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Dichloro(isopropylamido)bis(isopropylamine)(isopropylimido)tantalum(V), a monomeric Ta^V compound with imido, amido and amino moieties

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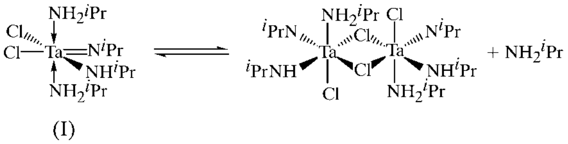
The title compound, $[Ta(C_3H_7N)(C_3H_8N)Cl_2(C_3H_9N)_2]$, is the first monomeric example of a metal complex that features imido, amido and amino moieties in the same molecule. The Ta atom has distorted octahedral coordination, with the imido moiety *trans* to chlorine and the pseudo-axial ligands bent away from the imido moiety. Principal dimensions include Ta=N = 1.763 (8) Å, Ta—N(H) = 1.964 (7) Å, and Ta—N(H$_2$) = 2.247 (7) and 2.262 (7) Å.

Comment

The synthesis of the title compound, $Ta(N^iPr)(NH^iPr)(NH_2{}^iPr)_2Cl_2$, (I), was first reported by Bates *et al.* (1985) and was originally proposed to be dimeric with the formula $[TaCl(\mu\text{-}Cl)(N^iPr)(NH^iPr)(NH_2{}^iPr)Cl_2]_2$ by analogy with the previously reported structure of dimeric $[TaCl(\mu\text{-}Cl)(N^tBu)(NH^tBu)(NH_2{}^tBu)Cl_2]_2$ (Jones *et al.*, 1984). Compound (I) was later studied by Jayaratne *et al.* (1996) who proposed a monomeric formulation based on ^{1}H and ^{13}C NMR spectroscopy data.



(I)

Our interest in this compound was sparked by our studies of imine metathesis by metal–imido complexes of the general formula $CpTa(=NR)Cl_2$ (Burland *et al.*, 2002). Our mechanistic work had suggested the possible involvement of metal–amido complexes in the reaction mechanism. We decided to survey metal–amido complexes previously reported in the literature in order to develop the tools necessary to help us identify possible intermediates in our reactions. We were immediately struck by the title compound, (I), as it contained all three nitrogen moieties that were of interest to us. A search of the Cambridge Structural Database (Allen, 2002) for metal complexes with imido, amido and amino groups yielded hits for only two complexes, both centrosymmetric dimers; these were the Ta complex reported by Jones *et al.* (1984) mentioned above (CSD refcode CEDTOU), and the isostructural vanadium complex (CSD refcode DAJCOG; Preuss *et al.*, 1985).

In the structure of the title imide/amide/amine complex, (I) (Fig. 1), the distinction between imide, amide and amine N atoms was clear from the Ta—N dimensions (Table 1) and also by the location of the amide and amine H atoms *via* difference maps. The imido Ta=N bond length of 1.763 (8) Å is typical for monomeric tantalum imides (Wigley, 1994), but long compared with the unusually short Ta=N bond length of 1.61 (3) Å reported for the dimeric ^{t}Bu analog by Jones *et al.* (1984). The nearly linear C—N—Ta bond angle [173.8 (8)°] is consistent with a high degree of π-bonding with the metal.

The Ta—N(H) bond length [1.964 (7) Å] of the amido moiety has a formal bond order of one and is nearly 0.2 Å longer than the Ta=N bond length. The Ta—N—C bond angle [135.8 (11)°] indicates that, as with the imide, there is some metal–lone pair overlap. In the dimeric ^{t}Bu analog, the Ta—N amide bond is short at 1.86 (3) Å and exhibits an unusual almost linear Ta—N—C bond angle of 160 (2)°.

The Ta—N(H$_2$) bond lengths and Ta—NH$_2$—C bond angles of the two amine moieties of (I) (Table 1) are similar, with mean values of 2.255 (8) Å and 118.8 (19)°. The amine dative interaction is again weaker than that of the amide, as indicated by the elongation of approximately 0.3 Å of the Ta—N bond length. The dative amine bond for the dimeric ^{t}Bu analog is similar, with a Ta—N bond length of 2.23 (3) Å and a Ta—N—C angle of 126 (2)°.

In the crystal, the molecules of (I) are linked by N—H···Cl hydrogen bonds (Table 2) about inversion centers, generating chains extending in the *b* direction.

As proposed by Jayaratne *et al.* (1996), we have shown that the structure of (I) is indeed monomeric and as such is

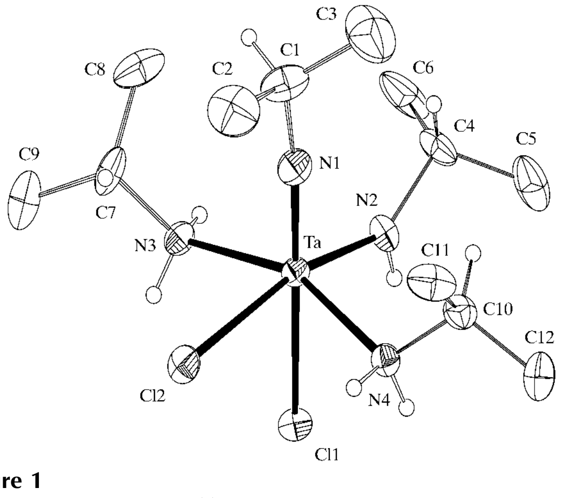


Figure 1
A view of the molecule of (I) with ellipsoids drawn at the 30% probability level. Methyl-H atoms have been omitted for clarity and only one of the two possible orientations of the disordered isopropyl groups is shown.

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potentially a very useful reference compound for comparison of amino, amido and imido bond lengths and angles. It is analogous to the structure of the alkyl/alkylidene/alkylidyne compound $W(CH_2CMe_3)(CHCMe_3)(CCMe_3)(dmpe)$ [dmpe is 1,2-bis(dimethylphosphino)ethane] reported by Churchill & Youngs (1979) (CSD refcode DMPMPW10) that is often cited for comparisons of metal–carbon bond lengths.

We used two-dimensional heteronuclear multiple-bond correlation (HMBC) NMR spectroscopy to fully assign the ^{1}H and ^{13}C NMR spectra of (I). We also report the ^{14}N and ^{15}N NMR spectroscopy data for this compound. The ^{1}H NMR spectrum of (I) depends on concentration. At low concentrations, the NH_2 protons of the amine moiety appear as a broad singlet in the δ 3.2–3.4 region of the spectrum. At higher concentrations, the amine protons shift upfield and become distinctive multiplets. It seems likely that the title compound is in equilibrium with a dimeric form that is analogous to that reported previously for the ^{t}Bu derivative.

Experimental

The title compound was synthesized as described by Jayaratne *et al.* (1996) from the reaction of $TaCl_5$ with ^{i}PrNH$_2$. Recrystallization by slow evaporation of toluene from a solution of the compound afforded colorless crystals suitable for X-ray analysis. ^{1}H NMR spectroscopic analysis of the crystals showed that little or no decomposition had occurred during recrystallization.

^{1}H, ^{13}C and ^{15}N NMR spectra were recorded on a Bruker AF500 or AF300 NMR spectrometer. Chemical shifts for ^{1}H and ^{13}C are referenced to the residual protio impurity in the deuterated solvent. ^{15}N chemical shifts are referenced to formamide used as an external standard. ^{14}N NMR spectra were recorded by Dr M. Minelli, Grinnell College, Iowa, on a Bruker AC 300 MHz NMR spectrometer with a 10 mm broadband probehead (^{109}Ag–^{31}P) with digital tuning. Neat nitromethane was used as the external reference (0 p.p.m.).

^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 0.83 [*d*, 6H, $^3J_{HH} = 6.00$ Hz, $NH_2CH(C\mathit{H}_3)_2$], 0.86 [*d*, 6H, $^3J_{HH} = 6.00$ Hz, $NH_2CH(C\mathit{H}_3)_2$], 1.10 [*d*, 6H, $^3J_{HH} = 6.00$ Hz, $NHCH(C\mathit{H}_3)_2$], 1.30 [*d*, 6H, $^3J_{HH} = 6.00$ Hz, $NCH(C\mathit{H}_3)_2$], 3.38 [*br*, 6H, $N\mathit{H}_2CH(CH_3)_2$, $NH_2C\mathit{H}(CH_3)_2$], 4.52 [*sept*, 1H, 6.00 Hz, $NC\mathit{H}(CH_3)_2$], 4.70 [*m*, 1H, $NHC\mathit{H}(CH_3)_2$], 7.80 [*d*, 1H, $^3J_{HH} = 10.00$ Hz, $N\mathit{H}CH(CH_3)_2$]. ^{13}C {1H} NMR (75.4 MHz, $CDCl_3$, 298 K): δ 24.9 [$NH_2CH(\mathit{C}H_3)_2$], 26.5 [$NHCH(\mathit{C}H_3)_2$], 27.8 [$NCH(\mathit{C}H_3)_2$], 49.5 [$NH_2\mathit{C}H(CH_3)_2$], 60.0 [$N\mathit{C}H(CH_3)_2$], 60.2 [NH-H$(CH_3)_2$]. ^{14}N {^{1}H} NMR (21.69 MHz, CH_2Cl_2, 298 K): δ −31 [N-$CH(CH_3)_2$], −122 [$\mathit{N}HCH(CH_3)_2$], −321 [$\mathit{N}H_2CH(CH_3)_2$], −335 [N_2-$CH(CH_3)_2$]. ^{15}N NMR (50.68 MHz, C_6D_6, 298 K): δ −30.0 [*s*, $\mathit{N}CH$-$(CH_3)_2$], −115 [*d*, $\mathit{N}CH(CH_3)_2$, $J_{NH} = 6$ Hz], −314 [*t*, $\mathit{N}H_2CH(CH_3)_2$, $J_{NH} = 66$ Hz].

Crystal data

$[Ta(C_3H_7N)(C_3H_8N)Cl_2(C_3H_9N)_2]$
$M_r = 485.27$
Triclinic, $P\overline{1}$
$a = 9.5970$ (19) Å
$b = 10.073$ (2) Å
$c = 12.755$ (3) Å
$\alpha = 95.04$ (3)°
$\beta = 111.77$ (3)°
$\gamma = 113.46$ (3)°
$V = 1009.5$ (6) Å^3

$Z = 2$
$D_x = 1.596$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10$–30°
$\mu = 5.70$ mm^{-1}
$T = 210$ (2) K
Block, colorless
$0.34 \times 0.26 \times 0.14$ mm

Data collection

Siemens *P*3 diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.182$, $T_{max} = 0.450$
4079 measured reflections
3528 independent reflections
3098 reflections with $I > 2\sigma(I)$

$R_{int} = 0.072$
$\theta_{max} = 25.1$°
$h = -11 \rightarrow 0$
$k = -11 \rightarrow 11$
$l = -15 \rightarrow 15$
3 standard reflections every 200 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.109$
$S = 1.09$
3528 reflections
219 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0639P)^2 + 2.1304P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.44$ e Å^{-3}
$\Delta\rho_{min} = -1.36$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ta—Cl1	2.632 (2)	Ta—N2	1.964 (7)
Ta—Cl2	2.504 (3)	Ta—N3	2.262 (7)
Ta—N1	1.763 (8)	Ta—N4	2.247 (7)
N1—Ta—Cl1	177.8 (2)	N3—Ta—N4	158.0 (3)
N1—Ta—Cl2	97.7 (3)	N4—Ta—Cl1	84.06 (18)
N1—Ta—N2	98.5 (4)	N4—Ta—Cl2	82.11 (18)
N1—Ta—N3	98.3 (3)	Cl2—Ta—Cl1	83.43 (8)
N1—Ta—N4	98.0 (3)	Ta—N1—C1	173.8 (8)
N2—Ta—Cl1	80.4 (2)	Ta—N2—C4	135.8 (11)
N2—Ta—Cl2	163.7 (2)	Ta—N2—C4′	135.9 (14)
N2—Ta—N3	97.2 (3)	Ta—N3—C7	120.9 (5)
N2—Ta—N4	95.0 (3)	Ta—N4—C10	119.1 (10)
N3—Ta—Cl1	80.02 (19)	Ta—N4—C10′	116.3 (10)
N3—Ta—Cl2	81.1 (2)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D \cdots A$	D—H$\cdots A$
N3—H3$A\cdots$Cl1^{i}	0.90	2.65	3.473 (7)	153
N4—H4$A\cdots$Cl1^{ii}	0.90	2.75	3.547 (7)	148
N4—H4$B\cdots$Cl2^{ii}	0.90	2.71	3.456 (7)	141

Symmetry codes: (i) $1 - x, 2 - y, -z$; (ii) $1 - x, 1 - y, -z$.

The title compound crystallized in the triclinic system; space group $P\overline{1}$ was chosen and confirmed by the successful refinement. It became obvious during the refinement that two of the isopropyl groups (C4/C5/C6 and C10/C11/C12) were disordered. This was dealt with by generating models (C4/C5/C6 and C4′/C5′/C6′, and C10/C11/C12 and C10′/C11′/C12′) using appropriate DFIX restraints [Csp^3—Csp^3 = 1.52 (1) Å, Csp^3—N = 1.48 (1) Å and $CH_3\cdots CH_3$ = 2.54 (1) Å]. Initially, tied-occupancy free variables were refined for each disordered isopropyl group, but as the refined values were not significantly different from 0.5, these occupancies were subsequently fixed at 0.5. Difference maps clearly revealed the amino- and amido-H atoms. In the final refinement cycles, all H atoms were allowed for as riding atoms using the *SHELXL* HFIX commands (N—H = 0.90 Å and C—H = 0.96 and 0.98 Å). The maxima and minima in the final difference map were within 1 Å of the Ta atom.

Data collection: *P*3/*PC* (Siemens 1990); cell refinement: *P*3/*PC*; data reduction: *SHELXTL* (Sheldrick, 1997*a*); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*); molecular graphics: *PLATON* (Spek 2002); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1670). Services for accessing these data are described at the back of the journal.

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