A new double-cube nitride complex containing titanium and potassium

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The reaction of the imide–nitride complex [{Ti(η^5-C$_5$Me$_5$)-(μ-NH)}$_3$(μ_3-N)] with potassium iodide in pyridine at room temperature affords the adduct di-μ-iodido-1:1′$\kappa^4 I$-bis{tri-μ_3-imido-1:2:3$\kappa^3 N$;1:2:4$\kappa^3 N$;1:3:4$\kappa^3 N$-μ_3-nitrido-2:3:4$\kappa^3 N$-tris-[2,3,4(η^5)-pentamethylcyclopentadienyl](pyridine-1κN)-*tetrahedro*-potassiumtrititanium(IV)}, [K$_2$Ti$_6$(C$_{10}$H$_{15}$)$_6$I$_2$N$_2$(NH)$_6$-(C$_5$H$_5$N)$_2$] or [(C$_5$H$_5$N)(μ-I)K{(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}]$_2$. The crystal structure contains two [KTi$_3$N$_4$] cube-type units held together by two bridging I atoms. There is a centre of inversion located in the middle of this unprecedented discrete K$_2$I$_2$ unit. The geometry around K is best described as distorted trigonal prismatic, with three imide groups, two bridging I atoms and one pyridine ligand.

Comment

Polynuclear transition metal nitride complexes exhibit singular structures. These compounds might be of interest as building blocks in the synthesis of metal nitride materials (Oyama, 1996) or as intermediates in dinitrogen fixation and activation processes (see, for example, Fryzuk & Johnson, 2000; Himmel & Reiher, 2006; Kozak & Mountford, 2004). However, a review of the literature reveals the lack of a systematic synthetic method for the preparation of these polynuclear complexes (Abarca *et al.*, 2003; Dehnicke & Strähle, 1992). In this context, the titanium imide–nitride compound [{Ti(η^5-C$_5$Me$_5$)(μ-NH)}$_3$(μ_3-N)], (I) (Abarca *et al.*, 2000; Roesky *et al.*, 1989), is able to incorporate metal centres, and we have extensively investigated the rational synthesis of a series of heterometallic nitride complexes with cube-type structures. In particular, ligand (I) entraps alkali metal halides to give stable molecular adducts of the type [XM\{(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] (M = Li and X = Br, I; M = Na and X = I) (García-Castro *et al.*, 2005). However, the analogous treatment of (I) with amides of group 1 elements affords edge-linked [M(μ_4-N)(μ_3-NH)$_2$\{Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}]$_2$ or corner-shared [M(μ_3-N)(μ_3-NH)$_5$\{Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}$_2$]

double-cube complexes, depending on the reagent ratio of (I) and the amide (*viz.* 1:1 or 2:1; Martín *et al.*, 2004).

The reaction of these edge-linked double-cube derivatives with metal halides has been used to prepare new heterometallic nitride complexes (García-Castro *et al.*, 2001). Over the course of these investigations, we attempted to synthesize a zinc double-cube compound by treatment of the potassium derivative with ZnI$_2$ in pyridine. After three days at room temperature, yellow crystals of [(C$_5$H$_5$N)(μ-I)K{(μ_3-NH)$_3$-Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}]$_2$, (II), were obtained in 27% yield. These crystals had a hexagonal prism shape and were air sensitive. Complex (II) was characterized by X-ray crystal structure determination, IR spectroscopy and CHN microanalysis. Compound (II) is not soluble in pyridine-d_5, and decomposes in benzene-d_6 or chloroform-d_1 to afford the imide–nitride ligand (I), KI and pyridine, precluding its characterization by NMR spectroscopy. Furthermore, a rational synthesis by reaction of (I) with KI in pyridine gave compound (II) in 73% yield.

[Ti] = Ti(η^5-C$_5$Me$_5$)

(I)

(II)

The structure of (II) (Fig. 1) contains two [KTi$_3$N$_4$] cube-type units linked by two bridging I atoms and related by a centre of inversion located in the middle of the planar K$_2$I$_2$ unit. The distance between the two K atoms is 4.629 (2) Å, clearly shorter than the K···K lengths found for [K$_6$I$_4$(dmp)$_8$]$^{2+}$ [dmp is 2,9-dimethyl-1,10-phenanthroline; 4.960 (1) and 5.010 (1) Å], in which three K$_2$I$_2$ fragments are held together (Buttery *et al.*, 2006). This phenanthroline derivative is the only compound in the Cambridge Structural Database (CSD, Version 5.32; Allen, 2002) containing I-bridged K$_2$I$_2$ units. Complexes with this type of unit, *viz.* M_2I$_2$, are common for the lighter alkali metal iodide complexes (see, for example, Barrett *et al.*, 2006; Fei *et al.*, 2003; Herberich *et al.*, 2005), but, to the best of our knowledge, there are no structural examples of compounds with discrete K$_2$I$_2$ units. The K—I bond lengths in (II) [3.553 (1) and 3.605 (1) Å] are slightly longer than the values found for the phenanthroline complex [3.303 (1)–3.581 (1) Å]. The I—K—I^i and K—I—K^i angles [symmetry code: (i) $-x + 1$, $-y + 1$, $-z + 2$] in our discrete unit [99.39 (3) and 80.61 (3)°, respectively] are quite different to the values found for the polynuclear [K$_6$I$_4$(dmp)$_8$]$^{2+}$ cation described by Buttery *et al.* (2006) [I—K—I = 85.78 (3)–88.77 (3)° and K—I—K = 89.23 (3)–97.39 (3)°].

The geometry around the potassium centre of (II) is best described as distorted trigonal prismatic, with the three imide groups of (I), two bridging iodide ligands and one N atom of

Figure 1
A perspective view of the molecule of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $-x + 1, -y + 1, -z + 2$.]

the pyridine group occupying the six coordination positions. The K—N bond lengths [2.962 (3)–3.089 (3) Å] are similar to those found for potassium complexes containing the neutral tridentate ligand N,N,N',N'',N''-pentamethyldiethylenetriamine [2.838 (3)–3.066 (5) Å; Althaus *et al.*, 1999; Craig *et al.*, 1996; Fanjul *et al.*, 2007]. Additionally, the K—N bond distances for (II) are longer than those found for the corner-shared double-cube complex [K(μ_3-N)(μ_3-NH)$_5$\{Ti$_3$-(η^5-C$_5$Me$_5$)$_3$(μ_3-N)\}$_2$] [2.958 (2) Å; Martín *et al.*, 2004], which presents intracube N—K—N angles [average 62.0 (1)°] very similar to those in (II) [60.70 (9)–62.09 (9)°]. The N$_{imide}$—K—I and N$_{imide}$—K—N$_{pyridine}$ angles are in the range 74.18 (6)–138.2 (1)°, whereas the N$_{pyridine}$—K—I angles are 92.89 (9) and 124.17 (8)°. The K—N$_{pyridine}$ bond length [2.896 (4) Å] compares well with those found in other potassium complexes containing a pyridine ligand [2.776 (3)–2.926 (2) Å; see, for example, Boyle *et al.*, 2003].

The Ti—N1 and Ti—N$_{imide}$ distances in (II) [average 1.939 (4) and 1.946 (5) Å, respectively] are slightly longer than those determined for the free ligand [1.913 (8) and 1.929 (8) Å; Roesky *et al.*, 1989] and close to those found for the potassium corner-shared double cube [1.928 (2) and 1.932 (6) Å; Martín *et al.*, 2004]. The average N$_{imide}$—Ti—N$_{imide}$ angle [104.0 (1)°] is similar to that observed in a

potassium double cube [104.1 (1)°], whereas it is narrower than the same angle in the structure of (I) [107.5 (7)°]. The remainder of the parameters within the tridentate organometallic ligand are similar to those of these cited complexes.

Experimental

[\{Ti(η^5-C$_5$Me$_5$)(μ-NH)\}$_3$(μ_3-N)], (I), and [K(μ_4-N)(μ_3-NH)$_2$-\{Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)\}]$_2$ were prepared according to the methods of Abarca *et al.* (2000) and García-Castro *et al.* (2001), respectively. A pyridine solution (15 ml) of [K(μ_4-N)(μ_3-NH)$_2$\{Ti$_3$(η^5-C$_5$Me$_5$)$_3$-(μ_3-N)\}]$_2$ (0.20 g, 0.15 mmol) was carefully layered with a pyridine solution (5 ml) of ZnI$_2$ (0.049 g, 0.15 mmol; Aldrich). The system was allowed to equilibrate for 3 d to afford yellow crystals of [(C$_5$H$_5$N)-(μ-I)K\{(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)\}]$_2$, (II) (yield 0.070 g, 27%). The following rational method of synthesis may also be employed. A 100 ml Schlenk flask was charged with (I) (0.30 g, 0.49 mmol), KI (0.080 g, 0.48 mmol; 98%, Aldrich) and pyridine (20 ml). The reaction mixture was stirred at room temperature for 20 h. The resultant pale-yellow solid was isolated by filtration, washed with pyridine (5 ml) and vacuum dried for 3 h to give (II) (yield 0.30 g, 73%). IR (KBr, $\tilde{\nu}$, cm^{-1}): 3315 (*w*), 2907 (*m*), 2855 (*m*), 1602 (*w*), 1584 (*m*), 1484 (*w*), 1438 (*m*), 1376 (*m*), 1218 (*w*), 1147 (*w*), 1069 (*w*), 1029 (*m*), 992 (*w*), 758 (*vs*), 713 (*s*), 676 (*vs*), 661 (*vs*), 643 (*s*), 606 (*m*), 575 (*s*), 472 (*m*), 423 (*m*). Analysis calculated for C$_{70}$H$_{106}$I$_2$K$_2$N$_{10}$Ti$_6$: C 49.26, H 6.26, N 8.21%; found: C 49.62, H 6.56, N 8.13%.

Crystal data

[K$_2$Ti$_6$(C$_{10}$H$_{15}$)$_6$I$_2$N$_2$(NH)$_6$-(C$_5$H$_5$N)$_2$]	β = 93.46 (1)°
M_r = 1707.05	γ = 115.55 (1)°
Triclinic, $P\bar{1}$	V = 2053.8 (6) Å^3
a = 11.298 (2) Å	Z = 1
b = 11.346 (2) Å	Mo $K\alpha$ radiation
c = 18.391 (3) Å	μ = 1.45 mm^{-1}
α = 101.66 (1)°	T = 200 K
	0.32 × 0.29 × 0.23 mm

Data collection

Nonius KappaCCD area-detector diffractometer	34701 measured reflections
Absorption correction: multi-scan (Blessing, 1995)	9150 independent reflections
T_{min} = 0.594, T_{max} = 0.827	6034 reflections with $I > 2\sigma(I)$
	R_{int} = 0.045

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.119	
S = 0.98	
9150 reflections	$\Delta\rho_{max}$ = 1.10 e Å^{-3}
433 parameters	$\Delta\rho_{min}$ = -0.82 e Å^{-3}

H atoms bonded to C atoms were introduced at calculated positions and refined using a riding model, with C—H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C) for the methyl groups of the cyclopentadienyl rings, and with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C) for the pyridine ligand. The H atoms of the imide groups were found in a

Table 1
Selected geometric parameters (Å, °).

K1—N12	2.962 (3)	Ti2—N12	1.936 (3)
K1—N13	2.986 (3)	Ti2—N23	1.950 (3)
K1—N23	3.089 (3)	Ti3—N13	1.947 (3)
K1—N101	2.896 (4)	Ti3—N23	1.949 (3)
K1—I1	3.553 (1)	Ti1—N1	1.936 (3)
K1—I1^i	3.605 (1)	Ti2—N1	1.943 (3)
Ti1—N12	1.949 (3)	Ti3—N1	1.939 (3)
Ti1—N13	1.944 (3)		
N12—K1—N13	62.09 (9)	N1—Ti1—N12	85.8 (1)
N12—K1—N23	60.70 (9)	N1—Ti1—N13	86.4 (1)
N13—K1—N23	60.71 (9)	N1—Ti2—N12	86.0 (1)
N12—K1—I1	123.11 (6)	N1—Ti2—N23	85.9 (1)
N12—K1—I1^i	74.18 (6)	N1—Ti3—N13	86.3 (1)
N12—K1—N101	138.2 (1)	N1—Ti3—N23	86.0 (1)
N13—K1—I1	79.45 (7)	Ti1—N1—Ti2	94.0 (1)
N13—K1—I1^i	124.46 (7)	Ti1—N1—Ti3	93.7 (1)
N13—K1—N101	111.3 (1)	Ti2—N1—Ti3	94.1 (1)
N23—K1—I1	132.43 (7)	Ti1—N12—Ti2	93.8 (1)
N23—K1—I1^i	123.68 (6)	Ti1—N12—K1	95.2 (1)
N23—K1—N101	79.8 (1)	Ti2—N12—K1	98.3 (1)
N101—K1—I1	92.89 (9)	Ti1—N13—Ti3	93.2 (1)
N101—K1—I1^i	124.17 (8)	Ti1—N13—K1	94.5 (1)
I1—K1—I1^i	99.39 (3)	Ti3—N13—K1	97.9 (1)
K1—I1—K1^i	80.61 (3)	Ti2—N23—Ti3	93.6 (1)
N12—Ti1—N13	104.0 (1)	Ti2—N23—K1	94.0 (1)
N12—Ti2—N23	103.9 (1)	Ti3—N23—K1	94.6 (1)
N13—Ti3—N23	104.1 (1)		

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

difference Fourier map at the final stages of the refinement procedure and were refined freely.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DIRAX/LSQ* (Duisenberg, 1992); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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