecule of acetonitrile solvate (Fig. 4).

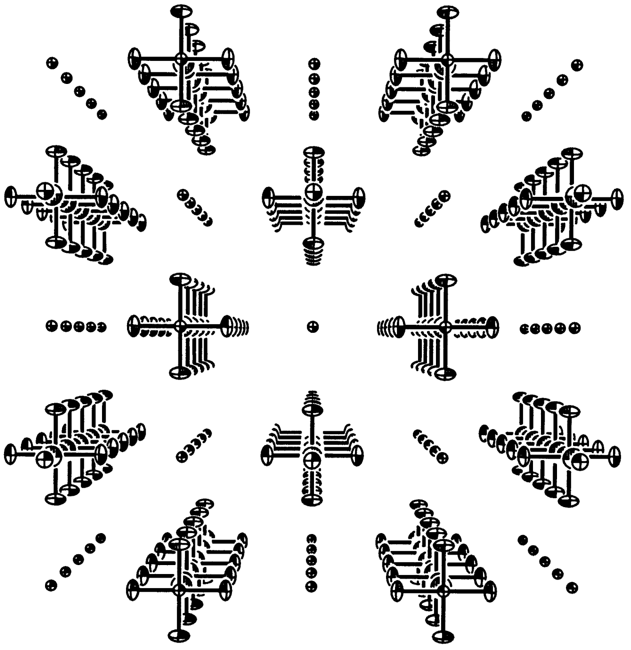

Fig. 3. Arrangement of anionic components within **1**.

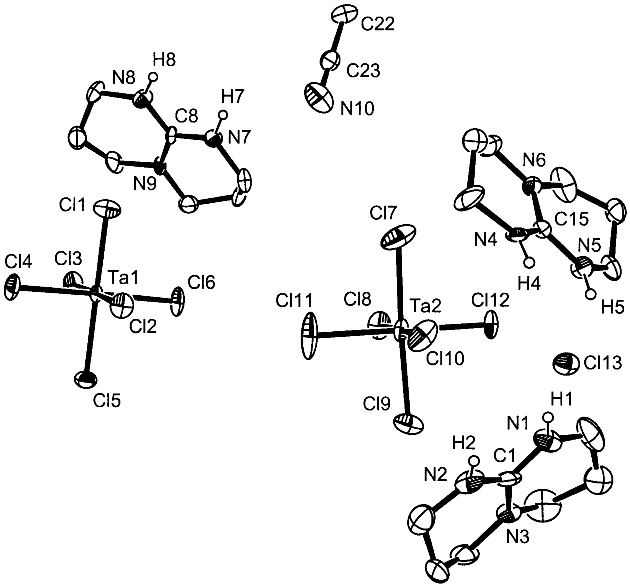

Fig. 4. Asymmetric unit for $[(\mathrm{hppH}_2)]_3[\{TaCl_6\}_2\{Cl\}]\cdot\mathrm{MeCN}$ (**2**), with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms, except N*H* of the cation, omitted for clarity.

In contrast to **1**, the X-ray data indicated well-defined cations with no unresolved disorder in the carbon/nitrogen positions, allowing location of the hydrogen atoms. The C–N distances within the core of the cation are very similar [1.29(2)–1.36(2) Å], suggesting a delocalisation of the positive charge across the CN_3 moiety, observed in other structurally characterised examples of the $[\mathrm{hppH}_2]^+$ cation [12]. The anions in the case of **2** are arranged in an $\cdots$**A**–**B**–**C**–**A**–**B**–**C**$\cdots$ pattern, where **A** = $\cdots\{TaCl_6\}\{TaCl_6\}\{TaCl_6\}\{TaCl_6\}\cdots$, **B** = $\cdots\{Cl\}\{TaCl_6\}\{Cl\}\{TaCl_6\}\cdots$ and **C** = $\cdots\{TaCl_6\}\{Cl\}\{TaCl_6\}\{Cl\}\cdots$ (Fig. 5a). Location of the N*H* atoms shows that intermolecular hydrogen bonding is present between the $[\mathrm{hppH}_2]^+$ cation and the chloride anion (strongest interactions illustrated in Fig. 5b), with distances and angles as listed in Table 3. There are no interactions present between the cations and the $[TaCl_6]^-$ anions.

In view of the fact that the mass spectral data indicated that two $[\mathrm{hpp}]^-$ ligands were coordinated to the tantalum, the bis(ligand) complex was targeted. The reaction between 2 equiv. of the in situ generated lithium salt of hppH with $TaCl_5$ in toluene afforded, after work-up, an orange solid which analysed correctly for the compound $(\mathrm{hpp})_2TaCl_3$ (**3**) [13]. Mass spectral data was in agreement with this formula, showing peaks at 562 $[M]^+$, and 527 $[M-Cl]^+$. The ^1H NMR spectrum ($CDCl_3$) was however more complicated than expected for the molecular species **3**, showing overlapping multiplets in the range 4.1–3.2 and at 2.0 ppm. The ^{13}C NMR experiment most clearly illustrated the presence of different environments for the $[\mathrm{hpp}]^-$ anion at low field, corresponding to the $C\mathrm{N}_3$ carbon atom of the

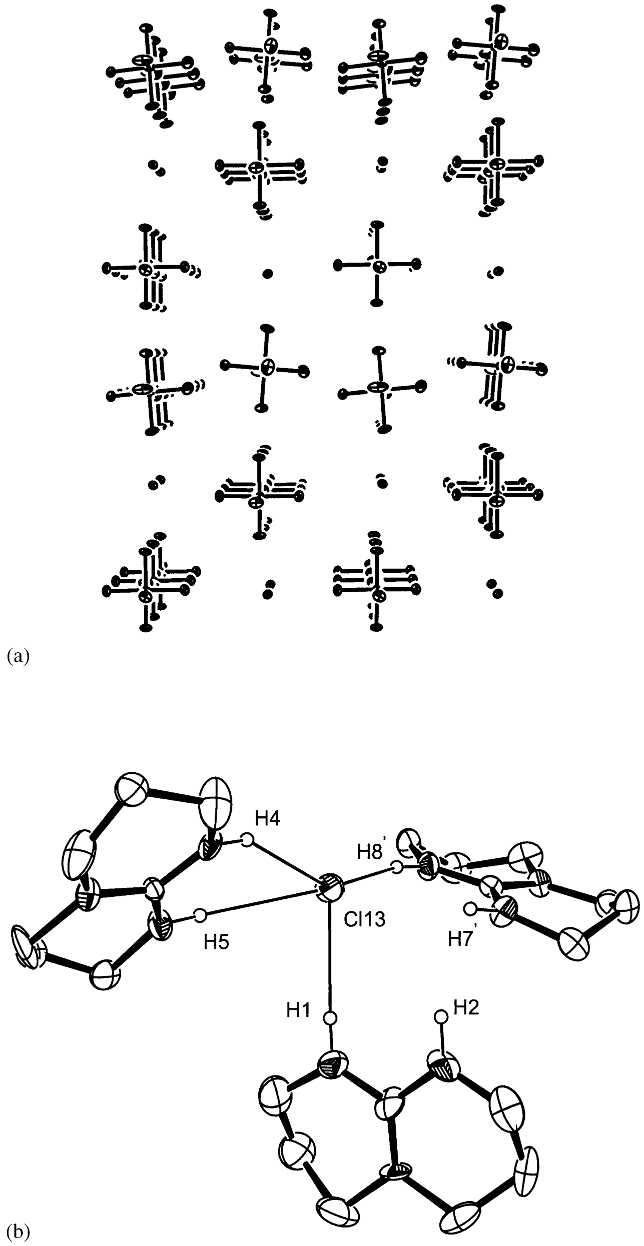

Fig. 5. (a) Arrangement of anionic components within **2**. (**b**) Interaction between $[(hppH_2)]_2$ and $[Cl]^-$ in **2**. Hydrogen atoms, except N*H* of the cation, omitted for clarity.

ligand, where signals were observed at 163.7 and 161.0 ppm. This suggests the presence of a mixture of compounds in the crude material, as only a single environment is expected for guanidinate anion in the bis(ligand) product **3**. Recrystallisation of the crude solid by layering a saturated CH_2Cl_2 solution with hexane afforded orange crystals that were subjected to X-ray diffraction analysis. The molecular structure revealed that rather than the molecular species **3**, the crystals consisted of the coordination isomer, $[Ta(hpp)_4]^+$ $[TaCl_6]^-$ (**4**). Crystal data is summarised in Table 1 and selected bond lengths and angles are collected in Table 4.

Table 2
Selected bond lengths (Å) and angles (°) for $[(hppH_2)]_3[\{TaCl_6\}_2\{Cl\}]\cdot MeCN$ (**2**)

Bond lengths			
C(1)–N(1)	1.33(2)	C(1)–N(2)	1.37(2)
C(1)–N(3)	1.29(2)	C(8)–N(7)	1.335(17)
C(8)–N(8)	1.332(18)	C(8)–N(9)	1.301(19)
C(15)–N(4)	1.31(2)	C(15)–N(5)	1.36(2)
C(15)–N(6)	1.33(2)		
Bond angles			
N(1)–C(1)–N(2)	116.9(16)	N(1)–C(1)–N(3)	119.4(18)
N(2)–C(1)–N(3)	123.6(16)	N(7)–C(8)–N(8)	117.6(12)
N(7)–C(8)–N(9)	120.6(13)	N(8)–C(8)–N(9)	121.7(12)
N(4)–C(15)–N(5)	116.6(12)	N(4)–C(15)–N(6)	122.2(13)
N(5)–C(15)–N(6)	121.0(14)		

Table 3
Bond lengths (Å) and angles (°) for intramolecular N*H*···$[Cl]^-$ interactions in **2**

Bond lengths			
H(1)–Cl(13)	2.377	H(2)–Cl(13)	3.246
H(4)–Cl(13)	2.499	H(5)–Cl(13)	2.471
H(7’)–Cl(13)	2.718	H(8’)–Cl(13)	2.389
Bond angles			
N(1)–H(1)–Cl(13)	167.49	N(2)–H(2)–Cl(13)	136.78
N(4)–H(4)–Cl(13)	152.01	N(5)–H(5)–Cl(13)	153.04
N(7)–H(7)–Cl(13)	147.50	N(8)–H(8)–Cl(13)	165.03

Compound **4** consists of a well-separated ion pair, with an eight coordinate tantalum centre subtended by four chelating guanidinate ligands in the cation and a regular octahedral $[TaCl_6]^-$ anion (Fig. 6). A compound containing $[Ta(hpp)_4]^+$ was recently reported by Cotton et al. [14], where the anionic component consisted of $[Ta(CO)_6]^-$ with tantalum in the (−1) oxidation state. In compound **4** however, both the cationic and anionic tantalum centres are present in the (+5) oxidation state. The geometry of the metal in the cation is best described as a distorted dodecahedron (Fig. 7), with approximate D_{2d} symmetry. Comparing

Table 4
Selected bond lengths (Å) and angles (°) for $[Ta(hpp)_4][TaCl_6]$ (**4**)

Bond lengths			
Ta(2)–N(1)	2.128(4)	Ta(2)–N(3)	2.219(3)
C(1)–N(1)	1.344(5)	C(1)–N(2)	1.339(5)
C(1)–N(3)	1.330(5)		
Bond angles			
N(1)–Ta(2)–N(3)	60.34(12)	N(1)–Ta(2)–N(1′)	157.20(17)
N(1′)–Ta(2)–N(3)	142.45(12)	N(1″)–Ta(2)–N(3)	80.01(13)
N(1‴)–Ta(2)–N(3)	82.85(13)	N(3)–Ta(2)–N(3‴)	124.61(10)
N(1)–C(1)–N(2)	124.5(4)	N(1)–C(1)–N(3)	109.7(4)
N(2)–C(1)–N(3)	125.8(4)		

Symmetry transformations used to generate equivalent atoms: $''''$ $-x+1/2, -y+1/2, z$; $'$ $-x+1/2, -y-1/2, z$; $''$ $y+1/2, -x, -z+1$; $'''$ $-y, x-1/2, -z+1$.

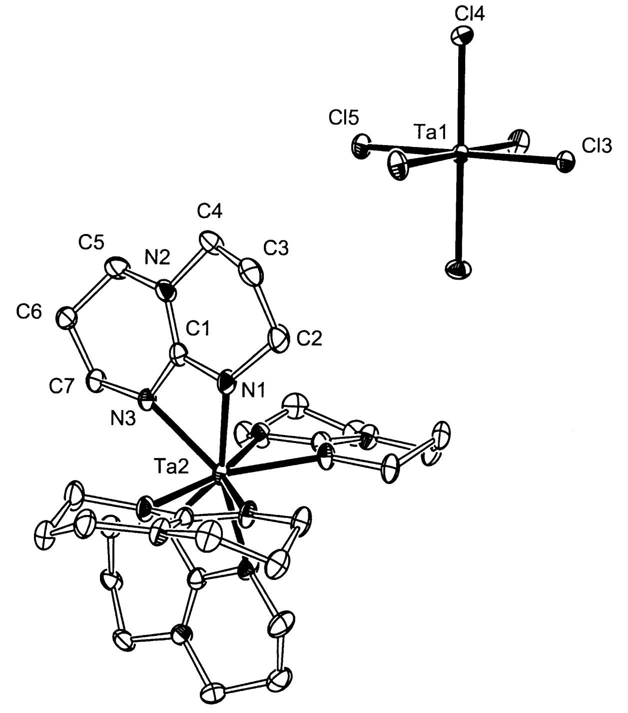

Fig. 6. Molecular structure of [Ta(hpp)$_4$][TaCl$_6$] (**4**), with thermal ellispoids drawn at the 30% probability level. Hydrogen atoms omitted for clarity.

the twist angle (ϕ) between intersecting trapezoids that are defined in **4** by the positions of the nitrogen atoms N(1), N(3), N(3′), N(1′) and N(1″), N(3″), N(3‴), N(1‴) [15], we observe a slightly greater distortion from ideal dodecahedral geometry (where $\phi = 0°$) in **4** ($\phi = 2.2°$) than in the previous example of this cation ($\phi = 1.4$, 1.6°). The Ta–N distances of **4** [2.128(4) and 2.219(3) Å] are in the range previously reported for this cation [2.08–2.25 Å] and compare favourably with other tantalum(V) guanidinate complexes [8,16]. Delocalisation of the negative charge through the CN$_3$ moiety is evident from the carbon–nitrogen bond lengths [1.330(5)–1.344(5) Å], which are similar to the values observed in related [hpp]$^-$ complexes of titanium [1.338(4)–1.347(4) Å] [5], and tin [1.302(12)–1.373(11) Å] [6].

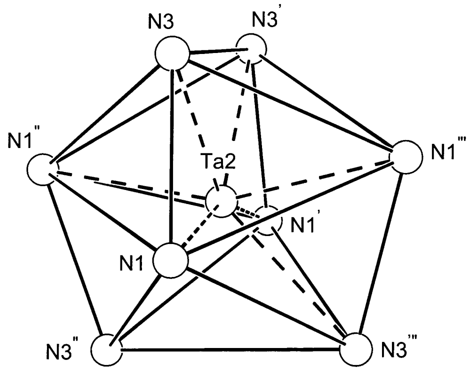

Fig. 7. Distorted dodecahredral arrangement of nitrogen atoms around the tantalum centre in the [Ta(hpp)$_4$]$^+$ cation.

In summary, mass spectral evidence indicates formation of the bis- rather than the mono-ligand compound from the stoichiometric reaction between hpp(SiMe$_3$) and TaCl$_5$. Attempted purification by crystallisation failed to give the desired product, and inadvertent hydrolysis afforded ionic complexes comprised of [hppH$_2$]$^+$ cations and [Cl]$^-$ and [TaCl$_6$]$^-$ anions in extended arrays linked by intermolecular hydrogen bonds. The reaction of 2 equiv. of the in situ generated lithium salt with TaCl$_6$ affords a mixture of (hpp)$_2$TaCl$_3$ (**3**), identified in the mass spectrum, and the coordination isomer [Ta(hpp)$_4$][TaCl$_6$] (**4**). The molecular structure of **4** was deduced from X-ray diffraction data, consisting of well-separated ion pairs with a distorted dodecahedral cation and a regular octahedral anion. Further work on the synthesis of Group 5 metal complexes incorporating the [hpp]$^-$ anion is in progress and will be reported in due course.

5. Crystal structure data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 207109, 207110 and 207111 for compounds **1**, **2** and **4**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

DBS wishes to thank CONICET (Consejo Nacional de Investigaciones Científicas y Técnicas) of Argentina for supporting a one-year collaborative project at the University of Sussex. We also wish to thank the University of Sussex for additional financial support, and acknowledge the use of the EPSRC's Chemical Database Service at Daresbury.

References

[1] J. Barker, M. Kilner, Coord. Chem. Rev. 133 (1994) 219.
[2] F.T. Edelmann, Coord. Chem. Rev. 137 (1994) 403.
[3] P.J. Bailey, S. Pace, Coord. Chem. Rev. 214 (2001) 91.
[4] S.L. Aeilts, M.P. Coles, D.C. Swenson, R.F. Jordan, Organometallics 17 (1998) 3265.
[5] M.P. Coles, P.B. Hitchcock, J. Chem. Soc., Dalton Trans. (2001) 1169.
[6] S.R. Foley, G.P.A. Yap, D.S. Richeson, Polyhedron 21 (2002) 619.

[7] M.K.T. Tin, G.P.A. Yap, D.S. Richeson, Inorg. Chem. 37 (1998) 6728.

[8] (a) M.K.T. Tin, N. Thirupathi, G.P.A. Yap, D.S. Richeson, J. Chem. Soc., Dalton Trans. (1999) 2947;
(b) N. Thirupathi, G.P.A. Yap, D.S. Richeson, Organometallics 19 (2000) 2573.

[9] N. Thirupathi, G.P.A. Yap, D.S. Richeson, Chem. Commun. (1999) 2483.

[10] G.M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, 1997.

[11] D. Kummer, S.H.A. Halim, W. Kuhs, G. Mattern, J. Organomet. Chem. 446 (1993) 51.

[12] (a) I. Díaz, V. Fernández, J.L. Martínez, L. Beyer, A. Pilz, U. Müller, Z. Naturforsch., Teil B 53b (1998) 933;
(b) A. Gleich, F.P. Schmidtchen, P. Mikulcik, G. Müller, J. Chem. Soc., Chem. Commun. (1990) 55;
(c) S.W. Ng, P. Naumov, S. Chantrapromma, S.S.S. Raj, H.-F. Fun, A.R. Ibrahim, G. Wojciechowski, B. Brzezinski, J. Mol. Struct. 569 (2001) 139;
(d) A. Meetsma, E. van Aken, H. Wynberg, Acta Crystallogr., Sect. C 48 (1992) 1874;
(e) F.A. Cotton, D.J. Timmons, Polyhedron 17 (1998) 179;
(f) K. Wijaya, O. Moers, A. Blaschette, P.G. Jones, Z. Naturforsch., Teil b 54 (1999) 1441;
(g) E. van Aken, H. Wynberg, F. van Bolhuis, J. Chem. Soc., Chem. Commun. (1992) 629;
(h) G. Müller, J. Riede, F.P. Schmidtchen, Angew. Chem., Int. Ed. Engl. 27 (1988) 1516;
(i) P.J. Murphy, H.L. Williams, D.E. Hibbs, M.B. Hursthouse, K.M. Abdul Malik, Chem. Commun. (1996) 445;
(j) P.J. Murphy, H.L. Williams, M.B. Hursthouse, K.M. Abdul Malik, J. Chem. Soc., Chem. Commun. (1994) 119;
(k) P.J. Murphy, H.L. Williams, D.E. Hibbs, M.B. Hursthouse, K.M. Abdul Malik, Tetrahedron 52 (1996) 8315;
(l) W. Peschke, P. Schiessl, F.P. Schmidtchen, P. Bissinger, A. Schier, J. Org. Chem. 60 (1995) 1039;
(m) E. van Aken, H. Wynberg, F. van Bolhuis, Acta Chem. Scand. 47 (1993) 122;
(n) M. Haj-Zaroubi, N.W. Mitzel, F.P. Schmidtchen, Angew. Chem., Int. Ed. 41 (2002) 104.

[13] The same product was obtained from the reaction of 2 equiv. of the silylated-guandine with $TaCl_5$.

[14] F.A. Cotton, C.A. Murillo, X. Wang, Inorg. Chim. Acta 300 (2000) 1.

[15] E.L. Muetterties, L.J. Guggenberger, J. Am. Chem. Soc. 96 (1974) 1748.

[16] M.K.T. Tin, G.P.A. Yap, D.S. Richeson, Inorg. Chem. 38 (1999) 998.