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Syntheses and Crystal Structures of Bis[2-(benzylamido)pyridine]trichloro Complexes of Niobium(V) and Tantalum(V)

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Bis[2-(benzylamido)pyridine]trichloroniobium(V) (**1**) and bis[2-(benzylamido)-pyridine]trichlorotantalum(V) (**2**) have been synthesised in a melt reaction of 2-(benzylamino)pyridine and corresponding metal(V) halide. Both complexes were crystallised from toluene which was used for extraction. Solvate molecules are also found in the solid-state structures; the Nb compound crystallises with two complex molecules and two solvate molecules in the asymmetric unit, whereas in **2** the number of metal complexes and toluene molecules in the asymmetric unit is one. Compound **1** crystallises in monoclinic space group $P2_1/c$ with unit-cell parameters of $a=18.292(8)$ Å, $b=19.904(15)$ Å, $c=17.646(10)$ Å and $\beta=109.47(4)$. Compound **2** crystallises in $P2_1/n$ with unit-cell parameters $a=9.227(8)$ Å, $b=20.005(7)$ Å, $c=16.804(6)$ Å and $\beta=100.08(5)$ Å. The coordination spheres around the transition metals are pseudo-pentagonal bipyramids.

Over 30 years ago Bradley and Thomas published syntheses for many amido complexes of niobium and tantalum, such as pentakis(dimethylamido)tantalum(V),[1] tetrakis(diethylamido)niobium(IV)[2] and pentakis(piperidino)tantalum(V).[3] In some cases mixed imido-amido complexes, e.g. tris(diethyamido)ethylimidotantalum(V), were obtained.[1] Many single-crystal structures of these and other amido complexes have been determined since. Pentakis(dimethylamido)- and pentakis(piperidino)-niobium(V)[4] complexes have been reported to have distorted tetragonal bipyramidal coordination in the solid state, whereas in tetrakis(diphenylamido)niobium(IV)[5] and *tert*-butylimidotris(dimethylamido)tantalum[6] the metals have disordered tetrahedral coordinations. Many of the heteroleptic complexes, such as $[Nb[N(SiMe_3)_2]_2Br_2]$,[5] $[Ta(N(SiMe_3)_2)_2Cl_2]$[7] and $[Ta[N(SiMe_3)_2]_2Cl_3]$,[8] contain trimethylsilylamide ligands. The most common synthesis method has been reaction between lithiated ligand precursors and metal halides. Chloro-amido complexes have also been prepared in direct reactions between ligand and metal chloride. When dimethylamine and tantalum(V) chloride were refluxed in benzene, three different species, $[TaCl_3(NMe_2)_2(NHMe_2)]$, $[TaCl_2(NMe_2)_3(NHMe_2)]$ and $[(TaCl_2(NMe_2)_2(NHMe_2))_2O]$, were obtained.[9]

Many niobium and tantalum complexes with nitrogen neutral Lewis donor nitrogen ligands have also been reported. Pyridine and its derivatives are common ligands in these complexes. Tetrachlorodi(pyridine)-tantalum(IV)[10] is known to be monomeric in the solid state, whereas related tantalum(III) compound achieves a similar six-coordination via two chloro bridges when the dimeric pyridine adduct, $Ta_2Cl_6(Py)_4$, is formed.[11] Adducts with multidentate pyridines have also been characterised; for example 2,2′,2″-terpyridine has been reported to form many complexes with niobium and tantalum tetra- and pentahalides.[12]

Many niobium and tantalum compounds with macrocyclic tetradentate ligands, e.g. dichloro(phtalocyanido)-niobium(IV),[13] are known. If the metal is at its highest oxidation state (V) in macrocyclic complexes, oxo derivative compounds, such as tri-μ-oxobis[5,10,15,20-tetraphenylporphyrinatoniobium(V)],[14] are predominant.

Our interest in niobium and tantalum complexes comes from their possible use as polymerisation catalysts. Studies of homogenous alkene polymerisation catalysts are predominated by metallocene derivatives.[15] The fact that metallocenes have been thoroughly studied and patented was a motivating factor for our study of alternate complexes. In the complexes studied the metal ions are at their highest oxidation state, because lower oxidation state complexes may form isolable complexes with alkynes and alkenes.[16,17]

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Experimental

All reaction steps were carried out under an argon atmosphere using standard Schlenk techniques. The crystals for the X-ray measurements were mounted on a glass fibre using the oil-drop method.[18]

Synthesis of [$NbCl_3(PyNBz)_2$]. Niobium(V) chloride, 2.36 g (8.73 mmol), and 2-(benzylamino)pyridine, 3.22 g (17.3 mmol), were melted at 100 °C for 30 min and extracted with toluene (60 ml) by refluxing for 2 h. The toluene solution was separated from the oily purple–black amorphous residue and filtered. Purple crystals were obtained after 15 h. The estimated yield of the crystalline material was 30%.

Synthesis of [$TaCl_3(PyNBz)_2$]. Tantalum(V) chloride, 1.36 g (3.89 mmol) and 2-(benzylamino)pyridine (m.p. 95–97 °C), 1.47 g (7.97 mmol), were heated at 100 °C. The melt started to turn red immediately. During the reaction gas formation was observed. After 1 h 30 ml of toluene were added, and the solution was refluxed for 2 h and filtered when hot through Celite. The solution was kept at room temperature and a few drops of *n*-hexane were added. Intense red crystalline blocks were obtained after 20 h. The yield of the crystalline material was 64%.

X-ray crystallography. Intensity data were recorded with a Rigaku AFC-7S diffractometer using graphite-monocromatised Mo$K\alpha$ ($\lambda = 0.7173$ Å) radiation. Reflection intensities over background were collected using 2θ–ω scans. Intensities of three standard reflections which were recorded after every 200 intensity scans showed only random fluctuations or slight decay (< 5%) during both data collections. The intensity data were corrected for Lorentz and polarisation effects and absorption (ψ-scan). Unit-cell dimensions were determined from 20 reflections ($4 < \theta < 15°$). The data set was processed to reflection files with TEXSAN single-crystal structure analysis software.[19] Structures were solved with the SHELXTL PC 4.1 program package[20] using direct methods which showed the positions of most of the non-hydrogen atoms. Refinement with full-matrix least-squares on F^2 was carried out with SHELXL93[21] using all collected reflections. In each case non-hydrogen atoms were refined anisotopically, except for the carbon atoms in solvate molecules [**1**, C(1c)–C(7c), C(1d)–C(7d) and **2**, C(31)–C(37)]. Both refinements resulted in large thermal parameters in the toluene carbon atoms. Additional refinement cycles were carried out in order to refine the site-occupancy factors; however, the refinements indicated full occupancies, and populations were therefore again fixed to 1.00. In both compounds hydrogen atoms were introduced in calculated positions with thermal parameters 1.3 times those of the parent atoms. Crystallographic data are presented in Table 1. Fractional atom coordinates for the complexes are presented in Tables 2 and 3. Structure factors and anisotropic thermal parameters are available from the authors on request.

Results and discussion

Most amido complexes of early transition metals have been prepared via reaction between a lithited ligand precursor[1–8] and a metal halide. Alternative methods have also been studied. For example, direct reaction between ammonia and tantalum(V) chloride results in several different species depending on the reaction temperature.[22] At low temperatures ammonia behaves as a neutral Lewis base, whereas at 0 °C mixed amido-ammonia complexes, such as $Ta(NH_2)_2(NH_3)_3Cl_3$, are formed. When the temperature is further raised to 170 °C $Ta(NH_2)_2Cl_3$ is formed. Similarly, dialkyl amides produce amido complexes because amine behaves as a H^+ acceptor. These reactions may also lead to mixed amido-amine complexes because dialkylamide is able to act as a neutral Lewis base.[9]

In our experiments direct reactions between 2-(benzylamino)pyridine and transition-metal(V) halides were used without a solvent. The ligand precursor, which has a suitable melting point (95–97 °C), was melted with niobium(V) chloride or tantalum(V) chloride at a temperature just above its melting point. Reactions produce a highly viscous, intensely coloured oily material which is partially soluble in toluene. The desired product is clearly the most soluble in toluene, because homomorphous large crystals are easily obtained from toluene. However, in the synthesis of $[Nb(BzNPy)_2Cl_3]$ a large fraction of the reaction products remained undissolved, probably as various hydro-

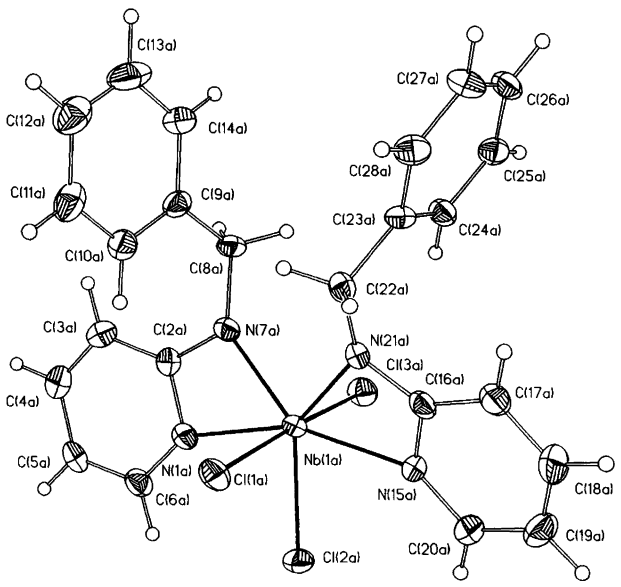

Fig. 1. Molecular structure of $[Nb(BzNPy)_2Cl_3]$ showing the labeling scheme. The other highly similar unit is numbered analogously to that presented. Displacement ellipsoids are drawn at the 30% probability level. The toluene solvate molecule is omitted for clarity.

Table 1. Crystal data for $[Nb(BzNPy)_2Cl_3]$ and $[Ta(BzNPy)_2Cl_3]$

Formula[a]	$C_{24}H_{22}Cl_3N_4Nb$	$C_{24}H_{22}Cl_3N_4Ta$
Relative formula mass[a]	565.71	635.75
Colour, habit	Deep purple, block	Dark red, prism
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$, No. 14	$P2_1/n$, No. 14
Temperature/K	193(1)	193(1)
a/Å	18.292(8)	9.227(8)
b/Å	19.904(15)	20.005(7)
c/Å	17.646(10)	16.804(6)
β/°	109.47(4)	100.08(5)
V/Å^3	6057(7)	3054(3)
Z	8	4
D_c/g cm^{-3}	1.443	1.622
Crystal size/mm	0.55 × 0.45 × 0.35	0.50 × 0.50 x 0.45
F(000)	2688	1472
μ/mm^{-1}	0.689	3.888
Transmission range	0.8483–1.0000	0.8384–1.0000
2θ range/°	5–50	5–53
Independent reflections	9380	5999
Observed reflections [$F > 4\sigma(F)$]	7423	5454
Parameters	633	318
Extinction correction	None	0.003(1)
Refinement method on F^2	Full-matrix least squares	Full-matrix least squares
Final R [$F > 4\sigma(F)$]	$R_1 = 0.0887$	$R_1 = 0.0582$
	$wR_2 = 0.2283$	$wR_2 = 0.1588$
R indices (all data)[b]	$R_1 = 0.1078$	$R_1 = 0.0628$
	$wR_2 = 0.2448$	$wR_2 = 0.1627$
S (Goodness of fit, F^2)[c]	1.022	1.069
Residual e-density /e Å^{-3}	2.291 and −1.077	3.252 and −2.575
Weights ($P = (F_o^2 + 2F_c^2)/3$)	$[\sigma^2(F_o^2) + (0.1632P)^2 + 11.2206P]^{-1}$	$[\sigma^2(F_o^2) + (0.1627P)^2 + 11.6292P]^{-1}$

[a] Toluene solvate, C_7H_8 92.14 g mol^{-1}, excluded.
[b] $R = \Sigma||F_o| - |F_c||/|F_o|$ with $F > 4\sigma(F)$, function minimized is $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)]]^{0.5}$
[c] $S = [\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)]^{0.5}$

chloride adducts of the reactants. In contrast, the crude product of $[Ta(BzNPy)_2Cl_3]$ is highly soluble in toluene and was obtained with good yield. It seems likely that hydrochloric acid was at least partially vaporised during the reaction.

Although both complexes have very similar bonding patterns they are not crystallographically isostructural. The niobium compound (Fig. 1) crystallises with two complex molecules and two toluene solvate molecules in the asymmetric unit, whereas one complex and one toluene molecule form the asymmetric unit in the tantalum compound (Fig. 2). Both complexes crystallise in space group No. 14. The coordination spheres of the metals can be regarded as pseudo-pentagonal bipyramids (Fig. 3). Two chloro ligands occupy the axial positions of the polyhedra, and a pentagonal plane is formed from two pairs of nitrogen atoms and the third chloro ligand. The pentagonal plane (Fig. 2) is quite distorted for two reasons: (i) the atoms are not lying exactly in the plane and (ii) all *cis*-angles deviate from the ideal 72°. The former phenomenon can be seen as a tilt caused by the coordinating 2-amidopyridine: one of the nitrogen atoms of the ligand is ca. 0.20(3) Å above plane and twists the other dental nitrogen atom the same amount down from the plane. The latter behaviour (ii) is caused by the small N–M–N angle in the chelate ring: because of the rigid 2-(phenylamido)pyridine with small bite all *cis*-angles in the pentagonal plane deviate from an ideal 72°. Nitrogen–metal–nitrogen angles in the chelate ring are small and they vary only little. In $[NbCl_3(PyNBz)_2]$ they are between 60.5(2) and 60.9(2)° and in $[TaCl_3(PyNBz)_2]$ 60.8(2) and 60.8(2)°. Both these reasons lead to a situation in which all other *cis*-angles in the pentagonal plane are clearly over 72°. All N–M–Cl(2) *cis*-angles in both structures are around 78(1)° and N–M–N angles involving the amido bonds are the widest, namely 84.8(2)

Table 2. Atomic coordinates and equivalent isotropic displacement parameters for $[Nb(BzNPy)_2Cl_3]$

Atom	$10^4x/a$	$10^4y/b$	$10^4z/c$	10^3U_{eq}[a]/Å^2
Nb(1a)	3832(1)	1524(1)	6324(1)	31(1)
Cl(1a)	2977(1)	2187(1)	5281(1)	45(1)
Cl(2a)	2750(1)	743(1)	6105(1)	47(1)
Cl(3a)	4620(1)	780(1)	7333(1)	47(1)
N(1a)	3931(4)	880(3)	5315(4)	38(2)
C(2a)	4589(4)	1199(4)	5327(4)	34(2)
C(3a)	4926(5)	1040(4)	4748(5)	43(2)
C(4a)	4585(5)	548(5)	4207(5)	51(2)
C(5a)	3899(5)	230(4)	4196(5)	45(2)
C(6a)	3594(5)	408(4)	4772(5)	44(2)
N(7a)	4765(3)	1653(3)	5937(4)	36(1)
C(8a)	5520(4)	1981(4)	6183(5)	41(2)
C(9a)	5589(5)	2562(4)	5654(5)	40(2)
C(10a)	4975(5)	2757(4)	4978(5)	45(2)
C(11a)	5050(6)	3304(5)	4525(6)	56(2)

Table 2. (continued)

Atom	$10^4x/a$	$10^4y/b$	$10^4z/c$	10^3U_{eq}[a]/Å^2
C(12a)	5732(7)	3651(5)	4733(7)	64(3)
C(13a)	6340(6)	3464(5)	5399(8)	69(3)
C(14a)	6282(5)	2922(5)	5861(6)	54(2)
N(15a)	3339(4)	1825(4)	7280(4)	37(2)
C(16a)	3720(4)	2415(4)	7394(4)	37(2)
C(17a)	3590(5)	2899(5)	7923(5)	46(2)
C(18a)	3074(6)	2747(6)	8297(6)	62(3)
C(19a)	2694(6)	2133(5)	8181(6)	59(3)
C(20a)	2825(5)	1679(5)	7654(5)	47(2)
N(21a)	4184(4)	2416(3)	6938(4)	35(1)
C(22a)	4535(4)	3056(4)	6833(4)	36(2)
C(23a)	5217(4)	3229(4)	7560(5)	34(2)
C(24a)	5591(4)	2778(4)	8151(4)	38(2)
C(25a)	6205(4)	2957(5)	8813(5)	43(2)
C(26a)	6477(5)	3614(5)	8898(5)	45(2)
C(27a)	6116(5)	4073(5)	8316(6)	52(2)
C(28a)	5498(5)	3893(4)	7660(5)	46(2)
Nb(1b)	8914(1)	3350(1)	11220(1)	31(1)
Cl(1b)	8047(1)	2680(1)	10182(1)	43(1)
Cl(2b)	7835(1)	4132(1)	11031(1)	43(1)
Cl(3b)	9714(1)	4090(1)	12226(1)	48(1)
N(1b)	8436(4)	3019(3)	12184(4)	36(1)
C(2b)	8808(4)	2437(4)	12260(4)	37(2)
C(3b)	8672(5)	1924(5)	12753(5)	47(2)
C(4b)	8145(6)	2063(5)	13138(6)	56(2)
C(5b)	7780(5)	2669(5)	13048(6)	55(2)
C(6b)	7935(5)	3151(5)	12558(5)	49(2)
N(7b)	9271(3)	2450(3)	11802(4)	38(2)
C(8b)	9604(4)	1819(4)	11658(5)	37(2)
C(9b)	10285(4)	1597(4)	12363(5)	36(2)
C(10b)	10564(5)	936(5)	12400(6)	51(2)
C(11b)	11183(6)	717(5)	13056(7)	64(3)
C(12b)	11534(5)	1152(6)	13665(7)	63(3)
C(13b)	11263(5)	1802(5)	13654(6)	51(2)
C(14b)	10645(4)	2023(4)	13001(5)	38(2)
N(15b)	9003(4)	4001(4)	10207(4)	41(2)
C(16b)	9676(4)	3713(4)	10238(4)	37(2)
C(17b)	10063(5)	3915(4)	9719(5)	44(2)
C(18b)	9726(6)	4427(5)	9172(5)	50(2)
C(19b)	9029(5)	4719(5)	9160(5)	51(2)
C(20b)	8684(5)	4486(4)	9685(5)	46(2)
N(21b)	9848(3)	3233(3)	10825(4)	36(1)
C(22b)	10596(4)	2907(4)	11072(5)	41(2)
C(23b)	10676(5)	2384(4)	10469(5)	40(2)
C(24b)	10073(5)	2196(5)	9800(5)	49(2)
C(25b)	10161(6)	1732(5)	9263(6)	54(2)
C(26b)	10889(7)	1431(5)	9394(7)	65(3)
C(27b)	11479(7)	1611(6)	10071(8)	76(3)
C(28b)	11391(5)	2075(5)	10619(7)	59(3)
C(1c)	6786(6)	−355(6)	10564(7)	66(3)
C(2c)	7548(7)	−216(6)	10747(8)	80(3)
C(3c)	7940(9)	62(8)	11531(9)	100(4)
C(4c)	7523(8)	222(7)	12035(9)	94(4)
C(5c)	6772(8)	85(7)	11770(9)	98(4)
C(6c)	6412(7)	−199(6)	11084(7)	76(3)
C(7c)	6350(9)	−664(8)	9797(9)	113(5)
C(1d)	8138(9)	432(8)	9116(9)	96(4)
C(2d)	7492(9)	853(9)	9021(10)	111(5)
C(3d)	6828(9)	714(8)	8455(9)	105(5)
C(4d)	6699(10)	250(9)	7952(10)	113(5)
C(5d)	7311(10)	−207(9)	8012(10)	118(5)
C(6d)	8025(9)	−114(8)	8566(9)	95(4)
C(7d)	8876(14)	513(12)	9689(14)	199(10)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Atomic coordinates and equivalent isotropic displacement parameters for for $[Ta(BzNPy)_2Cl_3]$.

Atom	$10^4x/a$	$10^4y/b$	$10^4z/c$	10^3U_{eq}[a]/Å^2
Ta(1)	1075(1)	3362(1)	8594(1)	39(1)
Cl(1)	433(2)	2721(1)	9661(1)	50(1)
Cl(2)	−793(2)	4164(1)	8832(1)	52(1)
Cl(3)	1625(3)	4069(1)	7560(1)	57(1)
N(1)	2329(7)	3994(3)	9567(4)	45(1)
C(2)	3625(9)	3693(4)	9529(5)	42(2)
C(3)	4922(9)	3864(4)	10044(5)	48(2)
C(4)	4832(10)	4357(4)	10609(6)	54(2)
C(5)	3487(10)	4671(4)	10648(5)	51(2)
C(6)	2257(9)	4471(4)	10117(5)	47(2)
N(7)	3324(7)	3213(3)	8935(4)	44(1)
C(8)	4553(9)	2883(4)	8662(5)	48(2)
C(9)	5298(9)	2357(4)	9250(5)	47(2)
C(10)	6562(11)	2054(5)	9085(8)	69(3)
C(11)	7276(15)	1575(6)	9613(11)	93(4)
C(12)	6732(14)	1404(7)	10296(9)	88(4)
C(13)	5486(14)	1706(5)	10461(7)	68(3)
C(14)	4776(11)	2180(4)	9939(5)	54(2)
N(15)	−855(8)	3051(3)	7684(4)	46(2)
C(16)	−245(9)	2457(4)	7557(5)	45(2)
C(17)	−1024(11)	1975(5)	7055(6)	56(2)
C(18)	−2434(11)	2141(5)	6677(6)	63(2)
C(19)	−3029(11)	2752(6)	6803(6)	63(2)
C(20)	−2209(10)	3208(5)	7313(6)	55(2)
N(21)	1150(8)	2447(3)	7990(4)	44(2)
C(22)	1940(9)	1830(4)	8130(5)	42(2)
C(23)	2623(9)	1619(4)	7413(5)	43(2)
C(24)	2667(10)	2035(4)	6764(5)	51(2)
C(25)	3292(9)	1830(5)	6111(6)	55(2)
C(26)	3871(11)	1203(6)	6101(7)	65(3)
C(27)	3855(12)	777(5)	6751(7)	68(3)
C(28)	3218(10)	982(4)	7399(6)	57(2)
C(31)	−2719(37)	4382(16)	5067(21)	227(14)
C(32)	−3181(18)	4577(8)	5803(10)	98(4)
C(33)	−4452(25)	4394(12)	5977(14)	143(7)
C(34)	−5076(33)	4612(14)	6602(17)	173(9)
C(35)	−4293(25)	5007(11)	7114(14)	136(7)
C(36)	−3013(23)	5186(10)	7062(12)	124(6)
C(37)	−2338(24)	4992(10)	6401(13)	132(6)

[a] See Table 2.

and 85.4(2)° in $[NbCl_3(PyNBz)_2]$ and 83.9(3) in $[TaCl_3(PyNBz)_2]$. Also, the equatorial chloro ligands show slight distortion regarding their *trans*-orientations. Cl(1)–M–Cl(3) angles between the axial positions are 175(1)° and Cl_{axial}–M–$X_{equatorial}$ angles deviate typically between 3 and 5° from the ideal 90° in both structures.

M–Cl distances are longest for the equatorial chloro ligands: in $[Nb(BzNPy)_2Cl_3]$ the distances are 2.446(2) Å in both molecules, whereas in the Ta–Cl_{axial} bond the distance is 2.440(2) Å. M–Cl distances for atoms lying in axial positions are between 2.378(2) and 2.394(2) Å in $[Nb(BzNPy)_2Cl_3]$ compared with 2.362(2) and 2.363(2) Å found in $[Ta(BzNPy)_2Cl_3]$. Metal–nitrogen distances differ only slightly from the literature values.[4,9,23] The M–N_{amido} bonds are similar or only slightly longer than the previously reported ones. In $[NbCl_3(BzNPy)_2]$ complex units all M–N_{amido} bond lengths are 2.055 Å within statistical error, whereas in pentakis(dimethylamido)niobium(V) and the analogous

Table 4. Selected bond lengths (in Å) and angles (in °) in $[Nb(BzNPy)_2Cl_3]$.

	Mol. a	Mol. b
Nb(1)–N(1)	2.250(6)	2.256(6)
Nb(1)–N(7)	2.055(6)	2.061(7)
Nb(1)–N(15)	2.243(6)	2.256(6)
Nb(1)–N(21)	2.068(6)	2.063(6)
Nb(1)–Cl(1)	2.378(2)	2.391(2)
Nb(1)–Cl(2)	2.446(2)	2.446(2)
Nb(1)–Cl(3)	2.394(2)	2.394(2)
N(1)–Nb(1)–N(7)	60.9(2)	60.5(2)
N(1)–Nb(1)–N(15)	154.9(2)	156.0(2)
N(1)–Nb(1)–N(21)	144.2(2)	142.7(2)
N(7)–Nb(1)–N(15)	143.5(2)	143.1(2)
N(7)–Nb(1)–N(21)	85.4(2)	84.8(2)
N(15)–Nb(1)–N(21)	60.6(2)	60.7(2)
N(1)–Nb(1)–Cl(1)	84.8(2)	95.1(2)
N(7)–Nb(1)–Cl(1)	94.5(2)	85.2(2)
N(15)–Nb(1)–Cl(1)	96.2(2)	85.3(2)
N(21)–Nb(1)–Cl(1)	86.5(2)	95.2(2)
N(1)–Nb(1)–Cl(2)	77.7(2)	77.9(2)
N(7)–Nb(1)–Cl(2)	138.2(2)	136.7(2)
N(15)–Nb(1)–Cl(2)	77.4(2)	78.2(2)
N(21)–Nb(1)–Cl(2)	136.3(2)	138.4(2)
N(1)–Nb(1)–Cl(3)	92.8(2)	85.1(2)
N(7)–Nb(1)–Cl(3)	87.9(2)	98.7(2)
N(15)–Nb(1)–Cl(3)	84.2(2)	92.7(2)
N(21)–Nb(1)–Cl(3)	97.8(2)	87.1(2)
Cl(1)–Nb(1)–Cl(2)	86.65(8)	87.23(8)
Cl(1)–Nb(1)–Cl(3)	175.22(8)	175.67(8)
Cl(2)–Nb(1)–Cl(3)	88.81(8)	88.60(8)

Table 5. Selected bond lengths (in Å) and angles (in °) in $[Ta(BzNPy)_2Cl_3]$.

Ta(1)–N(1)	2.225(7)	Ta(1)–Cl(1)	2.362(2)
Ta(1)–N(7)	2.075(7)	Ta(1)–Cl(2)	2.440(2)
Ta(1)–N(15)	2.223(7)	Ta(1)–Cl(3)	2.363(2)
Ta(1)–N(21)	2.099(6)		
N(1)–Ta(1)–N(7)	60.8(2)	N(7)–Ta(1)–Cl(2)	138.6(2)
N(1)–Ta(1)–N(15)	156.2(2)	N(15)–Ta(1)–Cl(2)	78.0(2)
N(1)–Ta(1)–N(21)	142.5(3)	N(21)–Ta(1)–Cl(2)	137.5(2)
N(7)–Ta(1)–N(15)	142.4(3)	N(1)–Ta(1)–Cl(3)	92.8(2)
N(7)–Ta(1)–N(21)	83.9(3)	N(7)–Ta(1)–Cl(3)	87.5(2)
N(15)–Ta(1)–N(21)	61.0(3)	N(15)–Ta(1)–Cl(3)	84.9(2)
N(1)–Ta(1)–Cl(1)	85.3(2)	N(21)–Ta(1)–Cl(3)	97.9(2)
N(7)–Ta(1)–Cl(1)	94.8(2)	Cl(1)–Ta(1)–Cl(2)	87.37(8)
N(15)–Ta(1)–Cl(1)	95.4(2)	Cl(1)–Ta(1)–Cl(3)	175.78(8)
N(21)–Ta(1)–Cl(1)	85.9(2)	Cl(2)–Ta(1)–Cl(3)	88.57(8)
N(1)–Ta(1)–Cl(2)	78.3(2)		

pyrrolidine complex a $M–N_{amido}$ distance range of 1.977(17)–2.056(13) Å has been reported.[4] The values found in $[Ta(BzNPy)_2Cl_3]$, 2.075(7) and 2.099(6) Å, are longer than the related amido bond lengths [1.954(5) and 1.963(5) Å] in trichlorobis(dimethylamido)dimethylamino tantalum(V).[9] The average lengths of the $M–N_{pyridine}$ bonds in $[Nb(BzNPy)_2Cl_3]$ [2.25(1) Å] and in $[Ta(BzNPy)_2Cl_3]$ [2.22(1) Å] are comparable to those observed in 2,2′-bipyridyldichloro(trimethyl)tantalum(V)[23] [2.29(2) Å].

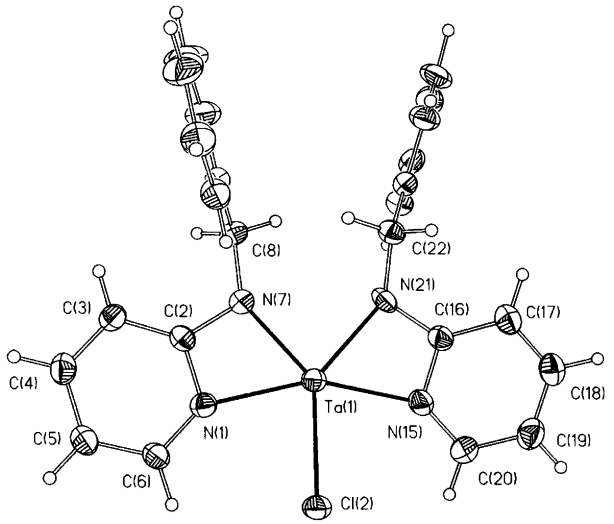

Fig. 2. View of $[Ta(BzNPy)_2Cl_3]$ showing the pentagonal plane from the direction of Cl(1). Displacement ellipsoids are drawn at the 30% probability level. Cl(1) and Cl(3) atoms and the toluene solvate molecule are omitted for clarity.

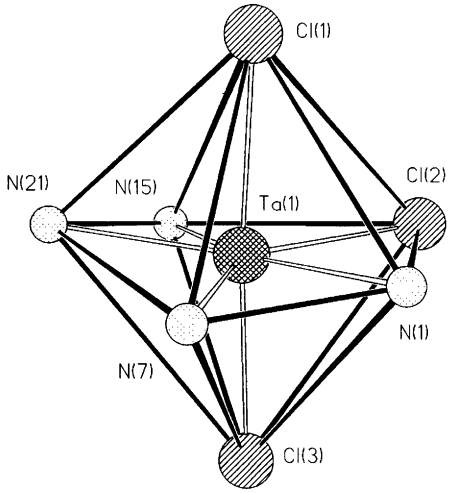

Fig 3. Distorted pseudo pentagonal bipyramidal coordination sphere of $[Ta(BzNPy)_2Cl_3]$.

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